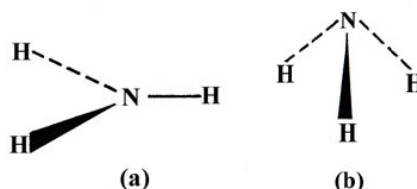# 6.5: Molecular Geometry

The theory of valency which we have been developing is known as **valence bond theory**. One further feature of this theory is that it may be used to predict (or in some cases, rationalize) the observed geometries of molecules By the geometry of a molecule we mean the relative arrangement of the nuclei in three-dimensional space. For example, assuming the two O-H bonds in the water molecule to be similar and hence of the same length, the angle formed by the two O-H bonds (the HOH angle could conceivably posess any angle from 180° to some relatively small value. All we demand of our simple theory is that it correctly predict whether the water molecule is linear (bond angle = 180°) or bent (bond angle less than 180°) Or as another example, it should predict whether the ammonia molecule is planar (a) or pyramidal (b).

The observed geometry of a molecule is that which makes the energy of the system a minimum. Thus those geometries will be favoured which (i) concentrate the largest amount of charge density in the binding region and thus give the strongest individual bonds, and (ii) keep the nuclei as far apart as possible (consistent with (i)), and hence reduce the nuclear replusions. Consider again the two possibilities for the water molecule It is clear that the linear form (a) will have a smaller energy of nuclear repulsion from the hydrogens than will the bent form (b).

If the amount of electron density which could be concentrated in the regions between the nuclei in each *[Math Processing Error]* bond (i.e., the strength of each *[Math Processing Error]* bond) was independent of the bond angle, then clearly the linear form of the water molecule would be the most stable. This would be the situation if all the atomic orbitals which describe the motions of the electrons were rigidly spherical and centred on the nuclei. But this is not the case. As was stressed earlier in our discussion of atomic orbitals, the motion of electrons possessing angular momentum because they occupy orbitals with $l \neq 0$ is concentrated along certain axes or planes in space. In particular the three p orbitals are a maximum along the three perpendicular axes in space. The valence bond theory of the water molecule describes the two O-H bonds as resulting from the overlap of the H $1s$ orbitals with the two half-filled $2p$ orbitals of the oxygen atom. Since the two $2p$ orbitals are at right angles to one another, valence bond theory predicts a bent geometry for the water molecule with a bond angle of 90°.

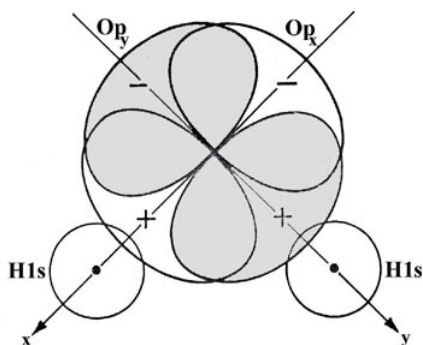The overlap of the orbitals is shown schematically in .

Fig. 6-16. A pictorial representation of the overlap of *[Math Processing Error]* and *[Math Processing Error]* orbitals on the oxygen with the 1s orbitals of two H atoms.

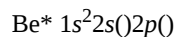File failed to load: https://cdnjs.cloudflare.com/ajax/libs/mathjax/2.7.3/jax/output/HTML-CSS/jax.js

The actual bond angle in the water molecule is 104.5°. The opening of the angle to a value greater than the predicted one of 90° can be accounted for in terms of a lessening of the repulsion between the hydrogen nuclei. The **assumption** we have made is that the maximum amount of electron density will be transferred to the binding region and hence yield the strongest possible bond when the hydrogen and oxygen nuclei lie on the axis which is defined by the direction of the $2p$ orbital. For a given internuclear separation, this will result in the maximum overlap of the orbitals. Because an orbital with l ¹ 0 restricts the motion of the electron to certain preferred directions in space, bond angles and molecular geometry will be determined, **to a first rough approximation**, by the inter-orbital angles.

In the valence bond description of ammonia, each N-H bond results from the overlap of an H $1s$ orbital with a $2p$ orbital on N. All three $2p$ orbitals on N have a vacancy and thus three bonds should be formed and each HNH angle should be 90°, i.e., ammonia should be a pyramidal and not a planar molecule. The NH_3 molecule is indeed pyramidal and the observed HNH angle is 107.3°. The actual bond angle is again larger than that predicted by the theory.

It might be argued that since the N atom possesses a half-filled $2p$ shell (its electronic configuration is $1s^22s^22p^3$), its density distribution is spherical and hence the N atom should not exhibit any directional preferences in its bonding. This argument is incorrect for the following reason. The density distribution is obtained by squaring the wave function. The wave function which properly describes the system must be obtained first, then squared to obtain the density. The wave function which describes the ammonia molecule consists of products of hydrogen $1s$ orbital functions with the nitrogen $2p$ orbital functions. (A product of orbitals is the mathematical statement of the phrase "overlap of orbitals" in valence bond theory.) The density distribution obtained by squaring the product of two orbitals is **not** the same as that obtained from the sum of the squares of the individual orbitals. Thus in the valence bond theory of molecular electronic structure the directional properties of the valence orbitals play an important role. By assuming that the most stable bond results when the two nuclei joined by the bond lie along the axis defined by the orbitals and considering the bonds to a first approximation to be independent of one another, we can predict the geometries of molecules.

Hybridization

The BeH_2 molecule is linear and the two Be-H bonds are equivalent. The valence bond description of BeH_2 accounted for the two-fold valency of Be (which has the ground state configuration $1s^22s^2$) by assuming the bonding to occur with a promoted configuration of Be:

Be* $1s^22s()2p()$

At first sight this suggests that the two Be-H bonds should be dissimilar and not necessarily 180° apart because one bond results from the overlap with a $2s$ orbital and the other with a $2p$ orbital on Be. We can, however, account for the equivalence of the two Be-H bonds and for the linearity of the molecule within the framework of the theory. There is no **a priori** reason for assuming that the one bond will result from the overlap with a $2s$ orbital and the other from the overlap with a $2p$ orbital. In the most general treatment of the problem, each bond to a hydrogen could involve both the $2s$ and the $2p$ orbitals. That is, we can "mix" or **hybridize** the valence orbitals on the Be atom. In fact, by taking each valence orbital on Be to be an equal part of $2s$ and $2p$, we can obtain two equivalent hybrid orbitals which are directed 180° apart. The two hybrid orbitals will form two equivalent bonds with the H $1s$ orbitals whose total bond strength will be larger than that obtained by forming one bond with a $2p$ and the other with a $2s$ orbital on Be.

The construction of the hybrid orbitals is accomplished by taking the sum and the difference of the $2s$ orbital and one of the $2p$ orbitals, say the $2p_x$ orbital, both orbitals being centred on the Be nucleus. This is illustrated in Fig. 6-17.
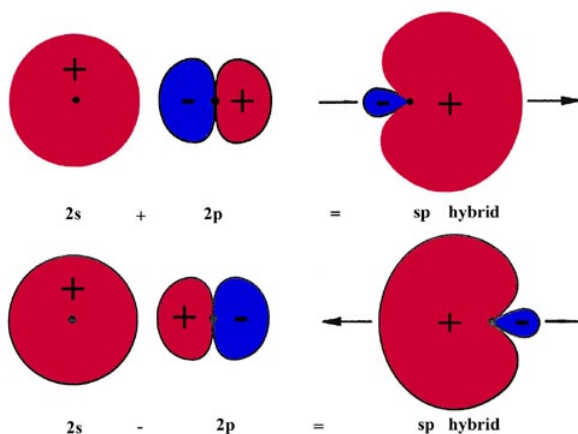
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Fig. 6-17. The construction of sp hybrid orbitals from a 2s and 2p atomic orbital on Be.

Since the $2p$ orbital has a node at the nucleus the $2p$ orbital wave function has opposite signs on each side of the nodal plane indicated in the figure. Both orbitals are positive on one side and the orbital functions add at each point in space. On the other side of the nodal plane, the orbitals are of opposite sign and their sum yields the difference between the two functions at every point in space. The addition of a $2s$ and $2p_x$ orbital concentrates the wave function and hence the charge density on the positive side of the x-axis. Obviously the combination $(2s - 2p_x)$ will be similar in appearance but concentrated on the negative side of the x-axis. These combinations of the $2s$ and $2p$ orbitals yield **two** hybrid orbitals which are equivalent and oppositely directed. Since each of the hybrid orbitals is constructed from equal amounts of the $2s$ and $2p$ orbitals they are termed "sp hybrid" orbitals.

The linear nature of BeH_2 can be explained if it is assumed (as is true) that the best overlap with both H $1s$ orbitals will result when the valence orbitals on the Be are sp hybrids (Fig. 6-18).
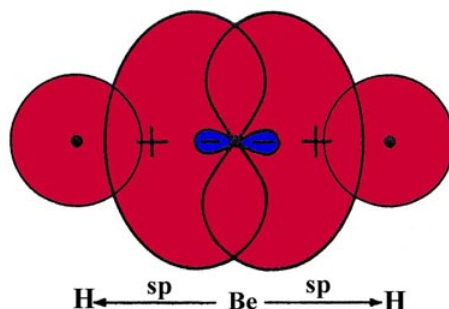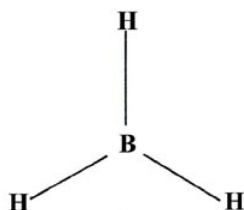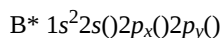

Fig 6-18. A pictorial representation of the overlap of two sp hybrid orbitals on Be with H 1s orbitals to form BeH2.

The three B-H bonds in BH_3 are equivalent and the molecule is planar and symmetrical:

The promoted configuration of boron with three unpaired electrons is
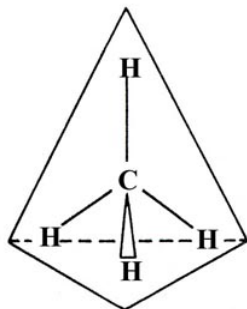
B* $1s^2 2s() 2p_x() 2p_y()$

In this case we must construct three equivalent hybrid orbitals from the three atomic orbitals $2s$, $2p_x$, and $2p_y$, on boron. The $2p_x$ and $2p_y$ orbitals define a plane in space and the three hybrid orbitals constructed from them will be projected in this same plane. Since the hybrid orbitals are to be equivalent, each must contain one part $2s$ and two parts $2p$. They will be called "sp^2" hybrid
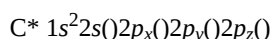
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orbitals. The three orbital combinations which have the above properties are indeed directed at 120° to one another. The planar, symmetrical geometry of BH_3 can be accounted for in terms of sp^2 hybridization of the orbitals on boron.

The four C-H bonds in CH_4 are equivalent and the molecule possesses a tetrahedral geometry:
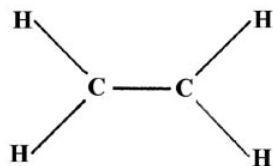

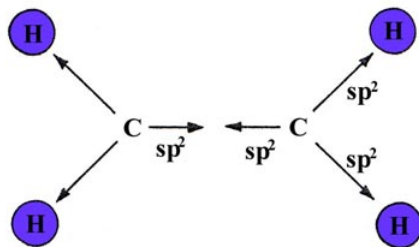The promoted configuration of carbon with four unpaired spins is

C* $1s^2 2s()2p_x()2p_y()2p_z()$

Four equivalent hybrid orbitals can be constructed from the $2s$ and the three $2p$ orbitals on carbon. Each orbital will contain one part $2s$ and three parts $2p$, and the hybrids are termed sp^3 hybrids. Only one such set of orbitals is possible and the angle between the orbitals is 109°28′, the tetrahedral angle. The tetrahedral geometry of CH_4 is described as resulting from the sp^3 hybridization of the valence orbitals on the carbon atom.
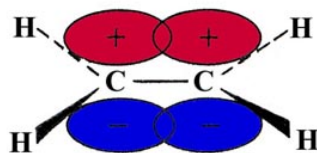
The three hybridization schemes which have been presented are sufficient to account for the geometries of all the compounds formed from elements of the first two rows of the periodic table (those with $n= 1$ or $n = 2$ valence orbitals). Consider, for example, the unsaturated hydrocarbons. The ethylene molecule, C_2H_4, possesses the planar geometry indicated here,
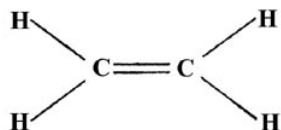

where the bond angles around each carbon nucleus are approximately 120°. Three bonds in a plane with 120° bond angles suggests sp^2 hybridization for the carbon atoms. Two of the sp^2 hybrids from each carbon may overlap with H $1s$ orbitals forming the four C-H bonds. The remaining sp^2 hybrids on each carbon may overlap with one another to form a bond between the carbons:

The sp^2 hybrids are denoted by arrows in the above diagram to indicate their directional dependence. If these bonds are formed in the x-y plane, using the $2p_x$ and $2p_y$ orbitals of the carbon atoms, a singly-occupied $2p_z$ orbital will remain on each carbon. They will be directed in a plane perpendicular to the plane of the molecule:

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The overlap of the two $2p_z$ orbitals above and below the plane of the molecule will result in a second electron pair bond between the carbon atoms. The bonds formed in the plane of the molecule are called s (sigma) bonds, while those perpendicular to the plane are called p bonds. Since the overlap of the orbitals to form a p bond is not as great as the overlap obtained from s bonds (which are directed along the bond axis), p bonds in general are weaker than s bonds. A Lewis structure for the C_2H_4 molecule is expressed as

indicating that there is a double bond between the carbon atoms, i.e., the density from two pairs of electrons binds the carbon atoms.

The energy required to break the carbon-carbon double bond in ethylene is indeed greater than that required to break the carbon-carbon single bond in the ethane molecule, H_3C-CH_3. Furthermore, the chemical behaviour of ethylene is readily accounted for in terms of a model which places a large concentration of negative charge density in the region between the carbon atoms. The physical evidence thus verifies the valence bond description of the bonding between the carbons in ethylene.

Our final example concerns another important possible hybridization for the carbon atom. The acetylene molecule, C_2H_2, is a linear symmetric molecule: H-C-C-H. The linear structure suggests we try *sp* hybridization for each carbon, one hybrid overlapping with a hydrogen and the other with a similar hybrid from the second carbon atom. This will produce a linear s bond framework for the molecule:
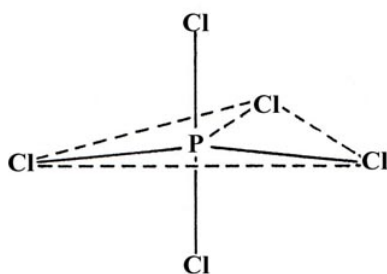

The *sp* hybrids are denoted by arrows in the above diagram. If the *sp* hybrids are assumed to be directed along the *x*-axis, then the remaining singly-occupied $2p_y$ and $2p_z$ orbitals on each carbon may form p bonds. The $2p_y$ orbitals on each carbon may overlap to form a p bond whose density is concentrated in the *x-y* plane, with a node in the *x-z* plane. Similarly the $2p_z$ orbitals may form a second p bond concentrated in the *x-z* plane, with a node in the *x-y* plane. Acetylene will possess a triple bond, one involving three pairs of electrons, between the carbon atoms. The Lewis structure is drawn as
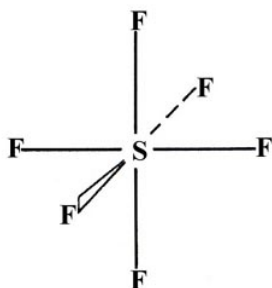

where it is understood that one of the C-C bonds is a s bond while the other two are of the p-type. The chemistry and properties of acetylene are consistent with a model which places a large amount of charge density in the region of the C-C bond.

Hybridization schemes involving *d* orbitals are also possible. They are important for elements in the third and succeeding rows of the periodic table. Although the elements of the third row do not possess occupied 3*d* orbitals in their ground electronic configurations, the 3*d* orbitals of phosphorus, sulphur and chlorine are low enough in energy that promoted configurations involving the 3*d* orbitals may be reasonably postulated to account for the binding in compounds of these elements. One consequence of the "availability" of the 3*d* orbitals is that there are many exceptions to the octet rule in compounds of the third row elements. For example, in PCl_5 there are ten valence electrons involved in the bonding of the five chlorines to the phosphorus. A hybridization scheme based on the promotion of one 3*s* electron of phosphorus to a 3*d* orbital to yield five "dsp^3" hybrid orbitals correctly predicts the trigonal bypyramidal structure of PCl_5:

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As a final example consider the molecule SF_6 in which all six S-F bonds are equivalent and the geometry is that of a regular octahedron (one F atom centred in each face of a regular cube):

This geometry and number of bonds can be accounted for by assuming the promotion of one $3s$ and one $3p$ electron to two of the $3d$ orbitals on the sulphur atom. This hybridization yields six equivalent "d^2sp^3" hybrid bonds which are indeed directed as indicated in the structure for SF_6.

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