❖ Bent's Rule and Energetic of Hybridization

The success of the valence-shell-electron-pair-repulsion (VSEPR) theory in rationalizing various molecular geometries is quite remarkable as far as simplicity is concerned. However, the failure of VSEPR theory in the case of transition metal complexes or some other serious limitations like inert-pair effect in some main group compounds are also undeniable facts that need to be addressed in a more sophisticated way. The limited applicability of VSEPR theory is actually rooted in the fact that it does not consider any wave-mechanical picture of atomic structure; in other words, as the VSEPR theory does not talk in terms of atomic orbitals, it is quite bound in terms of flexibility required to model the chemical bonds. However, as we know that the Lewis ideas of electron sharing inspired not the Sidgwick and Powell only, but some other physicists like Walter Heitler and Fritz London also. Whilst on the one side the Sidgwick and Powell were working on the VSEPR theory, which was completely immune to the concept of orbitals; Heitler and London were treating the chemical bond in a hundred percent wave-mechanical framework. In 1926, Walter Heitler found out how to use Schrödinger's wave equation to show that the single electron wave-functions of two hydrogen atoms interact with each other to form a covalent bond. Soon after that, he and his associate Fritz London worked on some more theoretical details of the theory and labeled it as valence bond theory (VBT). Thought the VBT was quite effective in the calculation of bonding properties of the H_2 molecule, it was still unable to rationalize complex molecules. Later, an American chemist, Linus Pauling modified the Heitler-London theory by incorporating two key concepts, resonance (1928) and orbital hybridization (1930).

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The initial development of the concept of orbital hybridization was to explain the structure of simple molecular geometries like CH_4, BF_3 or $BeCl_2$. The methane molecule had actually been the test case for all bonding theories at that time. Before 1874, the CH_4 molecule was thought to be of square planar geometry with a carbon atom in the center.

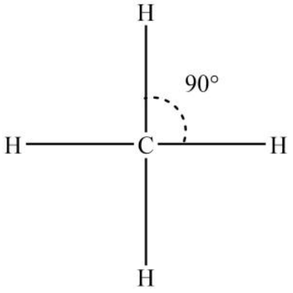

Figure 27. The visualization of the structure of methane before 1874.

Now today it might seem very funny but at that time this structure was quite reasonable because it could explain the observed magnetic moment which is zero for methane. The square planar structure has four C−H bonds of equal length and all adjacent bonds at 90°; the cancellation of two opposite dipole moments from two trans bonds would also give a zero dipole moment. However, if we attach four different groups to the carbon, the resulting molecule is actually optically active i.e. it would rotate the plane of polarized light in left or right; and therefore, it must exist as two isomers (enantiomeric pair). It is possible only if the arrangement of groups around central carbon is tetrahedral rather square planar; because the later one would exist as three isomers, all optically inactive.

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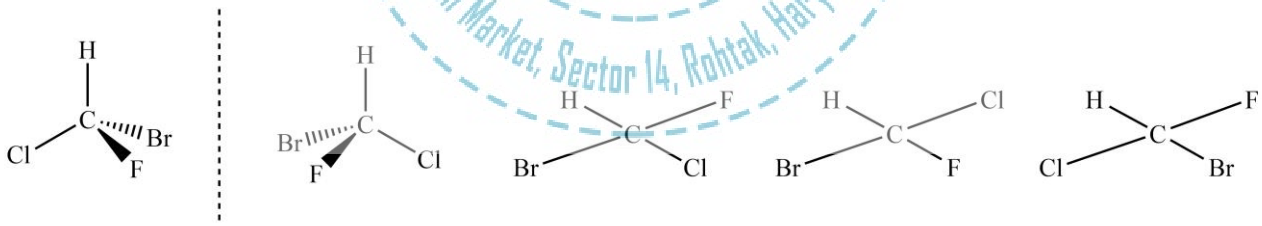

Two optical isomers of asymmetric carbon

Three geometrical isomers of asymmetric C in square-planar structure
All are optically inactive

Figure 28. Isomers for asymmetric carbon in tetrahedral and square-planar geometry.

A Dutch physical chemist, Jacobus Henricus van't Hoff, was the first to formulate the three-dimensional carbon. In 1874, he showed that a tetrahedral arrangement of four different groups around a carbon atom is the only way to give rise to two optical isomers. Using the same theory, he also explained the three isomers of tartaric acid, one enantiomeric pair, and one meso form. The tetrahedral coordination around carbon was also proved in 1913 when X-ray diffraction studies of diamond showed a bond and angle of 109°28′.

Now although the VSEPR theory, a successor of Lewis idea (1913), explained the tetrahedral coordination in CH_4 molecule by minimum repulsion of four bond pairs; it did not help us to understand the nature of the orbitals involved in the bonding. Linus Pauling in 1931 Pauling pointed out that, in the frame of simple "valence bond theory", a carbon atom can form four bonds by using one s and three p orbitals by promoting its one $2s$ electron to empty $2p_z$ orbital and thus creating four half-filled orbitals. However, it might would mean that a C atom creates three bonds at right angles (from use of p subshell) and a fourth bond (weaker one) using the s wave-function in some arbitrary direction (this fourth C−H bond would be maximum away from the other three bonds if it is put at 135°) as shown below.

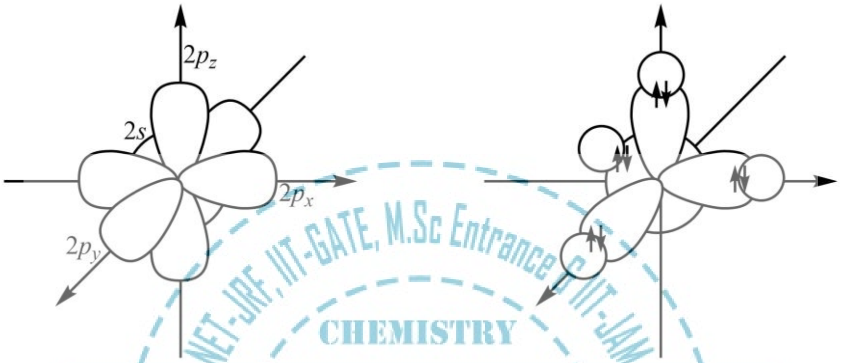

Figure 29. The possible bonding mode in CH_4 molecule from valence bond theory without considering orbital hybridization (one lobe of p-orbitals in the right image are omitted for clarity.

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The experimental results like four equal bonds separated by a bond angle of 109.5° or the zero dipole moment cannot be explained by the structure given above. Hence, the aforementioned geometry was a wrong proposal for sure because, besides the bond angle anomaly, it would give rise to small dipole due to the difference in electronegativity between C (2.5) and H (2.2). Moreover, according to simple valence bond theory, as the bonding of hydrogen is happening with one s and three p orbitals of carbon, we should expect one s–s bond to be shorter than three s–p bonds.

To explain this situation, Pauling thought that what would happen if instead of using pure one s and three p wave functions, we use a linear combination of these four. Now though there can be an infinite number of linear combinations of these four single-electron-wave-functions, one should not forget that every single electron-electron-wave-functions must be normalized and orthogonal to others. Linus Pauling found that out of infinite linear combinations, there are only four expressions that are normalized as well as orthogonal to each other. When he plotted these four linearly combined functions in space round carbon nucleus, they were of the same shape, same energy and were oriented at 109°28′. Linus Pauling created the tetrahedral frame of half-filled orbitals, ready for overlap with approaching hydrogens. This was a revolutionary step, he called these functions as hybrid orbitals.

Hybridization is the intermixing of atomic orbitals of different energies and shapes so as to produce new orbitals with the same energy and equivalent shape.

➢ ***Characteristic Features of Hybridization***

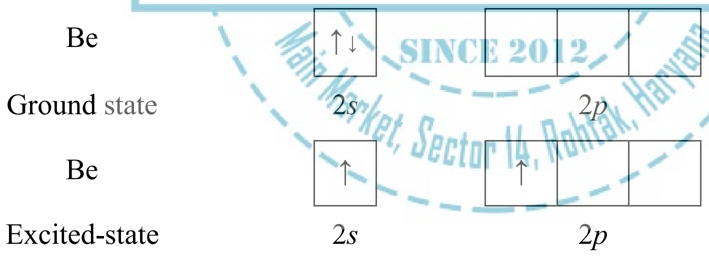
The orbital hybridization in the main group or the transition metal compounds has the following characteristic features:

1. The number of hybrid orbitals is the same as the number of atomic orbitals intermixed.
2. Hybrid orbitals are equivalent in shape and have the same energies.
3. Hybrid orbitals form stronger bonds than their pure atomic counterparts.
4. Hybrid orbitals are directed in specific directions and therefore control the geometry of the molecule.
5. Only valence shell orbitals take part in hybridization.
6. There should be only a small energy difference in the orbitals undergoing hybridization.
7. Electron promotion is not a necessary condition to be followed.
8. In addition to the half-filled orbitals, fully filled and empty orbitals can also undergo hybridization.

➢ ***Types of Hybridisation***

Hybrid orbitals are assumed to be the mixtures of atomic orbitals, superimposed on each other in various proportions. For example, in the CH_4 molecule, the hybrid orbital of C, which forms a carbon-hydrogen bond consists of 25% *s*-character and 75% *p*-character and is thus labeled as sp^3 hybridized. The main types of hybridization are as follows.

1. *sp*-hybridization: One *s* and one *p*-orbitals intermix to form two hybrid orbitals oriented at 180° from each other and form the basis for the linear geometry of $BeCl_2$, BeH_2, BeF_2 like molecules.



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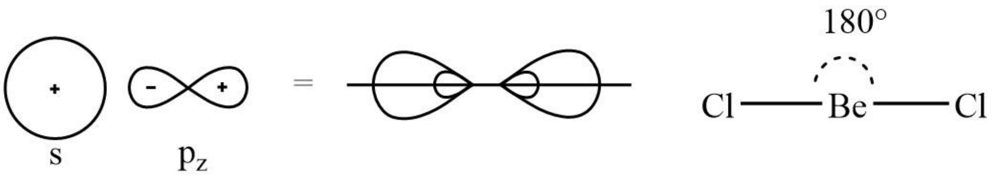

Figure 30. Pictorial representation of *sp*-hybrid orbitals e.g. $BeCl_2$ molecule.

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2. *sp*^{2}-hybridization: One *s* and two *p*-orbitals intermix to form three hybrid orbitals oriented at 120° from each other and form the basis for the trigonal geometry of BF_3 type molecules.

	2*s*	2*p*		
B Ground state	↑↓	↑		
B Excited-state	↑	↑	↑	

Which gives

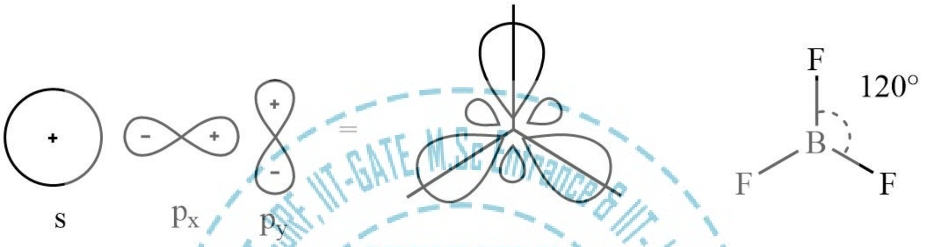

Figure 31. Pictorial representation of sp^2 hybrid orbitals e.g. BF_3 molecule.

3. *sp*^{3}-hybridization: One *s* and three *p*-orbitals intermix to form four hybrid orbitals oriented at 109°28ˈ from each other and form the basis for the tetrahedral geometry of BF_3 type molecules.

	2*s*	2*p*		
C Ground state	↑↓	↑	↑	
C Excited-state	↑	↑	↑	↑

Which gives

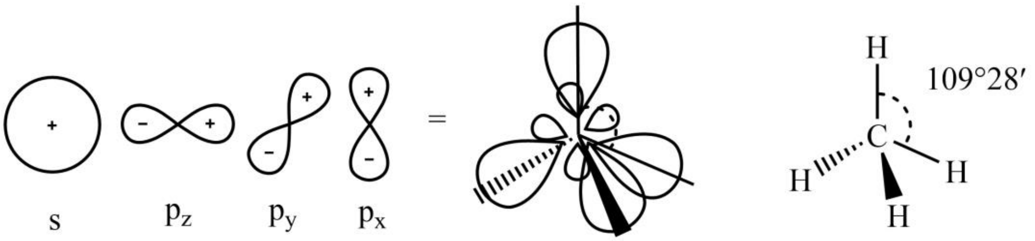

Figure 32. Pictorial representation of sp^3 hybrid orbitals e.g. CH_4 molecule.

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4. *sp^3d*-hybridization: One *s*, three *p* and one *d*-orbitals intermix to form five hybrid orbitals where three hybrid orbitals are oriented at 120° and at 90° from two axial bonds to form the basis for the trigonal bipyramidal geometry of PF_5 type molecules.

P	↑↓	↑	↑	↑					
Ground state	3*s*	3*p*			3*d*				
P	↑	↑	↑	↑	↑				
Excited-state	3*s*	3*p*			3*d*				

Which gives

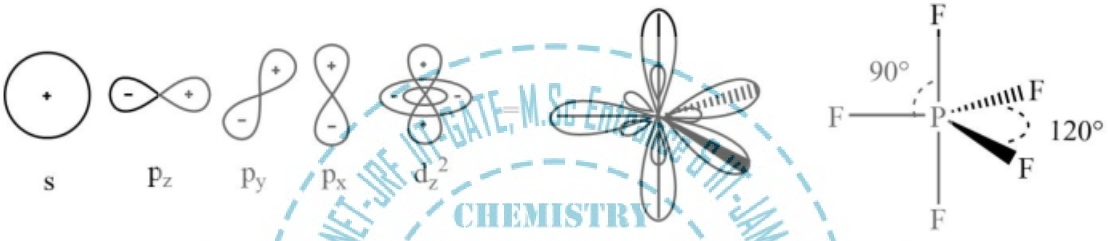

Figure 33. Pictorial representation of sp^3d hybrid orbitals e.g. PF_5 molecule.

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5. *sp^3d^2*-hybridization: One *s*, three *p* and two *d*-orbitals intermix to form six hybrid orbitals where each orbital is at 90° from 4 and at 180° from one to form the basis for the octahedral geometry of SF_6.

S	↑↓	↑↓	↑	↑					
Ground state	3*s*	3*p*			3*d*				
S	↑	↑	↑	↑	↑	↑			
Excited-state	3*s*	3*p*			3*d*				

Which gives

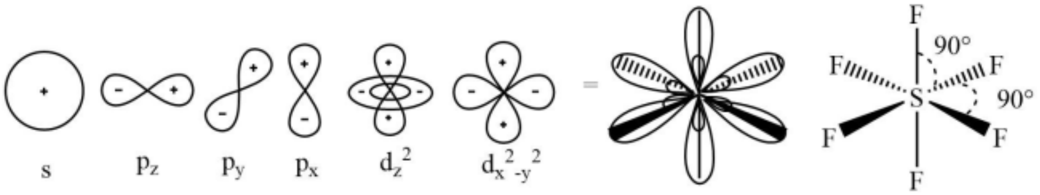

Figure 34. Pictorial representation of sp^3d^2 hybrid orbitals e.g. SF_6 molecule.

6. *sp^3d^3*-hybridization: One *s*, three *p* and three *d*-orbitals intermix to form seven hybrid orbitals where five equatorial hybrid orbitals are oriented at 72° from each other and at 90° from two axial hybrid orbitals to form the basis for the pentagonal bipyramidal geometry of IF_7 type molecules.

I	↑↓	↑↓ ↑↓ ↑	
Ground state	5*s*	5*p*	5*d*
I	↑	↑ ↑ ↑	↑ ↑ ↑
Excited-state	5*s*	5*p*	5*d*

Which gives

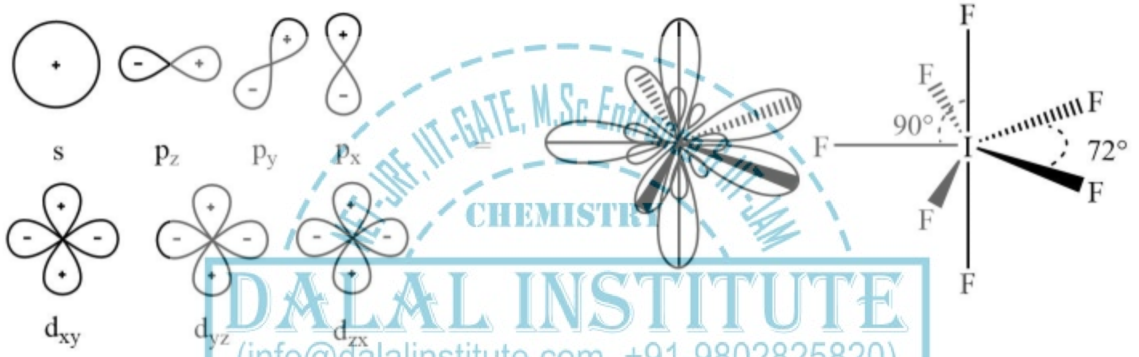

Figure 35. Pictorial representation of sp^3d^3 hybrid orbitals e.g. IF_7 molecule.

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➢ *Some Other Less Common Hybridization Schemes*

Besides the simple and hyper-valent molecules like IF_7, there are also some less common hybridization schemes as given below.

1. *dsp^2*-hybridization: One *d*, two *p* and one *s*-orbitals intermix to form four hybrid orbitals which are oriented at 90° to each other and form the basis for the square planar geometry of tetra-coordinated molecules.

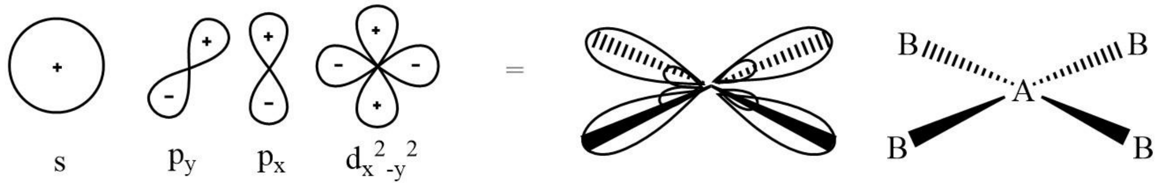

Figure 36. The pictorial representation of dsp^2 orbitals hybridization scheme forming the basis for square planar geometry.

2. *sp*^{3}*d*-hybridization: One *s,* three *p* and one *d*-orbitals intermix to form five hybrid orbitals which are oriented at 90° to each other and form the basis for square pyramidal geometry of penta-coordinated molecules.

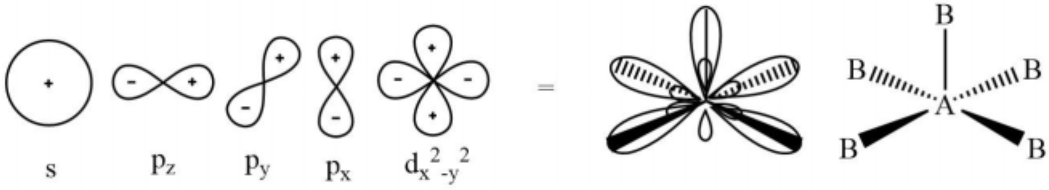

Figure 37. The pictorial representation of sp^3d hybrid orbitals forming the basis for square pyramidal geometry.

3. *sp*^{3}*d*^{2}-hybridization: One *s,* three *p* and two *d*-orbitals intermix to form six hybrid orbitals which are oriented towards the corners of a trigonal prismatic geometry in hexa-coordinated molecules.

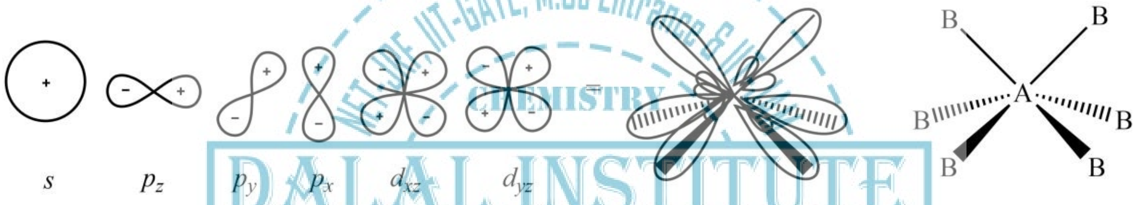

Figure 38. The pictorial representation of sp^3d^2 orbitals hybridization scheme forming the basis for trigonal prismatic geometry.

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4. *sp*^{3}*d*^{3}-hybridization: One *s,* three *p* and three *d*-orbitals intermix to form seven hybrid orbitals which are oriented towards the corners of a mono-capped trigonal-prismatic geometry in hepta-coordinated molecules.

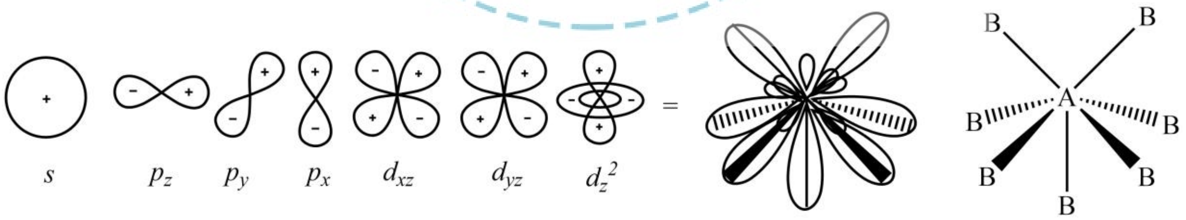

Figure 39. The pictorial representation of sp^3d^3 orbital hybridization scheme for the formation of mono-capped trigonal-prismatic geometry.

However, main group Compounds rarely show these hybridizations like dsp^2-square planar or sp^3d-square pyramidal geometry due to stability issues which makes them more predictable structure than transition metal complexes.

➢ *Bent's Rule*

The introduction of the concept of hybridization by Linus Pauling was a huge success in the rationalization of the chemical bond, especially in the organic compounds. However, in the 1940s it became apparent that a lot of molecular geometries, including even the simple ones, show slight deviations from the predictions of orbital hybridization concept of valence bond theory. For instance, consider the case of H_2O molecule; where the H−O−H bond angle is 104.5°, which far less than the normal tetrahedral angle of 109.5°. Besides the isovalent species like H_2O or NH_3, the conventional hybridization theory was also unable to explain why the Cl−C−Cl and Me−C−Me bond angles in sp^3-hybridized CCl_2Me_2 are 108.5° and 113°, respectively.

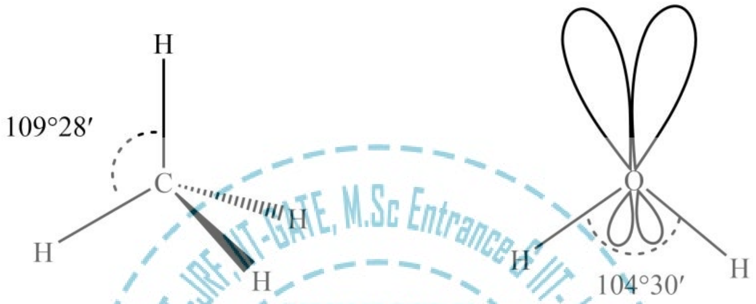

Figure 40. The comparison of the bond angle of methane and water though both have of sp^3 hybridization.

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In 1947, a British chemist, A. D. Walsh tried to explain such inconsistencies by describing a correlation between the electronegativity of ligand attached to carbon and the hybridization scheme involved. it was suggested that hybridization may yield orbitals with different magnitude of *s* and *p* character. In 1961, Henry A. Bent published a more sophisticated treatment of the problem that correlated the molecular structure, hybridization scheme of the central atom, and the electronegativity strengths of the attached groups. The work is generally labeled as Bent's rule and is based upon the perturbation theory which suggests that isovalent hybridization should transfer more *s*-character towards more electropositive substituents to maximize the bonding energy. This can be explained in terms of electron density available for bonding. The more electropositive groups would be able to withdraw more electron density from *p*-orbital than *s*-orbital.

In the compounds containing mixed substituents and hybridized orbitals, a trend has been observed according to which atomic s-character tends to concentrate in the orbitals that are directed towards electropositive groups and atomic p-character tends to concentrate in the orbitals that are directed towards electronegative groups.

Valence orbitals for main group elements consist of *s* and *p* orbitals with s-orbital having lower energy, which means that the bonding orbital is lower in energy and shape more like *s*-orbital rather than *p*-orbital. However, in the case where the central atom or ion has a lone pair, it will be having large s-character because *s*-orbital are closer to the nucleus, allowing greater stabilization for the lone pair. The deviation of molecular geometries from their perfectly tetrahedral, octahedral or other symmetrical counterparts can be explained and predicted by examining the substituent groups and lone pair of electrons.

➢ *Applications of Bent's Rule*

The Bent's rule can be used to rationalize many aspects of structure, bonding, spectra and the physical and chemical properties of a wide range of compounds. Some of the important applications of Bent's rule which are quite popular in the field of chemical science are given below.

1. Bond angles: *i)* In $A(Cl)_2(Me)_2$ molecules, where A is C, Si, Ge, Sn or Pb; the Cl–A–Cl bond angle is smaller than that of Me–A–Me bond angle. With high electronegativity halogen substituent Cl, more *p*-character is concentrated in A–Cl bond than A–Me bonds. Subsequently, bonds with greater *p*-character have smaller bond angles than those with *s*-character because *s*-orbitals are closer to the nucleus and hence exert larger inter-electronic repulsion producing higher bond angles.

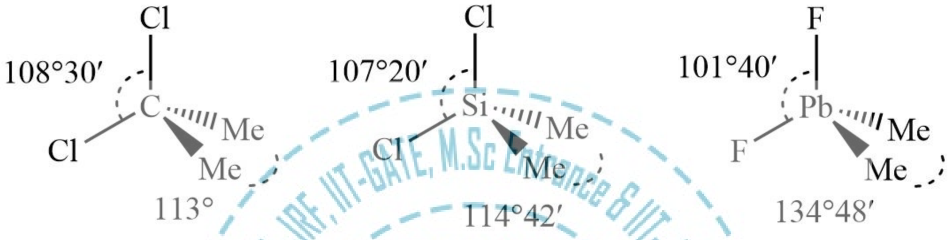

Figure 41. Increasing p-character in A–X bond, decreasing halogen–A–halogen bond angle.

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ii) In SF_4, the bond angle of axial F–S–F bond is 173° (ideally 180°) and the equatorial F–S–F bond angle is 101° (ideally 120°). The axial, as well as equatorial bond angles, are decreased slightly due to increased s-character of the lone pair and more *p*-character in bond pairs. Furthermore, thionyl tetrafluoride shows the same trend but the slightly higher bond angle between equatorial fluorines than that of sulfur tetrafluoride. This anomaly can be explained in terms of comparatively larger *s*-character in equatorial fluorines as the lone pair has been replaced by a more electronegative oxygen atom.

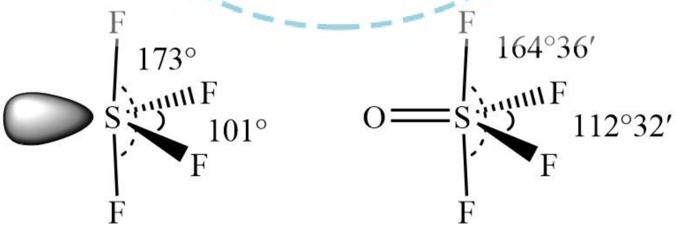

Figure 42. SF_4 molecule and SOF_4 molecules.

iii) As one moves left to right in the figure given, the substituents become more electronegative and the bond angle between them decreases. According to Bent's rule, as the electronegativity strength of substituents increase, orbitals rich in *p*-nature will be oriented towards those substituents. From the abovementioned argument, it will reduce the bond angle; which is in good agreement with the experimental data. If we compare this justification with VSEPR theory, the VSEPR model cannot explain why the angle in dimethyl ether is larger than the normal tetrahedral angle of 109.5°. In the prediction of the bond angle in H_2O molecule, Bent's rule proposes that the hybrid orbitals which are rich in *s*-character should be oriented towards more electropositive lone pairs, whilst the orbitals of more *p*-nature should point towards the hydrogens. This enhanced *p*-character in orbitals decreases the corresponding bond angle to less than the normal tetrahedral of 109.5°. The same reason can be applied to NH_3 molecule, the other canonical cases of this kind.

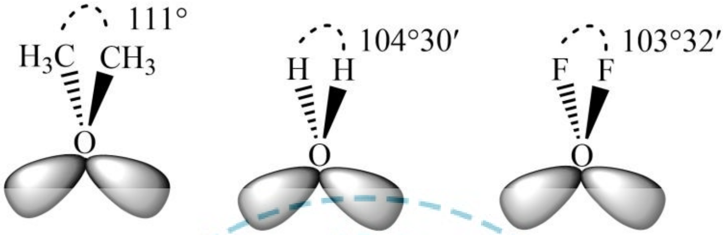

Figure 43. The decreasing trend of the B–A–B bond angle between substituents with increasing electronegativity.

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2. Bond lengths: *i)* The bond lengths can also be changed by changing the hybridization or by adding electronegative groups to the central atoms. If a molecule geometry has X–A–Y component, replacement of the group X by a more electronegative substituent would manipulate the hybridization of the central atom and reduces the neighboring A–Y bond length. Now owing to the higher electronegativity of fluorine than hydrogen, the carbon of fluoromethane will direct its hybrid orbitals with the higher *s*-character towards the three H groups rather than the fluorine. In the case of difluoromethane, only two hydrogens are present, so the *s*-character in total is pointed towards them is less and more is pointed towards the two fluorine groups. This reduces the carbon–fluorine bond lengths relative to the fluoromethane molecule.

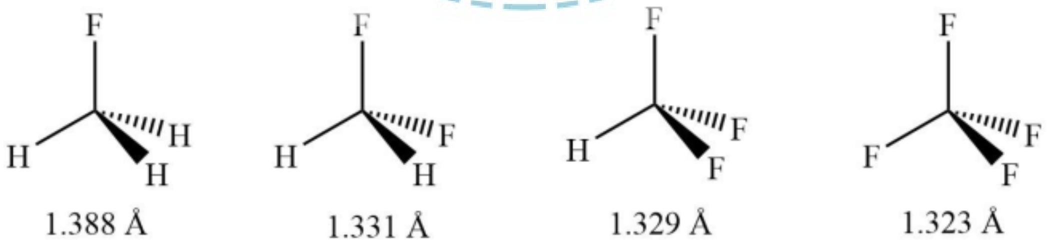

Figure 44. The decreasing trend of average carbon–fluorine bond lengths as we move from CH_3F to CF_4 molecular geometries.

This pattern continues to the CF_4 whose carbon–fluorine bonds have the largest *s*-character (25%) and the shortest bonds in the whole series.

ii) The same pattern also continues for the chlorinated equivalents of CH_4, though the effect is less efficient because the chlorine is of lower electronegativity strength than the fluorine.

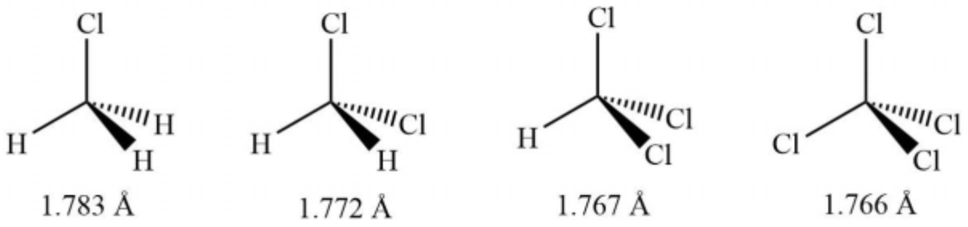

Figure 45. Average carbon–chlorine bond length.

The abovementioned cases seem to prove that the atomic radius of chlorine is less significant than its electronegativity strength because the prediction based on steric factors alone would yield the opposite pattern due to greater setting-apart tendency of larger chlorine groups. As the steric clarification is in contradiction with the experimental results, Bent's rule plays a significant role in structure elucidation.

iii) A similar trend is observed for single, double and triple carbon–carbon bonds, as the change of hybridization scheme from sp^3 to sp-type would lead to more *s*-character and therefore shorter bond.

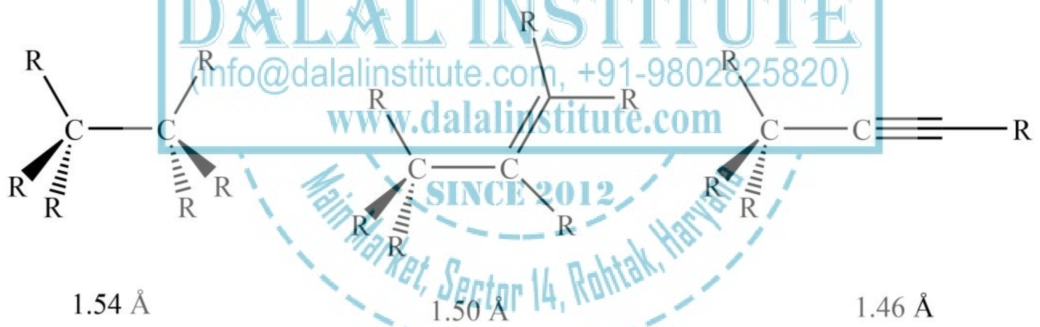

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Figure 46. Average carbon–carbon bond length with changing hybridization.

3. J_{CH} coupling constants: Bent's rule is very much effective in explaining the variation of carbon-hydrogen coupling constant with increasing electronegativity strength of the attached substituents. The ^1H-^{13}C coupling constants (J_{CH}) measured from nuclear magnetic resonance (NMR) spectra is one of the most direct scales that can be used to estimate the magnitude of *s* character in a bonding overlap between carbon and hydrogen.

Now as we know from the quantum theory that the J_{CH} values will be much greater in bonds with more *s* character than the one with the less. Therefore, as the electronegative character of the attached group increases, the magnitude of *p*-character oriented towards the corresponding group increases as well. This induces more *s* character in the bonds directed towards the methyl protons; which in turn, increases the J_{CH} coupling constants.

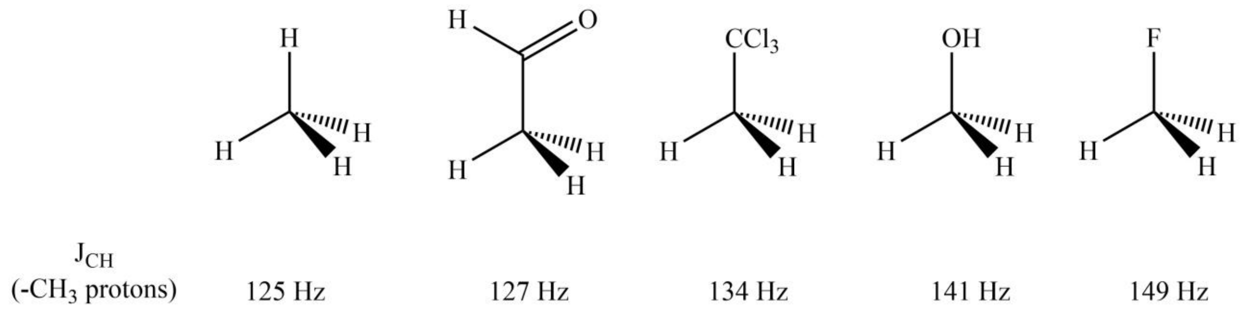

Figure 47. The variation of carbon-hydrogen coupling constants (J_{CH}) with increasing electronegative strength of the attached group.

4. Inductive effect: One of the most important phenomena in the field of organic chemistry, the inductive effect, can also be rationalized with the help of Bent's rule. The phenomenon of inductive effect is actually the passing of charge via the covalent bonds and Bent's rule offers a reasonable mechanism for such observations by exploiting the differences in the hybridization scheme involved. It has been observed that with the increase in the electronegativity strength of the groups attached to the central carbon, the electron-withdrawing power of the central carbon also increases and can be measured by the polar-substituent-constant values. According to the Bent's rule, the increase in the electronegativity of the groups attached would attract more *p* character towards them; consequently, leaving higher *s* character for the C−R bond. Now because the s orbitals have higher electron-density near the nuclei than their *p* counterparts, a shift of electron density towards the carbon in the C−R bond is expected; which in turn would make the central carbon atom more electron-withdrawing to the ligand attached i.e. R.

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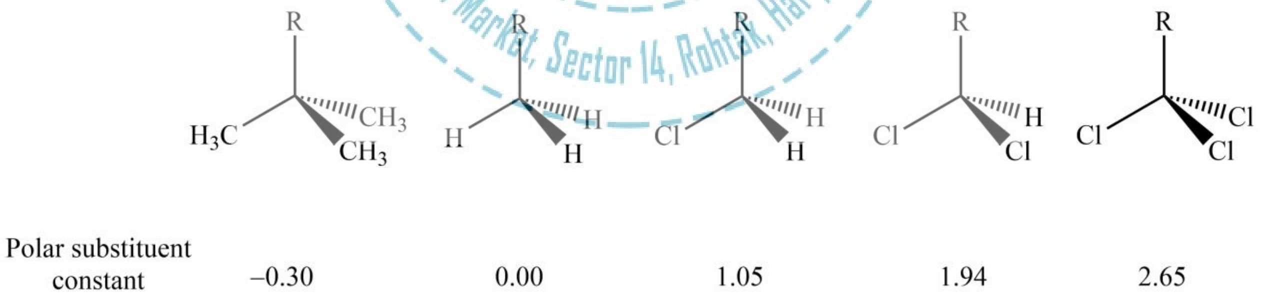

Figure 48. The variation polar-substituent-constants with increasing electronegative strength of the attached group.

In words, we can say that the electron-withdrawing capability of the substituents-attached is transferred to the neighboring carbon atoms in the carbon chain under consideration. This is exactly the same conclusion what the inductive effect states.

➢ *Exceptions of Bent's Rule*

The general statement of Bent's rule, atomic *s*-character concentrates in orbitals directed towards electropositive substituents, is true only for main group compounds. However, transition metal complexes show quite strange behavior. It has been observed that the group four transition metals Ti–Hf do not rigorously follow Bent's rule. With these complexes, the more electronegative substituents have larger bond angles indicating greater s-character. This can be explained by the fact that the *d*-orbitals in transition metals are generally lower in energy than *s*-orbital. Thus, more electronegative substituents will be attracted to the high lying *s*-orbitals. Transition metal orbitals are sd^3 hybridized with very little contribution from *p*-orbitals.

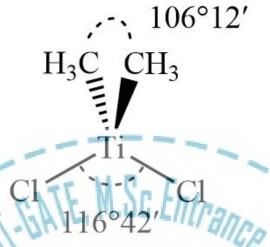

Figure 49. Distorted structure of $TiMe_2Cl_2$.

The broad form of Bent's rule can be stated as follows, "The energetically low-lying valence orbital concentrates in bonds directed towards electropositive substituents". This satisfies both the main group and transition metal complexes.

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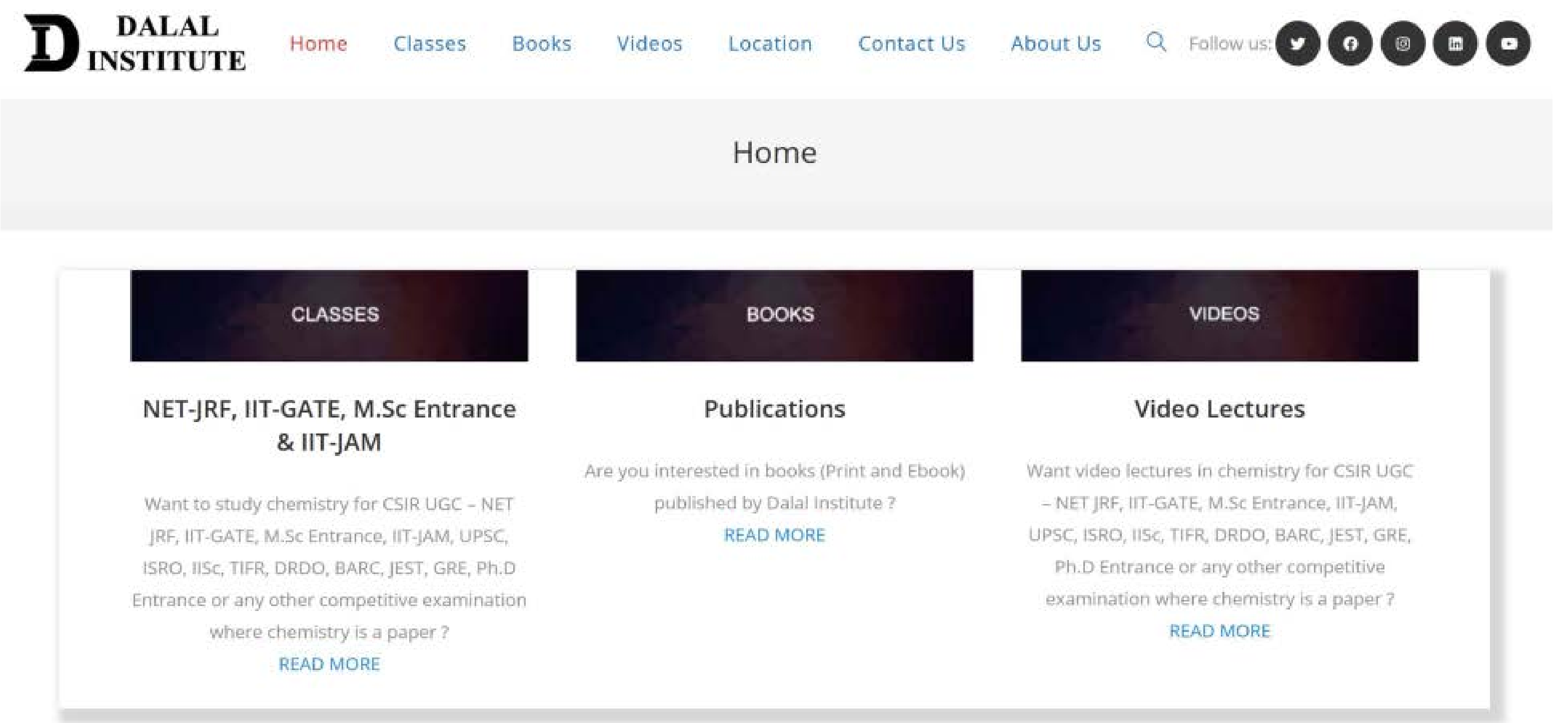

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