Commentary

Teaching Molecular Geometry with the VSEPR Model

by Ronald J. Gillespie

The VSEPR model is widely known and is widely used for understanding and predicting molecular geometry, so it might seem that there is little more to say on the topic. However, there are several reasons for writing this commentary:

- The VSEPR model is taught mainly as an empirical model at the freshman level and its usefulness in more sophisticated forms, particularly at higher levels, is not so widely known.

- The physical basis of the model is not always understood, thus, it is often taught incorrectly.

- It is not always fully appreciated that the VSEPR model is completely independent of the valence bond theory and consequently the two are often confused.

Empirical Version

The simplest presentation of VSEPR is the empirical model based on the assumption that the valence shell electron pairs in a Lewis structure keep as far apart as possible, that is, they appear to repel each other *(1–7)*. This assumption leads to the well-known shapes for AX_nE_m molecules, where A is the central atom, X a ligand, and E a lone pair. Deviations from the regular polyhedral shapes are rationalized by the following well-known assumptions or rules:

1. Lone pairs repel more strongly than bond pairs.

2. The repulsion exerted by a bond pair decreases with increasing electronegativity of the ligand.

3. Multiple bonds repel more strongly than single bonds.

These rules can be rationalized in terms of the regions where an electron pair is most probably to be found, called electron pair domains.

Electron Pair Domain Version

The idea that the exact position of an electron cannot be determined and that it can conveniently be represented by a probability or charge cloud is usually presented early in any introduction to bonding. This provides the background for a version of the VSEPR model in which each valence shell electron pair is represented by a charge cloud or domain in which it is most probably to be found *(2, 3, 4, 6)*. The differences between the shapes and sizes of bonding and non-bonding domains then gives a rationalization for the rules used to account for deviations from shapes based on the regular polyhedra. A bonding domain is confined to the region between two atomic cores, whereas a lone-pair domain is attracted by only one core so it spreads out as much as possible around this core and has a greater angular spread than a bonding pair domain, causing angles between lone pairs and bonding pairs to be larger than between bonding pairs. Increasing the electronegativity of the

ligand decreases the size of a bonding pair domain, causing it to occupy less space in the valence shell of the central atom, A, thus decreasing the angles involving this bond. Multiple bonds increase in size as the number of electron pair domains in the bond (one, two, or three pairs) increases, so that bond angles increase with increasing bond multiplicity.

At this level the VSEPR model provides an explanation for the geometry of a very large number of the simple AX_mE_n molecules that are encountered in a general chemistry course, although there are exceptions that can only be understood in terms of a more sophisticated treatment of the model *(2, 3, 4, 6)*. Many instructors will not wish to go further than this basic level in presenting the VSEPR model in their first-year classes. However, it is important that instructors should have some understanding of the physical principles underlying the VSEPR model and, in particular, of why electron pairs are almost always found in pairs and why they appear to repel each other. And, of course, this is also important for students in higher level classes. This understanding is provided by the Pauli principle, which describes a very important and fundamental property of electrons that has far-reaching consequences in chemistry.

Pauli Principle

In the presentation of the VSEPR model as an empirical model no explanation is given of the nature of the repulsive forces between electron pairs or of why electrons in molecules are almost always found in pairs. It is sometimes stated that the repulsive forces between electron pairs are electrostatic, but this is not correct because the repulsive forces between electron pairs arise mainly from the operation of the Pauli principle. If only electrostatic forces were operating there would be no reason for electron pairs to form. In its most general form the Pauli principle states that the wave function for a many-electron molecule must be antisymmetric to electron interchange *(8–11)*. Its consequence is that electrons with the same spin have a zero probability of being found at the same location, and an increasing probability of being found at an increasing distance apart. In other words, electrons with the same spin keep as far apart as possible, while electrons of opposite spin have no effect on each other and may even be found at the same position in space if electrostatic repulsion is ignored *(8–11)*. It can, perhaps, be useful to think of opposite spin α and β (or spin-up and spin-down) electrons as existing in two independent "worlds" (two independent, but overlapping, sets of three dimensions) in which, if we ignore their mutual electrostatic repulsion, the α electrons do not "see" the β electrons in the other "world" and so they have no influence on each other's behavior, whereas electrons of the same spin in the same "world" have to share the space available to them and thus, keep as far apart as possible. This tendency for same spin electrons to keep apart is often referred to as a "Pauli
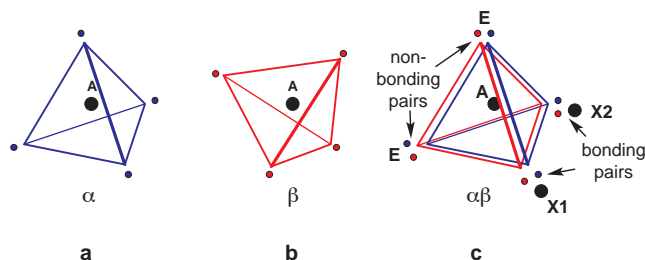
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Figure 1. The Pauli principle determines the most-probable distribution of the electrons in a valence shell. (a) The most-probable relative arrangement of four α-spin electrons. (b) The most-probable relative arrangement of four β-spin electrons. Both arrangements may adopt any relative orientation in space. (c) In the presence of the nuclei of two combining ligands (X1 and X2), as in H_2O or SCl_2, the two tetrahedra are brought into approximate coincidence at these two positions (and therefore at all four tetrahedral positions), thus forming two bonding pairs and two lone pairs (E) with an overall tetrahedral arrangement.
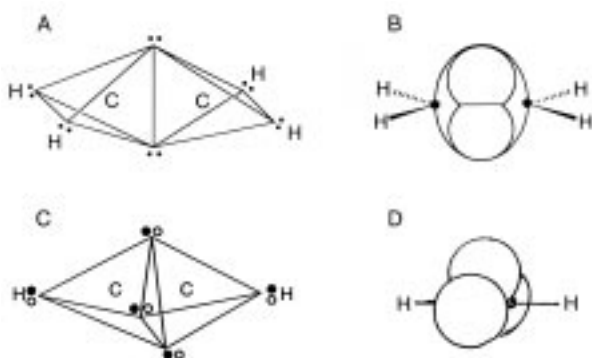

Figure 2. VSEPR theory descriptions of multiple bonds. (A) Electron pair arrangement in a double bond, (B) the domain representation of a double bond, (C) electron pair arrangement in a triple bond, and (D) the domain representation of a triple bond.

force" as, for example, when we talk about the Pauli repulsion between closed-shell atoms that prevents any substantial overlap of molecules. No further explanation of the Pauli principle can be given: it is a fundamental property of an electron, like its mass and charge. First-year students, of course, normally meet the Pauli principle in the context of the orbital model in the form that no more than two electrons, which must be of opposite spin, can occupy an orbital. This less general form of the Pauli principle must also be accepted without further explanation as a fundamental property of electrons.

In an AX_n molecule in which A has an octet of electrons and there are at least two ligands X, the Pauli principle, together with electrostatic attraction between the electrons and the positive core of the ligands, leads to the formation of four pairs of electrons of opposite spin with a *most-probable* tetrahedral arrangement (Figure 1). This is the arrangement that keeps four electrons of α spin as far apart as possible, and four electrons of β spin similarly as far apart as possible, while α- and β-electrons may come together to form a pair as a consequence of the attraction of the positive core of a ligand. It is important to emphasize that this is not the actual arrangement of the electrons, but only an arrangement that is more probable than any other. How much more probable depends on the strength of the attraction provided by the ligands. In the absence of the ligands, the electron density distribution of an atom is spherical, but with increasing electronegativity of the ligands the valence shell electrons become increasingly localized into pairs *(9).* Similarly, 10-electron valence shells have a most-probable arrangement of five pairs of opposite spin electrons with a trigonal bipyramidal geometry and six pairs an octahedral geometry. Thus the Pauli principle provides the physical basis for the domain version of the VSEPR model.

Two or even three separate bonding electron-pair domains can be localized between two atomic cores, provided

that the attraction exerted by the atomic cores is strong enough to overcome the mutual repulsion of the electrons. This attractive force increases with increasing electronegativity and decreases with increasing size of the atoms concerned. Thus, multiple bonds tend to be restricted to small atoms with large electronegativities (such as C, N, and O), while multiple bonds between larger atoms with smaller electronegativites are much less common. The Pauli principle leads to a description of a multiple bond as consisting of two or three of the four valence shell electron-pair domains around each of the multiply bonded atoms (Figure 2). This description is very similar to the "old-fashioned" model of multiple bonds that represented them as formed by the sharing of the edges or faces of two tetrahedra and as is often represented in ball-and-stick molecular models by bent bonds.

Comparison: VSEPR Model and Valence Bond Theory

It is important to recognize that the VSEPR model provides an approach to bonding and geometry based on the Pauli principle that is completely independent of the valence bond (VB) theory or of any orbital description of bonding. The VB theory is often taught at more or less the same time as the VSEPR model, and this can be a source of considerable confusion, as it can lead to the belief that the VSEPR model depends on, or is derived from, the VB theory, where-as, in fact, it is completely independent of the VB theory. The VB theory gives a simple and very approximate *description* of the bonding in a molecule, but in general it does not predict geometry. It assumes that a bond between two atoms may be described as being formed by the overlap of a singly occupied atomic orbital on one atom and a singly occupied orbital on the other atom. It is also assumed that a bond is formed in the direction in which an orbital, such as a p orbital, is most concentrated. For molecules such as CH_4, NH_3, and H_2O, this assumption does not predict the correct shapes: the concept of hybridization was introduced by Pauling *(12).* If it is *assumed* that the four bonds in methane are equivalent so that four equivalent hybrids are needed to describe them, then, using only the available s and p orbitals to construct the

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equivalent hybrids, these turn out to be the four tetrahedral sp^3 hybrids. In this limited sense the VB theory might be said to predict the geometry of CH_4 and give an approximate prediction of the geometry of H_2O and NH_3. However, there is no a priori reason for the assumption that the four bonds in methane are equivalent and that the four corresponding orbitals must therefore be equivalent. Unfortunately hybridization is frequently not fully explained so that just how this process of "mixing" atomic orbitals produces four orbitals of such a different shape from the atomic s and p orbitals is not clear to the student. Even the shapes of the atomic s and p orbitals are a mystery for most students, as no justification for them is normally given at the introductory level. They are often presented as the shapes of the corresponding electron density distribution rather than as the wave function (orbital) with its appropriate signs. Without these signs the formation of hybrid orbitals cannot be explained.

It cannot be too strongly emphasized that hybridization is not a physical phenomenon, but only a mathematical device that ensures that a bond can be described in terms of the overlap of a single orbital on one atom with a single orbital on the other atom. Hybridization does not produce any change in the electron density of an *isolated* free atom, which is always spherical. A change in the electron density only occurs with bond formation and a corresponding concentration of electronic charge in the bonding regions. In general the VB theory does not predict molecular shape, but only provides a method for describing the bonding in terms of the overlap of two appropriate orbitals when the geometry is known. For example, the deviation of the bond angle from the tetra-hedral angle in H_2O and NH_3 cannot be predicted by the VB theory, although the VSEPR theory predicts these bond angles to be $<109.5°$.

Multiple Bonds and VSEPR and MO Theories

Multiple bonds are described by the VSEPR theory, as shown in Figure 2. It can be seen that the VSEPR theory predicts the planar geometry of the ethene molecule. Moreover, because the two electron pairs forming the double bond are attracted towards each other by the carbon nuclei, the angle between them at the carbon atom decreases and the HCH angle correspondingly increases to a value larger than $109.5°$. The experimentally observed angle is $116°$.

The multiple bonds in ethene and ethyne are, however, described in a different way in the vast majority of introductory texts using a type of "hybrid" MO–VB description. This description necessitates the introduction of two additional new concepts: (1) Two p orbitals can overlap in a "sideways" manner rather than overlap in the direction in which they are most concentrated; (2) The same set of s and three p orbitals can be hybridized in different ways, to give four sp^3 orbitals in methane, three sp^2 orbitals in ethene (leaving a p orbital "unhybridized"), and into two sp orbitals and two "unhybridized" p orbitals in the case of the ethyne molecule, making the concept of hybridization even more mysterious for the student. The sp^2 hybrid orbitals are generally intro-

duced with the justification that ethene is known to be a planar molecule with $120°$ (actually $116°$) bond angles at carbon. So this bonding description clearly does not provide an *explanation* of the geometry. The VSEPR description of double and triple bonds is quite straightforward and leads to the correct prediction of geometry while it does not need the introduction of the concepts of "sideways overlap"and different types of hybrid orbitals.

This "VB–MO" description of the bonding in ethene is often extended to give a rough MO description of the bonding in benzene. However, the resonance description is quite adequate for the first-year course. This same type of bonding description, which is essentially an MO description, is also frequently used to describe diatomic molecules such as N_2, O_2, NO, and CO, particularly to account for the paramagnetism of the oxygen molecule. However, the bonding in all these molecules (with the exception of O_2), can be described by the VSEPR model if in odd-electron molecules a single unpaired electron is treated like a pair. So it is important to consider whether it is really worthwhile to introduce a whole new description of bonding just to account for an interesting, but by no means particularly important, property of oxygen. Moreover, Linnett has shown in his double-quartet model that a modification of the VSEPR model that recognizes that the electrons in linear molecules are not necessarily all paired, gives a satisfactory explanation of the paramagnetism of oxygen *(10)*.

VSEPR and Chemistry Majors' Courses

If the VSEPR model is presented at the empirical level or in its domain version (as is usually the case in the general chemistry course), the Pauli principle in its more general form should be presented in a higher-level course, including its importance for understanding the VSEPR model, as well as the Linnett model *(10)*. A course on bonding and geometry or an inorganic course would be a suitable place for this material. The inorganic course in particular provides many opportunities for elaborating and exemplifying the VSEPR model *(3, 4, 8)*. Finally, the deeper understanding of the model provided by the AIM analysis of the Laplacian of the electron density and the electron localization function (ELF) could be discussed at the graduate level *(13, 14)*.

Conclusions and Recommendations

1. In view of the limitations of both the VB and MO theories for understanding molecular geometry and the difficulties they introduce for the student, the first introduction to molecular geometry should be through the simple and easily understood VSEPR model. Most instructors will probably not wish to go further than the empirical version or its domain version, leaving a treatment of the Pauli principle and its importance for an understanding of the VSEPR model to later courses. Nevertheless it is important that instructors teaching the VSEPR model should have a good understanding of its physical basis.

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2. The introduction of the VB theory should follow the VSEPR model, emphasizing that it is quite independent from the VSEPR model. Like VSEPR it provides a useful yet approximate description of bonding; unlike VSEPR, it does not provide an explanation for molecular geometry.

3. As the usual hybrid VB–MO description of the bonding in ethene and related molecules introduces new concepts that are difficult for the student to understand, and because it does not explain, for example, molecular geometry including the planarity of the ethene molecule, there is no reason for it to be introduced in the general chemistry course. In contrast, the VSEPR model gives a perfectly satisfactory description of the bonding that follows directly from the Lewis model and provides an explanation of molecular geometry.

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Ronald J. Gillespie is in the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1; gillespi@mcmaster.ca.