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VB and MO: Two Powerful Theories that Nicely Complement One Another

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Abstract: Introductory chemistry textbooks often present valence bond theory as useful, but incorrect and inferior to molecular orbital theory, citing the electronic structure of O_2 and electron delocalization as evidence. Even texts that initially present the two theories on equal footing, use language that biases students toward the MO approach. However, these "failures" of VB are really just misconceptions and/or misapplications of the theory. At their theoretical limits, both VB and MO are equivalent, they simply approach that limit from different sides. Certain concepts may be easier to grasp with one theory or the other so that having a commanding knowledge of both is extremely beneficial. However, presenting one theory as superior to the other suppresses the ability to look at a problem from both sides and is therefore detrimental to students and the whole of chemistry. It is time for VB and MO to be taught on equal footing like the complementary theories they are.

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Introduction: The chemical bond is one of the fundamental pillars of chemistry. However, it is also one of the most difficult concepts for beginning students to grasp. Most introductory chemistry textbooks start the discussion of chemical bonding with Lewis structures, connecting atoms to each other, and with VSEPR theory, giving students an idea of the three-dimensional shape of molecules, based on the concept of electron repulsion. This then leads into valence bond (VB) theory and hybrid orbitals.

Finally, molecular orbital (MO) theory is introduced, and is often presented as a better or more correct theory with statements such as, "(VB) is a significant oversimplification that we partially compensate for by hybridization. Nevertheless, we can do better",[1] "some aspects of bonding are better explained by a more sophisticated model called molecular orbital theory",[2] and "molecular orbital theory is more powerful than valence bond theory because the orbitals reflect the geometry of the molecule to which they are applied."[3]

These texts then support their claims with statements such as: "this simple valence bond picture can't be right because it predicts that the electrons in (O_2) are *spin-paired*."[4] This supposed failure of VB to predict the electronic structure of O_2 is a common theme, even in texts that initially present VB and MO as equally useful theories that both have strengths and weaknesses.[5–8] Further support for the superiority of MO theory is taken from electron delocalization in molecules such as ozone where in VB "it appears that the two oxygen-oxygen bonds differ from each other",[1] and benzene where "the most accurate picture of the ⊠ electrons is (…) in accordance with the molecular orbital theory approach."[1]

Herein, we argue that VB and MO are equally valid approaches for the study of chemical bonding and, in particular, that VB does not break down in certain molecular species as has often been claimed. Our aim is to try to change the way VB is presented in introductory textbooks and thus its perception among working chemists (whose lingua franca is anyway the VB language). This commentary is directed to the chemical educator who may not be well-versed in the nuances of VB and MO theories. For a more detailed account, we refer the interested reader to previous work[9–11] and references therein.

VB and MO equivalency: Before specifically addressing the electronic structure of O_2 and electron delocalization, it should be noted that both VB and MO theories are exactly the same in their theoretical limits and, as such, any result that can be obtained with one can also be obtained with the other. The exact limit in MO theory requires building the wavefunction as a superposition of electronic configurations that allow for excitation of all electrons into all possible orbitals. On the other hand, the exact VB wavefunction is a superposition of configurations that include all spin pairings of all electrons in all orbitals. The equivalence of MO and VB has been known since the 1930s[12,13] and is particularly straightforward to prove for H_2.[9,14] Extensions to multi-electron/multi-orbital systems only requires more mathematics, but lead to the same conclusion – the two theories are identical even though their representations are different.[11,14–17] Yet despite these two theories being fundamentally the same, they have historically often been viewed as diametrically opposed to one another.[11,18]

Although mathematically equivalent, in the exact limit, MO and VB converge toward that limit along different directions. As the names suggest, valence *bond* theory considers a molecule as a collection of bonds, whereas *molecular* orbital theory views the molecule as a whole. At the introductory level, neither theory is discussed anywhere close to its theoretical limit. VB is presented as a single configuration of electrons in hybrid orbitals, spin paired in bonds, while MO is presented as a single configuration of molecular orbitals arranged in order of increasing energy and filled with electrons in accordance with Hund's rule. However, even at these simplest levels of approximation, MO and VB are not as different as they may seem and can be transformed back and forth even at the least accurate MO level of Hückel theory.[19] Furthermore, it is well known that if a set of orbitals is an acceptable solution to the Schrödinger equation, then any unitary transformation of those orbitals is also an acceptable solution. In fact, mathematically rigorous localization techniques,[20,21] yield hybrid orbitals, much like in VB theory. This transformation can be visualized with easy to use and freely available programs such as IBOVIEW[22]. While such programs are backed by rigorous theory, students (or educators) do not need to understand the intricacies of this theory in order to see the different orbital representations producing the same results and thereby understand their equivalence.

Despite this equivalency, it has been suggested that hybrid orbitals are "inappropriate models for the description of electronic energies and electron density within a molecule (as indicated by) photoelectron spectroscopic evidence"[23] and were "simply chosen by Pauling (…) so as to correspond to the supposed localized electron pair chemical bonds."[24] While such a claim is now widely recognized as unfounded,[25] and has been repeatedly refuted in great detail both in this journal[26–29] and elsewhere,[10,11,14] it is instructive to briefly summarize the situation here. The argument against hybrids goes that the photoelectron spectrum (PES) of methane shows two peaks in a 3:1 intensity ratio, corresponding to the triply degenerate t_2 and non-degenerate a_1 MOs, respectively, while the VB picture of methane shows four equivalent C-H bonds, supposedly leading to a single PES peak at odds with the experimental results.

This simple argument fails to consider that the PES measures the energetic difference between CH_4 and CH_4^+ and *not* the energy of the four equivalent C-H bonds in CH_4. If we start with the notion that CH_4^+ has three equivalent C-H bonds and one that is unique, having just a single electron, then there is of course no way to decide which of the C-H bonds is missing an electron. The correct wavefunction is thus a symmetry-adapted combination of the four possibilities (corresponding to ejecting one electron from each C-H hybrid) leading to two states with distinct energies: one that is triply degenerate and the other that is non-degenerate, exactly as is observed in the experimental PES.[14,27]

Misconceptions of VB: In the end, any "failure" of VB theory is also a failure of MO theory so that claims that MO correctly predicts the magnetic properties of the O_2 molecule while VB does not must be fundamentally flawed. Such statements most likely arise from the oversimplified assumption that VB and Lewis structures are the same thing. For example, the commonly drawn Lewis structure of O_2,  $:\ddot{O}=\ddot{O}:$, shows all electrons spin paired, resulting in an erroneously non-magnetic singlet state. On the other hand, the MO treatment of this molecule places a single electron in each component of the doubly degenerate ⊠* MO, correctly predicting a magnetic triplet state.

It is somewhat surprising that the preceding argument is so prevalent in introductory chemistry textbooks given that Pauling's original VB treatment[30] of O_2 predicted two 3-electron ⊠ bonds, resulting in a triplet state in agreement with experiment. Despite numerous reiterations of Pauling's original correct VB treatment of O_2,[11,14,31,32] many introductory textbooks still cite this as an example of the failure of VB and a reason for the superiority of MO over VB. This error stems from the belief that VB **requires** all electrons to be spin paired whenever possible instead of adopting the electron pairing scheme that results in the lowest possible energy. This wrong belief has caused much of the chemical community to teach this erroneous view for the past 90 years or so.

An error many textbooks make in describing electron delocalization with VB is in assuming that VB only allows for one possible spin pairing, so that the concept of resonance must be invoked as some sort of correction factor to make the theory agree with experiment. However, resonance is an inherent part of VB theory and appeared in Pauling and Wheland's original VB description of benzene.[33] Resonance is not a correction factor added to a flawed theory, but rather a means of taking into account the quantum mechanical indistinguishability of electrons. Sometimes, as in the case of the π electrons of benzene, an electron is equally likely to pair with either of its nearest neighbors and therefore both possibilities must be considered. It has been further shown that the "Hückel rules" for aromaticity/antiaromaticity can be explained by symmetry mixing of VB structures.[34]

Conclusions: Although unitary orbital transformations, symmetry-adapted structure combinations, 3-electron bonds, and the details of VB structure mixing are beyond the scope of introductory chemistry courses, that is not a sufficient reason to present VB as a failed or flawed theory that is inferior to MO theory. This undue labeling biases students towards MO and prevents them from digging deeper into the intricacies of VB. Indeed, upper level Physical[35] and Inorganic[36] Chemistry textbooks often discuss MO in depth while barely going beyond the General or Organic Chemistry treatment of VB. Some of these students then go on to become future Chemistry teachers and perpetuate the myth they were taught as undergraduates.

One of the consequences of this longstanding bias is that much more time and effort has been put into the development of MO rather than VB approaches. In addition, many powerful concepts initially developed by application of VB theory, such as oriented external electric field catalysis,[37] two state reactivity,[38] and charge-shift bonding[39] have been slow to take hold among the chemical community due to a misplaced general mistrust of VB. Despite this not so encouraging environment, there have been notable advances in VB theory[40–43] such as the BOVB[44] and SCGVB[45] methods. Like the many different flavors of MO methods, these different versions of VB complement each other and agree on their predictions of fundamental molecular properties such as those described herein.

Both VB and MO are equally valid attempts to conceptualize the process by which atoms or larger fragments come together to make molecules. These two theories are simply different ways of looking at the same problem and each of them has its strengths and weaknesses, so that certain concepts may be easier for some students to understand from one framework or the other. Of course, a different student may be more comfortable with the other framework for the same exact problem. When VB is labeled as a failure, students question the point in learning it rather than focusing on the "correct" MO theory. Let us stop this erroneous view which has been taught to generation of chemists for the past 90 years or so! More even-tempered language in introductory textbooks would enforce the idea of embracing both VB and MO theories and the benefits of looking at a problem from multiple viewpoints.

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