On the Role of d Orbital Hybridization in the Chemistry Curriculum

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In many respects, the chemical bond is at the heart of chemistry, and therefore chemical bonding theory must be taught at the introductory level. Chemical bonding is usually first presented at the general chemistry level by introducing valence bond (VB) theory as a means to explain the molecular shapes derived from the valence shell electron pair repulsion (VSEPR) model. After developing the concepts of hybridization and resonance, molecular orbital (MO) theory is presented as an alternative view. MO theory is often presented as a superior or more advanced theory citing "failures" of VB such as the paramagnetism of O_2 and the explanation of excited electronic states.

However, a more in-depth application of VB *(1)* shows that resonance between two paramagnetic structures with two 3-electron π bonds (Figure 1A) is more stable than resonance between two diamagnetic spin paired structures each with a 2-electron π bond and a 4-electron repulsion (Figure 1B). The correct ordering of the low-lying excited states of O_2 can then be obtained through a four-structure VB calculation involving the four structures in both A and B. Thus, the "failures" of VB are really just due to oversimplifications. While it could be argued that VB theory fails because it requires an overly complex application to describe something as simple as the electronic structure of O_2, it could also be argued that MO theory fails because it requires an overly complex application to describe something as simple as the bent structure of water. Of course, MO theory does elegantly describe the correct structure of water, but only by an application that is beyond the scope of most introductory level chemistry courses.

Students often wonder why they have to learn two complicated theories that describe the same thing. If one theory is better, why not learn that one and forget about the other? It is important to emphasize to students that neither theory is correct. By definition a theory is never correct. In addition, neither theory is better than the other. They approach the exact wavefunction from different directions[1] owing to differing approximations and each has its strengths and weaknesses *(2)*. The reason students need to be well versed in both is so that they can be adept at using the theory that best fits the problem at hand. For example, MO theory provides a clear picture of magnetic properties, spectroscopy, and delocalized bonding situations while VB works well for chemical structure, localized bonding, and bond making and breaking. In addition, it is useful for students to be able to mix the two theories where appropriate as in the case of ozone where the σ framework can be nicely explained using VB and sp^2 hybrid orbitals while the delocalized π orbitals can be described by MO.

A particularly interesting problem for both theories is the explanation of the bonding in molecules with more than eight electrons around the central atom (hypervalent) such as octahedral SF_6. Most general chemistry texts do not attempt an explanation using MO theory and make use of six sp^3d^2 hybrid bond orbitals on the sulfur in a VB description. However, both MO *(3)* and VB *(4)* calculations have shown that the extent of d-

orbital hybridization in hypervalent molecules such as SF_6 is negligible. Although d orbitals do contribute to the overall bonding as polarization functions *(3e, 4)*, correlation functions *(3f)*, and as a means of stabilizing fluorine lone pairs *(3e)*, the stability of these molecules has more to do with the size of the central atom and to the high electronegativity of the outer atoms.

However, the idea of spd hybridization still appears in many undergraduate chemistry text books despite strong evidence to the contrary. Perhaps the reason is that the use of spd hybridization is so simple and conforms to the 2 electron bond picture seen in Lewis structures. However, as correctly stated by Schreiner, "the convenience of visually pleasing explanations for intricate chemical phenomena must not outweigh proper physical descriptions" *(5)*. In addition, most of the previous work on this subject focuses on d-orbital participation to the ground-state wavefunctions of hypervalent molecules rather than directly on the spd hybridization schemes currently taught. This article seeks to enforce sp^3d^2 hybridization in SF_6 and compare it to situations where d orbitals are not allowed to participate at all. A qualitative description of bonding in SF_6 will then be developed[2] and the role of d-orbital hybridization in the chemistry curriculum will be discussed.
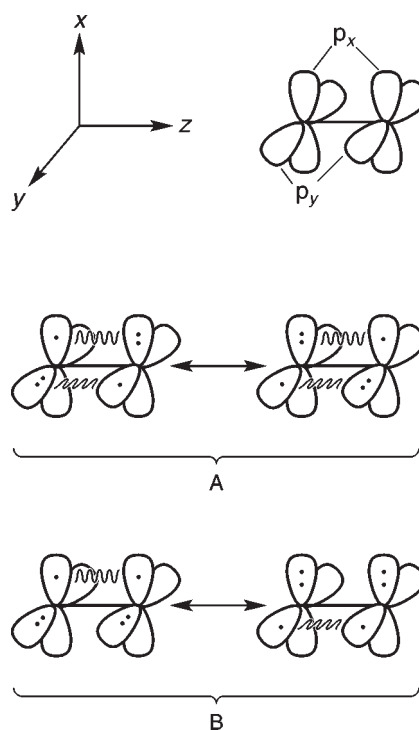

Figure 1 Application of VB shows that resonance between two paramagnetic structures with two three-electron π bonds (A) is more stable than resonance between two diamagnetic spin paired structures each with a 2-electron π bond and a 4-electron repulsion (B).
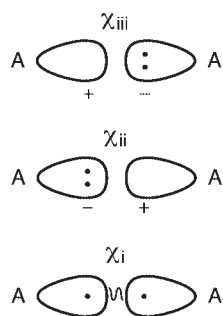
Figure 2. A VB description of the a σ bond in a diatomic AA would include three structures: χ_i is referred to as the Heitler–London (HL) structure and χ_{ii} and χ_{iii} are ionic structures.

Table 1. Relative Energies[a] of SF_6

Entry	d Orbitals[b]	Forced Hybrids[c]	Structures	Energy/ (kcal mol^{-1})
1	x		1	1305.8
2	x	x	1	1852.7
3		x	12	706.0
4			1	305.5[d]

[a]Energies relative to S + 6F at the ROHF/LANL2MB level. [b]x indicates sulfur d orbitals included in the calculation. [c]x indicates sulfur orbitals constrained to the hybridization scheme described in the text. [d]RHF/LANL2MB.

Theoretical Methods

The GAUSSIAN98 (6) suite of programs was used to optimize the geometrical parameters of SF_6 at the B3LYP (7)/6-31G* (8) level of theory. This combination of the B3LYP density functional method that includes some degree of electron correlation and the 6-31G* "double-ζ plus polarization" basis set yields geometric parameters in good agreement with experimental values (9). VB calculations (10) were then performed at this optimized geometry using the XMVB program (11). In the XMVB program electrons are paired to make structures analogous to common Lewis structures. For example, a VB description of the a σ bond in a diatomic AA would include three structures of the type shown in Figure 2 where χ_i is referred to as the "Heitler–London" (HL) (12) structure and χ_{ii} and χ_{iii} are "ionic" structures. These three structures can then be combined to create the VB wavefunction,

$$\Psi_{VB} = c_1\chi_i + c_2\chi_{ii} + c_3\chi_{iii} \tag{1}$$

All VB calculations utilized the LANL2MB basis set. This basis set is made up of the LANL2 effective core potential (13) that approximates core electrons (S:1s2s2p, F:1s) as an electrostatic potential while the valence electrons are described by a minimal basis set made up of a single basis function for each atomic orbital (AO). Owing to the absence of d functions in the LANL2MB basis set, for the calculations involving d orbitals (Table 1), a d-type function was added to the sulfur basis (14). Although this basis set is too small to be useful for quantitative results, it is sufficient for the qualitative bonding descriptions proposed herein.

Only electrons directly involved in bonding were included in the VB calculations (i.e., no contribution from fluorine lone pairs). All other electrons were frozen in MOs calculated at the restricted Hartree–Fock (RHF) (15) level. In each case, the fluorine s and p AOs directed towards the sulfur are free to mix in order to lower the overall SF_6 energy. The sulfur 3s, 3p, $3d_{z^2}$, and $3d_{x^2-y^2}$ AOs are either free to mix or constrained as described in the next section.

Although resonance mixing with ionic VB structures is expected to be important for an accurate bonding description (16), consideration of all possible electron spin pairings in order to create all possible VB structures would be both impractical and would confuse the desired qualitative SF_6 bonding description. Therefore, only "chemically significant" VB structures analogous to common Lewis structures were considered herein.

All energies are reported in kcal mol^{-1} relative to a sulfur atom and six fluorine atoms completely separated and calculated with the restricted open-shell Hartree–Fock (ROHF) (17) method along with the LANL2MB basis set.[3] In all calculations the sulfur atom lies at the origin with fluorine atoms along the x, y, and z Cartesian axes. The notation "$\phi_{a^{+(-)}}$" is used to indicate a hybrid, lying on the "a" axis in the positive (negative) direction. Readers requiring further details concerning theoretical methods are asked to contact the author directly.

Results and Discussion

When the 3s, $3p_{x,y,z}$, and $3d_{x^2-y^2}$ sulfur AOs are free to mix in any proportion to form six bonding orbitals on the central sulfur, the resulting energy is 1305.8 kcal mol^{-1} (entry 1, Table 1) with sulfur orbital mixing as described by

$$\phi_{z^+} = 0.768\,s + 0.635\,p_z - 0.079\,d_{z^2}$$
$$\phi_{z^-} = 0.768\,s - 0.635\,p_z - 0.079\,d_{z^2}$$
$$\phi_{y^+} = 0.768\,s + 0.635\,p_y + 0.040\,d_{z^2} + 0.069\,d_{x^2-y^2}$$
$$\phi_{y^-} = 0.768\,s - 0.635\,p_y + 0.040\,d_{z^2} + 0.069\,d_{x^2-y^2} \tag{2}$$
$$\phi_{x^+} = 0.768\,s + 0.635\,p_x + 0.040\,d_{z^2} - 0.069\,d_{x^2-y^2}$$
$$\phi_{x^-} = 0.768\,s - 0.635\,p_x + 0.040\,d_{z^2} - 0.069\,d_{x^2-y^2}$$

The sum of the squares of the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbital coefficients are both only 0.019 indicating that the d orbitals contribute far less than would be required for complete sp^{3}d^2 hybridization[4] in agreement with previous calculations (3, 4). If the hybrids are forced to adopt an sp^{3}d^2 configuration as in

eq 3, the total energy is substantially higher at 1852.7 kcal mol^{-1} (entry 2, Table 1).

$$\phi_{z^+} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_z - \frac{1}{\sqrt{3}}d_{z^2}$$

$$\phi_{z^-} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_z - \frac{1}{\sqrt{3}}d_{z^2}$$

$$\phi_{y^+} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_y + \frac{1}{\sqrt{12}}d_{z^2} + \frac{1}{\sqrt{4}}d_{x^2-y^2}$$

$$\phi_{y^-} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_y + \frac{1}{\sqrt{12}}d_{z^2} + \frac{1}{\sqrt{4}}d_{x^2-y^2} \qquad (3)$$

$$\phi_{x^+} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_x + \frac{1}{\sqrt{12}}d_{z^2} - \frac{1}{\sqrt{4}}d_{x^2-y^2}$$

$$\phi_{x^-} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_x + \frac{1}{\sqrt{12}}d_{z^2} - \frac{1}{\sqrt{4}}d_{x^2-y^2}$$

The problem of how to explain the bonding in SF$_6$ remains. Calculations do not support the use of sp^{3}d^2 hybrid orbitals, but how can six bonds be formed from one s and three p orbitals on S? The MO description of SF$_6$ *(18)* involves a combination of the sulfur 3s and 3p$_{x,y,z}$ AOs with a$_{1g}$, t$_{1u}$, and e$_g$ symmetry-adapted combinations of orbitals on an octahedral fragment composed of all six fluorine atoms as shown in Figure 3. Note that the highest occupied e$_g$ MOs are located exclusively on the fluorines (and distributed across all six fluorines) in agreement with the experimental observation that hypervalent molecules are most stable when the outer atoms have high electronegativity. Thus, the six bonds in SF$_6$ can be considered to be made up of four bonding orbitals and two nonbonding orbitals located primarily on the fluorines resulting in a bond order of 2/3 for each S−F bond and an energy of 305.5 kcal mol^{-1} (entry 4, Table 1).

From a VB standpoint, the bonding in SF$_6$ can be described using two, 2-electron bonds from sulfur sp hybrids pointing 180° away from each other and two, 2-electron bonds from sulfur p orbitals with the remaining four electrons located on two fluorine atoms as shown in Figure 4. Four resonance structures can be drawn keeping the sulfur sp hybrids pointing along the z axis and distributing nonbonded electrons among all fluorines as shown in Figure 5 (including formal charge). Eight more resonance structures can then be drawn with the sp hybrids lying along the x and y axes resulting in a 12-structure VB calculation with an energy of 706.0 kcal mol^{-1} (entry 3, Table 1), well below the forced sp^{3}d^2 result (entry 2, Table 1). Thus, the four sulfur s and p AOs mix to form four bonding orbitals that are spread over six bonding regions through resonance mixing.[5]

It is interesting to note the similarities between this VB description of SF$_6$ and the MO description presented above. Both place partial negative charge on the fluorines and both have a formal S−F bond order of 2/3. In addition, the linear four electron F−S−F bonding unit, made up of an electron in a p orbital on the sulfur spin paired with a fluorine electron and two electrons on the fluorine directly opposite, is similar to the four-electron, three-center (4e3c) bonding concept *(19)* previously used to describe bonding in hypervalent molecules *(20)*.
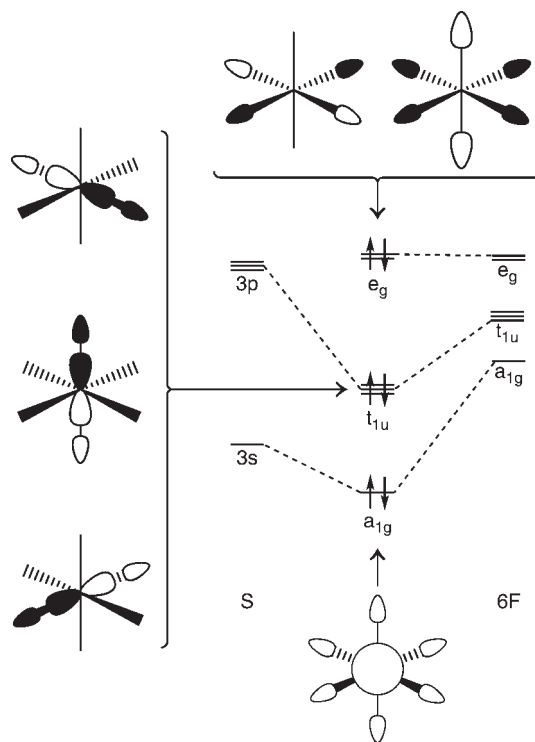

Figure 3. The MO description of SF$_6$ *(18)* involves a combination of the sulfur 3s and 3p$_{x,y,z}$ AOs with a$_{1g}$, t$_{1u}$, and e$_g$ symmetry-adapted combinations of orbitals on an octahedral fragment composed of all six fluorine atoms.
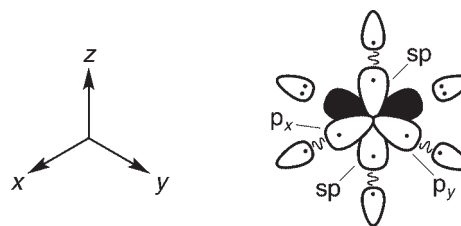

Figure 4. From a VB standpoint, the bonding in SF$_6$ can be described using two, 2-electron bonds from sulfur sp hybrids pointing 180° away from each other and two, 2-electron bonds from sulfur p orbitals with the remaining four electrons located on two fluorine atoms.
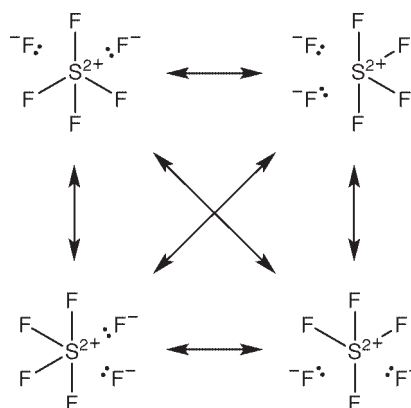

Figure 5. Four resonance structures can be drawn keeping the sulfur sp hybrids pointing along the z axis and distributing nonbonded electrons among all fluorines.

The Role of d Orbital Hybridization in the Chemistry Curriculum

Although the idea of spd hybridization is simple enough for general chemistry students to grasp and it works well to describe the bonding in hypervalent molecules, it is fundamentally flawed and therefore, in the author's opinion, should be removed from the general chemistry curriculum. However, the MO and VB treatments presented above, though having a sound theoretical base, may be beyond the scope of most general chemistry courses. The question is not how to teach bonding in hypervalent molecules to general chemistry students, but whether or not general chemistry students need a detailed description of bonding in hypervalent molecules.

Most general chemistry students will not go beyond a second-year organic course where bonding in the vast majority molecules can be adequately explained by sp, sp^2, and sp^3 hydrid orditals and simple Lewis structures. Although these students do not need an in-depth MO or VB description of chemical bonding, it is important for them to realize that they are learning an overly simplified model that does not hold in all situations. In many cases a strict sp, sp^2, or sp^3 hybridization scheme is inadequate even among molecules containing second-period atoms *(21)*, and an accurate picture of electronic structure cannot be represented by a single Lewis structure because Lewis structures "contain no quantitative information about atomic orbital involvement" *(3c)*.

After seeing molecules like SF_6 when discussing VSEPR and learning about hybridization in first row molecules, the curious general chemistry student will want to know about the bonding in hypervalent molecules. Bonding in hypervalent molecules can be introduced at a surface level as a means of illustrating some key scientific concepts rather than diving into the details of MO and VB theories.

For example, students can be told that bonding in hypervalent molecules is beyond the scope of general chemistry but involves resonance mixing among several VB structures some of which are ionic in nature. While not going into detail, this simple statement lets students know that there is more to chemistry than their first-year course (a point that is sometimes lost on first-year students). Interested students may be inspired to continue in chemistry to learn more. In addition, mentioning resonance mixing and the importance of ionic structures (a quick description of "ionic" structures may be necessary) prepares students for what will come in organic chemistry.

The role of d orbitals in hypervalent molecules serves as a good example of present day theory change. Students often see the scientific method as something that happened in the 1800s and in the present day all chemistry is known. Hybridization was a good theory based on the experimental evidence of the day. However, new computational methods have allowed chemists to probe deeper into the nature of bonding than ever before and as a result, evidence has been uncovered that casts doubt on sp^3d^2 hybridization. As instructed by the scientific method, when new evidence comes along that refutes an old theory a new theory must be developed. Although most general chemistry textbooks still rely on sp^3d^2 hybridization to explain bonding in SF_6, some are starting to acknowledge the limitations of this model *(22)*.

Furthermore, students often want their theories to be correct in *all* situations. Although at first chemistry may appear to have either right or wrong answers, at the forefront there

are no right answers only new discoveries. The idea of hybridization works well for carbon and first row molecules where the energetic cost of utilizing high-energy p orbitals is outweighed by the energetic advantage of increased bonding. This is not the case for SF_6 where use of d orbitals in hybrids is energetically unfavorable. Thus, hybridization is shown to not be an all-inclusive phenomenon, but rather a means by which a molecule sometimes can obtain the lowest energy possible.

Students continuing their study of chemistry will take advanced-level courses where more in-depth MO and VB descriptions of chemical bonding in hypervalent molecules can be presented. In addition, SF_6 serves as a good example of how MO and VB are not so at odds as many people think, but rather offer similar explanations from different perspectives. The reason that multiple theories such as MO and VB exist is because they are useful in different situations. In addition, SF_6 illustrates that both MO and VB are more complex than they may seem at first. This is a common theme in chemistry education where information is first presented at a simple level that can then be built upon in later courses.

For example, the concept of bond order is easy to use and useful for many simple molecules. In SF_6, however, the 2/3 bond order obtained by counting bonds (VB) or bonding orbitals (MO) fails to explain why the S−F bond in SF_2, with an apparent bond order of 1, has a slightly longer bond length (1.591 Å) *(23)* than the S−F bond in SF_6 (1.561 Å) *(23)*. A more in-depth treatment of the hybridization in SF_2 *(24)* shows that the 2s AO mixing coefficient is $1/\sqrt{8}$ as opposed to $1/\sqrt{6}$ in SF_6 where the s AO is evenly distributed over 6 bonds. Thus, the smaller s AO character of the S−F bond in SF_2 results in a longer bond length.

Furthermore, SF_6 provides an opportunity to discuss the importance of ionic structures and resonance mixing of ionic with covalent structures in VB theory. From an MO standpoint, fragment orbital mixing to form delocalized MOs in polyatomic molecules can be discussed. Furthermore, SF_6 illustrates that the concept of the 2-electron bond is not as all-encompassing as students would like. Deviations such as 4c3e bonds (which can be discussed from the standpoint of MO or VB or both) arise when they lower the total energy of the molecule.

Conclusions

In SF_6, d orbitals on the sulfur contribute far less than would be required for sp^3d^2 hybrid bonding orbitals. When complete sp^3d^2 hybridization is enforced, the total energy is substantially higher than alternative bonding descriptions with no sulfur d-orbital contribution. This is in agreement with previous studies that showed the d orbitals in SF_6 act as polarization functions, correlation functions, and to stabilize fluorine lone pairs rather than forming hybrids. Therefore, although attractive in their simplicity, sp^3d^2 hybrid orbitals should not be used to explain the structure and bonding of SF_6. Although not studied herein, the role of d orbitals in other hypervalent molecules is expected to be similar thus eliminating the need for spd hybridization in any form.

Although likely beyond the scope of most general chemistry courses, alternative bonding descriptions can be formulated that do not require d-orbital participation and highlight some of the more advanced points of MO and VB theories appropriate for upper-level classes. From the perspective of

molecular orbital theory, four bonding and two nonbonding MOs can be created by mixing the 3s and 3p AOs of sulfur with six orbitals formed from an octahedral F_6 fragment. From the perspective of valence bond theory, the 3s and 3p AOs of sulfur form 4 bonding orbitals that are distributed over the six S—F bonding sites through resonance mixing. The similarity in these descriptions serve as a good example of the similarities in MO and VB theories.

In the general chemistry curriculum SF_6 serves as a good example of present day theory change. Although most general chemistry texts still adhere to the sp^3d^2 hybridization model to explain the bonding in SF_6, the situation is slowly changing. Theories, by definition, are never "correct". They are simply models that help us understand a particular chemical phenomenon (in the present case, chemical bonding). Furthermore, SF_6 serves as a reminder that the bonding theories taught in general chemistry are overly simplified and are not applicable to *all* situations. These ideas are essential for chemistry students to grasp early on before theories get more complicated and the number of "correct" answers become fewer and fewer.

Notes

1. In their complete application, both MO and VB will converge on the exact wavefunction. For MO theory, this requires *all* electronic excitations into *all* virtual orbitals (full-CI) and for VB theory, this requires *all* possible pairings of *all* electrons in *all* orbitals. For practical reasons, neither complete application is possible thus necessitating various degrees of approximation.

2. For a more quantitative description of bonding in hypervalent molecules the reader is referred to refs *3* and *4* and references therein.

3. The small and inflexible LANL2MB basis set has more difficulty describing the bonding situations than for atomic calculations. Therefore, the error in the SF_6 calculation is greater than for S + 6F leading to positive relative energies.

4. Complete sp^3d^2 hybridization would require mixing in two full d orbitals. If one considers the "d^2" to mean that only two d orbitals contribute *to some extent*, then the hybridization in PF_5 would have to be sp^3d^3 because, by symmetry, the $3d_{z^2}$, $3d_{x^2-y^2}$, and $3d_{xy}$ orbitals all contribute to the bonds *to some extent*.

5. The 12-structure VB calculation is still incomplete and therefore substantially above the MO calculation. A complete VB description requires structures of the F· :S ·F and F: S :F type as well as ionic structures as described in Figure 2. A more complete VB picture can be found in ref *4*.

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