

Topic 7

Valence Bond Theory (Hybridization)

7.1 Contents in Brief

- Understanding hybrid atomic orbitals
- sp , sp^2 , sp^3 , sp^3d and sp^3d^2 hybridization
- Compounds involving lone pairs in hybrid orbitals
- The relationship between VSEPR and hybridization at the central atom

7.2 Introduction

A Lewis structure models the number of electrons around each atom in a covalent molecule and assigns the electrons in bonds and in lone pairs (Topic 5). The shape of a molecule can be predicted by adapting the Lewis structure using the VSEPR model (Topic 6). Valence Bond (VB) theory describes a model of how the atomic orbitals of the constituent atoms overlap to achieve the molecular shape predicted by the VSEPR model. Unlike Molecular Orbital (MO) theory (Topic 4), VB theory is a

localized electron model of covalent bonding that is more easily applied to complicated polyatomic molecules and ions of the main group elements.

7.3 Hybrid Atomic Orbitals

VB theory considers covalent bonding to result from the overlap of atomic orbitals, one orbital (and one electron) from each of two interacting atoms. When the atomic orbitals contain unpaired electrons the newly-formed bonding orbital becomes occupied (a bonding pair) and a covalent bond results as described for the MO model in Topic 4.6. A σ bond can be formed by the overlap of two s orbitals, an s orbital and a p orbital, or by the overlap of two p orbitals, as shown in Figure 7.1. The shading of the orbitals in Figure 7.1 indicates the relative sign of the wave function.

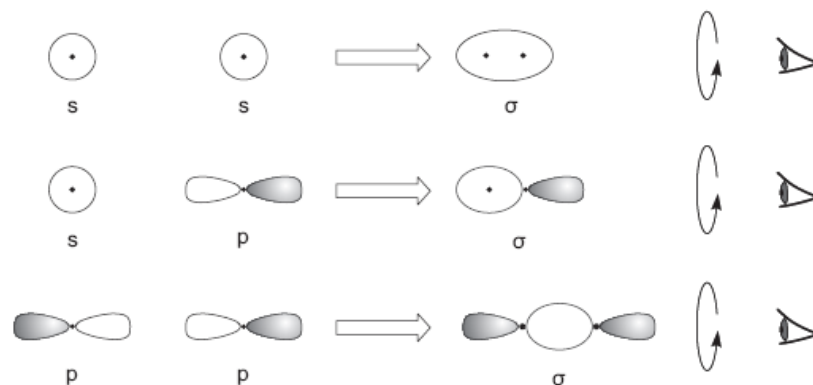


Figure 7.1: Overlap of s and p atomic orbitals to form σ -bonds according to VB theory. Dots represent the positions of the nuclei. Shading (white or grey) denotes the relative sign of the wave function.

The bonds shown in Figure 7.1 have a symmetrical distribution of electron density about the internuclear axis (*i.e.*, the sign of the wave function is the same in all directions away from the line connecting the nuclei of the bonded atoms). Bonds formed

by this type of orbital overlap are termed σ (sigma) bonds, which is the same label as that used in MO theory (Topic 4.6).

In molecules with three or more atoms, the s and p atomic orbitals are not necessarily aligned in the same directions as the atom-atom vectors in the molecules. For example, the C–H bonds in methane are formed using valence s and p atomic orbitals on carbon. However, the three p orbitals of the carbon atom are oriented at 90° to one another, and thus are not aligned to accommodate the tetrahedral H–C–H bond angles of 109° that are measured experimentally and predicted using VSEPR theory. Therefore, it is not obvious how simple s and p atomic orbitals on carbon can be used to develop an orbital-based bonding model for methane. The s and p atomic orbitals have different energies in the free atom as shown in Figure 7.2. However, they can be mathematically mixed (or hybridized) to give hybrid orbitals that are equivalent in energy (degenerate) as shown in Figure 7.2 for methane, and give the appropriate tetrahedral geometry. VB theory is often called “hybridization theory”.

To help visualize the combination (hybridization) of s and p atomic orbitals (AOs) on a given atom, consider the linear combination of s and p orbitals, depicted in Figure 7.3, to produce hybrid sp atomic orbitals.

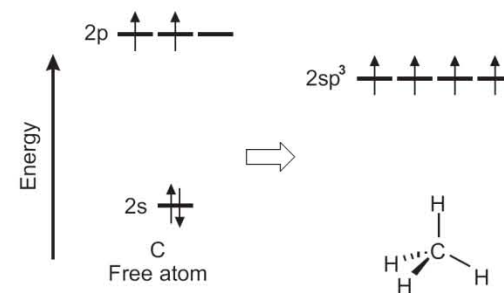


Figure 7.2: Energy levels of 2s and 2p atomic orbitals of carbon and the corresponding four degenerate $2sp^3$ hybrid orbitals in methane.

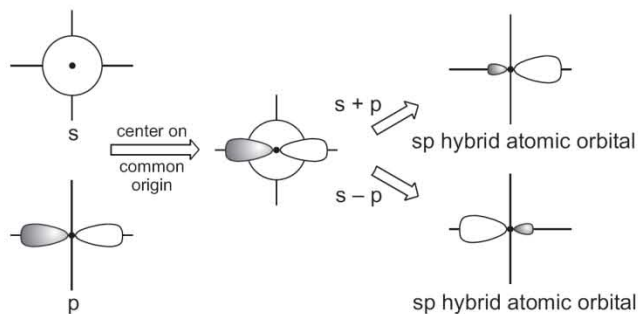


Figure 7.3: Visualizing hybridization of an s and p orbital.

This process is conceptually similar to the formation of molecular orbitals from atomic orbitals (Topic 4.5), with the exception that the newly formed hybrid orbitals are centered on a single atom. An s orbital is a spherically symmetric mathematical

function that has the same sign of the wave function in all directions away from the nucleus. In contrast, the dumbbell-like wave function describing a p orbital features one mathematical sign in one lobe (e.g., positive, represented as light colored) and the other mathematical sign in the other lobe (e.g., negative, represented as dark). Linear combinations, one additive and one subtractive, give two new functions, $(s + p)$ and $(s - p)$, that are hybrids of s and p with each orbital featuring s and p characteristics. One of the new hybrid AOs is oriented along the $+x$ direction and one along the $-x$ direction, as required to rationalize a 180° bond angle at the carbon center in molecules such as ethyne ($\text{H}-\text{C}\equiv\text{C}-\text{H}$).

Hybrid orbitals maximize σ overlap and give the molecular shapes that are predicted using the VSEPR model. Hybridization (mixing) of the 2s and three 2p atomic orbitals of carbon in methane gives four sp^3 hybrid orbitals that are directed at angles of 109° towards the four hydrogen atoms, as illustrated in Figure 7.4.

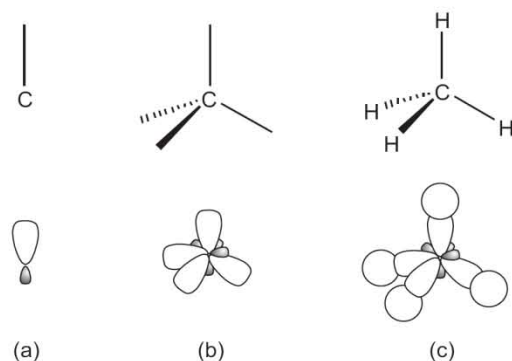


Figure 7.4: (a) Shape of a 2sp^3 orbital of carbon (b) tetrahedral arrangement of four 2sp^3 orbitals (c) overlap of four sp^3 orbitals with four H $1s$ orbitals in methane.

Each sp^3 orbital in the hybridized carbon atom in methane accommodates a single electron. The overlap between each sp^3 hybrid orbital and a $1s$ orbital of a hydrogen

atom (containing a single electron) results in a σ bonding overlap, with each of the newly formed C–H bonding orbitals accommodating two electrons.

The trigonal planar VSEPR geometry is modeled by sp^2 hybridization, in which mixing of one 2s and two 2p orbitals gives three degenerate sp^2 orbitals with an angle of 120° between them. This leaves one unhybridized 2p orbital perpendicular to the trigonal plane that can be used for π overlap (π bond). Figure 7.5 shows the energy of orbitals of the carbon centers in ethene, C_2H_4 . The energy difference between the three sp^2 orbitals and the unhybridized 2p orbital is smaller than the electron-pair repulsion energy that would be encountered if the “fourth electron” were paired up in a $2sp^2$ orbital. As shown in Figure 7.6, overlap of two sp^2 hybrid orbitals (one from each carbon atom) gives a C–C σ bond. The two carbon centers are close enough to enable the unhybridized 2p orbitals to overlap (one electron from each carbon center) in a sideways fashion to give in-phase π overlap (a π bond) between the carbon atoms. The alignment needed for the overlap of the 2p orbitals means that the π bond would be broken if one carbon trigonal plane were rotated relative to the other.

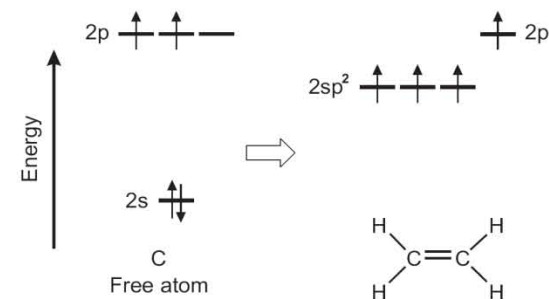


Figure 7.5: Hybridization of one 2s and two 2p atomic orbitals of each carbon atom in ethene to form three degenerate sp^2 hybrid orbitals. One unhybridized 2p orbital is used to form π overlap with the unhybridized 2p orbital of the neighboring carbon atom.

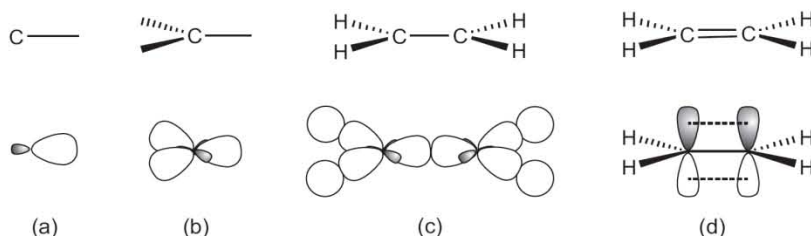


Figure 7.6: (a) Shape of a sp^2 orbital of carbon (b) trigonal planar arrangement of three sp^2 orbitals at each carbon atom in ethene (c) σ -overlap between two carbon atoms and σ -overlap of four terminal sp^2 orbitals with four H 1s orbitals (d) π -overlap of two unhybridized 2p orbitals on neighboring carbon atoms.

Double bonds contain one σ bond and one π bond. Triple bonds contain one σ bond and two π bonds in a linear geometry for carbon, which is modeled by sp hybridization. Mixing of one 2s and one 2p orbital gives two degenerate sp orbitals

that have an angle of 180° between them. This leaves two unhybridized 2p orbitals that can be used for in-phase π overlap (or π bonding). Figure 7.7 shows the energy of the orbitals used for bonding in ethyne, C_2H_2 . The bonds along the molecular axis for this linear molecule are achieved using hybrids composed of s and p orbitals on each carbon center. The two remaining p orbitals on each carbon center effect in-phase π overlap in two perpendicular planes as shown in Figure 7.8.

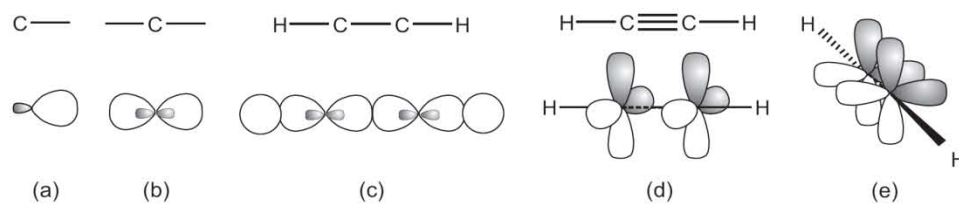


Figure 7.8: (a) Shape of a sp orbital of carbon (b) linear arrangement of two sp orbitals at each carbon atom in ethyne (c) σ overlap between two carbon atoms and σ overlap of two sp orbitals with two H 1s orbitals (d) π overlap of two pairs of unhybridized 2p orbitals on neighboring carbon atoms (e) end-on view of π overlap in (d).

Hybridization or orbital mixing can be invoked for all of the VSEPR geometries (Topic 6). Table 7.1 is derived from Tables 6.2 and 6.3 and shows how the number of VSEPR pairs at an atomic center relates to the hybridization of the atomic orbitals at that center. Atomic centers with two VSEPR pairs adopt sp hybridization to accommodate the two pairs in orbitals for σ bonding or lone pairs. Atomic centers with three VSEPR pairs adopt sp^2 hybridization to accommodate the three pairs. Atomic centers with four VSEPR pairs adopt sp^3 hybridization, centers with five VSEPR pairs are sp^3d hybridized and with six VSEPR pairs are sp^3d^2 hybridized.

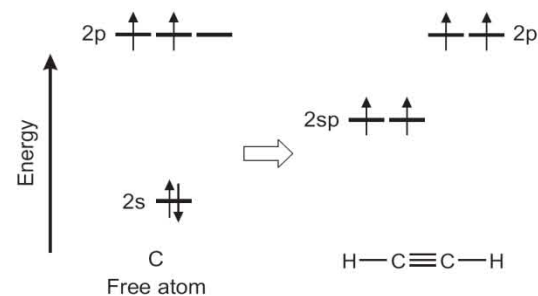
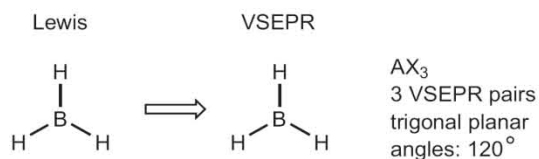


Figure 7.7: Hybridization of one 2s and one 2p atomic orbital of each carbon atom to form two degenerate sp hybrid orbitals on carbon in ethyne. Unhybridized 2p orbitals are used to form π overlap with unhybridized 2p orbitals on the neighboring carbon atom.

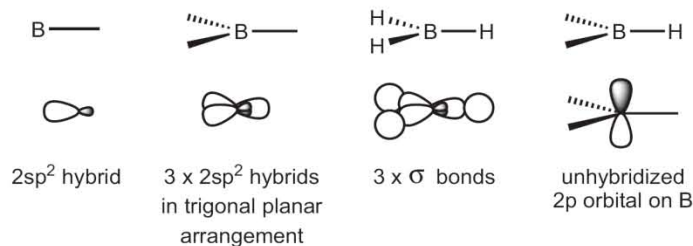
Table 7.1: Relationship between VSEPR number and hybridization.

VSEPR formula	Example	No. of VSEPR pairs, $n + m$	VSEPR shape (polygon)	Hybridization at A
AX_2	$BeCl_2$	2	linear	sp
AXE	CO	2	linear	sp
AX_3	BF_3	3	trigonal planar	sp^2
AX_2E	NO_2^-	3	trigonal planar	sp^2
AXE_2	O_2	3	trigonal planar	sp^2
AX_4	NH_4^+	4	tetrahedral	sp^3
AX_3E	NH_3	4	tetrahedral	sp^3
AX_2E_2	H_2O	4	tetrahedral	sp^3
AXE_3	HF	4	tetrahedral	sp^3
AX_5	PF_5	5	trigonal bipyramidal	sp^3d
AX_4E	$BrCl_4^+$	5	trigonal bipyramidal	sp^3d
AX_3E_2	ClF_3	5	trigonal bipyramidal	sp^3d
AX_2E_3	XeF_2	5	trigonal bipyramidal	sp^3d
AX_6	SF_6	6	octahedral	sp^3d^2
AX_5E	ICl_5	6	octahedral	sp^3d^2
AX_4E_2	XeF_4	6	octahedral	sp^3d^2

AX_3E_3 and AX_2E_4 have yet to be observed experimentally and are therefore omitted from this table.

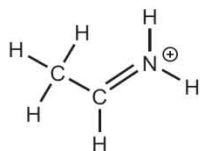
Example 7.1: Drawing hybrid orbitalsDescribe the hybridization at B in BH_3 .

For Lewis procedures, see Topic 5.4, for VSEPR procedures, see Topic 6.4. The trigonal planar VSEPR geometry is modeled by sp^2 hybridization, a mixing of one 2s and two 2p orbitals on B that gives three energy-equivalent (degenerate) 2sp^2 orbitals with an angle of 120° between them. This leaves one unhybridized 2p orbital perpendicular to the trigonal plane. Following the same process as that illustrated in Figure 7.5 for the hybrid orbitals of the carbon centers in ethene, the three 2sp^2 orbitals of B will each contain one electron and will overlap with the 1s orbitals from each of the three hydrogen centers (each containing one electron) to form three σ bonds, as illustrated in Figure 7.6 for the orbitals of carbon in ethene. The unhybridized 2p orbital is perpendicular to the trigonal plane of the molecule and is vacant.



Exercise 7.1

For the Lewis structure shown below, describe the hybridization at nitrogen and carbon.



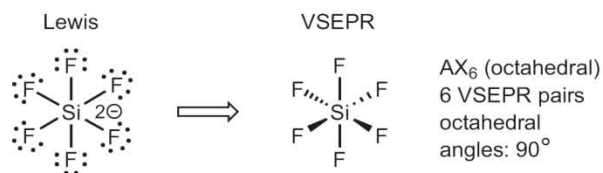
7.4 Hybridization in Compounds Containing the Heavy Elements

Molecules and molecular ions with a central atom that is a heavy element can accommodate ten or more bonding and nonbonding electrons. To a simple approximation, this can be attributed to the availability of d orbitals, which are not accessible for the elements of rows 1 and 2. Lewis structures of molecules with a heavy element as a central atom can be drawn with an “expanded valence”. For example, ten electrons surround phosphorus in the trigonal bipyramidal phosphorus pentachloride and twelve electrons surround sulfur in the octahedral sulfur hexafluoride (see Topics 5 and 6). To obtain hybrid orbitals with the appropriate orientation for the bonds in trigonal

bipyramidal or octahedral molecules, one d orbital is hybridized with the s and p orbitals to create five sp^3d hybrids for trigonal bipyramidal structures, and two d orbitals are hybridized with s and three p orbitals to create six sp^3d^2 orbitals for octahedral structures.

Example 7.2: Hybrid orbitals in compounds containing the heavy elements

Describe the hybridization in SiF_6^{2-} .



For Lewis procedures see Topic 5.4, for VSEPR procedures, see Topic 6.4. The octahedral VSEPR geometry is modeled by sp^3d^2 hybridization, a mixing of one 3s, three 3p orbitals and two 3d orbitals on Si to give six degenerate $3sp^3d^2$ orbitals with an angle of 90° between them.

Exercise 7.2

Describe the hybridization at phosphorus in:

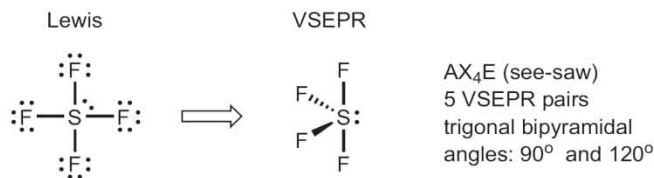


7.5 Compounds Involving Lone Pairs in Hybrid Orbitals

Hybrid orbitals also accommodate lone pairs of electrons. For example, water (H_2O) and ammonia (NH_3) are formed using 2sp^3 orbitals (tetrahedral VSEPR shape). The lone pairs occupy 2sp^3 hybrid orbitals, as shown for water in Figure 7.9. The experimentally observed bond angle in H_2O is less than 109° (the predicted tetrahedral angle) because of greater repulsion between the lone pairs than between the two bonding pairs of electrons. As such, the atoms are somewhat “pushed together” by the lone pairs repelling each other and so the bond angle is reduced.

Example 7.3: Hybrid orbitals containing lone pairs

Describe the hybridization at sulfur in SF_4 .



For Lewis procedures see Topic 5.4, for VSEPR procedures, see Topic 6.4. The trigonal bipyramidal VSEPR geometry is modeled by sp^3d hybridization, a mixing of one 3s , three 3p orbitals and one 3d orbital on S to give five degenerate $3\text{sp}^3\text{d}$ orbitals with angles of 90° and 120° between them. The five degenerate $3\text{sp}^3\text{d}$ orbitals have an energy that is an average of the 3s , 3p and 3d orbitals involved.

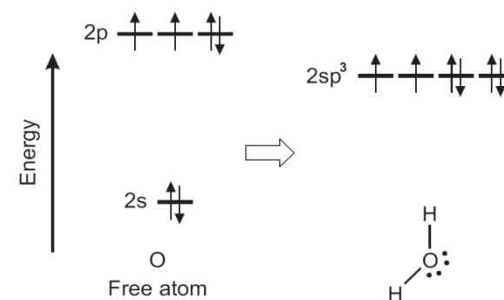


Figure 7.9: Hybridization of oxygen atomic orbitals in water.

Exercise 7.3

Describe the hybridization at xenon and at fluorine in XeF_2 .

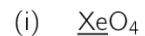
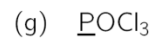
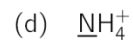
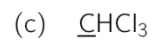
7.6 Summary

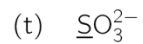
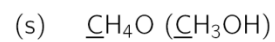
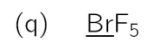
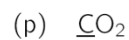
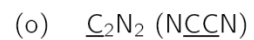
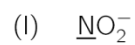
VB theory defines the hybridization (mixing) of atomic orbitals to generate new “hybridized” atomic orbitals of the appropriate shape to enable the best orbital overlap within a particular VSEPR polygon molecular shape. For linear VSEPR shapes, sp hybridization is adopted; for trigonal planar VSEPR shapes, sp^2 hybridization is adopted; for tetrahedral VSEPR shapes, sp^3 hybridization is adopted; for trigonal bipyramidal VSEPR shapes, sp^3d hybridization is adopted; for octahedral VSEPR shapes, sp^3d^2 hybridization is adopted. The components of the localized bonding model (Lewis structures, VSEPR theory and VB theory) predict shapes of molecules and provide an understanding of the chemical bonding involved.

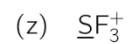
7.7 Additional Exercises

Exercise 7.4

Draw the best Lewis structure and determine the hybridization of the underlined atom in each of the following molecules.







7.8 Answers to Exercises 7

7.1 N, sp^2 ; C, sp^2 ; C, sp^3

7.2 (a) sp^3 (b) sp^3d

7.3 Xe, sp^3d ; F, sp^3

7.4 For best Lewis structures, refer to Topic 5.11.

(a) sp	(b) sp^3	(c) sp^3	(d) sp^3	(e) sp^3	(f) sp^3	(g) sp^3
(h) sp^3	(i) sp^3	(j) sp^3	(k) sp^3	(l) sp^2	(m) sp^2	(n) sp^2
(o) sp	(p) sp	(q) sp^3d^2	(r) sp^3d^2	(s) sp^3	(t) sp^3	(u) sp^3
(v) sp^3	(w) sp^3	(x) sp^3d	(y) sp^3	(z) sp^3		

