Main Group Chemistry
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Lecture – 05
Structure and Bonding aspects:
Lewis Structures and VSEPR Theory

Once again, I welcome you all to my lecture series on the chemistry of main group elements. So far, I was discussing about the classification of elements and periodic properties and also I gave introduction to the type of compounds we come across among main group elements. Before I proceed to elaborate the chemistry of main group elements group wise, let me bring another important concept that is very important to understand the physical and chemical properties and also the reactivity of main group compounds that is structure and bounding aspects.

Let me begin with Lewis structures. We are all familiar with the Lewis structures.

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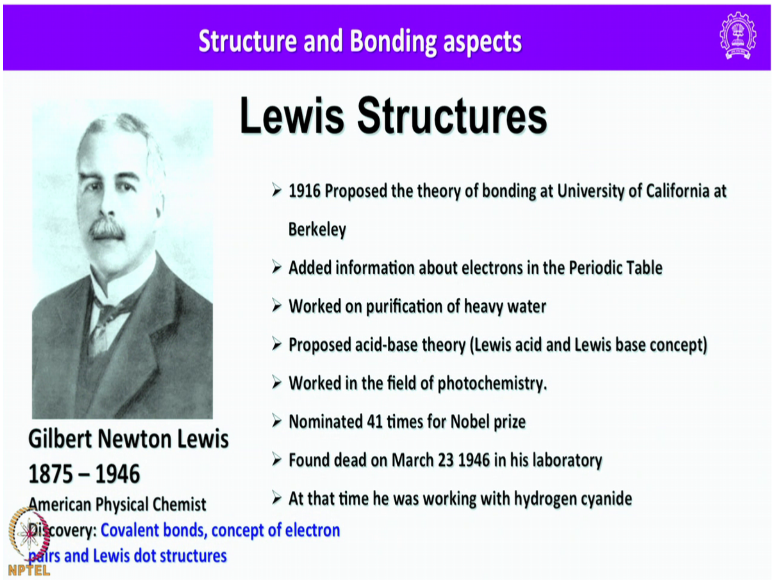

Structure and Bonding aspects

Lewis Structures

- 1916 Proposed the theory of bonding at University of California at Berkeley
- Added information about electrons in the Periodic Table
- Worked on purification of heavy water
- Proposed acid-base theory (Lewis acid and Lewis base concept)
- Worked in the field of photochemistry.
- Nominated 41 times for Nobel prize
- Found dead on March 23 1946 in his laboratory
- At that time he was working with hydrogen cyanide

Gilbert Newton Lewis
1875 – 1946
American Physical Chemist
Discovery: Covalent bonds, concept of electron pairs and Lewis dot structures

In fact, Lewis structure was proposed by Gilbert Newton Lewis in 1916 from University of California at Berkeley. And, besides working on structural aspects related to main group elements, he also added lot of information about electrons in the periodic table and also he worked on the purification of heavy water and he proposed acid-base theory and it is popularly known as Lewis acid-base concept and also he worked in the field of photochemistry. In fact, he was nominated 41 times for Nobel Prize and unfortunately, he was not given Nobel Prize and he found dead on March 23rd 1946, in his laboratory. At that time he was working with hydrogen cyanide, a deadly poisonous gas.

So, what are the postulates one has to follow before writing Lewis structure? So, one has to determine, how the atoms are bonded in a molecule. So, generally if there is only one of one element and multiple copies of another element the unique element is central. Commonly, hydrogen is always peripheral bonded to elements such as nitrogen, oxygen or sulphur and then we have to do the counting of electrons.

Essentially, counting the valence electrons of all atoms present in the molecule or ion of knowing the basic structure of the molecule we have to start placing the electrons around atoms. The first step is to determine the total number of electrons that are available for making bonding in Lewis dot structure. Here, we can use the help of group number of an element to indicate the number of valence electrons that it contributes to the molecule, for example; oxygen is in group 16, it gives 6 electrons.

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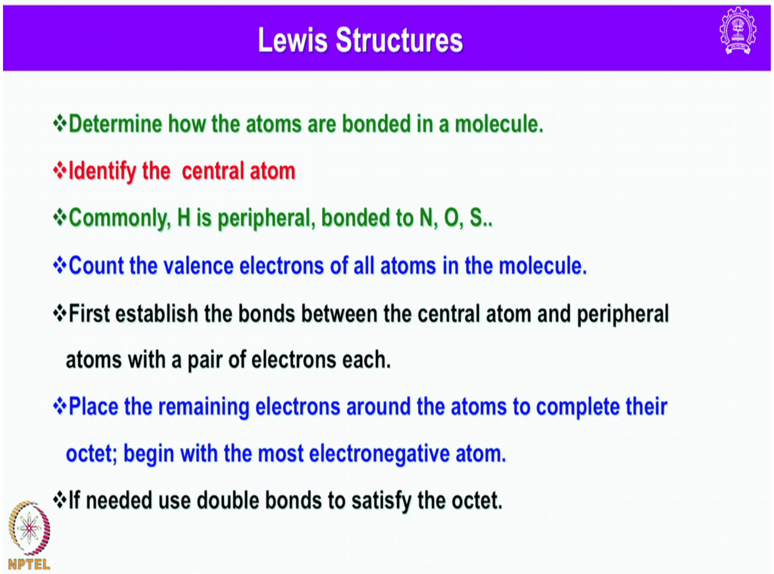

Lewis Structures

- ❖Determine how the atoms are bonded in a molecule.
- ❖Identify the central atom
- ❖Commonly, H is peripheral, bonded to N, O, S..
- ❖Count the valence electrons of all atoms in the molecule.
- ❖First establish the bonds between the central atom and peripheral atoms with a pair of electrons each.
- ❖Place the remaining electrons around the atoms to complete their octet; begin with the most electronegative atom.
- ❖If needed use double bonds to satisfy the octet.

So, what are the postulates one should remember I will repeat again; first, determine how the atoms are bonded in a molecule. And then, identify the central atom based on what had I said so far and again I am telling you hydrogen is always peripheral. Count the valence electrons of all atoms in the molecule. First establish the bonds between the central atom and peripheral atom with a pair of electrons each and place the remaining electrons around the atoms to complete their octet; begin with the most electronegative atom. If needed use double bonds to satisfy the octet. So, these are the few points, one should remember before initiating the process of writing Lewis structure.

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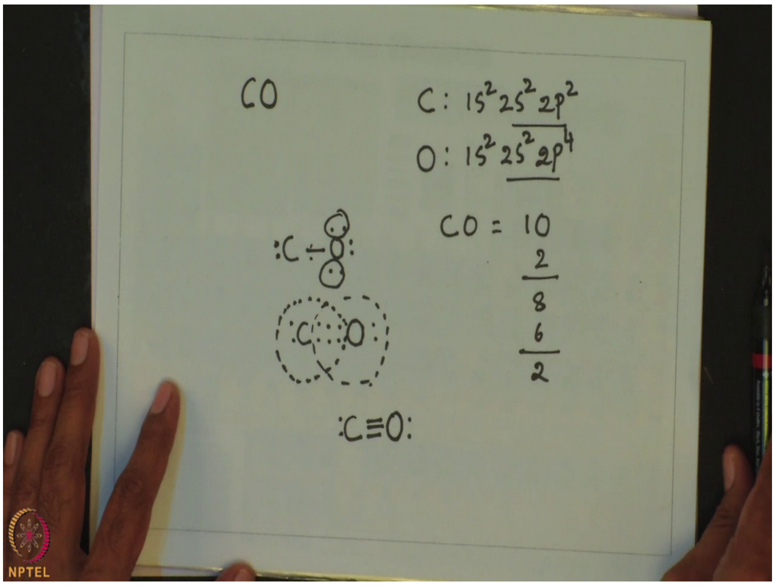

Let us consider in example. I will consider a simple example, such as CO. In CO, we have carbon and oxygen and we know the electronic configuration of carbon that is 1s 2, 2s 2 and 2p 2 and we also know the electronic configuration of oxygen 1s 2, 2s 2 and 2p 4. So, while writing the Lewis structure we should consider only the valence electrons. So, we have here 4 and here 6. So, total we have for CO – 10 electrons are there. So, here first write a bond here using 2 electrons and now we are left with 8 electrons and using these 8 electrons, let us first try to satisfy the octet of oxygen.

Now, oxygen has 2 electrons. It requires 6 more electrons; let us place in this fashion. So, 6 electrons are placed here. We are left with 2 electrons. These 2 electrons can come here. Now, if we look into carbon monoxide, oxygen has satisfied octet has 6 plus 2, 8 electrons whereas carbon has only 4 electrons. So, Lewis structure gives a satisfactory octet for carbon and oxygen. So, in that case what one should do is, we can consider transferring these electrons between oxygen and carbon in this fashion.

So, now, if I start counting these electrons along with these two; oxygen has 8 electrons. In a same way we can also consider carbon is satisfied having 8 electrons. So, thus Lewis structure gives a satisfactory bonding model for carbon monoxide. So, while writing carbon monoxide one can write like this or one can put a triple bond between c and o and complete it. So, this is how carbon monoxide has 3 bonds between carbon and oxygen. So, here the octet is satisfied.

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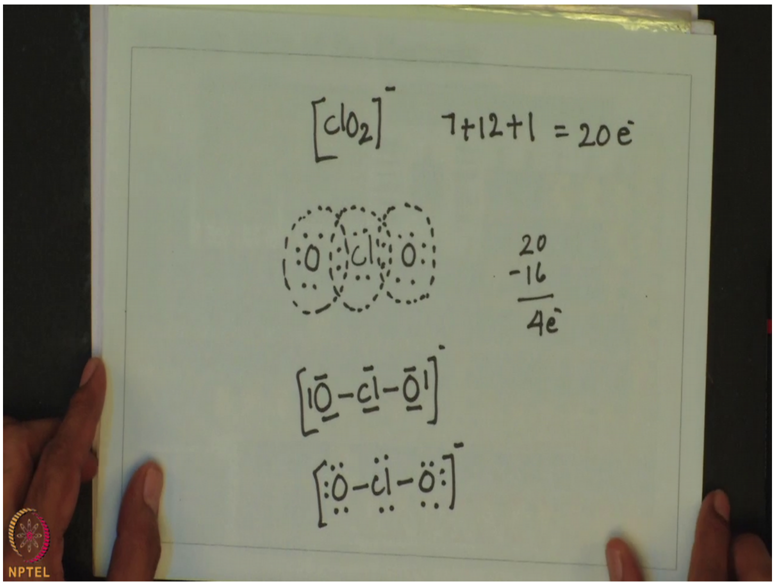

Let us look into another example such as, Cl O 2 minus. So, later I will tell you when we look into a species by simply looking to the Lewis dot structure we should be able to tell whether it exists in the cationic form, anionic form or neutral forms. So, here its say anionic form, it is in anionic form. So, Cl O 2 let us write in the same fashion. The total number of valence electrons that are available for making the bonds here, Cl has 7 electrons and oxygen totally we have 12 electrons, 6 plus 6 and 1 charge is there. So, we have a total of 20 electrons now. Here, chlorine is the central atom. It should be written like this and 2 are peripheral atoms. First, we should make a covalent bond by utilizing 2 electrons here, another 2 electrons here. So, we are left with now 16 electrons and oxygen being the most electro negative we should satisfy the octet of this one by adding 6 electrons for both oxygen atoms.

So, now, we have totally used 16 electrons and 4 electrons are left. These 4 electrons I place on chlorine. So, now, we first start counting all the 3 atoms have octet, that is, 4 pair of electrons. So, here there is no need to have any double bond. So, this is how the structure of

Cl O 2 minus can be explained using Lewis structure. So, this can also be written in another format or it can be, so, one can write either with solid line like this representing 2 electrons or one can simply write using the dot structure to complete this structure. So, this is how the Lewis dot structure successfully explains bonding in carbon monoxide and also Cl O 2 minus anion.

Let us look into some structure. In case of some structures Lewis structure cannot match the experimental observations. For certain atoms do not match the experimental observations, let us look into the simple examples such as format ion.

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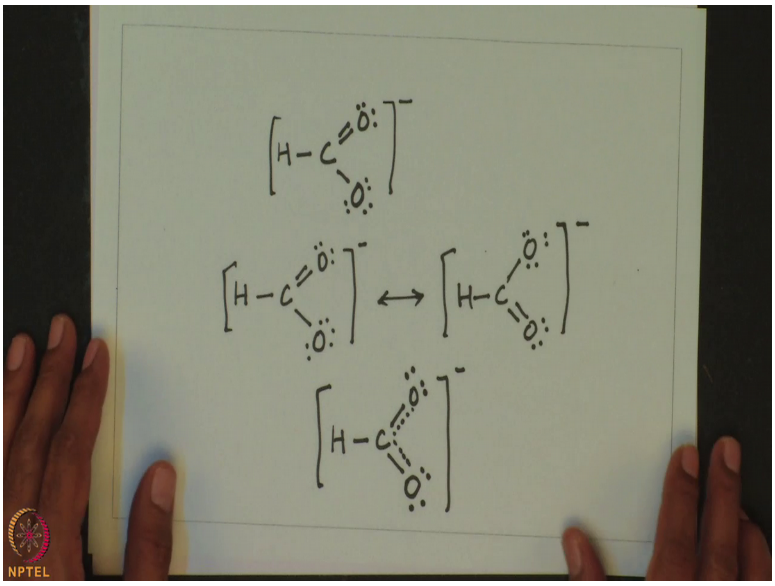

So, in case of format ions the bond lengths predicted by Lewis structure are incorrect. So, according to Lewis structure, so if you look this is how one can write the structure using Lewis method for format. So, here Lewis structure predicts 2 types of bonding for C O; one is C O double bond that is shorter and one C O single bond that is longer, but the x-ray structure determination has proved that both the bond distances are equivalent; that means, the molecule shows resonance and this resonance structure can be written in this fashion. So, the combined structure can be written in this form.

So, that means, if there are 2 or more identical options for a molecule to have double bonds the molecule will show resonance structures and these 2 resonance structures are shown here and because of this kind of resonance structure, what happens, both the C O bond distances are essentially equal; whereas Lewis dot structure identifies them as 2 separate entities and one is longer, one is shorter. That means, there is some limitations as far as Lewis model is concerned, what are the failures are limitations of Lewis model which we shall see now. A number of molecules with odd number of electrons exist and in case of Lewis structure we always count in pairs. So, when odd electron comes Lewis method faces to give a satisfactory structure.

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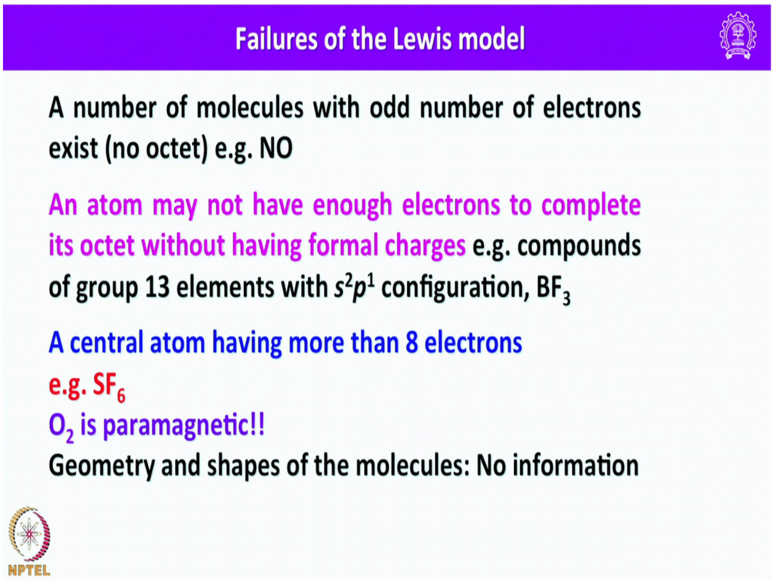

Failures of the Lewis model

A number of molecules with odd number of electrons exist (no octet) e.g. NO

An atom may not have enough electrons to complete its octet without having formal charges e.g. compounds of group 13 elements with s^2p^1 configuration, BF_3

A central atom having more than 8 electrons
e.g. SF_6
O_2 is paramagnetic!!
Geometry and shapes of the molecules: No information

For example; if we take NO, in this case we have 5 plus 6, 11 electrons are there. As a result, a satisfactory Lewis structure cannot be written for NO. An atom may not have enough electrons to complete its octet without having formal charges. This problem arises when you look into the compounds of group 13 elements, we have s2 p1 electronic configuration.

As a result, what happens, we will end up with only a 3 bonds and 6 electrons, example; BF 3 and another problem or limitation is when we look into molecules having more than 8 electrons, for example, sulphur hexafluoride we have 12 electrons are there and it does not say how to put the remaining 4 electrons and another important limitation is predicting the right structure of oxygen molecule. Oxygen molecule is paramagnetic, but Lewis structure does not depict this paramagnetic property. More than all these things, the major drawback of Lewis model is, it does not give any information about geometry and shapes of molecules.

So, in order to determine the molecular shapes and the geometries of main group compounds VSEPR theory was postulated. VSEPR is nothing, but, the valence shell electron pair repulsion theory. The expansion of abbreviation is self explanatory; valence shell, that means, we have to deal with valence shell and electrons means we are dealing with electrons present in valence shell and then the term repulsion comes, that means, when you are putting electrons into the valence shell there is some inter electronic repulsion and that means, how to minimise that one.

Valence electron pair repulsion theory essentially gives an idea of how to minimise the repulsion between the bonded pair as well low pair; that means, so, valence shell electron pair repulsion theory is based on the fact that the electrostatic repulsion of the electrons is reduced to a minimum when the various regions of high electron density assumes positions as apart as possible.

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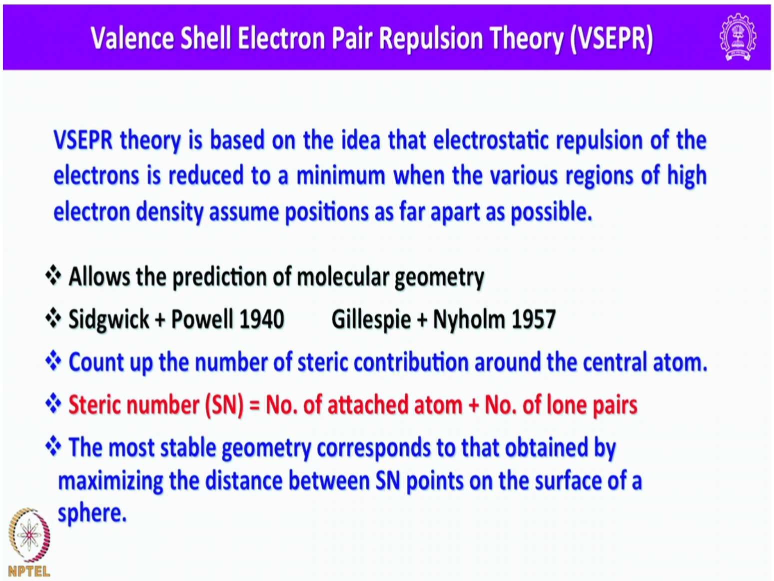

Valence Shell Electron Pair Repulsion Theory (VSEPR)

VSEPR theory is based on the idea that electrostatic repulsion of the electrons is reduced to a minimum when the various regions of high electron density assume positions as far apart as possible.

- Allows the prediction of molecular geometry
- Sidgwick + Powell 1940 Gillespie + Nyholm 1957
- Count up the number of steric contribution around the central atom.
- Steric number (SN) = No. of attached atom + No. of lone pairs
- The most stable geometry corresponds to that obtained by maximizing the distance between SN points on the surface of a sphere.

So, let us look into the concepts that are used in VSEPR theory and that means, essentially it is based on the electrostatic repulsion between the paired electrons, bonded electrons and unpaired electrons and how to place them surrounding the central atom to minimise these interaction between the lone pairs and bond pairs, and lone pairs and lone pairs, and bond pairs and bond pairs.

First, this concept was proposed by Sidgwick and Powell in 1940 and then in 1957, two more scientists Gillespie and Nyholm refined it and introduced the term called steric number. I would define what steric number is. First, we have to determine the steric contribution are in the central atom, by counting all the electrons very similar to Lewis structure and then we should arrive at a term called steric number and steric number is nothing, but the number of attached atoms plus number of lone pairs and number of attached atoms are essentially consuming 2 electrons to make a covalent bond and then number of lone pairs. Once if determine this steric number the most stable geometry corresponded to that can be obtained by maximizing the distance between the steric points on the surface of a sphere by keeping them as far away from each other as possible. So, these are the basic concepts used in valence shell electron pair repulsion theory.

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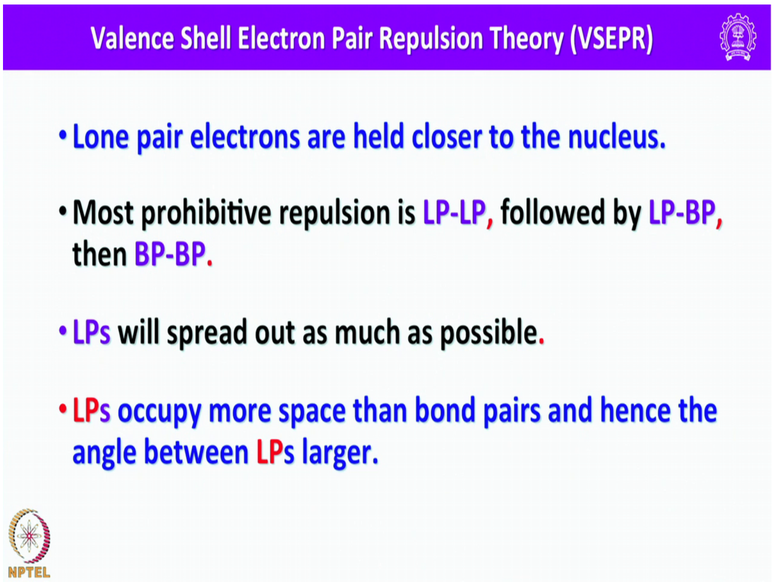

Valence Shell Electron Pair Repulsion Theory (VSEPR)

- Lone pair electrons are held closer to the nucleus.
- Most prohibitive repulsion is LP-LP, followed by LP-BP, then BP-BP.
- LPs will spread out as much as possible.
- LPs occupy more space than bond pairs and hence the angle between LPs larger.

So, let us look into few points again. Lone pairs of electrons; lone pair electrons are held closer the nucleus. So, most prohibitive repulsion is lone pair-lone pair, followed by lone pair-bond pair and then bond pair-bond pair. So, lone pairs will spread out as much as possible, that means, essentially lone pairs will occupy more space compared to bonded pairs and hence, the angle between the lone pairs will be always larger.

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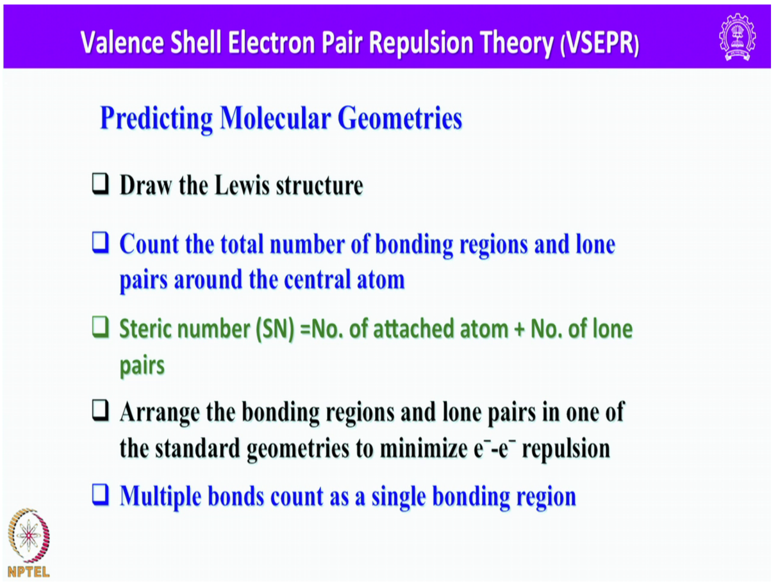

Valence Shell Electron Pair Repulsion Theory (VSEPR)

Predicting Molecular Geometries

- ☐ Draw the Lewis structure
- ☐ Count the total number of bonding regions and lone pairs around the central atom
- ☐ Steric number (SN) =No. of attached atom + No. of lone pairs
- ☐ Arrange the bonding regions and lone pairs in one of the standard geometries to minimize e^{-}-e^{-} repulsion
- ☐ Multiple bonds count as a single bonding region

So, for predicting in the molecular geometries, we need 2 important terms. First, we have to write a Lewis structure for a given molecule and then we have to count the total number of bonding regions and lone pairs around the central atom and determine the steric number. Again, steric number is nothing, but, the number of attached atom plus number of lone pairs. So, arrange the bonding regions and lone pairs in one of the standard geometries to minimise electron – electron repulsion. Multiple bonds count as a single bonding region.

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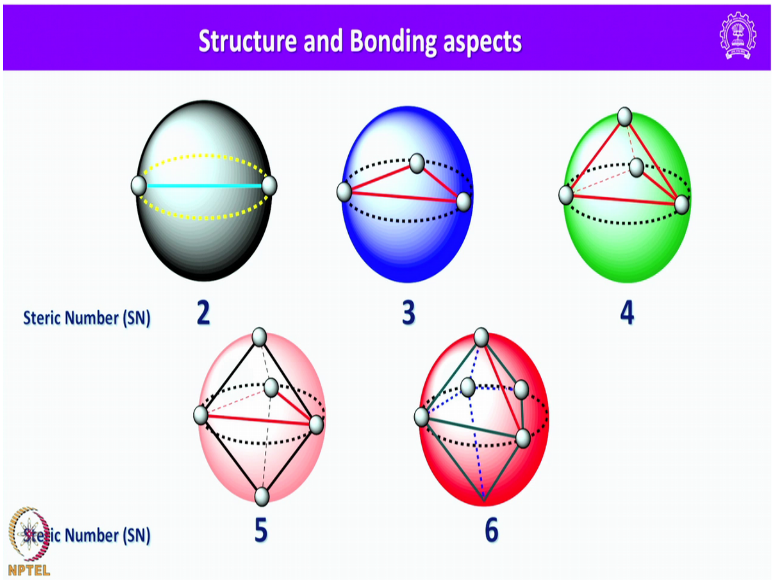

Structure and Bonding aspects

So, let us consider the geometries with different steric numbers. Steric numbers can be anywhere between 2 to 6. Of course, more will also come; let us first look into the steric numbers up to 6.

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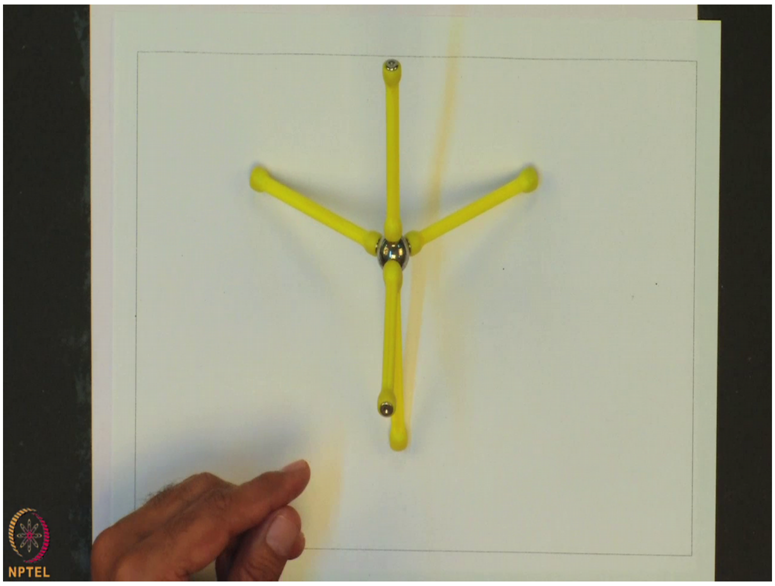

When the steric number is 2, the molecule will be linear and when the steric number is 3, molecule will be trigonal planar, something like this. So, when the molecule is linear the steric number 2 and when the steric number is 3. So, trigonal planar, the angles will be 120 degree and when the steric number is 4, they are tetrahedrally disposed something like this. This is symmetric tetrahedral with angles of 109.5 degree, something like this. When the steric number is 5 the geometry that should be used is trigonal bi-pyramidal, this is something like this. Here we have 2 types of bonds; one is 190 degrees and another one is 120 degrees. So, this is trigonal bi-pyramidal geometry and with steric number 6 octahedral geometry. So, this is how up to steric number one can assume the geometries like this.

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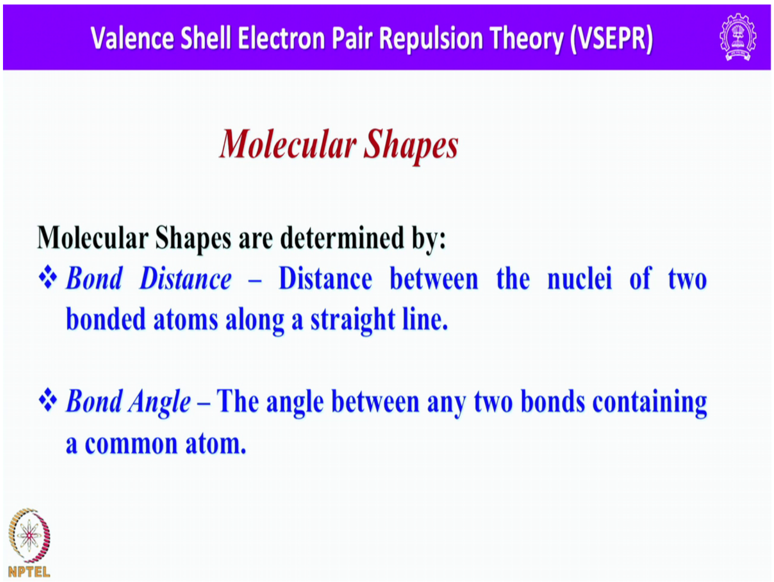

Valence Shell Electron Pair Repulsion Theory (VSEPR)

Molecular Shapes

Molecular Shapes are determined by:

- ❖ *Bond Distance* – Distance between the nuclei of two bonded atoms along a straight line.
- ❖ *Bond Angle* – The angle between any two bonds containing a common atom.

So, molecular shapes while determining molecular shapes we need 2 important terms, that is, bond distance and bond angle. The distance between the nuclear of 2 bonded atoms along a straight line is nothing, but the bond distance. The angle between any 2 bonds containing a common atom is essentially bond angle. So, in this you consider this molecule octahedral molecule, the distance from central atom to the peripheral atom is called bond distance and angle between these 2 atom at the central atom is called the bond angle. This is the bond angle and this is the bond distance.

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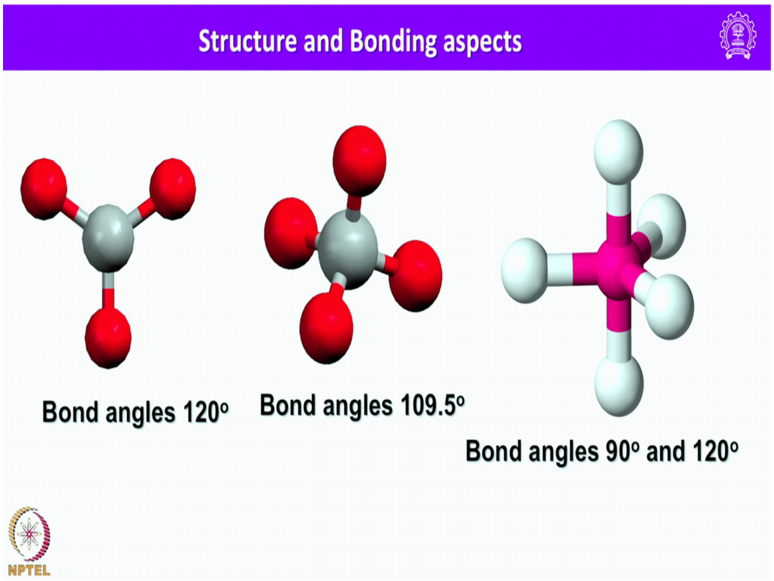

Structure and Bonding aspects

Bond angles 120°

Bond angles 109.5°

Bond angles 90° and 120°

So, this is trigonal planar molecule with coordination number with this trigonal planar molecule with steric number 3, bond angle is 120 and here it is a tetrahedral bond angle is 109.5 degree and here we have bond angles of 90 and 120 this is trigonal planar.

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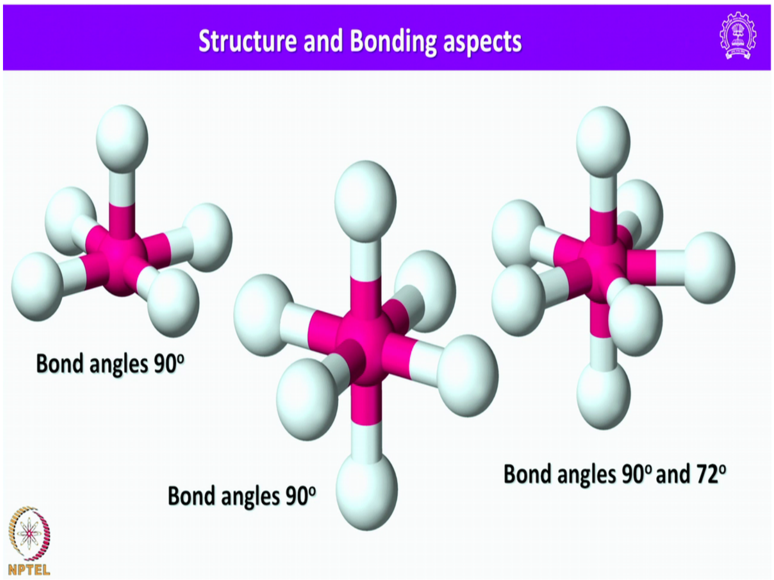

Structure and Bonding aspects

And here bond angle is 90. Of course, with steric number 5 we can have trigonal planar as well as square pyramidal geometry. So, one should remember main group compounds do not prefer to have square pyramid geometry, until and unless the sixth coordination is a lone pair. Otherwise preferred geometry for steric number 5 is trigonal bi-pyramidal. With coordination number 6 is octahedral geometry, with bond angle 90 degree and with coordination number 7, one can have pentagonal bi-pyramidal geometry. With bond angles 90 and 72; 72 will be between the equatorial ones and the axial one will make 90 degree with the equatorial atoms. So, this is the pentagonal bi-pyramidal geometry.

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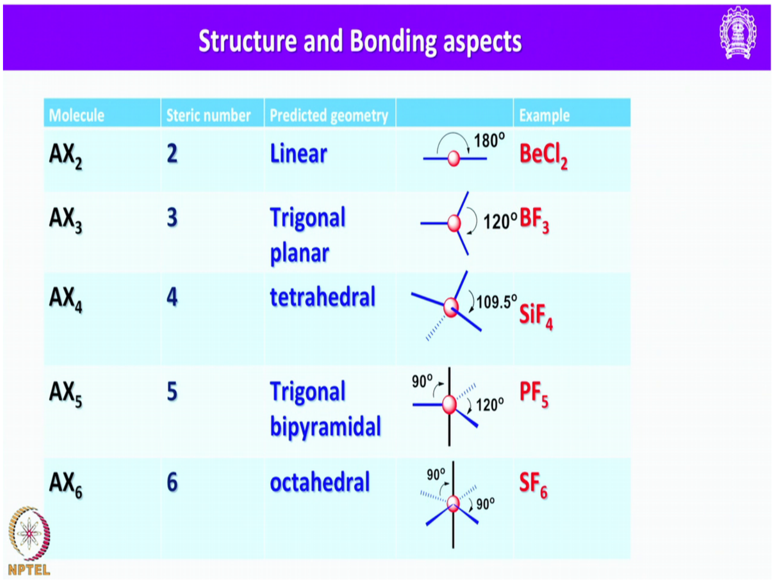

Structure and Bonding aspects

Molecule	Steric number	Predicted geometry		Example
AX_2	2	Linear	180°	$BeCl_2$
AX_3	3	Trigonal planar	120°	BF_3
AX_4	4	tetrahedral	109.5°	SiF_4
AX_5	5	Trigonal bipyramidal	90° 120°	PF_5
AX_6	6	octahedral	90° 90°	SF_6

So, here I have listed different kind of molecules we come across and the corresponding geometry and the angle with an example in each case. AX 2, steric number 2 and predicted geometry according to VSEPR theory is linear and of course, it is linear here, example; BeCl 2, beryllium dichloride, angle is 180 and when the molecule is AX 3 type where A is the central atom and X are the peripheral atoms, steric number 3. So, all are bonded pairs, trigonal planar and example is BF 3. When we have steric number 4 example is AX 4, tetrahedral geometry example is SiF 4 methane and other tetrahedral compounds having 4 bonded phase, here the angle is 109.5 and AX 5 trigonal bi-pyramidal angles are 90 and 120, example; PF 5 phosphorus pentafluoride and with AX 6, steric number 6, octahedral and here example is sulphur hexafluoride. So, these are about the steric number that accounts for only bonded pair.

Let us look in to the combination of both bonded pair and lone pairs. We have numerous examples of having both bonded pair and lone pair. So, in that case, geometry and shapes will be different where as in these cases what have shown here the geometry and the shape are essentially same. So far, we discussed about the molecules having only bonded pairs starting from steric number 2 to steric number 6 and also 7. In my next lecture, I will be discussing about the molecules have a both bonded pairs as well as lone pairs. So, let me conclude today’s talk and have pleasant chemistry learning and see you in my next lecture to learn more about the VSEPR theory.

Thank you very much.