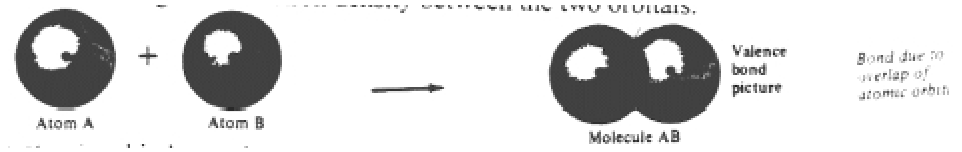
Modern Theories of Covalent Bonding

The VSEPR theory is a simple and useful tool in predicting molecular geometry of covalent molecules. However, there are several things that it does not do. It does not relate the shapes of molecules to the orbitals and energy levels of atoms. And it gives no picture of when, how, or why bonds form.

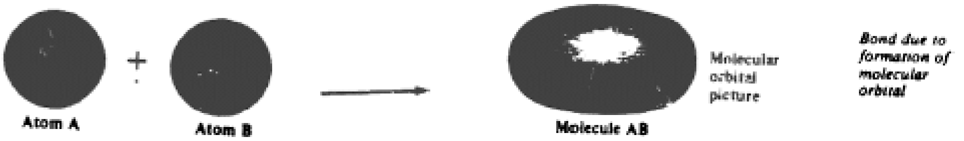
Two approaches are used to understand bonding in these terms:
1. the valence bond theory: VB theory
2. the molecular orbital theory: MO theory

In both theories, nuclei are imagined as attracted to an area of high electron density located along the line between the two nuclei - the bond axis. The bonding electrons are simultaneously attracted by both nuclei.
VB and MO theories differ in the way they construct a theoretical model of the bonding in a molecule.

In VB theory, a bond between two atoms is formed when a pair of electrons is shared by two overlapping atomic orbitals, one orbital from each of the atoms joined by the bond. The two electrons jointly occupy this region of space , or to overlap and forming a covalent bond. The two combining orbitals maintain their identity and overlap to give an area of greater electron density between the two orbitals.



In MO theory, atomic orbitals are pictured as combining to form molecular orbitals - new orbital that "belong" to the entire molecule or to groups of atoms, rather than to individual atoms. In this model the overlapping orbitals have combined and rearranged to give a single bonding molecular orbital with greater electron density between the two orbitals.

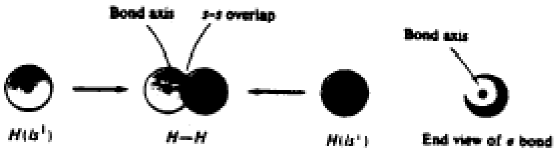


Both VB and MO theories are based on the mathematics of quantum mechanics. Both explain experimental facts such as the observed geometry of molecules, their molecular spectra or their bond energies, etc.

OVERLAP of ORBITALS:
Only one pair of electrons with their spins paired can be shared by two overlapping orbitals. The region of high electron density represented by the overlap indicates the covalent bond. The possibility for bond formation exists when two atoms can approach each other in such a way that occupied orbitals with similar energies are able to come into contact or overlap.
The greater the amount of overlap, the stronger the bond, lower the energy of the atoms (more stable the bonds).

Single Bonds in Diatomic Molecules

The simplest example of bond formation by atomic orbital overlap is given by the H_2 molecule. The single electron associated with each hydrogen atom occupies a spherical 1s orbital. Overlap of the two 1s orbitals allows pairing of the electron spins and the formation of a single covalent bond.

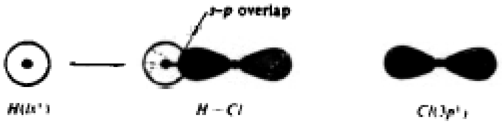


All bonds such as this, in which the region of highest electron density surrounds the bond axis are called σ bonds (sigma bonds). Only one sigma bond can form between any two atoms.

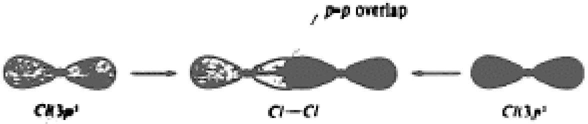
An *s* orbital and a *p* orbital (each of which contains a single electron) can also overlap to yield a sigma bond.

Example: H. $1s^1$
Cl. [Ne] $3s^2\ 3p_X^2\ 3p_y^2\ 3p_Z^1$

HCl molecule can be formed by the overlap of the 1s orbital of the hydrogen atom and the $3p_z$ orbital of the chlorine atom that holds a single unpaired electron.

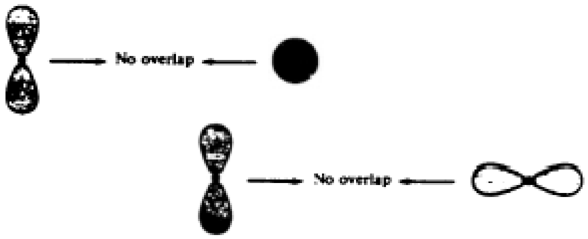


Similarly two *p* orbitals can overlap to produce a. sigma bond, if the overlapping orbitals lie along the same axis. For example, the chlorine - chlorine bond in the Cl_2 molecule can be described by the overlap of the two 3p orbitals, each containing one electron. However, to form a bond, the orbitals must approach end-on.



To form a bond, the overlapping orbitals must have the same symmetry with respect to the bond axis. The three p orbitals on a single atom are oriented in space at 90˚ to each other. Therefore, geometry does not allow bond formation between s and p orbitals when two atoms approach each other in certain ways.

A p orbital cannot overlap an s or another p orbital sufficiently to form a σ- bond when they approach as follows:



SINGLE BONDS IN POLYATOMIC MOLECULES: HYBRIDIZATION

Overlap of *s* and *p* orbitals as shown above cannot explain the bond lengths and bond angles in most molecules with more than two atoms. Furthermore the geometry observed cannot be explained by such overlap. For polyatomic molecules, we must explain not only the number of bonds formed but also their observed geometries.

In methane CH_4 the two *s* electrons and two *p* electrons from a C atom ($1s^22s^22p^2$) must each form a bond with a *1s* electron from a hydrogen H atom.

Differences in bond length and bond angle might be expected between C-H bonds from *s-p* overlap and those from *s-s* overlap.

However, experimental measurements show that the four C-H bonds in CH_4 are identical in length and form equal tetrahedral angles with each other.

The concept of hybridization was introduced to allow an explanation of molecular geometry in terms of atomic orbitals and VB theory.

Hybridization is the mixing of the atomic orbitals on a single atom to give a new set of orbitals called **hybrid orbitals** on that atom.

***s, p*, and *d* orbitals mix to form new atomic orbitals: hybrid orbitals**

Hybridization represents the blending of higher energy and lower energy orbitals to form orbitals of intermediate energy. The hybrid orbitals are still atomic orbitals and remain around a single nucleus.

The number of hybrid orbitals formed always equals the number of atomic orbitals that have combined.

sp hybrid orbitals are formed by mixing a *s* and a *p* orbital creating two new orbitals. Each *sp* hybrid orbital has a large lobe on one side of the nucleus and a smaller on the other side. For simplification smaller lobe is often omitted in drawings.

The *sp* hybrid orbitals form stronger bonds than *p* orbitals because they allow greater overlap.

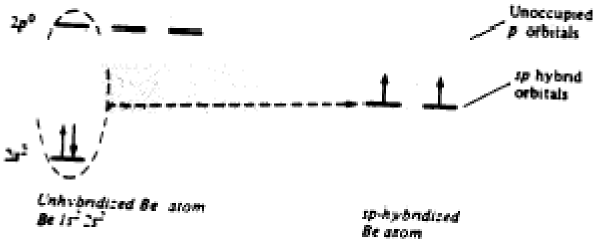
The large lobe occupies a greater region of space than the pure *p* orbital. This permits a greater degree of overlapping with the orbital of another atom resulting in the formation of a stronger bond.

The greater the overlap of two orbitals the stronger the bond.

The large lobes of the two *sp* hybrid orbitals point in opposite directions: 180^0 apart, linear molecule.

When two atomic orbitals are mixed, two hybrid orbitals are formed.

_sp_ Hybrid Orbitals: Consider $BeCl_2$:
The approach of the chlorine atoms causes a rearrangement of electrons and energy changes to take place in the beryllium atom.



One *s* orbital and one *p* orbital can hybridize to form two equivalent *sp* hybrid orbitals. The two hybrid orbitals have their large lobes pointing in opposite directions, 180^0 apart.

The promotion of a 2s electron to a 2p orbital in Be requires energy. Why, then, do we envision the formation of hybrid orbitals?

Hybrid orbitals have one large lobe ans can .: be directed at other atoms more effectively than can unhybridized atomic orbitals. Hence, they can overlap more strongly with the orbitals of other atoms than can atomic orbitals, and result in the formation of stronger bonds. The energy released by the formation of chemical bonds more than offsets the energy that must be expended to promote electrons.

Continuing the Saga of the Hybrid Orbitals

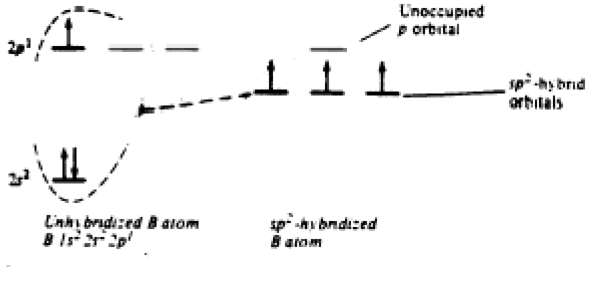
sp² Hybrid Orbitals

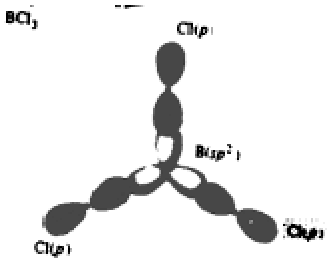
An sp^2 hybrid orbital results from the promotion of an *s* electron to a *p* orbital where hybridization occurs.

If an *s* and two of the *2p* orbitals combine, three hybrid orbitals, each similar to *sp* hybrid orbitals are formed, but they are termed sp^2 hybrid orbitals. This is because they are formed by mixing an $s + p + p$ orbitals. The superscript 2 signifies the number of *p* orbitals taking part in the formation of the hybrids.

Since three atomic orbitals were involved in the mixing, therefore three equivalent hybrid orbitals are formed. The spatial orientation will be that of planar triangular, with bond angles of 120^0.

Consider BCl_3:

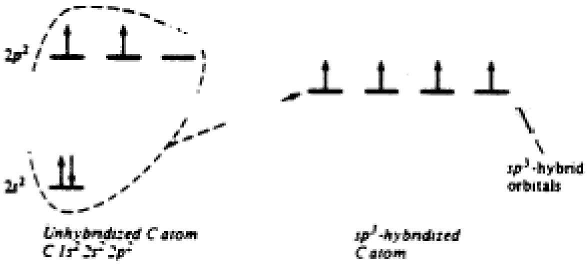




sp^3 Hybrid Orbitals

An sp^3 hybrid orbital involves one *s* and three *p* orbitals yielding four identical sp^3 orbitals, the larger lobes of which are directed towards the vertices of a regular tetrahedron and make an angle of 109.5^0 with each other. The sp^3 atomic orbital is more concentrated in direction than a *p* orbital, and is therefore able to overlap more extensively and form stronger bonds than a *p* orbital.

Consider CH_4:



Hybrid Orbitals in H_2O and NH_3

The sp^3 orbitals are also used in the bonding of both H_2O and NH_3, however the angles of the sp^3 orbitals are influenced and distorted by the presence of unbonded (lone) electron pairs.

sp^3d Hybrid Orbitals

The *s* and *p* orbitals of any atom give a maximum of four hybrid orbitals. Atoms of second-period elements which have only *s* and *p* orbitals can form no more than four hybrid orbitals and no more than four covalent bonds.

Beyond the second period atoms can form a larger number of covalent bonds by involving *d* orbitals in hybridization.

Example: PF_5

The geometry is explained by sp^3d hybridization: $s + p + p + p + d$ = five equivalent sp^3d hybrid orbitals. The geometry is trigonal bipyramidal with bond angles of 120˚ and four at 90˚.

Note: he order in which the orbitals of a hybrid set are written is the order of increasing *n*. Transition elements use the *(n-1)d, ns*, and *np* orbitals, and the d is written first: dsp^3 or d^2sp^3. Main-group elements use the *ns, np* and nd orbitals, and the *d* is written last: sp^3d or sp^3d^2.

sp^3d^2 Hybrid Orbitals

When six identical bonds are formed the central atom must use *d* orbitals. This is achieved by the promotion of an *s* and a *p* electron to *d* orbitals whereupon sp^3d^2 hybridization occurs. This gives an octahedral spatial orientation, bond angles of 90˚.

Example: SF_6

Review

Thus, the purpose of hybrid orbitals is to provide a convenient model for using valence bond theory to describe covalent bonds in molecules. One can not determine the hybrid orbitals used by a compound from the formula of a molecule alone, only when the molecular geometry is known, one can then employ the concept of hybridization to describe the atomic orbitals used by the central atom in bonding.

Hence the following steps are used to predict the hybrid orbitals used by an atom in bonding:

1. Draw the Lewis structure for the molecule or ion.
2. Determine the electron-pair geometry using the VSEPR model.
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometrical arrangement.

Geometrical Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	**Hybrid Orbital Set**	**Geometry**	**Examples**
s,p	Two *sp*	Linear, 180^0	BeF_2, $HgCl_2$
s,p,p	Three sp^2	Trigonal Planar, 120^0	BF_3, SO_3
s,p,p,p	Four sp^3	Tetrahedral, 109.5^0	CH_4, NH_3, H_2O, NH_4^{+1}
s,p,p,p,d	Five sp^3d	Trigonal Bipyramidal, 90^0, 120^0	PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2	Octahedral, 90^0	SF_6, ClF_5, XeF_4, SiF_6^{-2}

Example

Indicate the hybridization of orbitals employed by the central atom in each of the following: (a) NH_2^{-1}, (b) SF_4

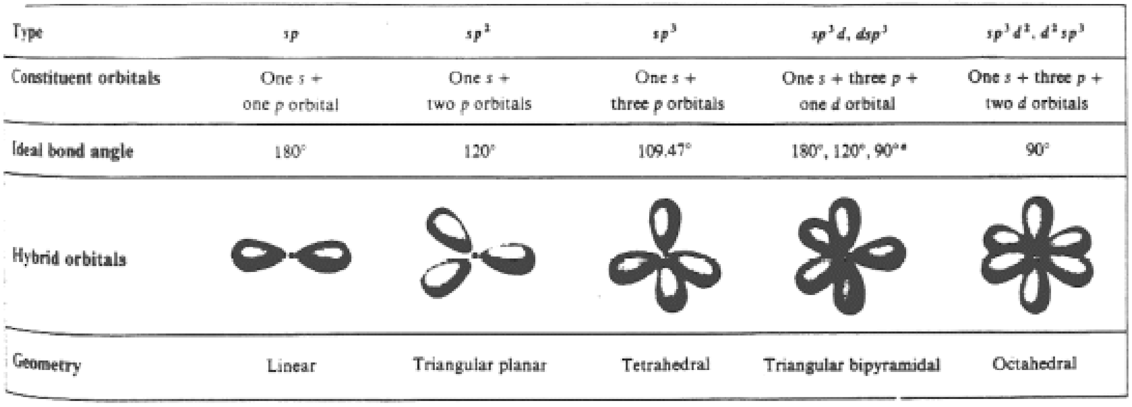
(a) First, determine the Lewis structure of NH_2^{-1} $[\mathrm{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}} :\mathrm{H}]^{-1}$

Second, determine the electron-pair geometry around N using the VSEPR model. Because there are four electron pairs around the N, thus the electron pair geometry is tetrahedral.
Third, specify the hybridization that gives a tetrahedral electron arrangement, i.e. sp^3. Two of the sp^3 hybrid orbitals contain non-bonding i.e. lone pairs of electrons, and the other two contain bonding pairs that are shared with hydrogen.
(b) SF_4: has 5 electron-pairs of electrons around S from the Lewis structure, giving rise to trigonal bipyramidal electron- pair geometry. With an expanded octet of 10 electrons, the use of d orbitals on the sulphur is required ... corresponding to the sp^3d hybridization. One of the hybrid orbitals contains a non-bonding pair of electrons, the other four are used in bonding.

Review Questions:

1. Describe the bonding in the F_2 molecule in terms of VB theory.
2. What are hybridized atomic orbitals? Why was the theory of hybridized orbitals introduced?
3.a. How would you designate the hybrid orbitals by "mixing" one d. one s and two p orbitals?
b. How many of the hybrid orbitals would be formed by the mixing?
4. What type of hybridization would you predict for molecules having the general formulas:
a. AB_3 b. AB_2E_2 c. AB_3E d. ABE_4 e. ABE_3 f. ABE_5
g. AB_2E_4 h. AB_3E_2 i. AB_4 j. AB_5 k. AB_5E 1. AB_4E_2
5. The bond angles in NH_3, H_2O and CH_4 are 107°. 104.5° and 109.5° respectively. How can these values be justified if sp^3 orbitals are involved in each case?
6. Predict the electron-pair geometry and the hybridization of the central atom in:
a) SO_3^{-2} (b) SF_6 (c) ClO_3^{-1} (d) $AlCl_4^{-1}$ (e) OF_2 (f) PF_6^{-1} (g) XeF_4 (h) PH_4^{+1}

Summary Table



Type	sp	sp^2	sp^3	sp^3d, dsp^3	sp^3d^2, d^2sp^3
Constituent orbitals	One s + one p orbital	One s + two p orbitals	One s + three p orbitals	One s + three p + one d orbital	One s + three p + two d orbitals
Ideal bond angle	180°	120°	109.47°	180°, 120°, 90°*	90°
Hybrid orbitals					
Geometry	Linear	Triangular planar	Tetrahedral	Triangular bipyramidal	Octahedral

Formation of sp^3d Hybridization