

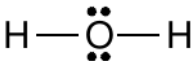
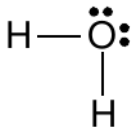
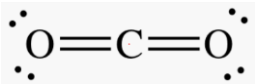

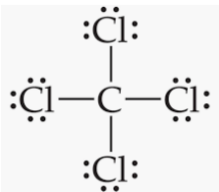
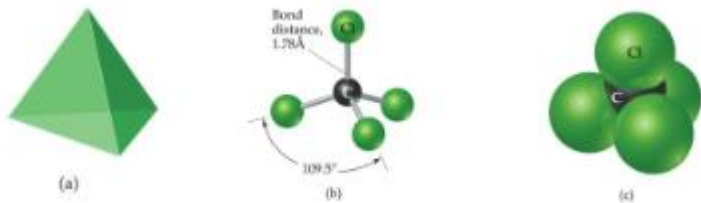


Learning Guide Module

Subject Code Chem 1 Inorganic Chemistry 1
Module Code 4.0 Chemical Bond
Lesson Code 4.3 Valence Bond Theory (Hybridization and VSEPR)
Time Limit 30 mins.

Components	Tasks	TA ^a	ATA ^b
Target 	<p>By the end of this module, the students will have been able to</p> <ol style="list-style-type: none"> 1. Predict the structures of polyatomic ions/molecules using the VSEPR. 2. Apply the hybridization theory to explain the geometric structures associated with different molecules (CH₄, H₂O, BeCl₂, NH₃, PCl₅, SF₆) 	1 min.	
Hook 	<p>Water! H₂O! From the formula and applying our knowledge on Lewis structures, we know that water has two bonds and they are Oxygen to Hydrogen bonds. But is that enough for us to answer questions like what makes it polar and what contributes to its unique increase of volume when it turns to ice? On the other hand, CO₂ which has also two bonds which are C=O bonds, is a nonpolar molecule. We will understand more their difference as we tackle theories on covalent bonding which are Valence Shell Electron Pair Repulsion Theory and Hybridization Theory.</p> <div style="text-align: center;">   </div> <p style="text-align: center;"><small>Source: Shape and Geometry of H₂O. Retrieved from Quora.com</small></p> <p>Figure 1. The Lewis structure of H₂O shows that there are 2 bonding pairs and 2 lone pairs around the central atom.</p> <p>There are many possible Lewis structures for some molecules yet these structures don't tell us the exact angles between bonds and lone electrons.</p> <div style="text-align: center;">  </div> <p style="text-align: center;"><small>Source: Lewis Structure for CO₂. Retrieved from coursehero.com</small></p> <p>Figure 2. The Lewis structure of CO₂ shows two double bonds attached to carbon.</p>	2 mins.	

<p>Ignite</p> 	<p>In the previous lesson, we used Lewis structures to visualize formulas of chemical compounds. However, Lewis structures do not show the actual 3-D shapes of molecules; they simply show the number and types of bonds. For example, the Lewis structure of CCl_4 tells us only that four Cl atoms are bonded to a central C atom:</p> <div style="text-align: center;">  </div> <p>Source: CCl_4 Lewis Structure. Retrieved from sciencetrends.com</p> <p>Figure 3. Lewis Structure of CCl_4</p> <p>The Lewis structure is just drawn with the atoms all in the same plane. As shown in Figure 3. However, the actual arrangement of CCl_4 is like the figure below.</p> <div style="text-align: center;">  </div> <p>Source: Chapter 9 Molecular Geometry and Bonding Theories. Retrieved from slideserve.com</p> <p>The molecular geometry of CCl_4 shows that the Cl atoms lie at the corners of a tetrahedron.</p> <p>If you wonder how chemists determine actual shape of molecules, well, there are various instrumental techniques such as X-Ray crystallography and other experimental techniques which can be used to tell us where the atoms are located in a molecule. (1)</p> <p>Molecular geometry is the three-dimensional arrangement of atoms in a molecule. It's very important because it affects a molecule's physical and chemical properties, such as melting point, boiling point, density, and the types of reactions it undergoes. Molecular geometry or molecular shape is determined by bond angles, the angles made by the lines joining the nuclei of the atoms in the molecule.</p> <p>We begin our discussion of molecular shapes with molecules (and ions) that, like CCl_4, which have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula AB_n in which the central atom A is bonded to n B atoms. For example, both CO_2 and H_2O are AB_2 molecules, whereas SO_3 and NH_3 are AB_3 molecules, and so on. (Chang, 2008)</p> <p>But the question is how can we predict the shapes of AB_n</p>	20 mins.	

molecules?

When A is a representative element (one from the s block or p block of the periodic table), we can answer these questions by using the valence-shell electron-pair repulsion (VSEPR) model.

THE VSEPR MODEL

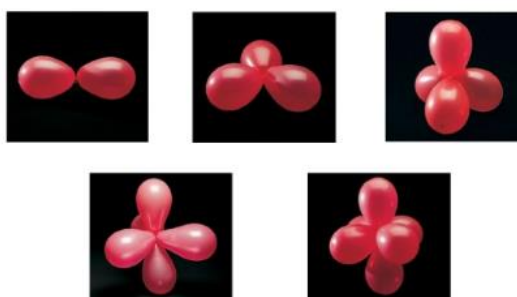
Imagine tying two identical balloons together at their ends as shown in Figure 5.



Source: Molecular Geometry with Balloons. Retrieved from carolina.com

Figure 5. The two balloons naturally orient themselves to point away from each other; that is, they try to “get out of each other’s way” as much as possible.

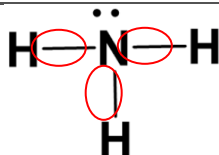
If we add a third balloon, the balloons orient themselves toward the vertices of an equilateral triangle, and if we add a fourth balloon, they adopt a tetrahedral shape. We see that an optimum geometry exists for each number of balloons. In some ways, the electrons in molecules behave like these balloons. (Silberberg, 2009)



Source: The Shapes of Molecules. Retrieved from slideshare.net

Figure 6. A balloon analogy for mutual repulsion of electron groups

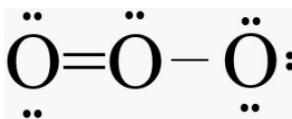
In order to understand the VSEPR model, it is very important that we know the number of **electron domains**, which can be compared to balloons previously, around the central atom. Electron domain refers to the number of lone pairs or bond locations around a particular atom in a molecule. Electron domains may also be called electron groups. For example, the Lewis structure of NH_3 has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):



Source: Hectro geometry. Retrieved from homeworklib.com

The nitrogen in ammonia is surrounded by four electron domains encircled in red.

Each multiple bond in a molecule also constitutes a single electron domain. Thus, the structure for O_3 has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):



Source: What are allotropes of oxygen? Retrieved from study.com

Figure 8. Lewis Structure of Ozone

In general, each nonbonding pair, single bond, or multiple bond is considered as a single electron domain around the central atom in a molecule.

The VSEPR model is based on the idea that electron domains are negatively charged and therefore repel one another. Like the balloons in Figure 6, electron domains try to stay out of one another's way. The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them. (Brown et.al,2012)

The arrangement of electron domains about the central atom of an AB_n molecule or ion is called its **electron-domain geometry**. In contrast, the **molecular geometry or shape** is the arrangement of **only the atoms in a molecule or ion**—any nonbonding pairs in the molecule are not part of the description of the molecular geometry.

Going further to our objective in determining the shape of any molecule, we first use the VSEPR model to predict the electron-domain geometry. From knowing how many of the domains are due to nonbonding pairs, we can then predict the molecular geometry or shape. Remember to ignore those domains that involve nonbonding electrons when talking about molecular shape.

Here are the general steps to predict the shapes of molecules or ions: (Brown et.al, 2012)

Step 1. Write the Lewis structure from the molecular formula to see the relative placement of atoms and the number of electron groups.

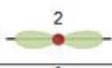













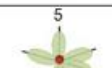





Step 2. Assign an electron domain or electron-group arrangement by counting all electron domains around the central atom, bonding plus nonbonding.

Step 3. Predict the ideal bond angle from the electron-group arrangement and the direction of any deviation caused by lone pairs or double bonds.

Step 4. Draw and name the molecular shape by counting bonding groups and nonbonding groups separately (see Table 1 for reference).

Referring to Table 1, notice that the bond angles decrease as the number of nonbonding electron pairs increases. It's because a nonbonding pair experiences less nuclear attraction, its electron domain is spread out more in space than is the electron domain for a bonding pair. As a result, electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles. In addition, electron domains for multiple bonds also exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds. (Brown et.al, 2012)

Table 1. Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
	Linear					
	Trigonal planar					
	Tetrahedral					
	Trigonal bipyramidal					
	Octahedral					

These geometries are important because they include all the shapes usually seen in molecules or ions that obey the octet rule.

Example.

Determine the electron domain geometry and the molecular shape of the following compounds:

- (a) PF_3
- (b) CBr_4

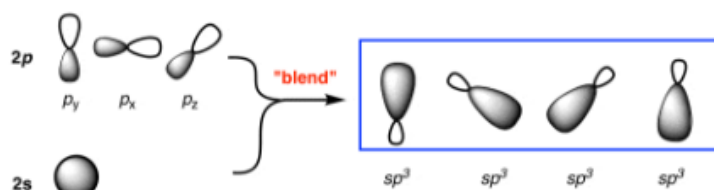
HYBRIDIZATION

The VSEPR model, does a surprisingly good job at

predicting molecular shape, but it cannot answer questions like why a CH_4 molecule should have a tetrahedral geometry. How can we reconcile the notion that covalent bonds are formed from overlap of atomic orbitals with the molecular geometries that come from the VSEPR model?

To begin with, we recall that atomic orbitals are regions in space where electrons are most probably found. Each type of orbital has unique shape. To explain molecular geometries, we can assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called **hybrid orbitals**. (Chang, 2008)

The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called **hybridization**. Just keep in mind that the total number of atomic orbitals on an atom remains constant, so *the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed*. (Brown et.al, 2012)



Source: What are hybrid orbitals? Retrieved from masterorganicchemistry.com

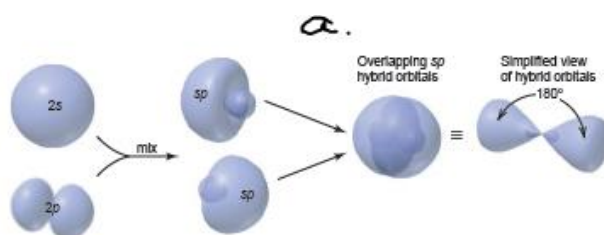
Figure 9. Same level ($n=2$) three p and one s orbitals can be hybridized to form four sp^3 orbitals. ($3+1=4$)

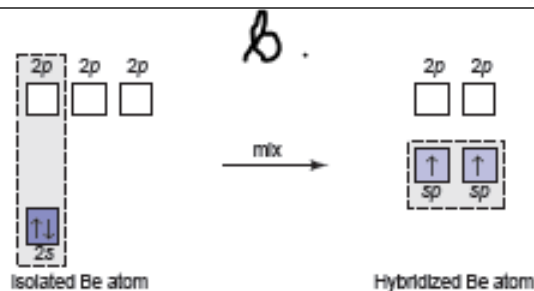
As we examine the **common types of hybridization**, notice the connection between the type of hybridization and certain molecular geometries predicted by the VSEPR model. (2)

a. sp Hybridization

Based on the VSEPR Model, when two electron groups surround the central atom, we observe a linear shape, which means that the bonding orbitals must have a **linear orientation**.

Valence Bond (VB) theory on hybridization explains this by proposing that mixing two nonequivalent orbitals of a **central atom, one s and one p**, gives rise to two equivalent **sp hybrid orbitals** that lie 180° apart (Figure 10a). (Silberberg, 2009)

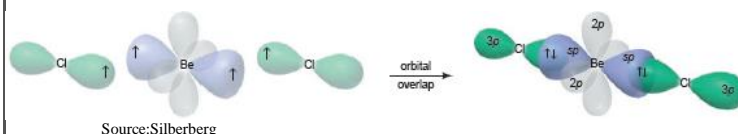




Source: Silberberg

Figure 10. In Be central atom, one 2s and one 2p atomic orbital mix to form two sp hybrid orbitals and the two other 2p orbitals remain unhybridized

In gaseous BeCl_2 , for example, the **Be atom** is said to be **sp hybridized**. The 2s and one of the three 2p orbitals of Be mix and form two sp orbitals. These overlap with 3p orbitals of two Cl atoms, and the four valence electrons—two from Be and one from each Cl—occupy the overlapped orbitals in pairs with opposite spins (Figure 11). The two unhybridized 2p orbitals of Be lie perpendicular to each other and to the bond axes. Thus, through hybridization, the paired 2s electrons in the isolated Be atom are distributed into two sp orbitals, which form two Be—Cl bonds. (Silberberg, 2009)



Source: Silberberg

Figure 11. BeCl_2 forms by overlap of the two sp hybrids with the 3p orbitals of two Cl atoms; the two unhybridized Be 2p orbitals lie perpendicular to the sp hybrids.

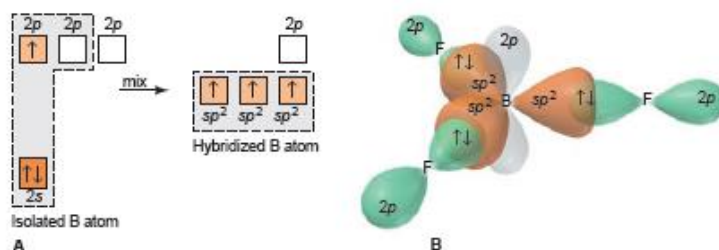
In summary, atom surrounded with 2 electron domains or electron groups are sp hybridized.

b. sp^2 Hybridization

In order to rationalize the **trigonal planar** electron-group arrangement and the shapes of certain molecules like BF_3 , we introduce the mixing of **one s and two p orbitals** of the central atom to give three hybrid orbitals that point toward the vertices of an equilateral triangle, their axes **120° apart**. These are called **sp^2 hybrid orbitals**. (Note that, hybrid orbital notation uses superscripts for the number of atomic orbitals of a given type that are mixed, not for the number of electrons in the orbital: here, one s and two p orbitals were mixed, so we have s^1p^2 , or sp^2 .) (Silberberg, 2009)

VB theory proposes that the central B atom in the BF_3

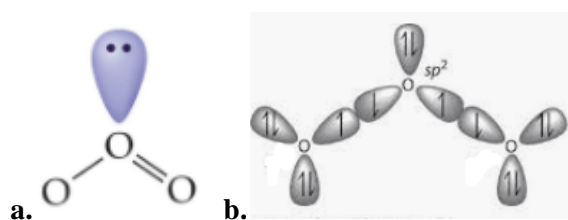
molecule is sp^2 hybridized. Figure 12 shows the three sp^2 orbitals in the trigonal plane, with the third 2p orbital unhybridized and perpendicular to this plane. Each sp^2 orbital overlaps the 2p orbital of an F atom, and the six valence electrons—three from B and one from each of the three F atoms—form three bonding pairs.



Source: Silberberg

Figure 12. a. The orbital diagram shows that the 2s and two of the three 2p orbitals of the B atom mix to make three sp^2 hybrid orbitals. The third 2p orbital remains empty and unhybridized. **b.** BF_3 forms through overlap of 2p orbitals on three F atoms with the sp^2 hybrids that lie 120° apart, and the unhybridized 2p orbital is perpendicular to the trigonal bonding plane.

To account for other molecular shapes within a given electron-group or electron domain arrangement, we postulate that one or more of the hybrid orbitals contains lone pairs. In ozone (O_3), for example, the central O is sp^2 hybridized and a lone pair fills one of its three sp^2 orbitals, so ozone has a bent molecular shape.



Source:09_Worked_Examples. Retrieved from studylib.net

Figure 13. a. The Lewis structure of Ozone shows one lone pair and 2 bonding (single and double bond) pairs. **b.** The sp^2 hybrid orbitals of central O overlap with the orbitals of outer oxygen atoms in ozone molecule.

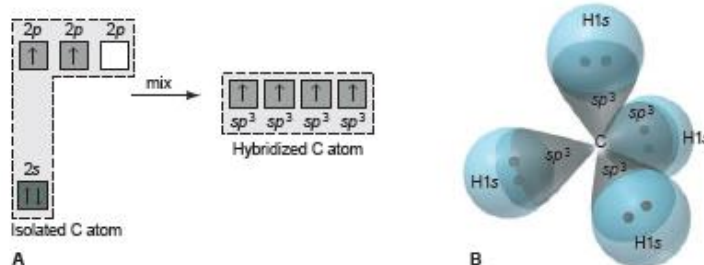
In summary, atom surrounded with 3 electron domains (whether bonding or nonbonding e- pairs) or electron groups are sp^2 hybridized.

c. sp^3 Hybridization

Now let's return to the question posed earlier about the orbitals in methane (CH_4), the same question that arises for any species with a tetrahedral electron group arrangement.

VB theory proposes that the **one s** and all **three p orbitals** of the central atom mix and form **four sp^3** hybrid orbitals, which point toward the vertices of a tetrahedron. As shown in Figure 14, the C atom in methane is sp^3 hybridized.

Its four valence electrons half-fill the four sp^3 hybrids, which overlap with the half-filled 1s orbitals of four H atoms and form four C—H bonds. (Silberberg, 2009)



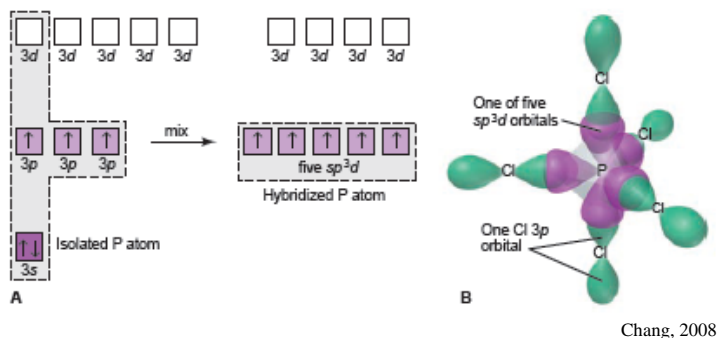
Source: Silberberg

Figure 14. **A.** The 2s and all three 2p orbitals of C are mixed to form four sp^3 hybrids. **B.** In methane, the four sp^3 orbitals of C point toward the corners of a tetrahedron and overlap the 1s orbitals of four H atoms.

In summary, atom surrounded with 4 electron domains or electron groups are sp^3 hybridized.

d. sp^3d Hybridization

For bigger molecules like PCl_5 , the VB model proposes that the one 3s, the three 3p, and one of the five 3d orbitals of the central P atom mix and form five sp^3d hybrid orbitals, which point to the vertices of a trigonal bipyramid.



Chang, 2008

Figure 15. The sp^3d hybrid orbitals in PCl_5

The orbital diagram above shows that one 3s, three 3p, and one of the five 3d orbitals of P central atom mix to form five sp^3d orbitals that are half-filled. Four 3d

orbitals are unhybridized and empty.

The trigonal bipyramidal PCl_5 molecule forms by the overlap of a 3p orbital from each of the five Cl atoms with the sp^3d hybrid orbitals of P (unhybridized, empty 3d orbitals not shown). (Brown.et.al,2012)

In summary, atom surrounded with 5 electron domains or electron groups are sp^3d hybridized.

e. sp^3d^2 Hybridization

To rationalize the shape of SF_6 molecule, the VB model proposes that the one 3s, the three 3p, and two of the five 3d orbitals of the central S atom mix and form six sp^3d^2 hybrid orbitals, which point to the vertices of an octahedron.

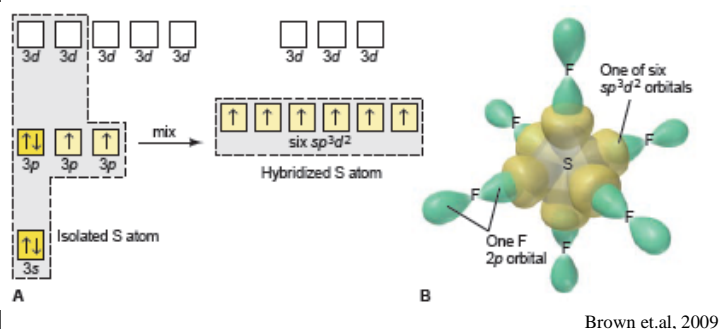


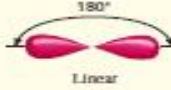
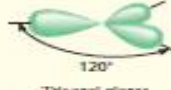
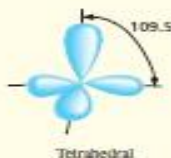
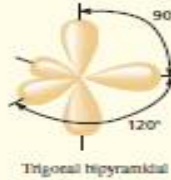
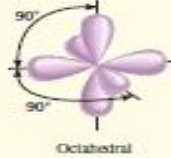
Figure 16. The sp^3d^2 hybrid orbitals in SF_6 .

The orbital diagram above shows that one 3s, three 3p, and two 3d orbitals of S central atom mix to form six sp^3d^2 orbitals that are half-filled. Three 3d orbitals are unhybridized and empty.

The octahedral SF_6 molecule forms from overlap of a 2p orbital from each of six F atoms with the sp^3d^2 orbitals of S atom (unhybridized, empty 3d orbitals not shown). (Brown et al, 2012)

In summary, atoms surrounded with 6 electron domains or electron groups are sp^3d^2 hybridized.

Table 2. Important Hybrid Orbitals and Their Shapes

Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, p	sp	2	 Linear	BeCl_2
s, p, p	sp^2	3	 Trigonal planar	BF_3
s, p, p, p	sp^3	4	 Tetrahedral	$\text{CH}_4, \text{NH}_4^+$
s, p, p, p, d	sp^3d	5	 Trigonal bipyramidal	PCl_5
s, p, p, p, d, d	sp^3d^2	6	 Octahedral	SF_6



Chang, 2008

Example:

Indicate the orbital hybridization around the central atom in:

- CO_2
- H_2O



<div>Navigate</div> <div></div>	<div>Formative assessment (Graded exercise 25/25)</div> <div>For your formal assessment, answer the following questions in a ½ sheet of paper, have it scanned and submit through our assigned learning platform.</div> <table><thead><tr><th>Compound</th><th>No. of Bonds</th><th>No. of Lone Pairs</th><th>e-Domain Geometry</th><th>Molecular Shape</th><th>Hybridization of Central Atom</th></tr></thead><tbody><tr><td>SF₆</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>SO₃</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>NO₂⁻</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>NH₃</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>ICl₄⁻</td><td></td><td></td><td></td><td></td><td></td></tr></tbody></table>	Compound	No. of Bonds	No. of Lone Pairs	e-Domain Geometry	Molecular Shape	Hybridization of Central Atom	SF ₆						SO ₃						NO ₂ ⁻						NH ₃						ICl ₄ ⁻						5 mins.	
Compound	No. of Bonds	No. of Lone Pairs	e-Domain Geometry	Molecular Shape	Hybridization of Central Atom																																		
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NH ₃																																							
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<div>Knot</div> <div></div>	<div>Summary of the lesson</div> <div>The VSEPR theory proposes that each group of electrons (single bond, multiple bond, lone pair, or lone electron) around a central atom remains as far away from the others as possible. The arrangement of electron domains around a central atom is called the electron-domain geometry; the arrangement of atoms is called the molecular geometry.</div> <div>On the other hand, hybridization allows us to explain how atomic orbitals mix and change their characteristics during bonding. Based on the observed molecular shape (and the related electron-group arrangement), we postulate the type of hybrid orbital needed. In certain cases, we need no hybridization at all.</div>	2 mins.																																					

^a suggested time allocation set by the teacher

^b actual time spent by the student (for information purposes only)

Endnotes

- (1) Structure Determination by X-Ray Crystallography. (https://www.youtube.com/watch?v=j4HgLf_eJoc)
- (2) VSEPR and Molecular Geometry. (<https://www.youtube.com/watch?v=Q9-JjyAEqnU>)

References

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Prepared by: Carren Anne Y. Dalisay	Reviewed by: Lester D. Mendoza
Position: Special Science Teacher II	Position: Special Science Teacher II
Campus: PSHS-SRC	Campus: Main