

A Conversation on VB vs MO Theory: A Never-Ending Rivalry?

ROALD HOFFMANN*

Department of Chemistry and Chemical Biology,
Cornell University, Baker Laboratory,
Ithaca, New York 14853-1301

SASON SHAIK*

Department of Organic Chemistry and
The Lise Meitner-Minerva, Center for Computational
Quantum Chemistry, Givat Ram Campus,
Jerusalem 91904, Israel

PHILIPPE C. HIBERTY*

Laboratoire de Chimie Physique, Groupe de
Chimie Théorique, Bât. 490, Université de Paris-Sud,
91405 Orsay Cédex, France

Received May 30, 2003

ABSTRACT

Quantum mechanics has provided chemistry with two general theories, valence bond (VB) theory and molecular orbital (MO) theory. The two theories were developed at about the same time, but quickly diverged into rival schools that have competed, sometimes fervently, on charting the mental map and epistemology of chemistry. Three practitioners of MO and VB theory talk — fighting a little, trying to understand — of the past and present of these two approaches to describing bonding in molecules.

RH = Roald Hoffmann, SS = Sason Shaik, PH = Philippe Hiberty

RH: I just saw this nice paper by you guys, on hydrogen abstraction reactions.

SS, PH: We hope you noticed the valence bond approach.

RH: I did, that's why I mentioned it. In your quiet way, both of you have done a lot to bring the community back to valence bond ideas.

Roald Hoffmann was born in Zloczów, Poland, in 1937, and after surviving the Nazi occupation came to the United States in 1949. He was educated at Stuyvesant High School in New York City, and at Columbia and Harvard Universities (where he studied with Martin Gouterman and William N. Lipscomb). After a Junior Fellowship at Harvard, he joined the faculty at Cornell University, where he has remained, now as the Frank H. T. Rhodes Professor of Humane Letters. He has won many of the awards of our profession. Aside from his work in theoretical chemistry, he is proud of being a teacher, who helped in the making of a video series on chemistry, "The World of Chemistry". Hoffmann is also a writer of essays, as well as poetry, nonfiction, and plays.

Sason Shaik was born in 1948 in Iraq. The family immigrated to Israel in the Exodus of the Iraqi Jewry. Has received his B.Sc. and M.Sc. in chemistry from Bar-Ilan University, and his Ph.D from the University of Washington. In 1978–1979 he spent a postdoctoral year with Roald Hoffmann at Cornell University. In 1980 he started his first academic position as a Lecturer at Ben-Gurion University, where he became Professor in 1988. He subsequently moved to the Hebrew University, where he is currently the director of The Lise Meitner-Minerva Center for Computational Quantum Chemistry. Among the awards he has received are the Lise-Meitner-Alexander von Humboldt Senior Award in 1996–1999, and the 2001 Israel Chemical Society Prize. His research interests are in the use of quantum chemistry, and in particular of valence bond theory, to develop paradigms which can pattern data and lead to the generation and solution of new problems.

SS: I still remember, Roald, while I was a Ph.D. student at the University of Washington, and you came to give the Walker–Ames lectures. After the second lecture, you invited all the students to drink beer in the local pub ...

RH: I think I was experimenting with a Harry Gray style for a while.

SS: ... I of course came too. After a few beers, I dared enough to ask you about science. I asked what did you think will be the major developments in quantum chemistry in years to come. You said, among other things, that VB theory would come back.

RH: Did I say that? I don't remember it.

SS: Yes, you did! As an avid student of MO theory then, I was shocked — how could such a prominent scientist utter this blasphemy? After all, VB theory was known during my student time as a flawed theory. Or simply a dead one. And lo and behold, a few years later here was I discovering VB theory with enchantment. As a postdoc in your lab, you were very kind to let me work on VB theory, even though it had nothing to do with the type of research you intended me to do. It is there where I developed the ideas that formed the basis for my own first VB paper. I am sure you were kind; were you also curious to see if your hunch about VB theory was correct?

RH: Maybe. I've always been ambivalent about VB. What is so closely tied to the chemist's bond concept, and so teachable at the beginning level, just had to have something right about it. So why wasn't there a good simple way to do calculations of value with VB theory?

PH: There is now! I am sure that chemists will eventually come back to VB theory. In fact, maybe they were never very far away.

RH: What do you mean?

PH: Well, the reason valence bond theory was so immediately accepted in the thirties, when Pauling explained it to the chemical community, is quite clear. The imagery and symbolism of valence bond theory touched directly familiar chemical epistemology. Take, for example, the description of benzene with the two Kekulé structures; it was *so* close to what chemists were imaging benzene to be. They were just waiting for a rationalization of Kekulé's idea!

Philippe C. Hiberty was born in 1948 in Paris. He studied theoretical chemistry at the University of Paris-Sud in Orsay. He prepared the French equivalent of an M.Sc. degree under the supervision of Professor W. J. Hehre, and then he completed his Ph.D. degree under the supervision of Professor L. Salem in Orsay and got a research position at the Centre National de la Recherche Scientifique (CNRS). In 1979 he started his postdoctoral research with Professor J. I. Brauman at Stanford University and then with Professor H. F. Schaefer, III, at Berkeley. He went back to Orsay to join the Laboratoire de Chimie Théorique, where he started developing a research program based on valence bond theory. He became Directeur de Recherche in 1986, and in addition to his research position he now teaches quantum chemistry at the Ecole Polytechnique in Palaiseau. He received the Grand Prix Philippe A. Guye from the French Academy of Sciences in 2002. His research interests are, among others, in the application of quantum chemistry and valence bond theory to the fundamental concepts of organic chemistry.

Moreover, the fundamental element of Pauling's theory was simply the chemical bond, which goes back to early chemical concepts and discovery of valency.

RH: What a stroke of genius, that portmanteau word "valence bond"!

PH: Yes, the whole of chemistry is connected to the idea of a chemical bond.

RH: Which Lewis gave an electronic formulation to, at roughly the same time as Bohr's orbital model was conceived.

SS: In fact, despite what physicists like to think, the first theory of the chemical bond was Lewis's.

RH: Was it inspiration or a lucky accident?

SS: Lewis had been seeking an understanding of the behavior of strong and weak electrolytes in solution, and like the biblical Saul who went to look for his father's asses and found a kingdom, so Lewis found the concept of the chemical bond as an intrinsic property that stretches between the covalent and ionic extremes. Gavroglu and Simões call Lewis, "the wonderful matchmaker", and give him credit even for resonance theory. Pauling's 1931 papers clearly linked his extension of Heitler–London's seminal account of the bonding in H₂ to Lewis's chemical theory. In fact, the first edition of Pauling's book is dedicated to Lewis, and Lewis's 1916 paper is cited in the preface.

RH: Linked it so well that poor John Slater, who in the same year independently developed similar concepts, just had no chance. Hardly a bashful man himself, he just couldn't match Pauling's expository skills. Nor Linus's natural way of engaging the chemical psyche.

PH: Neither, it seems, could Mulliken and Hund, as they built their molecular orbital theory in the thirties.

RH: Nor Erich Hückel, undervalued by his mentor Debye and by other physicists, ignored by the forces that were in synthetically minded German organic chemistry, his natural audience.

SS: Yes, chemistry owed Hückel a lot, but Jerry Berson explains so well why his work did not have an impact. Roald, why do you think Pauling had this hold on the chemist's imagination?

RH: It was curious, if you think about it, because VB theory took hold without, as far as I can see, any critical or risky predictions.

SS: Not that you need those, despite scientists' myths about what makes people accept theories. This is the general conclusion of historian of science Stephen Brush ...

RH: ... a Coulson student

SS: ... and not only about the dynamic of theory change in chemistry. Here is a fitting quote from your recent *American Scientist* article: "... what matters [*in why people buy a theory*] is a heady mix of factors in which psychological attitudes figure prominently."

RH: I think one reason chemists believed Pauling (and his apostle/expositor to the organic community, Wheland) is because he not only capitalized on what was already there — the idea of covalent and ionic bonds. But also, and this is largely forgotten, Pauling was not just a theoretician — he was America's premier structural chemist. I would guess that at the time that great Cornell book, *The Nature of the Chemical Bond*, was written, Pauling and his students had done half the crystal structures known. And they made electron diffraction a practical technique. Pauling spoke to chemists of the physical structure of the molecules they cared about, and even though he was a theorist, he spoke with unparalleled experimental authority.

SS: Yes, Pauling's colossal achievement not only addressed chemists in their own familiar language, it also managed to show them that their language had a formal basis rooted in the new quantum mechanics. This must have had a tremendous psychological impact on the ego of chemists. So what went wrong? How did it happen that molecular orbital theory, far from synthetic chemists' consciousness in 1940, was dominant in their outlook by 1955? And mind you, in that period came the War, when people didn't think much except about survival!

RH: Three things, I think: Pauling's personal failings as a scientist, the failings of VB theory, and ...

PH: Just a minute, we can agree about Pauling's failings; after all, he was human. But failures of VB theory? A myth! How can you hold on to this *canard*?

RH: Let me finish. And, third, the successes of MO ways of thinking. But first on Pauling and the ways he damaged his own credibility: he ignored MO theory to a degree that was clearly perceived by the community as blind, if not unethical. His interests (and great, great creative powers) also shifted to biological problems. And, finally, he lost touch with the explosion in structure and reactivity, to an extent that the third edition of *The Nature of the Chemical Bond* is ... an embarrassment. I remember meeting him in 1962, when I interviewed for a job at Caltech — and there he was, arguing for B₁₂H₁₂ when B₁₂H₁₂²⁻ (predicted a closed-shell molecule from MO arguments by Longuet-Higgins and Roberts) already existed!

SS: OK, Roald, we agree that Pauling did not develop VB theory beyond the point that satisfied ... him. And then he left chemistry in favor of biology. This still does not explain why chemists would suddenly abandon such a cozy theory?

RH: That's the point — the theory collapsed (in terms of its influence) when Pauling left the field. That was because Pauling — as long as he stayed in touch with the realities of chemistry — was a natural, masterly propagandist. Not because the theory had value in and of itself.

SS: I beg to differ; there was so much in VB theory that made sense, that told a chemical story rather than a physical one. Brush writes that even Mulliken admitted that the MO picture was less intuitive than the VB picture.

The imagery used by Hückel to explain why the MO picture appealed to him is based on a vibrating string, where the motion takes place through the effect of neighboring elements, but is delocalized through the whole string.

A vibrating string! Can you imagine a more alien picture to chemistry than that? Why on earth, then, would they suddenly drop a chemical theory in favor of a physical theory that views molecules as “strings”?

RH: Hey, maybe we were in on string theory before contemporary physics.

SS: Joking is fine, but let me make it even harder on you, Roald: was there ever a real reason to favor one theory over the other? When prominent advocates such as Slater and van Vleck wrote in so many words that the two theories are ultimately equivalent?

RH: Let’s just talk about that for a moment. They are equivalent for H_2 , i.e., VB + ionic structures = MO + configuration interaction = different orbitals for different spins, as we teach our students. But go a tad beyond H_2 and they become at the zeroth level – that’s the level practicing chemists find theory of use – nonequivalent.

PH: I disagree. A simple way to see the MO–VB equivalence in polyatomic molecules is to start from the MO wave function and to localize the orbitals. This does not change the total wave function and gives you a picture of the molecule that is very close to the VB one (this is what van Vleck showed). The equivalence carries over to the electron-correlated level. Already in the forties Coulson and Fischer proposed a clever way to write a VB function which is now the essence of modern methods, like the generalized valence bond method of Goddard. Each bond is described as a pair of overlapping orbitals, each of which being slightly delocalized on the other center.

RH: That’s what I meant by different orbitals for different spins.

PH: Which implies that such a VB description of the chemical bond already includes a good deal of electron correlation, while MO theory needs a complicated wave function with hundreds of configurations to achieve the same exactness.

RH: Philippe, this is sophistry. Each wave function explores correlation space, so to speak, in a different way. For one molecule a VB function tells you which configurations are important; for another the MO function guides you to the weights to be given to important ionic states.

SS: So, with equivalency being recognized so early, why, against all logic, should chemists have followed the pied piper of MO to immerse themselves in this strange physical theory rather than stay with their good old friend, VB theory?

RH: Gee, that’s not the way people who knew Robert Mulliken would characterize him, as a pied piper. And though Charles Coulson was a wonderful teacher, in person and in his *Valence* book, he was not an intellectual seducer.

Maybe MO stands for *more opportunities*. Sure, it began on the physical side, but step by step MO theory converted one community after another – first physicist-type spectroscopists working on diatomics (take the bond length trends in the excited states of C_2) in the thirties, then more chemical one trying to understand polyatomics through Walsh’s rules, then the ESR community by spin densities, and physical organic chemists through the best demonstration of them all – synthesis – of the stability of various Hückel systems, and inorganic chemists through Leslie Orgel’s studies and the Dewar–Chatt–Duncanson picture.

And VB theory – well, after Pauling it degenerated to unproductive counting of resonance structures. And its failures, from O_2 to cyclobutadiene, were apparent. And you guys were still in diapers.

SS: Please, those supposed failures are a calumny. We’ve written briefly about them elsewhere, but let us recount the story here.

Take for example the celebrated “failure” concerning the O_2 molecule. Maybe this matter is as shrouded in mystery as the discovery of the element that you and Carl Djerassi wrote about. Very curious about the myth that almost “killed” VB theory, we went back to the original papers to see with our own eyes whether Pauling had ever said that O_2 must have a doubly bonded singlet ground state, $O=O$. And guess what? In his landmark paper, Pauling was very careful to describe the molecule with two three-electron bonds, and so did Wheland in his book, and Pauling in his popular undergraduate textbook.

RH: I learned chemistry from it at Columbia ...

SS: Pauling taught that O_2 is paramagnetic with two three-electron bonds. And not only that: in a 1934 *Nature* paper, Heitler and Pöschl considered the O_2 molecule with VB principles and argued lucidly that, “The $^3\Sigma_g^-$ term [is the one] giving the fundamental state of the molecule.” It is true that Pauling did not acknowledge the earlier MO prediction of Lennard-Jones ... The Lennard-Jones paper is cited, but only as the origin of the term symbols Pauling was going to use for molecules such as C_2 , N_2 , etc.

RH: Typical ...

SS: But this is a personal failing, Pauling’s, not the theory’s. Scientifically, I find no reason to patch this “failure” onto VB theory. It is beyond me how the myth of this “failure” grew and spread so widely.

RH: Well, an 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 $O=O$.

PH: ... a naïve application.

SS: You’re creating a paper tiger, Roald. As I told you, the simplest VB theory has no trouble with dioxygen.

RH: It’s pretty complicated, what you have to do to get it right.

SS: Not at all! In fact, there exists a qualitative VB theory that expresses energies in terms of β and S parameters,

just like qualitative MO theory. This back-of-an-envelope theory tells you immediately that the diradical option, two three-electron bonds in the π system, is favored over the double-bonded option that displays one π bond and one four-electron repulsion in the other π plane.

PH: The same model leads you immediately to a simple derivation, one that any graduate student can master, that explains, almost trivially, the aromaticity/antiaromaticity concept and the $4n+2/4n$ rule as applied to cyclic ions like cyclopropenium, cyclopentadienyl. This was published first in 1963 by Fischer and Murrell. You can read about this in a recent paper we dedicated to Jack Dunitz.

Even if the demonstration of the Hückel rule is less direct in the VB scheme than in the MO one, what matters is that this rule as well as the concepts of aromaticity and antiaromaticity are accounted for in both MO and VB theories.

SS: Let me second Philippe's comment, and emphasize again that the negative image of VB theory is based on myths. VB theory was once poorly applied and forever marked as a failure. Does this make scientific sense to you, Roald?

RH: You're right, Sason and Philippe: I shouldn't have said that these are failures. But even so, even though all of these chemical conclusions could have been obtained from VB theory, they weren't. Look, people want theories to make predictions, preferably risky ones. They also want theories that explain many things, that tell a good story, that form a framework for understanding (actually VB theory did, but only because Lewis's bond, the chemist's bond, is such a useful concept). Theories should be portable, used by anyone. Why do you think the orbital symmetry control ideas of Woodward and myself made such an impact? They could be understood and applied by any intelligent graduate student.

PH: Wait a minute; you can have a VB-based theory of pericyclic reactions. Oosterhoff came up with one right away. Goddard followed with his phase continuity principle.

RH: After we did it.

PH: Even if after, still it is important to show that VB theory has this capability. The Woodward–Hoffmann rules transcend MO theory, and hence can be formulated in both languages.

RH: After the fact, *havivi*. Molecular orbital theory is so simple.

SS: Only because we have had two generations of textbooks. And great teachers, like you, Charles Coulson, Edgar Heilbronner, Lionel Salem, and the late Jeremy Burdett. VB theory had no chance because our generation was taught that it is a flawed theory, despite the absurdity of this judgment. I find it like a war of religions; one of the two parties must die. An active VB theory, living side by side with MO theory, would have certainly done these things.

RH: Maybe, in some alternative universe. MO theory is productive, right here, in ours. It gives people ideas for

experiment, for new molecules. Tell me something new, tell me something important that was predicted by VB theory in the last 60 years. Or, if not predicted, just explained more neatly.

PH: I'll give you some. I'll talk about concepts and paradigms, and not touch on all the methodological developments by so many ingenious people ... Roy McWeeny, Bill Goddard, David Cooper, Mario Raimondi, Gabriel Balint-Kurti, Joop van Lenthe and the late Joe Gerratt, and recently Wei Wu and Qianer Zhang, and ...

SS: Spare your breath, Philippe; the man asked for some stories!

PH: Here's one, and not even ours: You can cast VB theory into the formalism of Heisenberg, or magnetic, Hamiltonians. These are great tools that can deal with ground and excited states. Ovchinnikov and Malrieu separately used this approach for conjugated hydrocarbons and metallic clusters. You can predict relative stabilities of different isomers of polyenes, Hund's rule violations, and the ground-state multiplicities of exotic compounds like trimethylenemethane and so on, with a single drawing of the most spin-alternant structure. So simple and beautiful!

SS: A new bonding type that was found through a VB model is the ferromagnetic bonding that Paul Schleyer, Bill Goddard, and we discovered in lithium clusters with maximum spin and no electron pairs. These clusters are reminiscent of Bose–Einstein condensates, but they can be bound by as much as 12 kcal/mol per single Li atom. Imagine, bonding without electron pairs or doubly occupied MOs, which can reach 12 kcal/mol per atom! The effect of promotion energies, which is a VB concept, was highlighted so nicely by Bill Goddard and Emily Carter in their treatment of multiple bonding. It is now accepted that this is the stumbling block for descriptions of multiple bonding between heavy elements, and the peculiar geometries of some of these molecules, such as trans-bent double bonds or bridged structures.

PH: A story in which the two of us were involved is that of delocalization in benzene. It took 12 years to drive home the notion that the π -electrons of benzene have a dual property: On the one hand, the π -system is distortive and prefers a bond-alternated structure, on the other hand it is stabilized by resonance. I remember my shock when I saw the paper Sason submitted to *Nouveau Journal de Chimie* in 1984.

SS: Don't be shy, Philippe — tell the full story! You thought I was crazy. This is what you told me in my first day in Orsay.

PH: I thought the idea was either crazy or ingenious. But remember, Sason, I was one of the seven referees of your paper and, despite my suspicion about your sanity, I was in favor of accepting it.

SS: You mean the paper, or my sanity?

PH: The paper. It took me a little longer to get used to your kind of sanity. Eventually it was my turn to be taken

as a lunatic (by some referees), when I joined you in this long fight against prevailing opinions.

The idea took hold; finally, a beautiful connection to experiment was made by Haas and Zilberg, who showed that the frequency of the bond-alternating vibrational mode is exalted in the ${}^1B_{2u}$ excited state of benzene. This is general. For example, the Siegel molecule, tris-1,3-cyclobutano-benzene, which exhibits bond alternation in the ground state, acquires a local D_{6h} symmetry in its first excited state. Just imagine, you disrupt the π -delocalization by excitation and the deformed benzene nucleus regains its D_{6h} structure!

SS: We tend to focus too much on organic chemistry. There's Clark Landis's great work in applying VB theory to transition metal complexes with unusual structures. Mike Robb, Fernando Bernardi, and Massimo Ollivucci showed the importance of VB ideas in photochemistry. In fact, in the dynamics community there is an uninterrupted chain of VB usage from London, through Eyring, M. Polanyi, and all the way to Wyatt, Truhlar, and others in the present. And let's not forget what physicists did with VB theory, for example Anderson's treatment of metals and other materials in terms of resonating valence bonds.

Aren't these VB success stories?

RH: Sason, Philippe — I do like these stories. I also am not stupid, I know of others — the old and still impressive story of the avoided crossing of ionic and covalent curves, which makes such easy sense in a VB perspective, for instance. Or the properties of conical intersections in general.

I do note a curious inversion from what happened in the thirties in how *physical* these tales sound — spin states, spectroscopies. I don't think you'll convert organic chemists with them.

PH: Yes, Roald, Pauling was smart enough to disguise all these "physical" elements of VB and packaged it as simple resonance theory. This was good for the 1930s, but now chemists have more theoretical savvy, and can digest these bits of physics, couldn't they?

RH: Maybe. Some of them think theory is computation, and dignify that with the name of physical insight. The best physicists I've known — people like Ed Purcell — were after a quality of understanding that is ... almost chemical.

SS: Perhaps we're all off track. The MO–VB swings may have had nothing to do at all with "failures" of one theory and "successes" of another — in the end what tipped the balance in favor of MO may have been simply the computer implementation of MO-based theories. Chemists are a practical lot; they simply went where they could calculate.

RH: As they are doing now with the software available — it's amazing what gains prominence just because there is a button in *Gaussian* to do it!

But I still want to hear what modern VB theory has given us.

PH: Let me give you something more chemical then. A general mechanism for barrier formation is provided

by the valence bond state correlation diagram (VBSCD). The VBSCD leads to a general expression for an activation barrier, and allows correlations, or predictions of reaction barriers to be made from simple properties of the reactants, or substituent effects, solvent effects, etc. For example, S_N2 barriers are simply related to the ionization potential of the nucleophile and the electron affinity of the substrate. For radical reactions, and in particular hydrogen abstractions, the barrier is related to the singlet–triplet gap of the bond that is broken. The model is very general and applies to all kind of reactions.

SS: The prediction that nucleophilic attacks on cation radicals should follow the LUMO is a VB prediction. Similarly, the prediction that radical substitution reactions proceed by inversion of configuration or with a certain regioselectivity can be made only with VB theory, and so is the derivation of selection rules for electron transfer and substitution reactions of radical ions with nucleophiles and electrophiles.

Stereochemistry and predictions of barriers from simple properties of reactants — aren't these real, novel, predictive, and interpretative contributions to chemistry?

RH: I like these stories. But they are drops upon the ocean.

SS: From drops come brooks, then mighty rivers. It matters how people are taught. Your own work has played a significant role in brainwashing the community (maybe the way Pauling did in his time), so that they think MOs are the only thing there.

RH: We have to get out of this ... unseemly discussion somehow. You know, out there are people who don't believe that either orbitals or resonance structures exist, and that it's all densities.

SS: Yes, some of my best friends. But, I doubt that chemists will replace their orbitals and resonance structures with something that is only computable like density; that is, if they want to think about chemistry. The greater danger I see is that, because of the facility of doing calculations these days, chemists will simply drop the entire qualitative wisdom of both VB and MO theory. How many chemists you think still remember to do Hückel theory?

RH: I have an idea. A standard technique in marriage counseling (and I do think that MO and VB are a partnership) is to have the two parties stop and repeat, with an effort at understanding, what was said by the *other* partner. Can we try that?

PH: Let's. Here is what I think MO theory is good at: MO theory is more portable in all problems where the delocalized description of electrons is essential for understanding the phenomenon. As such, it is great for large molecules. For these, MO wave functions are compact while VB wave functions are cumbersome. For example, MO theory is excellent for understanding chemical structures of molecules such as ferrocene, where classical VB representations look somewhat ... repulsive. This is why

the MO picture for these exotic molecules was perceived as so refreshingly elegant when it was first presented by Dunitz and Moffitt.

SS: Your own investigations of many molecules highlighted time and again this elegance, and generated beautiful paradigms like the isolobal analogy. The Wade–Mingos rules for clusters have not yet found an easy analogue within VB theory. Electronic spectra, photoelectron spectra, electron transmission spectra, electron momentum spectra – all these are more easily interpreted with MOs. In reactivity too, stereochemical problems are easier to grasp and predict with MO theory, as demonstrated by the Woodward–Hoffmann rules and by frontier MO theory.

RH: VB theory is superb at relating localized chemical actions to each other. This is why your correlations of configurations are such an economic way of analyzing many kinds of reactivity. VB is the natural language for questions which broach electron dynamics – how is charge transferred, how do electrons move in the course of reaction? It has this natural connection to spin Hamiltonians, with an easy way into describing all kinds of magnetic phenomena.

PH: Could we just forget about this “what’s good about this theory or the other” stuff? I would rather speak about the bridges between the theories – you should like this, Roald: you devoted your Nobel lecture to building bridges. Around the seventies, some methods were developed to map MO-based wave functions to VB wave functions. Any MO-based wave function can be written as a linear combination of VB structures; the reverse is of course true also.

RH: A good connection between the theories is in fact made by thinking of localized orbitals, which are very much the orbitals of valence bond thinking. For those properties of a molecule that depend on all the occupied MOs, either viewpoint – “canonical” delocalized MOs, or localized orbitals (i.e., VB) – will give the same results. Such properties are total energy, distances, total dipole moment, etc. For those properties that depend on one orbital (ionization, electron affinity), or two (spectroscopy), or some subset of orbitals, one could begin from a localized VB viewpoint (e.g. as you have done for the C–H bond ionizations in CH_4^+). But one would be led back to the canonical MOs. They give a more direct entry to the problem.

The really interesting question to me is, what kind of observable is reactivity? Does it depend on one orbital (frontier control) or many?

SS: Let me respond in Philippe’s spirit of building bridges. It depends on the type of reactivity problem. The stereochemical intricacies of many reactions depend on a single orbital (one from each reactant of course). In some cases, the stereochemistry depends on a product of two orbital overlaps, as in radical substitution reactions. Regioselectivity depends on a mixture of factors: usually one factor is a single orbital effect and the other is a

collective all-electron effect. Promotion energies between orbitals determine barriers.

PH: Roald, what Sason and you have said just proves that there is a nice bridge that walks you from MO to VB and vice versa.

RH: Shall we call it by the lovely French word, *passerelle*?

SS: I like it. The MO–VB struggle may have been important once, when the rivalry sharpened the chemist’s abilities to use quantum mechanics as a thinking tool in chemistry.

However, what is understandable and may even have been necessary in the fifties is now obsolete, unwarranted, and counterproductive. Seventy odd years after the nascence of the rivalry, today theoreticians and experimental chemists ought to know that there are two ways of describing electronic structure, which are complementary rather than exclusive of each other. If they seem different, it may be that because the truncation of the theories at their simplest form created a situation of incommensurate theories, to use Thomas Kuhn’s idea.

PH: The two theories are not really different. They are rather two representations, differently costumed shadows of the same reality. Done well, done rigorously, VB and MO theory converge to the same exact description. Each simple representation has characteristic advantages (so there’s life for shadows): 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.

RH: Taken together, MO and VB theories constitute not an arsenal, but a tool kit, simple gifts from the mind to the hands of chemists. Insistence on a journey through the perfervid bounty of modern chemistry equipped with one set of tools and not the other puts one at a disadvantage. Discarding any one of the two theories undermines the intellectual heritage of chemistry.

We are grateful to many colleagues for their helpful comments. We owe special thanks to Don Truhlar for his thorough and thoughtful critique of this work. We thank Louise Spence for her valuable advice, and Jerry Ohlinger’s Movie Material Store for some movie stills, including the one used on the cover.

Supporting Information Available: For the interested reader, additional references are collected in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

To Read

Berson, J. A. *Chemical Creativity: Ideas from the Work of Woodward, Hückel, Meerwein and Others*; Wiley-VCH: Weinheim, 1999.

Brush, S. G. Dynamics of Theory Change in Chemistry: Part 1. The Benzene Problem 1865–1945. *Stud. Hist. Philos. Sci.* **1999**, *30*, 21.

Brush, S. G. Dynamics of Theory Change in Chemistry: Part 2. Benzene and Molecular Orbitals, 1945–1980. *Stud. Hist. Philos. Sci.* **1999**, *30*, 263.

Nye, M. J. *From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines 1800–1950*; University of California Press: Berkeley, CA, 1993.

Servos, J. W. *Physical Chemistry from Ostwald to Pauling*; Princeton University Press: Princeton, NJ, 1990.

Gavroglu, K. K.; Simões, A. The Americans, the Germans, and the beginning of quantum chemistry: The confluence of diverging traditions. *Hist. Stud. Phys. Biol. Sci.* **1994**, *25*, 47–110.

AR030162A