

VALENCE–SHELL ELECTRON–PAIR REPULSION (VSEPR) THEORY

A. BACKGROUND: VALENCE BOND THEORY

IMPORTANT NOTE: The information in this background section goes beyond what is required for Chemistry 11. However, this section is included to let you better understand why molecules bond together in specific shapes.

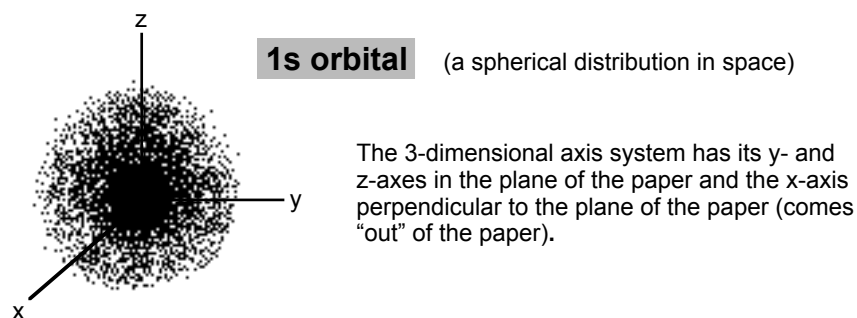
Valence Bond (VB) Theory proposes that “overlapping” of atomic VALENCE orbitals results in forming a COVALENT BOND between two atoms.

We have seen how electrons can be added to atoms to fill s-, p- and d-orbitals. Now we must look at the actual shapes of those orbitals as they are filled.

The Shapes of Electron Orbitals in an Isolated Atom

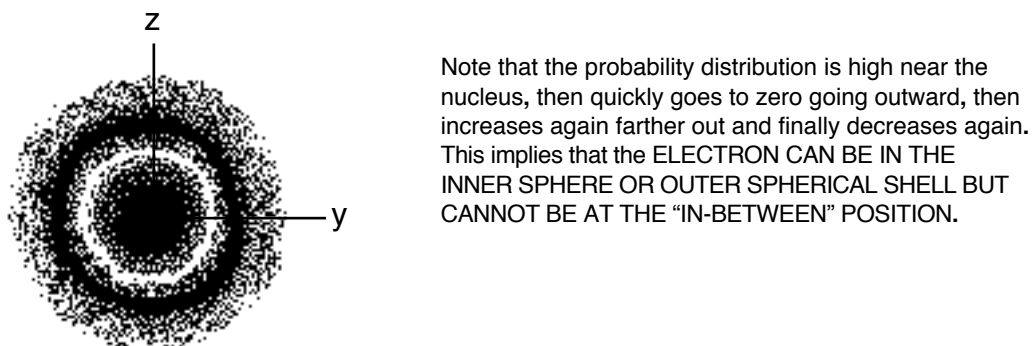
Definition: The **ELECTRON DENSITY** in an orbital is the probability of finding an electron at a given point in the orbital.

The electron density is a purely mathematical function and differs for each type of orbital. As a result, the shape of each type of orbital differs from the shapes of other types. Plotting the radial behaviour (outward from the origin) *versus* angular behaviour (3–dimensional rotation about the origin) of the 1s electron density gives the orbital shape shown below. (Think of a 1s electron as being represented by a bright blue light: bright at the centre but quickly tapering off in all directions within a short distance from the centre.)

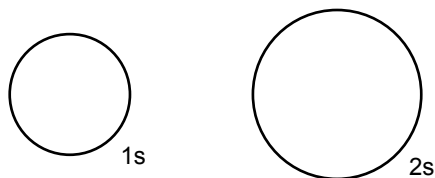


The greatest probability of finding an electron is near the nucleus; the electron density decreases in all directions as the distance from the nucleus increases.

A cross–section through the yz–plane of the 2s orbital shows the following electron density. (It looks somewhat similar to the above diagram because the electron density is the same in every direction.)

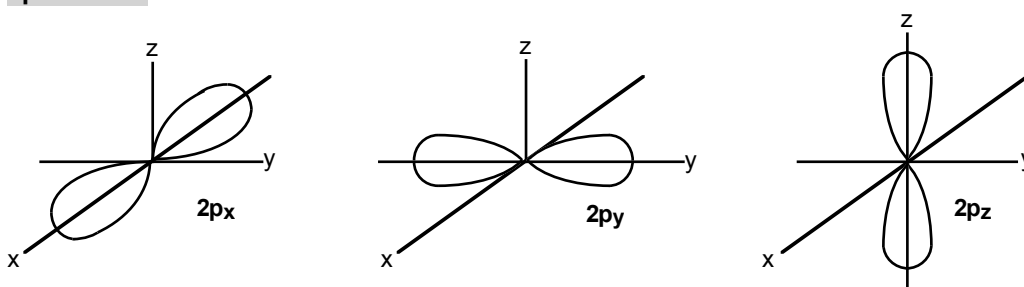


Because an orbital is described by a mathematical probability function having no definite boundaries (it tapers off rapidly, but never becomes zero), an orbital is frequently represented by a SURFACE enclosing 90% of the total electron probability. The 1s and 2s orbital surfaces are shown below:



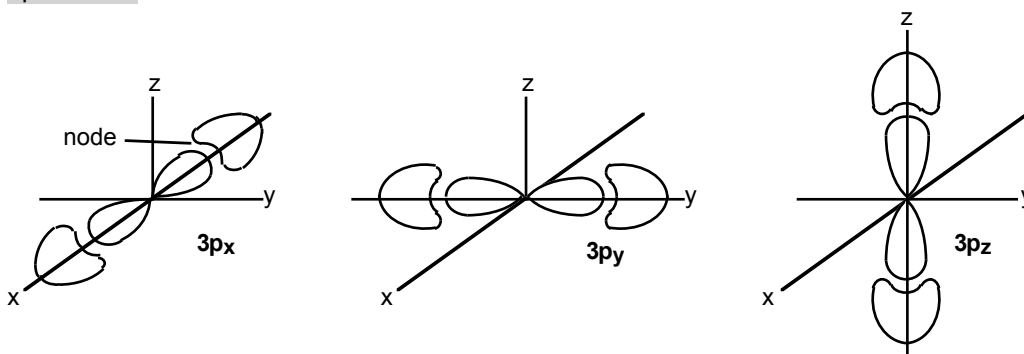
The shapes of the orbitals below are represented as surfaces to help you visualize the way the orbitals are arranged in space.

2p-Orbitals



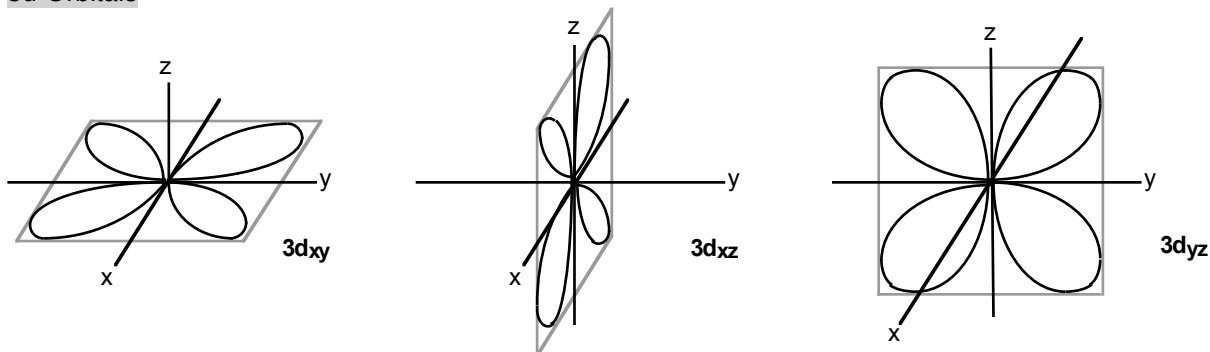
Each of the “carrot” shapes is called a “LOBE”. The “x” in “2p_x” indicates that the orbital lobes lie along the x-axis.

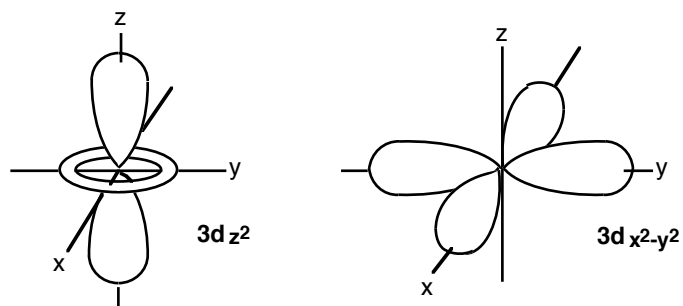
3p-Orbitals



The region between regions of non-zero electron probability where the probability of finding an electron drops to zero is called a “node”.

3d-Orbitals

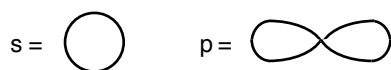




Forming Bond Orbitals By Overlapping Atomic Orbitals

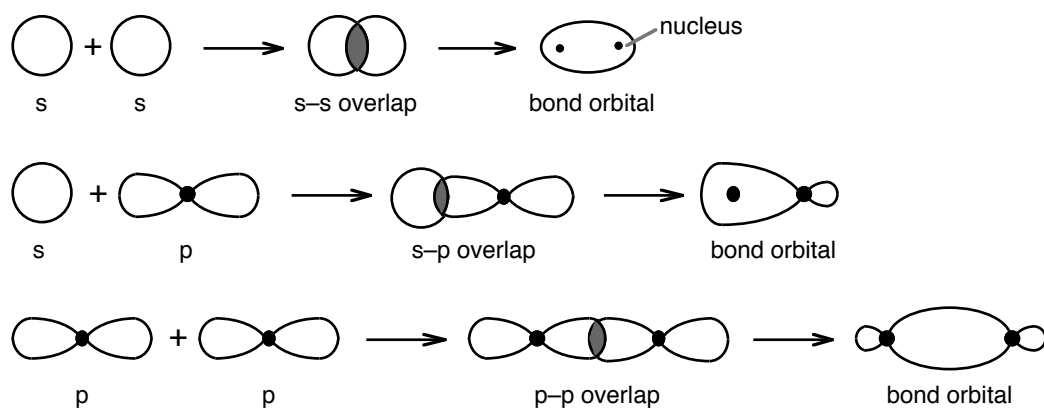
Valence bond theory assumes that when **atomic orbitals** overlap with each other, they form a new type of orbital called a **bond orbital**. This orbital overlap to form new bond orbitals is analogous to two water droplets on a glass surface touching each other and blending into a new, larger drop.

If we represent the “s” and “p” atomic orbitals as shown below,



three examples of bond orbital formation can be seen in the following example.

EXAMPLE:



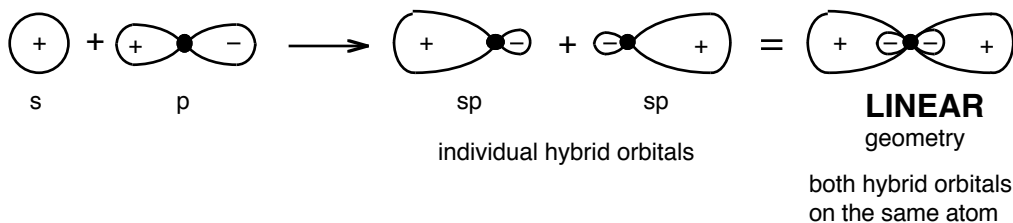
Hybridization

Mixing atomic orbital wave functions creates new orbitals that are combinations or “hybrids” of atomic orbitals. The hybridization of atomic orbitals is the basis of the orbital shapes and geometric orientations used in the valence-shell electron-pair repulsion theory in the upcoming Section B.

The more two orbitals on different atoms overlap, the stronger the bond between the atoms. The advantage of hybrid orbitals is that they overlap better with other orbitals and therefore form stronger bonds.

(a) sp Hybrid Orbitals

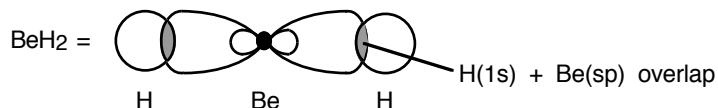
An “sp” hybrid orbital is formed by mixing an “s” with a “p” atomic orbital **from the same atom**. Because 2 orbitals are mixed together, 2 new orbitals are produced, only now they are “mixed” (or hybrid) orbitals. (One cup of applesauce plus one cup of cranberries, put into a blender, yields 2 cups of “cranapple” sauce.)



The two hybrid orbitals take on a linear (straight-line) arrangement to minimize the repulsion between electrons in the two orbitals.

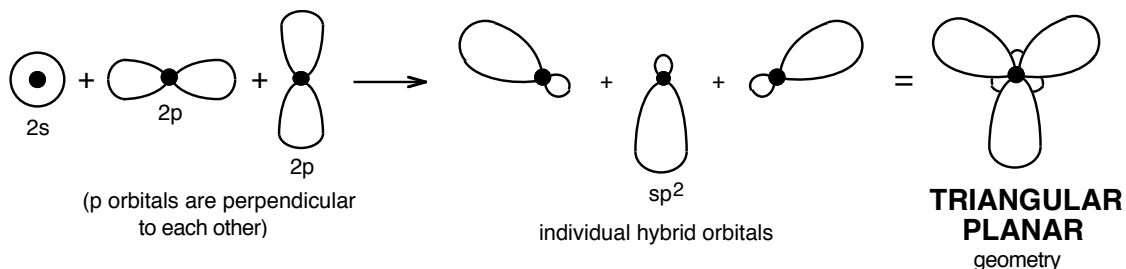
Analogy: Two tear-drop shaped balloons tied end-to-end push each other until they are 180° apart.

EXAMPLE: Beryllium uses sp hybrid orbitals when bonding with hydrogen.



(b) sp² Hybrid Orbitals

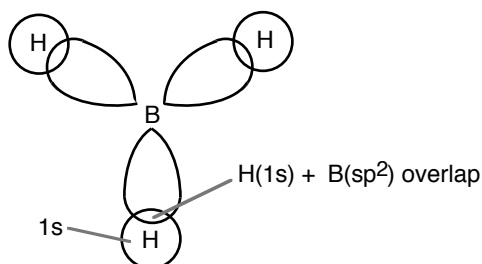
An “sp²” hybrid orbital is formed by mixing an “s” with TWO “p” atomic orbitals from the same atom.



The three hybrid orbitals have a triangular planar arrangement to minimize the repulsion between electrons in the three orbitals.

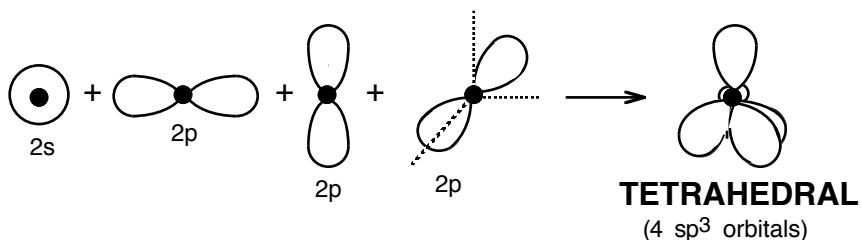
Analogy: Three tear-drop shaped balloons tied together push each other until they are 120° apart.

EXAMPLE: Boron uses sp² hybrid orbitals when bonding with hydrogen.



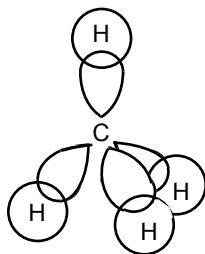
(c) sp^3 Hybrid Orbitals

An " sp^3 " hybrid orbital is formed by mixing an "s" with THREE "p" atomic orbitals from the same atom. Again, since 4 atomic orbitals are mixed and 4 hybrid orbitals are produced.



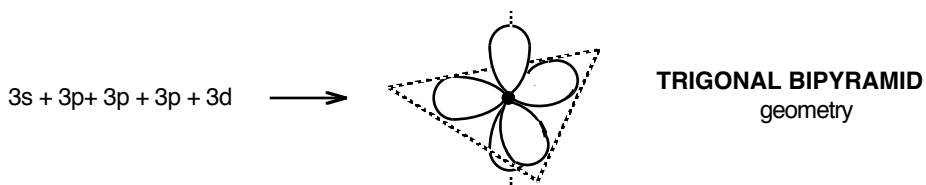
Analogy: Four tear-drop shaped balloons tied together push each other until they are 109° apart.

EXAMPLE: Carbon uses sp^3 hybrid orbitals when bonding to hydrogen.

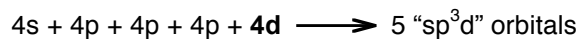


(d) sp^3d Hybrid Orbitals

An " sp^3d " hybrid orbital is formed by mixing an "s" orbital with THREE "p" orbitals and ONE "d" orbital from the same atom.



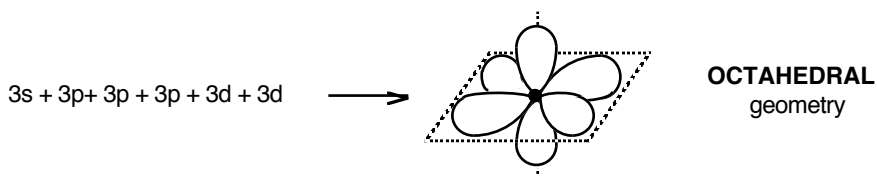
Note that this hybrid makes use of an unoccupied d-orbital with relatively low energy.



The use of sp^3d orbitals (and sp^3d^2 , below) is illustrated in Section B.

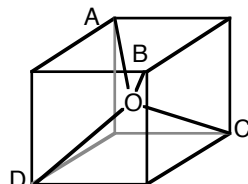
(e) sp^3d^2 Hybrid Orbitals

An sp^3d^2 hybrid orbital is formed by mixing an "s" orbital with THREE "p" orbitals and TWO "d" orbitals from the same atom.



EXERCISE:

- Predict the angles between each of the following.
 - two sp orbitals.
 - two sp^2 orbitals.
 - two adjacent sp^3d orbitals. Note that there are 2 different possible angles involved.
 - two adjacent sp^3d^2 orbitals.
 - NASTY! (for math freaks only) Predict the angle between two sp^3 orbitals (Hint: In the following diagram A, B, C, D are the corners of a tetrahedron. The tetrahedron rests inside a cube and O is at the exact center of the cube.)



B. VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR) THEORY

VALENCE BOND THEORY assumes that bonds form by overlapping orbitals on adjacent atoms, so that electrons in overlapping atomic orbitals are shared by both atoms. The valence bond theory also assumes that the more orbitals overlap, the more electrons are shared and the stronger the bond. This increased sharing of electrons causes atoms to position themselves to allow the maximum possible orbital overlap.

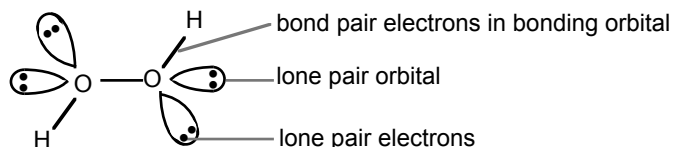
A simple version of valence bond theory is called the **VALENCE-SHELL ELECTRON-PAIR REPULSION THEORY (VSEPR Theory)**.

The following additional definitions are used.

BONDING ORBITALS, BONDING PAIR. These terms refer to orbitals that are directly involved in forming bonds, and to the pairs of electrons that occupy such orbitals. The electrons in a bond may come from either of the atoms involved in the bond.

LONE PAIR ORBITAL, LONE PAIR ELECTRONS. These terms refer to a valence orbital that contains electrons NOT directly involved in a bond.

EXAMPLE:



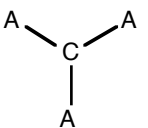
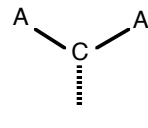
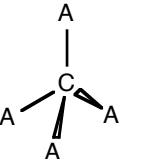
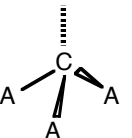
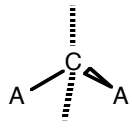
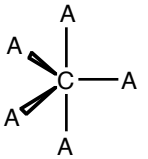
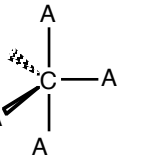
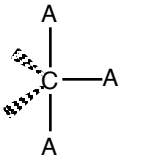
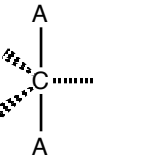
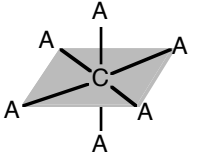
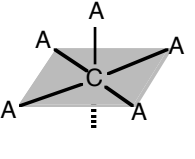
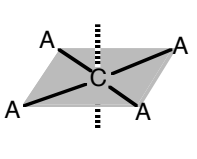
To simplify matters, valence bond theory assumes that lone pair orbitals and inner shell orbitals (that is, filled atomic orbitals) are unchanged when bonds form, and that the shape of filled atomic orbitals is not distorted by the presence of neighbouring atoms.

OCCUPIED valence orbitals in a **molecule** are somewhat different from orbitals in an **atom** and consist of “lobes” extending out from the atom in ONE direction. The position of these lobes, relative to each other, can be shifted around to minimize electrical repulsions existing between electrons in orbital lobes.

Because electrons repel each other, an atom's occupied valence orbitals **stay as far from each other as possible**. Lone pair electrons are confined to a small region of space around a single atom, whereas bond electrons move farther away from the central atom by shifting closer to the attached atom. Hence, bonding electrons suffer less repulsion from other central-atom electrons because the bonding electrons retreat farther from the central atom. As a result of differing amounts of repulsion for bond pair and lone pair electrons, the following rule applies.

$$\left(\begin{array}{c} \text{repulsion} \\ \text{between 2} \\ \text{LONE PAIRS} \end{array} \right) > \left(\begin{array}{c} \text{repulsion between} \\ \text{a LONE PAIR and a} \\ \text{BOND PAIR} \end{array} \right) > \left(\begin{array}{c} \text{repulsion} \\ \text{between 2} \\ \text{BOND PAIRS} \end{array} \right)$$

TABLE OF MOLECULAR SHAPES

Total number of orbitals	A = attached atom C = central atom — = bonding orbital = lone pair orbital
2	$\text{A} \text{ --- } \text{C} \text{ --- } \text{A}$ LINEAR
3	 TRIANGULAR PLANAR  V-SHAPED
4	 TETRAHEDRON  TRIGONAL PYRAMID  V-SHAPED
5	 TRIGONAL BIPYRAMID  IRREGULAR TETRAHEDRON  T-SHAPED  LINEAR
6	 OCTAHEDRON  SQUARE PYRAMID  SQUARE PLANAR

The VSEPR theory has a fairly general application, but is best suited to species where the central atom is a REPRESENTATIVE element; that is, an element which is NOT a transition metal.

The fact that some central atoms bond to 5 or 6 (or more) other atoms implies 10 or more electrons can exist in the valence shell. The ability of a central atom to accommodate 10 or 12 valence electrons is a result of involving one or more d-orbitals having a low-lying energy; this is where sp^3d and sp^3d^2 orbitals come in.

THE RULES OF THE GAME

- Write the Lewis structure for the molecule, as usual.
 - Count ALL the valence electrons, adding or subtracting electrons to allow for the overall charge.
 - Supply electrons to the surrounding atoms to bring them to a full-shell configuration.
 - Make sure there is AT LEAST ONE BOND between each attached atom and the central atom.
- Determine the number of left-over electrons on the central atom, that is “lone-pair electrons” (*lpe*), as follows.

$$\# \text{ of } lpe = (\text{total valence electrons}) - (\# \text{ of } e^- \text{ donated to other atoms})$$

- Determine the number of lone-pair orbitals (*lpo*) on the central atom required to hold the *lpe* as follows.

$$\# \text{ of } lpo = (\# \text{ of } lpe) / 2$$

If the number of *lpe* is an ODD number, round the number of *lpo* UP (because the odd electron occupies a full orbital).

- Determine the total # of orbitals required as follows.

$$\text{total \# orbitals} = (\# \text{ of attached atoms}) + (\# \text{ of } lpo)$$

- If the central atom is **not** in columns I, II or III, **and** if the central atom has less than an octet of electrons, form multiple bonds to the central atom.

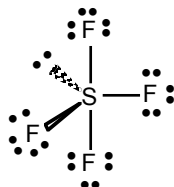
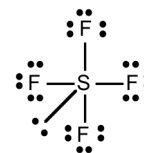
- Use the **Table of Molecular Shapes** (you will eventually have to memorize it) to assign a geometry based on

(A) the total # of orbitals, and (B) the # of *lpo*.

The presence of multiple bonds does not affect the geometry of the molecule. Double and triple bonds are treated as if they are “fat single bonds”.

EXAMPLE: What is the shape of SF₄?

- SF₄ has 34 e[−] (6 from S, 7 from each F)
- Assigning 8 e[−] to each F uses up 32 valence e[−]
- There are 34 − 32 = 2 *lpe*
- Therefore, there is $\frac{2}{2} = 1$ *lpo*
- Overall, there are 5 orbitals: 1 *lpo* + 4 attached atoms (see at right)
- S has 10 valence e[−] (5 orbitals x 2 e[−]), so no double bonds are required
- From the **Table of Molecular Shapes** we assign the following shape:

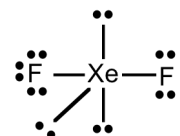


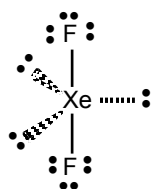
**IRREGULAR
TETRAHEDRON**

(based on a trigonal bipyramidal arrangement of orbitals)

EXAMPLE: What is the shape of XeF₂?

- XeF₂ has 22 e[−] (8 from Xe, 7 from each F)
- Assigning 8 e[−] to each F uses up 16 valence e[−]
- There are 22 − 16 = 6 *lpe*
- Therefore, there are $\frac{6}{2} = 3$ *lpo*
- Overall, there are 5 orbitals: 3 *lpo* + 2 attached atoms (see at right)
- Xe has 10 valence e[−] (5 orbitals x 2 e[−]), so no double bonds are required
- From the **Table of Molecular Shapes** we assign the following shape:



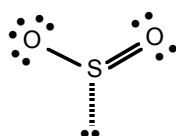
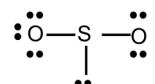


LINEAR

(based on a trigonal bipyramidal arrangement of orbitals)

EXAMPLE: What is the shape of SO_2 ?

- SO_2 has 18 e^- (6 from S, 6 from each O)
- Assigning 8 e^- to each O uses up 16 valence e^-
- There are $18 - 16 = 2$ ***lpe***
- Therefore, there are $2/2 = 1$ ***lpo***
- Overall, there are 3 orbitals: 1 ***lpo*** + 2 attached atoms (see at right)
- S only has 6 valence e^- , so a double bond is formed
- From the **Table of Molecular Shapes** we assign the following shape



V-SHAPED

(based on a triangular planar arrangement of orbitals)

EXERCISES:

2. Write the Lewis structures and predict the shapes of the following.

- | | | | | | |
|-------------------------|---------------------|----------------------|---------------------|------------------------------|---------------------|
| (a) SeF_4 | (e) IF_5 | (i) ClO_3^- | (m) SCl_2 | (q) ArF_3^+ | (u) FOO |
| (b) O_3 | (f) ClF_3 | (j) SbCl_5 | (n) SF_6 | (r) XeO_2F_2 | (v) IO_4^- |
| (c) ICl_5 | (g) BF_4^- | (k) I_3^- | (o) BeCl_2 | (s) KrF_4 | (w) ICl_4 |
| (d) SiF_6^{2-} | (h) AsF_5 | (l) ClO_2 | (p) NCl_3 | (t) PCl_3 | (x) BF_3 |

3. Write Lewis structures for the following and state the shape of the molecule around each bold atom.

