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Ministry of Higher Education & Scientific research
Al-Mustaqbal University
Science College
Biochemistry Department

Introduction in Chemistry

For

First Year Student/course 2

Lecture 5

By

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VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Definition: The Valence-Shell-Electrons-Pair-Repulsion Theory, (VSEPR) proposes that the stereochemistry of an atom in a molecule is determined primarily by the repulsive interactions among all the electron pairs in its valence shell.

Postulates of VSEPR Theory

1-The shape of the molecule is determined by repulsion between all of the electron pairs present in the valence shell

2-A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than the repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. The repulsive interactions decrease in the order:

Lone Pair- lone pair > Lone Pair- bond- pair > Bond Pair- bond pair.

LP-LP > LP-BP > BP-BP

3-The magnitude of repulsion between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atom.

4-Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond. Repulsive forces decrease sharply with increasing bond angle between the electron pairs

Limitations of VSEPR Theory:

Some significant limitations of the VSEPR theory include:

1-This theory fails to explain isoelectronic species (i.e. elements having the same number of electrons). The species may vary in shapes despite having the same number of electrons.

2-The VSEPR theory does not shed any light on the compounds of transition metals. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.

3-Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

Predicting the Shapes of Molecules:

The following steps must be followed in order to decide the shape of a molecule.

1- The least electronegative atom must be selected as the central atom (since this atom has the highest ability to share its electrons with the other atoms belonging to the molecule).

2- The total number of electrons belonging to the outermost shell of the central atom must be counted.

3- The total number of electrons belonging to other atoms and used in bonds with the central atom must be counted.

4- These two values must be added in order to obtain the valence shell electron pair number or the VSEP number.

How can the VSEPR Theory be used to Predict the Shapes of Molecules?

1-Total number of electron pairs around the central atom = ½ (number of valence electrons of central atom + number of atoms linked to central atom by single bonds)

- For negative ions, add the number of electrons equal to the units of negative charge on the ions to the valence electrons of the central atom.
- For positive ions, subtract the number of electrons equal to the units of positive charge on the ion from the valence electrons of the central atom.

2-The number of Bond pair = Total number of atoms linked to central atom by single bonds.

3-Number of lone pairs = Total number of electron – No of shared pair

What is VSEP Number?

The VSEP number describes the shape of the molecule, as described in the table provided below.

Each of these corresponding shapes can also be found in the illustration provided earlier. However, the VSEPR theory cannot be used to obtain the exact bond angles between the atoms in a molecule.

VSEPR notation gives a general formula for classifying chemical species based on the number of electron pairs around a central atom. Note, however, that not all *ABn* species have the same molecular geometry. For example, carbon dioxide and sulfur dioxide are both *AB*2 species, but one is linear and the other is bent. Sometimes, the notation is expanded to *ABnEm* to include lone pair electrons. This can get confusing, because water can be referred to as an *AB*2 species or an *AX*2*E* species, depending on the conventions the author or text chooses.

In general,

•A is used to represent the central atom;

•B or X is used to represent the number of atoms bonded to the central atom;

•E represents the number of lone pairs on the central atom (ignore lone pairs on bonded atoms).

The VSEPR model counts both bonding and nonbonding (lone) electron pairs, and calls the total number of pairs the steric number (SN). If the element A has m atoms bonded to it and n nonbonding pairs, then

$$SN=m+n \ldots\ldots \quad 1$$

SN is useful for predicting shapes of molecules. If X is any atom bonded to A (in single, double, or triple bond), a molecule may be represented by AXmEn where E denotes a lone electron pair. This formula enables us to predict its geometry. The common SN, descriptor, and examples are

given in the table below. Note that the SN is also called **the number of VSEPR pairs or number of electron pairs**

Molecular shapes and steric numbers (SN)		
Example	**SN**	**Descriptor**
$BeCl_2$, CO_2	2	**Linear**
BF_3, SO_3 SO_2E,	3	**Trigonal planar bent**
CH_4 **NH_3** **E** **H_2O** **E_2**	4	**Tetrahedral** **pyramidal bent**

PF_5 SF_4 E ClF_3 E_2	5	Trigonal bypyramidal butterfly T-shape
SF6, OIF5 BrF_5E XeF_4E_2	6	octahedral pyramidal square planar

Use VSEPR notation to represent the molecules O_3, O_2, CCl_4, NaCl, H_2O

O_3= AB2E O_2= ABE2 CCL_4= AB4 NaCl= its an ionic H_2O= AB_2E2

What would be the shape of the molecule if the VSEP number is 5?

The molecule would have a trigonal bipyramidal structure.

summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

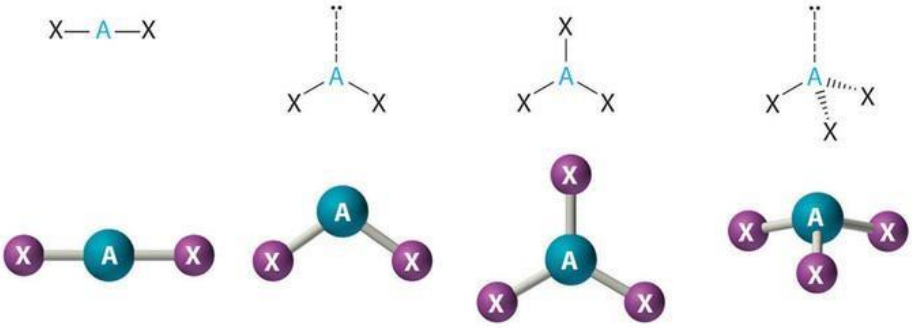
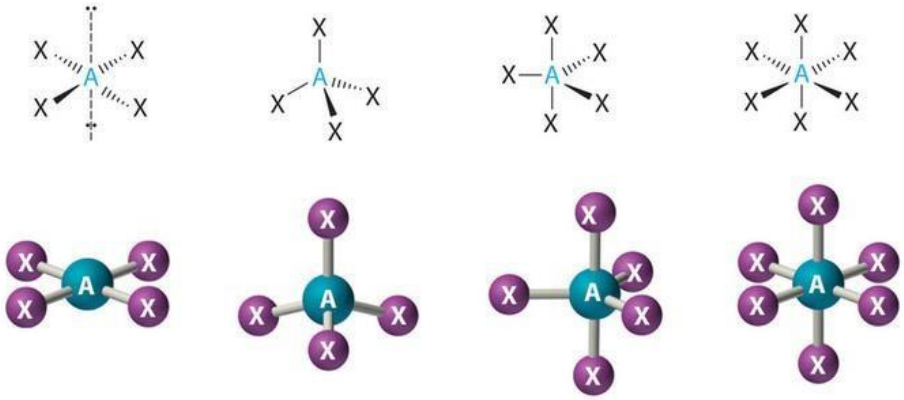
AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
				
Idealized Bond Angles	180°	<180°	120°	<120°
AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
				
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

Figure: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2 Molecules: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

H:Be:H or H—Be—H

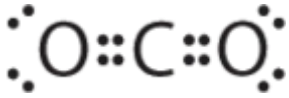
Lewis structure

2. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

3. From Figure below we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

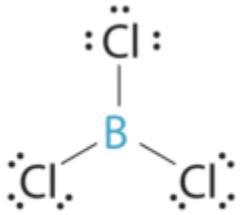
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear

Three Electron Groups

AX_3 Molecules: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



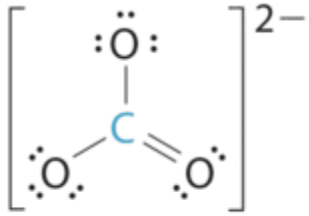
Lewis structure

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 1we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure

AX_3 Molecules: CO_3^{-2}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



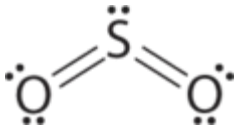
Lewis structure

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.

AX_2E Molecules: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



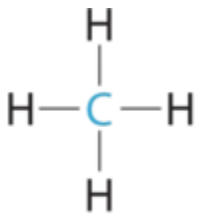
3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 10.2.410.2.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex. The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

Four Electron Groups

AX_4 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



Lewis structure

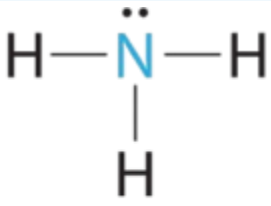
2. There are four electron groups around the central atom. As shown in Figure 10.2.210.2.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 1).

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 10.2.310.2.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions

AX_2E_2 Molecules: H_2O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

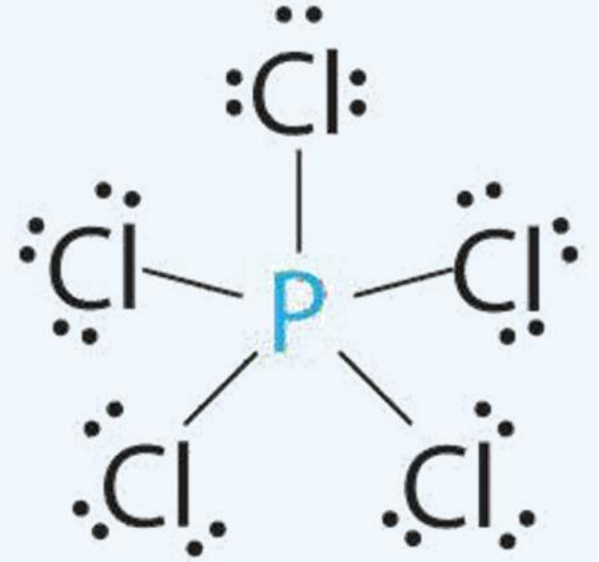
3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.

Five Electron Groups

AX_5 Molecules: PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is

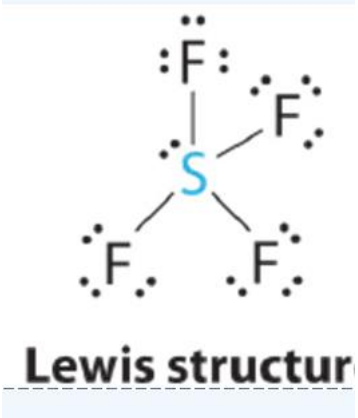


3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4-The molecular geometry of PCl_5 is trigonal bipyramidal, as shown in Figure 1. The molecule has three atoms in a plane in equatorial positions and two atoms above and below the plane in axial positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example

AX_4E Molecules: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 1

3-We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

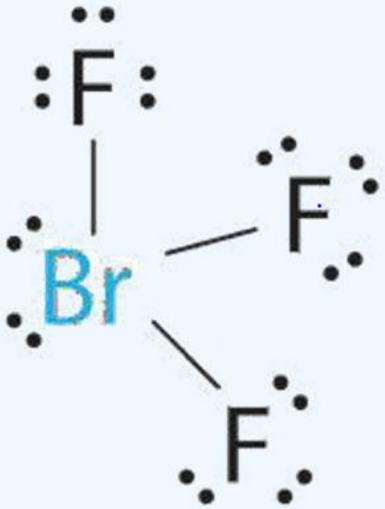
At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on

a trigonal bipyramid with a missing equatorial vertex; it is described as a seesaw. The Faxial–S–Faxial angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.

AX_3E_2 Molecules: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

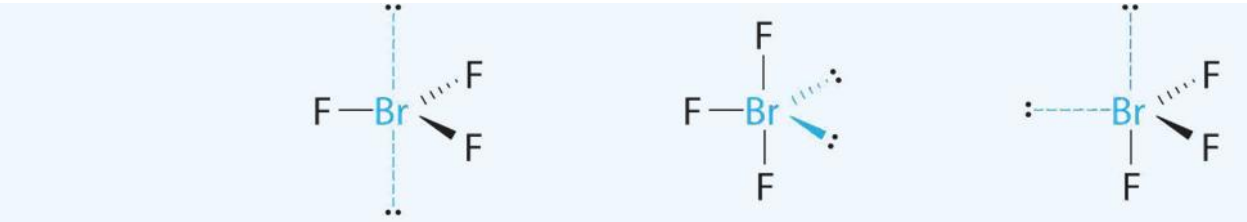


Lewis structure

2-There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3-With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial

positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4-The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions

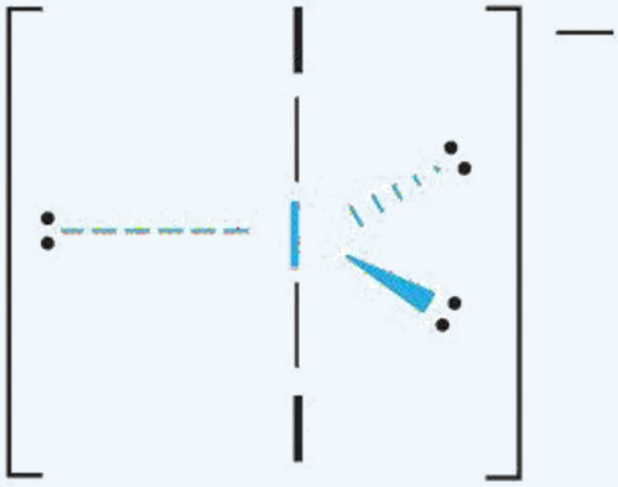
Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is

2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

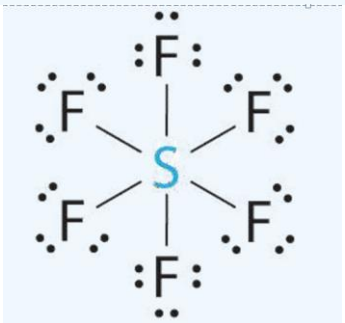
4-With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices

AX_6 Molecules: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is

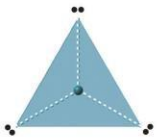
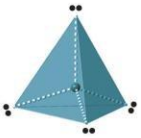
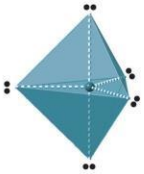
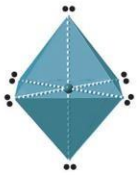
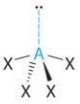
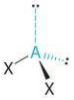
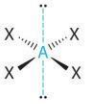


Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 10.2.210.2.2 that the geometry that minimizes repulsions is octahedral.
3. With only bonding pairs, SF6 is designated as AX6. All positions are chemically equivalent, so all electronic interactions are equivalent.

There are six nuclei, so the molecular geometry of SF6 is octahedral

Electron Groups	2	3	4	5	6
Molecular Geometry	 Linear	 Trigonal planar	 Tetrahedral	 Trigonal bipyramidal	 Octahedral
Zero Lone Pairs	Linear AX_2	 Trigonal planar AX_3	 Tetrahedral AX_4	 Trigonal bipyramidal AX_5	 Octahedral AX_6
One Lone Pair		 Bent (V-shaped) AX_2E	 Trigonal pyramidal AX_3E	 Seesaw AX_4E One axial lone pair	 Square pyramidal AX_5E
Two Lone Pairs			 Bent (V-shaped) AX_2E_2	 T-shaped AX_3E_2 Two axial lone pairs	 Square planar AX_4E_2
Three Lone Pairs				 Linear AX_2E_3 Three axial lone pairs	