

Lecture 9 February 4, 2019

Lewis Structures

Hybrid Orbitals

*Shapes of Molecules (Common
Stereochemistries in Main Group
Compounds)*

Two Electrons Shared between Two Atoms
Make a Bond! G.N. Lewis

(G. = Gilbert
N. = Newton
Lewis as in Lewis Structures!)

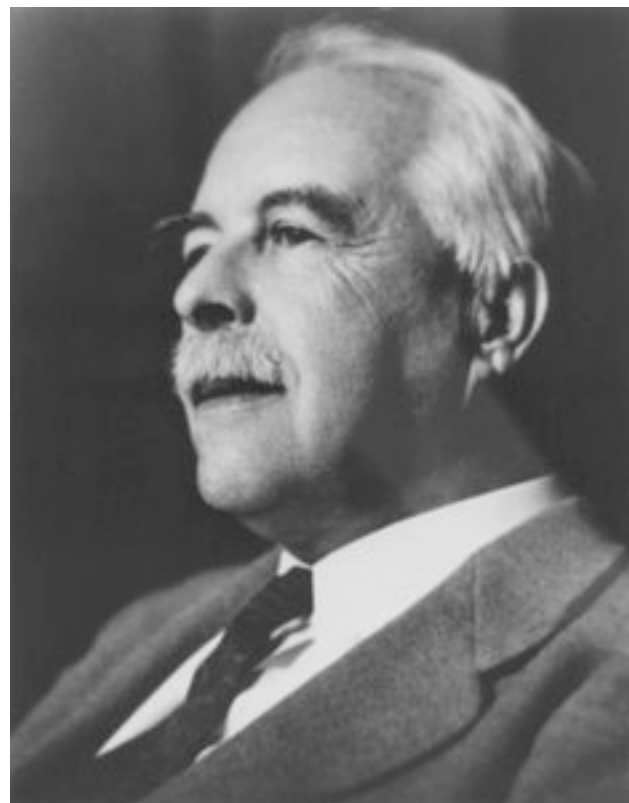
Lewis Structures and VSEPR:

Workshop Study

Simple Review videos

<https://www.youtube.com/watch?v=1ZlnzyHahvo>

https://www.youtube.com/watch?v=xNYiB_2u8J4



Rules for Oxidation State Assignment

Rule 1: The oxidation number of an element in its free (uncombined) state is zero — for example, Al(s) or Zn(s). This is also true for elements found in nature as *diatomic* (two-atom) elements and for sulfur, found as:

Rule 2: The oxidation number of a *monatomic* (one-atom) ion is the same as the charge on the ion

Rule 3: The sum of all oxidation numbers in a neutral compound is zero. The sum of all oxidation numbers in a *polyatomic* (many-atom) ion is equal to the charge on the ion that may have multiple oxidation states, if the other atoms in the ion have known oxidation numbers.

Rule 4: The oxidation number of an alkali metal (IA family) in a compound is +1; the oxidation number of an alkaline earth metal (IIA family) in a compound is +2.

Rule 5: The oxidation number of oxygen in a compound is usually -2 . If, however, the oxygen is in a class of compounds called *peroxides* (for example, hydrogen peroxide), then the oxygen has an oxidation number of -1 .

Rule 6: The oxidation state of hydrogen in a compound is usually +1. If the hydrogen is part of a *binary metal hydride* (compound of hydrogen and some metal), then the oxidation state of hydrogen is -1 .

Rule 7: The oxidation number of fluorine is always -1 . Chlorine, bromine, and iodine usually have an oxidation number of -1 , unless they're in combination with an oxygen or fluorine.

The Pauling Electroneutrality Principle:

Pauling's principle of electroneutrality states that each atom in a stable substance has a charge close to zero. It was formulated by Linus **Pauling** in 1948 and later revised.

Formal Charges: Keeping track of electrons leading to charge separation in a molecule:

Formal Charge

$$\text{FC} = \frac{\# \text{ Valence } e^- \text{ in Free Atom}}{\text{Total \# Nonbonding } e^-} - \frac{\text{Total \# Bonding } e^-}{2}$$

Lewis Structures: Do a Zillion.

Rules:

- 1) Octet Rule “Rules” > 90% time
- 1) The more electropositive element typically goes in center
--- **examples of exceptions: CH₄, NH₃, H₂O; Polyphosphates!**
- 2) Look for Resonance forms and choose best according to Pauling’s Electroneutrality Principle: smallest and least separation of formal charges

Pause: In Class Worksheet and Presentations on Board

Can Orbital Overlap Predict Molecular Shapes?

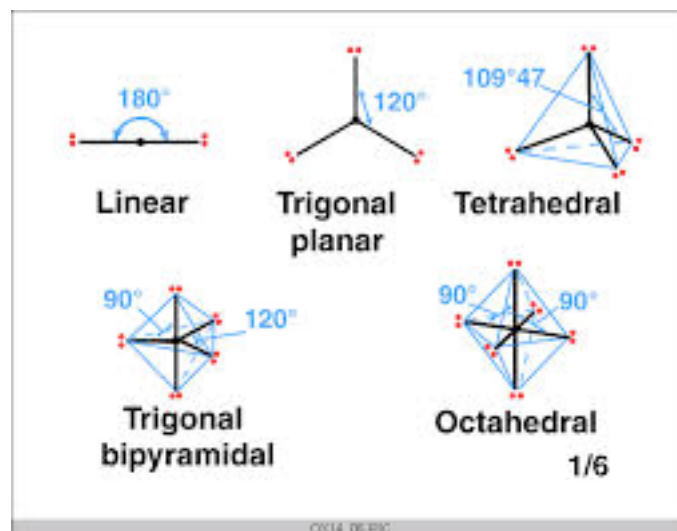
Consider: HF, H₂S, PH₃ Bonds of all can be ascribed to overlap of 3p valence orbital on F, S, or P with 1s H orbital

But: H₂O, NH₃, CH₄!!!

Need Hybrid orbitals: sp³

Valence Shell Electron Pair Repulsion *model*

- ✦ Is based on the number of regions of high electron density around the central atom
 - *Electron density*: The number of electrons in a unit volume.
- ✦ Can be used to predict the structure of a molecule
- ✦ Does fail in some cases; models are oversimplifications



Remember the following additional things:

1. Multiple bonds behave as a single electron pair bond for the purpose of VSEPR.
2. Order of repulsion between lone pair and lone pair (lp - lp), lone pair and bonding pair (lp - bp), and bonding pair and bonding pair (bp - bp) is $lp - lp \gg lp - bp > bp - bp$.

when a molecule has lone pairs of electrons , the bonding electron pairs are pushed closer and thus the bond angle is decreased.

<https://www.youtube.com/watch?v=1ZlnzyHahvo>
https://www.youtube.com/watch?v=xNYiB_2u8J4

In TBP, lone pairs go in Equatorial positions rather Than axial positions. This minimizes repulsions.

www.youtube.com/watch?v=nxebQZUVvTg

<http://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-13/>

<https://www.youtube.com/watch?v=1ZlnzyHahvo>

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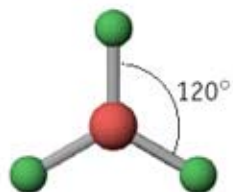
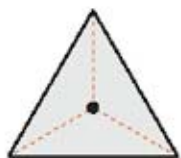
Linear



AX_2

Example: BeF_2

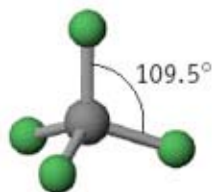
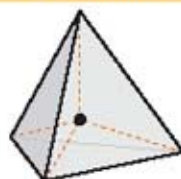
Trigonal-planar



AX_3

Example: BF_3

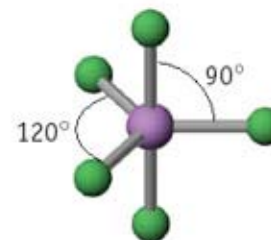
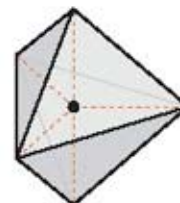
Tetrahedral



AX_4

Example: CF_4

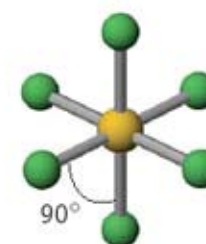
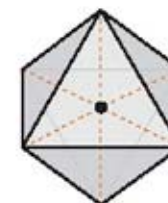
Trigonal-bipyramidal



AX_5



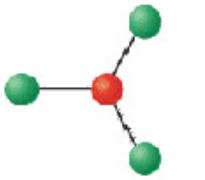
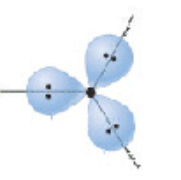
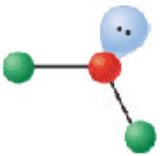
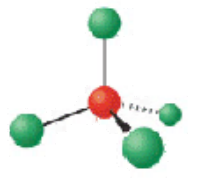
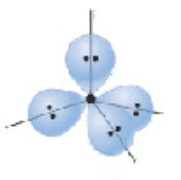
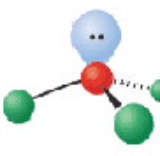
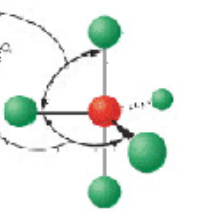
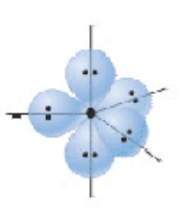
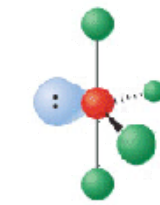
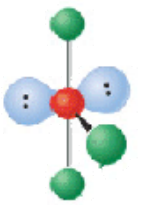
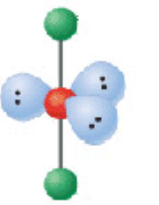
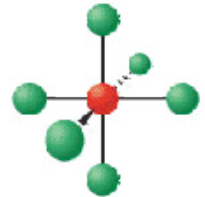
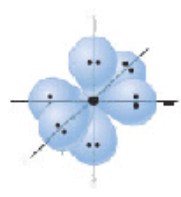
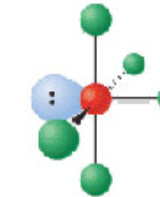
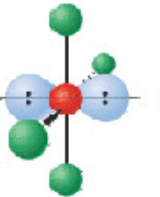
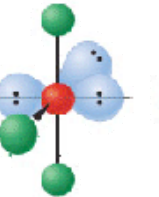
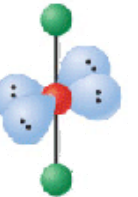
Example: PF_5

Octahedral

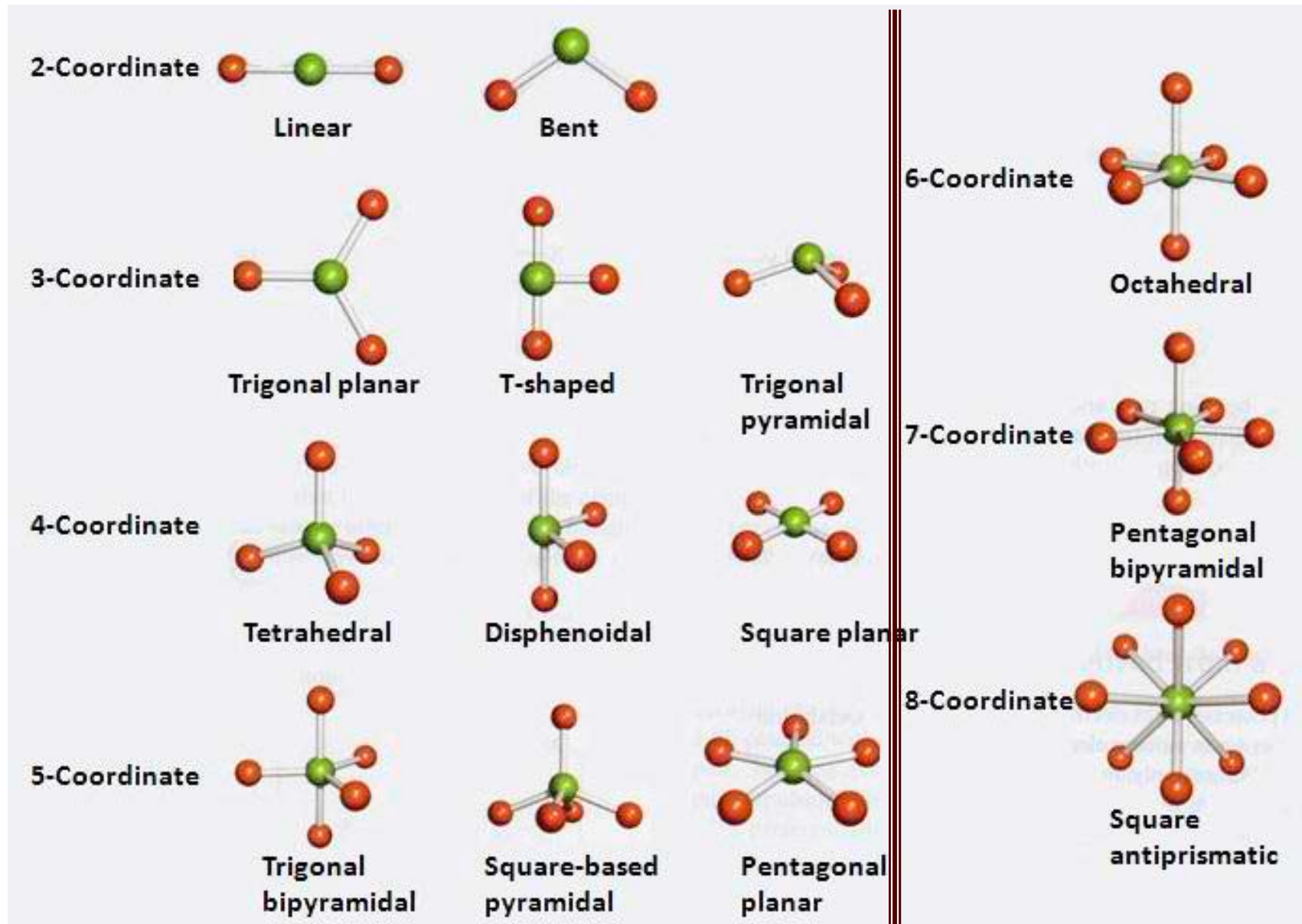


AX_6

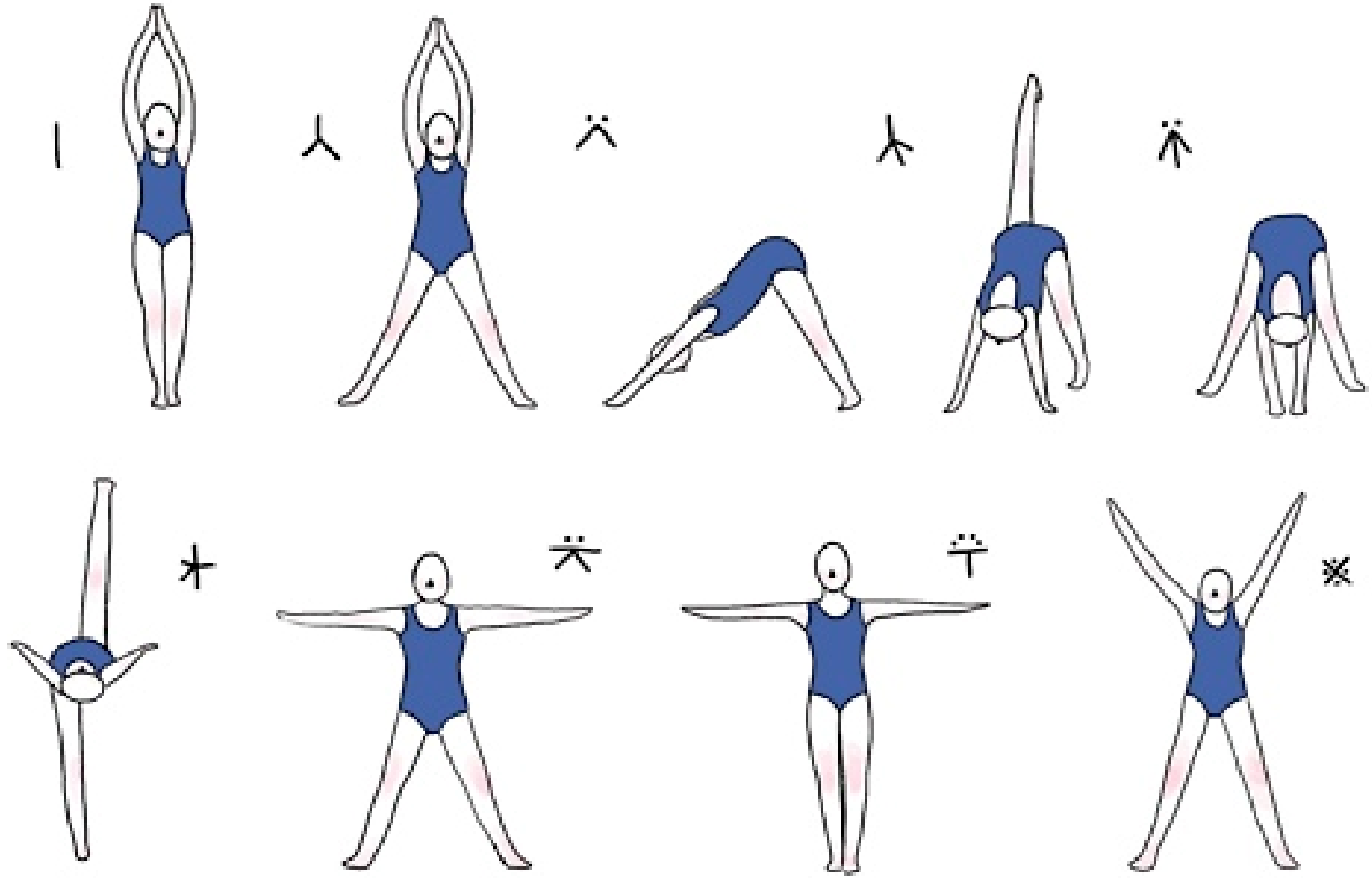
Example: SF_6

Bond angles	Spatial geometry	Electron pair geometry	Lone pair substitutions	Makeup of hybrid orbitals
180°	 Linear	 (<i>sp</i>)	...	$s + p_z$
120°	 Trigonal planar	 (<i>sp</i> ²)	 Bent	$s + p_x + p_y$
109.5°	 Tetrahedral	 (<i>sp</i> ³)	 Trigonal pyramidal	$s + p_x + p_y + p_z$
90°, 120°	 Trigonal bipyramidal	 (<i>dsp</i> ³)	 "Sawhorse"	$(s + p_x + p_y) + (p_z + d_{z^2})$
		 T-shaped	 Linear	
90°	 Octahedral	 (<i>d</i> ² <i>sp</i> ³)	 Square pyramidal	$(s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2})$
		 Square planar	 T-shaped	
			 Linear	



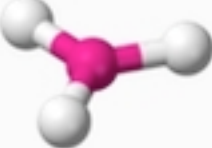
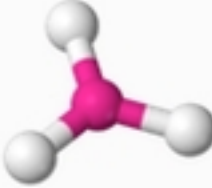
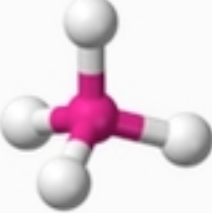
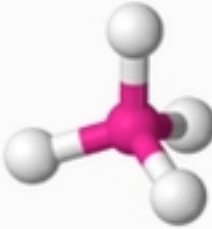

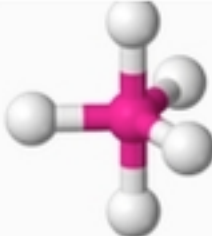


*Descriptions of geometries in mono-centric molecules: It is where
The atoms are. . .*





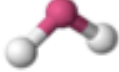


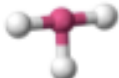


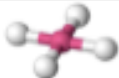



VSEPR YOGA









VSEPR and the AXE Description of Electron Arrangements




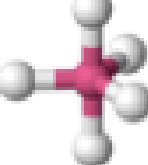

Molecule Type	Shape	Electron arrangement [†]	Geometry [‡]	Examples
AX_2E_0	Linear			$BeCl_2$, $HgCl_2$, CO_2
AX_3E_0	Trigonal planar			BF_3 , CO_3^{2-} , NO_3^- , SO_3
AX_4E_0	Tetrahedral			CH_4 , PO_4^{3-} , SO_4^{2-} , ClO_4^- , $TiCl_4$, XeO_4
AX_5E_0	Trigonal bipyramidal			PCl_5
AX_6E_0	Octahedral			SF_6 , WCl_6

VSEPR Theory

# of Atoms	# of electron pairs	Formula Type	Geometry	Bond Angle	Examples	Hybridization	Structure
3	0	AB ₂	Linear	180	CO ₂ , CS ₂ , BeH ₂		
3	1	AB ₂	Bent	117.5	GeCl ₂ , SO ₂ , NO ₂	sp ²	
3	2	AB ₂	Bent	105	H ₂ O, H ₂ S	sp ³	
4	0	AB ₃	Trigonal planar	120	BCl ₃ , AlBr ₃	sp ²	
4	1	AB ₃	Pyramidal	107	NH ₃ , PCl ₃ , AsBr ₃	sp ³	
4	2	AB ₃ (Inter halogen)	T-shaped	90, 180	ICl ₃ , BrF ₃	sp ³ d	
5	0	AB ₄	Tetrahedron	109.5	CCl ₄ , CH ₄ , SiBr ₄	sp ³	
5	1	AB ₄	Distorted tetrahedron (Seesaw)		SF ₄ , SBr ₄ , SeCl ₄	sp ³ d	
5	2	AB ₄	Square planar	90, 180	XeF ₄	sp ³ d ²	
6	0	AB ₅	Trigonal bipyramidal	90, 180, 120	PCl ₅	sp ³ d	
6	1	AB ₅ (Inter halogen)	Square pyramid		ClF ₅ , ICl ₅ , IBr ₅	sp ³ d ²	
7	0	AB ₆	Octahedron	90, 180	SF ₆	sp ³ d ²	

VSEPR Theory

# of Atoms	# of electron pairs	Formula Type	Geometry	Bond Angle	Examples	Hybridization	Structure
3	0	AB ₂	Linear	180	CO ₂ , CS ₂ , BeH ₂		
3	1	AB ₂	Bent	117.5	GeCl ₂ , SO ₂ , NO ₂	sp ²	
3	2	AB ₂	Bent	105	H ₂ O, H ₂ S	sp ³	
4	0	AB ₃	Trigonal planar	120	BCl ₃ , AlBr ₃ ,	sp ²	
4	1	AB ₃	Pyramidal	107	NH ₃ , PCl ₃ , AsBr ₃	sp ³	
4	2	AB ₃ (Inter halogen)	T-shaped	90, 180	ICl ₃ , BrF ₃ ,	sp ³ d	

5	0	AB ₄	Tetrahedron	109.5	CCl ₄ , CH ₄ , SiBr ₄	sp ³	
5	1	AB ₄	Distorted tetrahedron (Seesaw)		SF ₄ , SBr ₄ , SeCl ₄	sp ³ d	
5	2	AB ₄	Square planar	90, 180	XeF ₄ ,	sp ³ d ²	
6	0	AB ₅	Trigonal bipyramidal	90, 180, 120	PCl ₅ ,	sp ³ d	
6	1	AB ₅ (Inter halogen)	Square pyramid		ClF ₅ , ICl ₅ , IBr ₅	sp ³ d ²	
7	0	AB ₆	Octahedron	90, 180	SF ₆	sp ³ d ²	