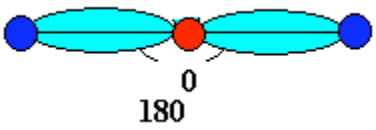
**VSEPR Theory**

VSEPR (an acronym for **V**alence **S**hell **E**lectron **P**air **R**epulsion) theory (theoretical model) is the procedure to predict the geometries of molecules. This is a theoretical model that works very well for simple molecules. **It simply says that the geometry (shape) of the molecule is dictated by the non-bonding electrons (or also known as lone electron pair(s)) sitting on the central atom**. Why the central atom? The answer to that question is this we are interested in predicting the geometry round only the central atom and not at all concerned with geometry around terminal atoms.

Now let us see how the non-bonding pair or pairs of electrons play a central role in determining the geometry. In an atom, the nucleus (red) is deeply buried in the negatively charged electron cloud (yellow) as shown below.

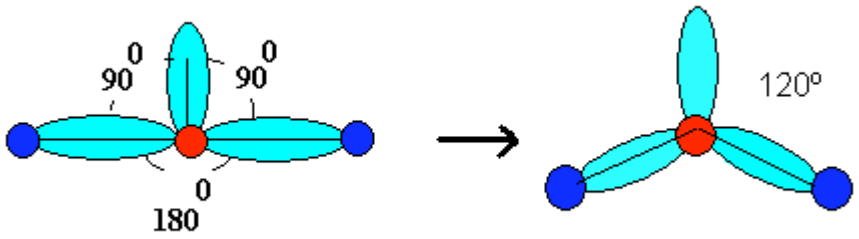
When atoms come closer, the electrons from one atom are repelled by the electrons of another atom. Therefore, this electron repulsion must be minimized in order for the molecule to become stable (stable means that it exists in nature for a long period of time). The central crux of the VSEPR theory is to minimize (or optimize) the electron repulsion in a given molecule.

Now, let us examine how the repulsion minimization evolves into a stable structure. In the following diagram two atoms (blue) are bonded to the central atom (red) and no non-bonding electrons exists on the central atom.




All electrons are engaged in bonding (cyan) on both sides of the central atom and as such the bond angle between the electrons is $180^0$. The angle is optimum because it minimizes the electron repulsion. If you bend the molecule slightly, up or down, you will introduce some repulsion that will lead to instability or repulsion.

Consider the following situation (central atom is indicated by red, bonded atoms by blue and electron density by cyan) where there exists non-bonding electrons on the central atom (left diagram).




You can see that there is a smaller distance between the non-bonding electrons and bonding electrons as indicated by the bond angle of $90^0$ that manifests in repulsion. On the other hand, the distance between bonding electrons is optimal as indicated by the bond angle of $180^0$. Therefore, the repulsion between the non-bonding electrons and bonding electrons needs to be minimized. This is achieved by pushing both bonds downwards until all the repulsions are minimized. This happens only when all the bond angles are equal to one another, that is, $120^0$(right diagram). This illustrates the importance and role of non-bonding electrons on the central atom.

The above provided explanation is easy to understand because it is a two-dimensional picture. If it is a three-dimensional picture, it is not so easy to understand. However, you should tune yourself in visualizing the shapes of the molecules in three-dimension.

When applying the VSEPR theory, you should remember few rules:

(a) If the groups/polyatomic ions are bonded to central atom, treat them as single atoms.
(b) The double bonds and triple bonds are treated as if they are single bonds. But keep in mind that single bonds and multiple bonds are not the same as the latter involves more electrons and hence electron density is higher.
(c) If Lewis structure gives two or more resonance structures, predict the geometry for any one of them because all the resonance structures yield the same geometry due to rule (b).

**Steps to Predict Geometry**

(a) Study all the geometrical shapes in terms of their requirements
(b) Write the Lewis structure
(c) Locate the central atom and terminal atoms
(d) Account for number of non-bonding electron pairs on the central atom
(e) With this information, predict the geometry.

**Word of caution:** In order to a create geometry, join only the terminal atoms. If electrons are present in terminal positions, ignore them because they are not part of the geometry.

To predict the geometry of molecules in a systematic manner and also to make your digesting process easier, the molecules are divided into two groups based on whether the central atom has non-bonding electrons or not. In all the following structures, A is the central atom, B are the terminal (bonded) atoms, groups, or polyatomic ions. I have used the word "entities" to mean atoms, groups or polyatomic ions. In addition, the dots represent electrons - one dot for one electron. Wherever applicable, the geometry is drawn in red and blue lines.

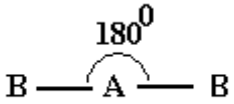
## Central Atom with No Non-bonding Electrons

This group consists of five main geometries ($AB_2$, $AB_3$, $AB_4$, $AB_5$, and $AB_6$). In the following sections, all the five categories are discussed with examples.

### I. Linear Structure ($AB_2$)

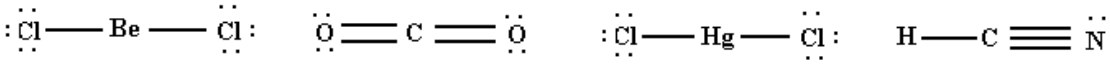
As far as predicting the geometry is concerned, $AB_2$ type is the simplest form. A is the central atom, B are bonded to the central atom, the bond angle BAB is $180^0$, and the central atom has no non-bonding electrons. This is type of geometry is known as a linear geometry. Therefore, linear structure is described by this geometry.

**Criteria for Linear Geometry**

| Geometry | Number of Terminal Entities (B) | Number of Non-bonding Electron Pairs | Bond Angles | Type |
|---|---|---|---|---|
|   | 2 | 0 | $180^0$ | $AB_2$ |

**Examples:** Beryllium chloride ($BeCl_2$), Carbon dioxide ($CO_2$), Mercury (II) chloride ($HgCl_2$), and Hydrogen cyanide (HCN).

The Lewis structures for these molecules are,



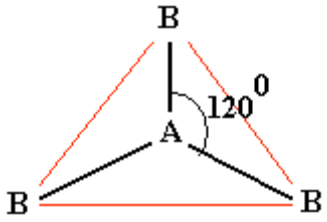
- Two atoms are bonded to central atoms.
- Terminal atoms obey the octet rule.
- The central atoms Be and Hg obey the rule of four and C obeys the octet rule.
- Central atoms have no non-bonding electrons
- Bond angles around central atoms are $180^0$

Hence, these molecules can be described by linear geometry or $AB_2$ type and thus are classified as **linear type** of molecules.

## II. Trigonal Planar Structure ($AB_3$)

This structure consists of three entities bonded to central atom, all three bond angles (BAB) are exactly the same, that is, $120^0$, and the central atom has no non-bonding electrons. This geometry is known as trigonal planar geometry that has 3 edges and 3 corners. Therefore, the trigonal planar structure is described this geometry.

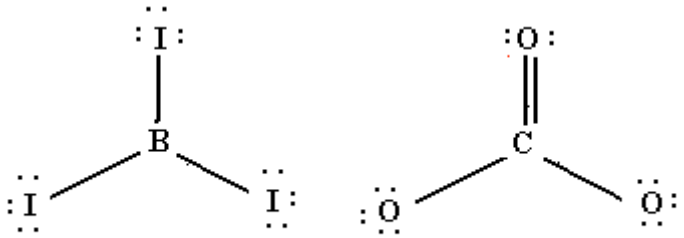
### Criteria for Trigonal Planar Geometry

| Geometry | Number of Terminal Entities (B) | Number of Non-bonding Electron Pairs | Bond Angles | Type |
|---|---|---|---|---|
|   | 3 | 0 | $120^0$ | $AB_3$ |

It is called trigonal planar ( some times also known as planar triangle) because all the atoms lie in the same plane, namely, the plane of the paper, and looks like a triangle when terminal atoms are connected (red lines).

**Example:** Boron triiodide **(**$BI_3$) and Carbonate ion ($CO_3^{2-}$).

Te Lewis structures for these are



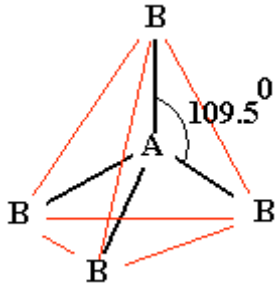
- Three atoms are bonded to central atoms.
- Central atom B in boron triiodide obeys the rule of six and the central atom C in carbonate ion obeys the octet rule.
- Terminal atoms obey the octet rule as you can see by eight electrons around them.
- The central atoms do not have non-bonding electrons and the bond angles around B and C are $120^0$.

Hence these structures can be described by trigonal planer geometry or $AB_3$ type and therefore are known as **trigonal planar** structures.

## III. Tetrahedral Structure ($AB_4$)

This type consists of four entities bonded to the central atom. All bond angles (BAB) are exactly the same, that is, $109.5^0$. This bond angle is known as tetrahedral angle. The central atom has no non-bonding electrons. This is type called tetrahedral geometry that has 4 faces, 4 corners, and 6 edges.

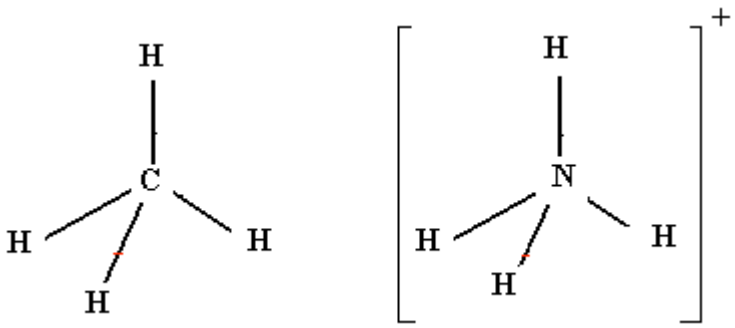
**Criteria for Tetrahedral Geometry**

| Geometry | Number of Terminal Entities (B) | Number of Non-bonding Electron Pairs | Bond Angles | Type |
|---|---|---|---|---|
|   | 4 | 0 | $109.5^0$ | $AB_4$ |

In this geometry, A is situated at the center of tetrahedron and four Bs occupy four corners of tetrahedron. The tetrahedron geometry is represented by red lines.

**Example:** Methane ($CH_4$) and Ammonium ion ($NH_4^+$).

The Lewis structures for these are

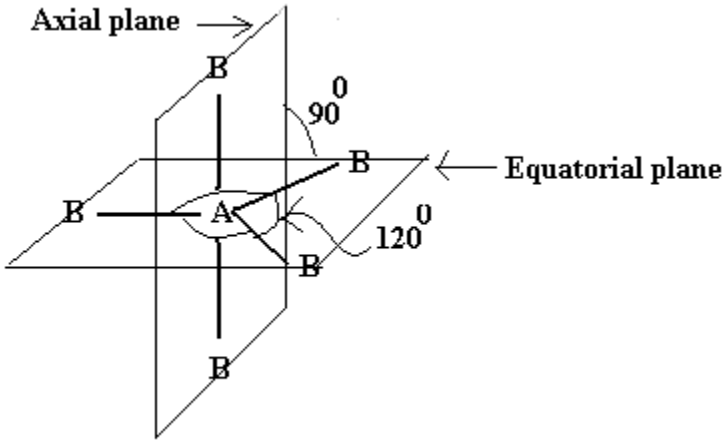



- Four H are bonded to central atoms
- Central atoms C and N are located at the center of the tetrahedron and obey the octet rule Terminal Hs occupy four corners and obey duet rule
- Central atoms have no non-bonding electrons and bond angles are tetrahedral angles

Since these structures satisfy the tetrahedral geometry or $AB_4$ type, they are classified as **tetrahedral** structures. Note that the + sign on the ammonium ion has nothing to do with the geometry.

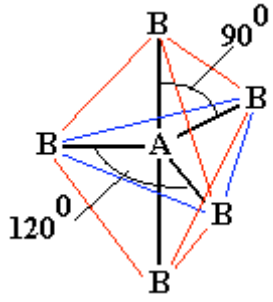
## IV. Trigonal Bipyramidal Structure ($AB_5$)

This type consists of five entities (B) bonded to the central atom A. The central atom has no non-bonding pair(s) of electrons, and there are three different bond angles; the angle between any two equatorial bonds is $120^0$, that between two axial bonds is $180^0$ (not shown in the diagram), and the angle between an axial bond and an equatorial bond is $90^0$. This geometry is known as trigonal bipyramidal that has 6 faces, 5 corners, and 9 edges.




Both axial and equatorial planes are perpendicular to each other. The central atom (A) is situated at the intersection of these planes. There are three atoms (B, A, and B) in axial plane and four atoms (B, A, B, B) in equatorial plane. The angle between both planes is $90^0$.

### Criteria for Trigonal Bipyramidal Geometry

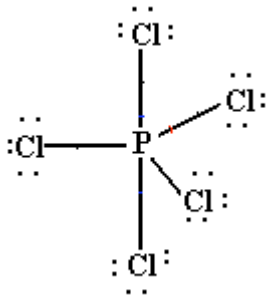
| Geometry | Number of Terminal Entities (B) | Number of Non-bonding Electron Pairs | Bond Angles | Type |
|---|---|---|---|---|
|   | 5 | 0 | $120^0$, $180^0$, $90^0$ | $AB_5$ |

The central atom A is located at the center of the geometry and five Bs occupy five corners. It is called trigonal bipyramidal structure because two pyramids (bipyramidal) located above and below the equatorial plane (indicated in red lines) are fused together at the triangle (trigonal) base (blue lines). The whole geometry is represented by the blue and the red lines.

NOTE: the pyramids in Egypt have square bases with 5 faces, 5 corners, and 8 edges. But the pyramids in trigonal bipyramidal structure have triangle base with 4 vertices.

**Example:** Phosphorus Pentachloride ($PCl_5$).

The Lewis structure for this molecule is

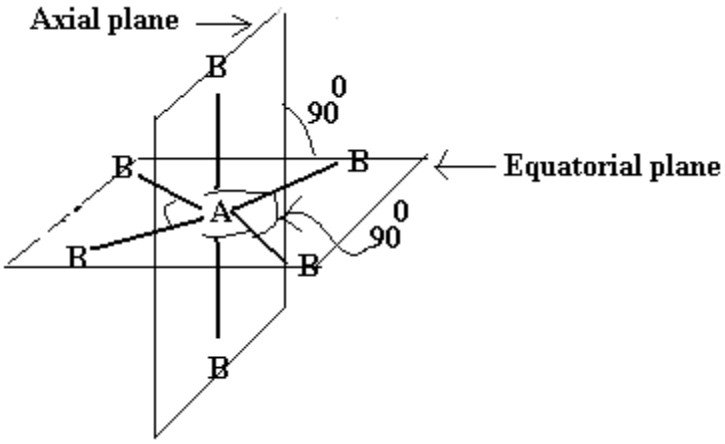



- The central atom P is located at the center of the trigonal bipyramid at the intersection of axial and equatorial planes
- Five atoms are bonded to the central atom P and occupy five corners
- Central atom has no non-bonding electrons
- Bond angles Cl-P-Cl in equatorial plane are $120^0$
- Bond angle between axial plane and equatorial plane is $90^0$
- Bond angle between P-Cl bonds in axial plane is $180^0$
- P obeys the rule of 10 and all Cl obey the octet rule.
- Pyramids, above and below the equatorial plane, are symmetrical.

Thus $PCl_5$ satisfies the requirements for trigonal bipyramidal geometry or $AB_5$ type and hence classified as **trigonal bipyramidal** structure.

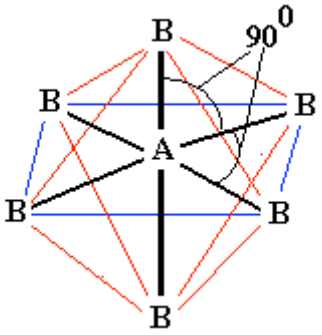
**V. Octahedral Structure ($AB_6$)**

This structure consists of six terminal entities (B) bonded to the central atom A. The central atom has no non-bonding pair(s) of electrons. All bond angles within the equatorial plane, within axial plane and between equatorial plane and axial plane are the same, namely, $90^0$. It has 8 (*octa*) faces, 6 corners, and 12 edges. This geometry represents the fusion of two pyramids at the square base.




Like trigonal bipyramid, this also has two planes (axial and equatorial) that are perpendicular to each other. The central atom (A) is at the intersection of these planes. There are three atoms (B, A, and B) in axial plane and fiver atoms (B, B, A, B, and B) in equatorial plane. All bond angles are $90^0$ except the angle between bonds in axial plane, which is $180^0$.

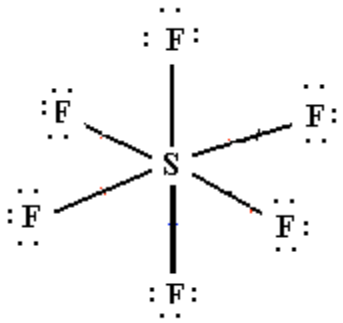
**Criteria for Octahedral Geometry**

| Geometry | Number of Terminal Entities (B) | Number of Non-bonding Electron Pairs | Bond Angles | Type |
|---|---|---|---|---|
|  | 6 | 0 | $90^0$ | $AB_6$ |



**Example:** Sulfur Hexafluoride ($SF_6$).

The Lewis structure for this molecule is




- Central atom S is located at the center of the octahedron at the intersection of axial and equatorial planes
- Six F atoms occupy six corners
- S obeys the rule of twelve and all terminal atoms obey the octet rule
- Pyramids, above and below the equatorial plane are symmetrical
- Central atom has non non-bonding electrons
- All bond angles are $90^0$

The $SF_6$ molecule satisfies all the requirements of octahedral geometry or $AB_6$ type and hence classified as **octahedral** structure.

## Précis

| | | |
|---|---|---|
| Linear | $AB_2$ type | $BeCl_2$ , $CO_2$ |
| Trigonal Planar | $AB_3$ type | $BI_3$ , $CO_3^{2-}$ |
| Tetrahedral | $AB_4$ type | $CH_4$, $NH_4^+$ |
| Trigonal Bipyramid | $AB_5$ type | $PCl_5$ |
| Octahedral | $AB_6$ type | $SF_6$ |

## Central Atom in Molecules with One or More Non-bonding Electrons

This section is forthcoming**.**