

Atomic Orbitals

Skills to develop

- Describe the shapes of ns , np , and nd atomic orbitals.
- Explain the variation of wavefunctions as the radius increases.
- Show how radial density changes as the radius increases.

Atomic Orbitals

Atomic orbitals are (energy) states or wave forms of electrons in the atom. If we insist on the particle nature of electrons, then the probability of finding an electron in an atomic orbital is proportional to the square of the wavefunction. The values of the wavefunction can be either positive or negative, but the probability is always a positive value.

Most of us are not used to thinking of electrons as waves, and we still refer to the density as the probability of finding the electron (a particle). The electron density diagrams given in many text books can be plotted using the appropriate wave functions. They are not the results of artists' imagination. In this demonstration, the computer will plot the densities according to an algorithm, which is based on the wavefunctions of various atomic orbitals.

The representation of [atomic orbitals](#) and their visualization has fascinated young and old scientists for ages. This link gives interesting pictures and movies. Congratulations to Dean Dager - dager@physics.ucla.edu, who has been a student winner twice in a row in Computer In Physics's Software Contest. His real-time visualization of the quantum mechanical [atomic orbitals](#) is a real treat.

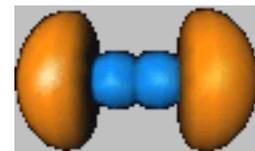
Some more links regarding atomic orbitals:

[Orbitron](#)

Dot-density as Electron-Density Plots

The probabilities of finding electrons anywhere in a three dimensional space around the hydrogen nucleus are proportional to the squares of the values of the wavefunction in the volume element corresponding to that space. Thus, the plot of probability should be done in a 3-dimensional space. However, such a plot not only requires a high degree of programming and viewing skills, it also takes a lot of computer time and a better monitor to do the job right. The next best way to represent them are looking at cross sections. This is the way we treat this subject here.

Lately, many diagrams to represent atomic orbitals have been made available via the web. The picture shown here is a $3p_z$ atomic orbital. [The learning matter of chemistry](#) is linked to a few useful places that provide various forms.

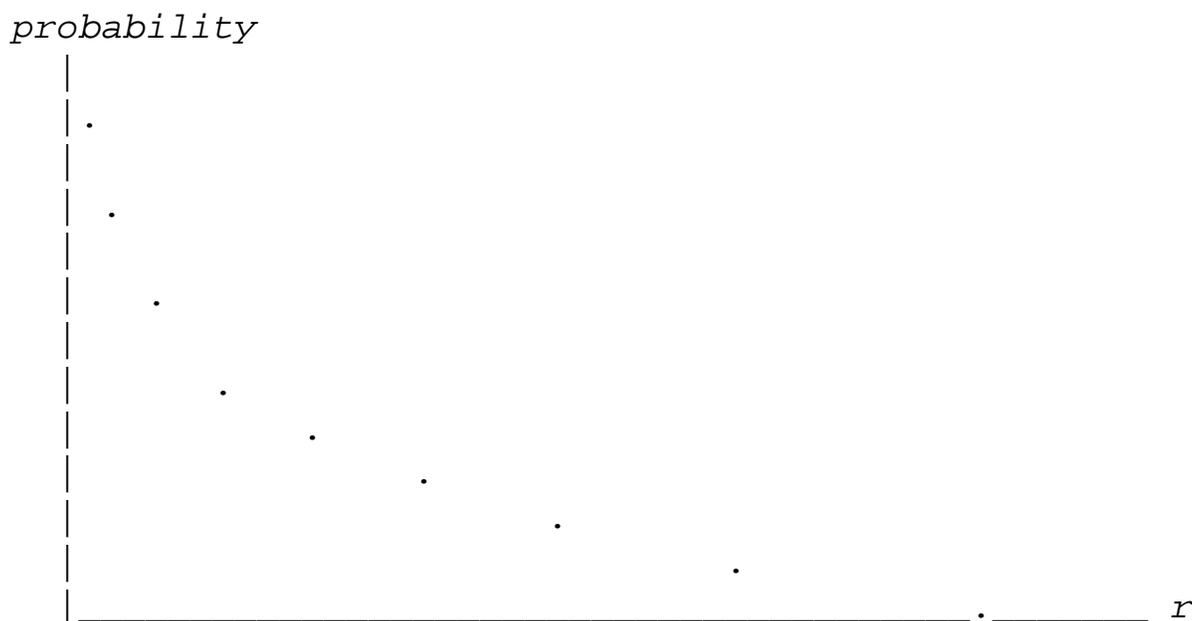


Two Forms of Electron Probability Density Plots

Each dot-density plot in this simulation is accompanied by two plots,

- (1) density versus radius r , and
- (2) radial density versus r .

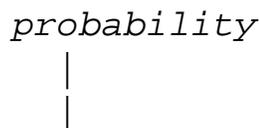
1. Density versus radius r : In this case, the square of the wave function is plotted against r . These plots are sometimes misleading. For example, the $1s$ orbital plot looks like

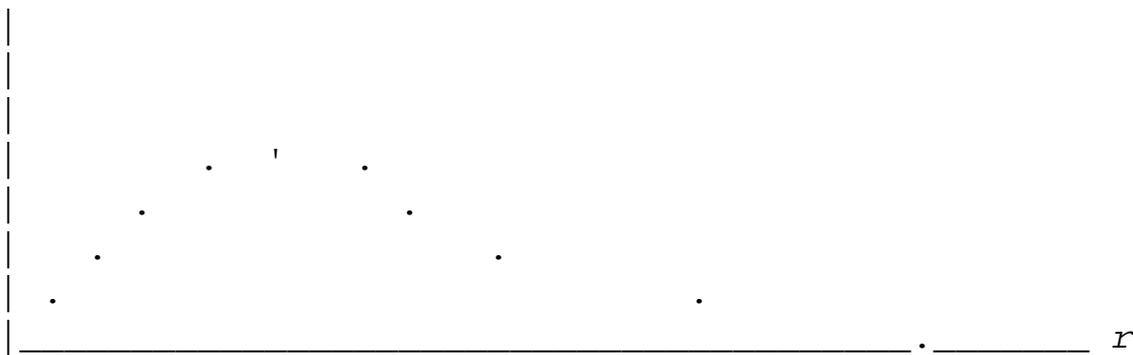


You may feel the probability of finding the electron is the highest in the nucleus, yet you have learned that the electron is most likely at a distance $r = 53$ pm from the center of the atom.

2. Radial density (RD) versus r : To really represent the probability of finding the electron at r at a given time, the radial distribution against r is often plotted. In this plot, instead of plotting square-of-the-wave-function, we modify square-of-the-wave-function by the volume associated with r , ($4\pi r^2$). This modification converts electron density to radial electron density.

The radial density plot of $1s$ orbital has a shape as shown below:





At the center of the atom, the value of the wavefunction is large, but when $r = 0$, the volume element ($4\pi r^2$) is almost zero when $r \rightarrow 0$. Thus, the radial distribution rises as r increases, reaching a maximum at some value of r . For the H atom, the maximum of the radial distribution is at $r = 53$ pm.

The Simulation of Electron Density

The simulation of electron density and showing orbitals is very well done in

The following program is no longer available, but the description is left here to you to use when you look at the above simulation

The computer plots of cross section of electron clouds for $1s$, $2s$, $2p$, $3s$, $3p$, and one $3d$ orbital are available. When the orbital is plotted the radial density is plotted versus r in the right lower corner of the screen. The function used for the plot is shown on the bottom of the screen. You do not need to copy the wave function, as you will get that later in a chemistry course.

The purposes of the computer simulation are given below:

1. To show you a simulated plot of the wavefunction by a desk top computer.
2. To show you the shapes of $1s$, $2s$, $2p$, $3s$, $3p$, and one $3d$ orbitals.
3. From the dot-density plots, please construct 3-dimensional pictures in your own mind.
4. From the plots, construct the nodal surfaces or planes in your mind.

Problems to Solve

1. Find the maximum radial distribution for $2s$, and $3s$ orbitals in Bohr's radius from the graph.

2. Find the maximum radial distribution for $3s$, $3p$, and $3d$ orbitals in Bohr's radius from the graph. Compare these three values and detect a trend as the azimuthal quantum number l increases.
3. Which orbital among $4s$, $4p$, $4d$, and $4f$ will have the smallest radius, at which the maximum radial distribution is found? This is an extension of 2.

The [Orbitron](#) is a link that gives wonderful views of the atomic orbitals.

Confidence Building Questions

- Which one of the following orbitals has one and only one nodal (spherical) shell or surface? $1s$, $2s$, $3s$, or $4s$.

If your answer is...I'm lost!

Consider...

An ns orbital has $(n-1)$ nodal shell(s). When $n = 2$, there is 1 nodal shell.

If your answer is...2s

Excellent...

How does an electron get through a nodal shell?

- Which one of the following orbitals has one and only one nodal plane? $1s$, $2s$, $2p_z$, $3s$, $3d_{xy}$.

If your answer is...I'm lost!

Consider...

The $2s$ orbital has a nodal shell, whereas the $2p_z$ orbital or $2p$ orbitals have a nodal plane.

If your answer is... p_z or $2p_z$

Excellent...

A nodal plane is a plane in which the probability of finding an electron is zero. The $2s$ orbital has a nodal shell, whereas the $2p_z$ orbital or $2p$ orbitals have a nodal plane.

- What shape do all s orbitals have?
 - a. spherical
 - b. dumbbell
 - c. donut
 - d. disk

If your answer is...I'm lost!

Consider...

Not all d orbitals have the same shape.

If your answer is...a

Excellent...

All p orbitals have a dumbbell shape, but from the plot, you should recognize the difference between $2p$ and $3p$ orbitals.

- **Although the maximum electron density of a $1s$ orbital is at the nucleus, why the radial density for this orbital is zero at the nucleus?**
 - a. The volume factor ($4\pi r^2$) is zero at $r = 0$.**
 - b. Electron can not get into a nucleus.**
 - c. No two particles can occupy the same space.**
 - d. The angular momentum keeps the electron away from the nucleus.**

If your answer is...I'm lost!

Consider...

Only a is accepted as the correct answer, although reasons given in other items sound all right.

If your answer is...a

Excellent...

Electron density means finding the electron per unit volume. Radial electron density means finding the electron at r .

- **What is the distance (in pm) for the maximum radial density of the $1s$ orbital in the hydrogen, H, atom.**

If your answer is...I'm lost!

Consider...

The Bohr's radius is 53 pm.

If your answer is...53 pm

Excellent...

The results is the same as Bohr's prediction.

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Valence Bond Theory and Hybrid Atomic Orbitals

Skills to develop

- Describe the valence bond (VB) approach to chemical bonding
- Demonstrate hybridization of atomic orbitals for VB
- Correlate the molecular shape to the hybrid atomic orbitals of some central atoms.
- Combine the concepts of **hybrid orbitals**, **valence bond theory**, **VSEPR**, **resonance structures**, and **octet rule** to describe the shapes and structures of some common molecules.

Valence Bond Theory and Hybrid Atomic Orbitals



This picture is an image of a Centaur from [Sphinx Stargate](#). The Centaur is a race of monsters in Greek mythology, **hybrid** animal having the head, arms and torso of a man united to the body and legs of a horse. **Mixing a number of atomic orbitals to form the same number of hybrid orbitals** to explain chemical bonding and shapes and molecular structures is a rather recent myth.

The most significant development in the first half of the 20th century is the human's ability to understand the structure of atoms and molecules.

Computation has made mathematical concepts visible to the extent that we now can *see* the atomic and molecular orbitals. On the other hand, Using everyday encountered materials or toys can also generate [beautiful illustrations of hybrid atomic orbitals](#).

The valence bond (VB) approach is different from the [molecular orbital \(MO\) theory](#). Despite their differences, most of their results are the same, and they are interesting.

The valence bond (VB) theory

The **valence-bond approach** considers the overlap of the atomic orbitals (AO) of the participation atoms to form a chemical bond. Due to the overlapping, electrons are localized in the bond region.

The overlapping AOs can be of different types, for example, a sigma bond may be formed by the overlapping the following AOs.

Chemical bonds formed due to overlap of atomic orbitals

<i>s-s</i>	<i>s-p</i>	<i>s-d</i>	<i>p-p</i>	<i>p-d</i>	<i>d-d</i>
H-H Li-H	H-C H-N H-F	H-Pd in palladium hydride	C-C P-P S-S	F-S in SF ₆	Fe-Fe

However, the atomic orbitals for bonding may not be "pure" atomic orbitals directly from the solution of the Schrodinger Equation. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The methods to get an AO with the proper character for the bonding is called **hybridization**. The resulting atomic orbitals are called **hybridized atomic orbitals** or simply **hybrid orbitals**.

We shall look at the shapes of some hybrid orbitals first, because these shapes determine the shapes of the molecules.

Hybridization of atomic orbitals

The solution to the Schrodinger Equation provides the wavefunctions for the following atomic orbitals:

$$1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, \text{ etc.}$$

For atoms containing two or more electrons, the energy levels are shifted with respect to those of the H atom. An atomic orbital is really the energy state of an electron bound to an atomic nucleus. The energy state changes when one atom is bonded to another atom.

Quantum mechanical approaches by combining the wave functions to give new wavefunctions are called **hybridization** of atomic orbitals. Hybridization has a sound mathematical foundation, but it is a little too complicated to show the details here. Leaving out the jargons, we can say that an imaginary mixing process converts a set of atomic orbitals to a new set of **hybrid atomic orbitals** or **hybrid orbitals**.

At this level, we consider the following hybrid orbitals:

$$\begin{aligned} &sp \\ &sp^2 \\ &sp^3 \\ &sp^3d \\ &sp^3d^2 \end{aligned}$$

The *sp* hybrid atomic orbitals

The *sp* hybrid atomic orbitals are

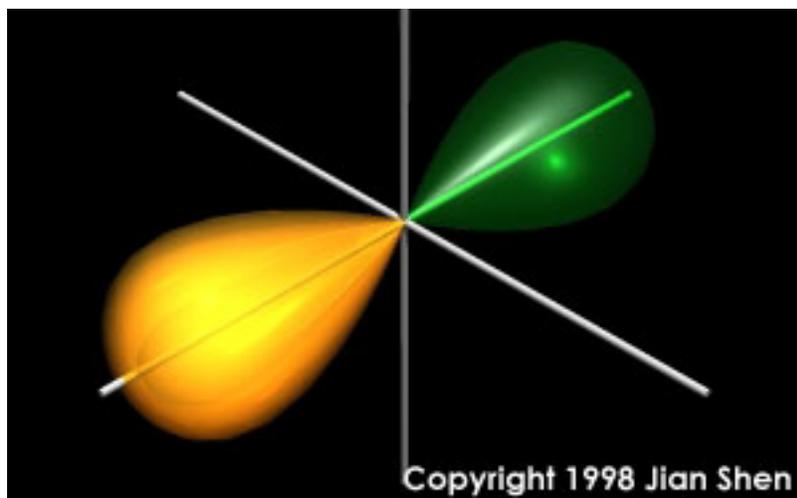


possible states of electron in an atom, especially when it is bonded to others. These electron states have half $2s$ and half $2p$ characters. From a mathematical view point, there are two ways to combine the $2s$ and $2p$ atomic orbitals:

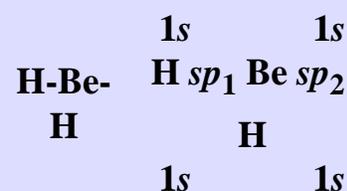
$$sp_1 = 2s + 2p$$

$$sp_2 = 2s - 2p$$

These energy states (sp_1 and sp_2) have a region of high electron probability each, and the two atomic orbitals are located opposite to each other, centered on the atom. The sp hybrid orbitals are represented by this photograph.



For example, the molecule H-Be-H is formed due to the overlapping of two $1s$ orbitals of 2 H atoms and the two sp hybridized orbitals of Be. Thus, the H-Be-H molecule is linear. The diagram here shows the overlapping of AOs in the molecule H-Be-H.



The ground state electronic configuration of Be is $1s^2 2s^2$, and one may think of the electronic configuration "before" bonding as $1s^2 sp^2$. The two electrons in the sp hybrid orbitals have the same energy.

You may say that the concept of hybridizing AOs for the bonding is just a story made up to explain the molecular shape of Cl-Be-Cl. You are right! The story is lovely and interesting, though.

In general, when two and only two atoms bond to a third atom and the third atom makes use of the sp hybridized orbitals, the three atoms are on a straight line. For example, sp hybrid orbitals are used in the central atoms in the molecules shown on the right.

**Linear
molecules**

ClBeCl

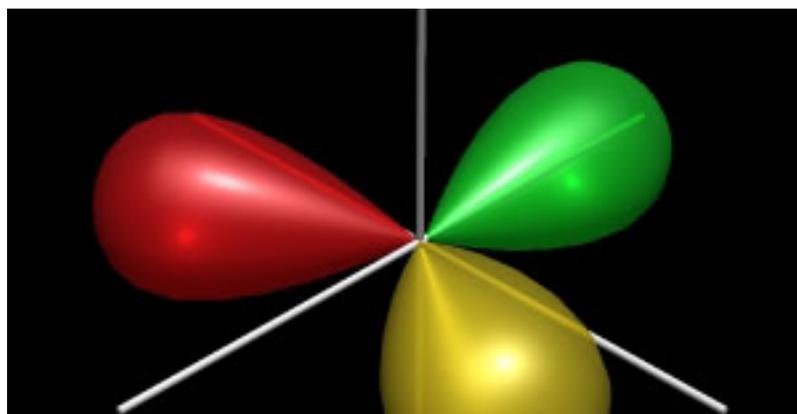
HCCH

HCN

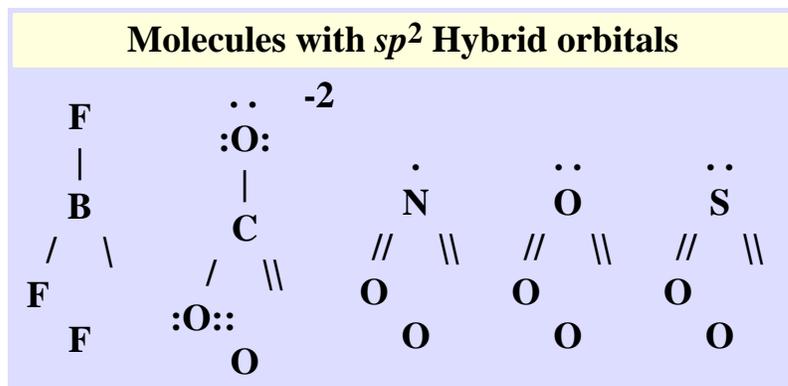
O=C=O

The sp^2 hybrid orbitals

The energy states of the valence electrons in atoms of the second period are in the $2s$ and $2p$ orbitals. If we mix two of the $2p$ orbitals with a $2s$ orbital, we end up with **three sp^2 hybridized orbitals**. These three orbitals lie on a plane, and they point to the vertices of an equilateral triangle as shown here.

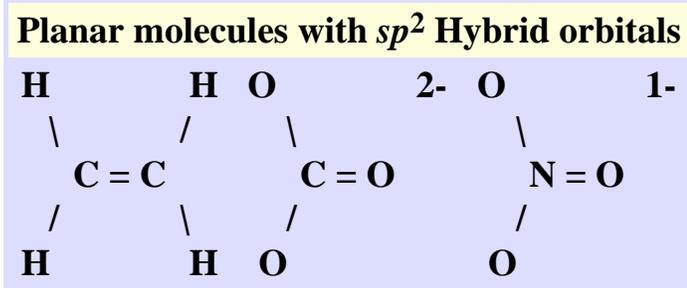


When the central atom makes use of sp^2 hybridized orbitals, the compound so formed has a trigonal shape. BF_3 is such a molecule:



Not all three sp^2 hybridized orbitals have to be used in bonding. One of the orbitals may be occupied by a pair or a single electron. If we do not count the unshared electrons, these molecules are bent, rather than linear. The three molecules shown together with the BF_3 molecule are such molecules.

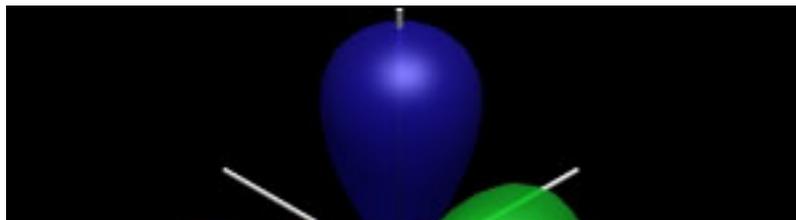
Carbon atoms also makes use of the sp^2 hybrid orbitals in the compound $H_2C=CH_2$. In this molecule, the remaining p orbital from each of the carbon overlap to form the additional pi, π , bond.



Other ions such as CO_3^{2-} , and NO_3^- , can also be explained in the same way.

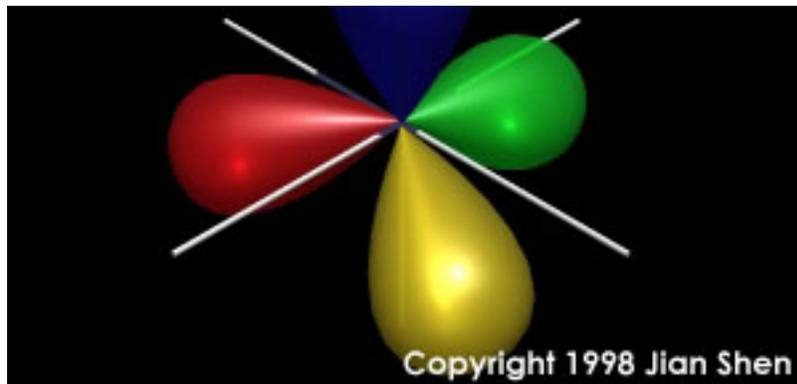
The sp^3 hybrid orbitals

Mixing one s and all three p atomic orbitals produces a set of four equivalent sp^3 hybrid atomic orbitals. The four sp^3



hybrid orbitals points towards the vertices of a tetrahedron, as shown here in this photograph.

When sp^3 hybrid orbitals are used for the central atom in the formation of molecule, the molecule is said to have the shape of a tetrahedron.

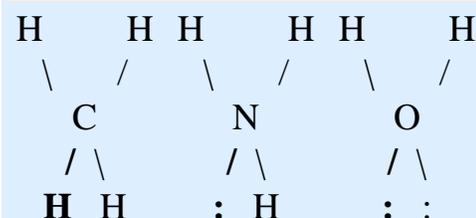


The typical molecule is CH_4 , in which the $1s$ orbital of a H atom overlap with one of the sp^3 hybrid orbitals to form a C-H bond. Four H atoms form four such bonds, and they are all equivalent. The CH_4 molecule is the most cited molecule to have a tetrahedral shape. Other molecules and ions having tetrahedral shapes are SiO_4^{4-} , SO_4^{2-} ,

As are the cases with sp^2 , hybrid orbitals, one or two of the sp^3 hybrid orbitals may be occupied by non-bonding electrons. Water and ammonia are such molecules.

The C, N and O atoms in CH_4 , NH_3 , OH_2 (or H_2O) molecules use the sp^3 hybrid orbitals, however, a lone pair occupy one of the orbitals in NH_3 , and two lone pairs occupy two of the sp^3 hybrid orbitals in OH_2 . The lone pairs must be considered in the VSEPR model, and we can represent a lone pair by E, and two lone pairs by E_2 . Thus, we have NH_3E and OH_2E_2 respectively.

Tetrahedral arrangements of CH_4 , NH_3E and OH_2E_2

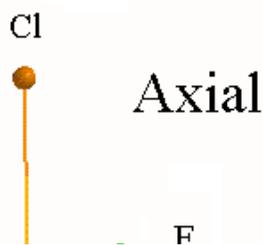


The *VSEPR number* is equal to the number of bonds plus the number of lone pair electrons. Does not matter what is the order of the bond, any bonded pair is considered on bond. Thus, the *VSEPR number* is 4 for all of CH_4 , $:\text{NH}_3$, $::\text{OH}_2$.

According to the VSEPR theory, the lone electron pairs require more space, and the H-O-H angle is 105 degrees, less than the ideal tetrahedral angle of 109.5 degrees.

The dsp^3 hybrid orbitals

The five dsp^3 hybrid orbitals resulted when one $3d$, one $3s$, and three $3p$ atomic orbitals are mixed. When an atom makes use of five dsp^3 hybrid orbitals to bond to five other atoms, the geometry of the



Confidence Building Questions

- **In terms of valence bond theory, how a chemical bond is formed?**

Discussion -

Molecular orbital theory considers the energy states of the molecule.

- **When one *s* and two *p* atomic orbitals are used to generate hybrid orbitals, how many hybrid orbitals will be generated?**

Discussion -

Number of orbitals does not change in hybridization of atomic orbitals.

- **In the structures of SO_2 and NO_2 , what are the values of the bond angles?**

Discussion -

Since the lone electron pair in $:\text{SO}_2$ and lone electron in $\bullet\text{NO}_2$ takes up more space, we expect the structure to distort leaving a smaller angle than 120 between the bonds.

- **What is the geometrical shape of the molecule CH_4 , methane?**

Discussion -

The 4 H atoms form a tetrahedron, and methane has a tetrahedral shape.

- **What do you expect the bond angles to be in the NH_4^+ ion?**

Discussion -

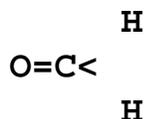
The structure of this ion is very similar to that of CH_4 .

- **What hybrid orbitals does the C atom use in the compound $\text{H-C}\equiv\text{C-H}$, in which the molecule is linear?**

Discussion -

Sigma (σ) bonds are due to sp hybrid orbitals, and 2 p orbitals are used for pi (π) bonds. The two sigma bonds for each C are due to overlap of sp hybrid orbitals of each C atom.

- **What hybrid orbitals does C use in the molecule:**



This is a trigonal planar molecule. It is called formaldehyde, a solvent for preserving biological samples. The compound has an unpleasant smell.

Skill -

The C atom has 3 *sigma* (σ) bonds by using three sp^2 hybrid orbitals and a *pi* (π) bond, due to one $2p$ orbital.

- **What is the shape of the molecule SF_6 ?**

Discussion -

Since the S atom uses d^2sp^3 hybrid orbitals, you expect the shape to be octahedral. The F atoms form an octahedron around the sulfur.

- **Phosphorus often forms a five coordinated compound PX_5 . What hybrid orbitals does P use in these compounds?**

Discussion -

A total of 5 atomic orbitals are used in the hybridization: one $3d$, one $3s$ and three $3p$ orbitals. The dsp^3 hybrid orbitals of P give rise to a trigonalbipyramidal coordination around the P atom.

The energy of d orbitals in N is not compatible with $2s$ and $2p$ orbitals for hybridization. Thus, you seldom encounter a compound with formula NX_5 with N as the central atom.

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Hybrid Orbitals in Carbon Compounds

Skills to develop

- Describe the hybrid orbitals used in the formation of bonding for each atom in some carbon containing compounds
- Calculate formal charge for each atom in some carbon containing compounds
- Draw resonance structures for some organic compounds

Hybrid Orbitals in Carbon Compounds

Diamond crystals such as the one shown here is appreciated by almost everyone, because of their hardness, sparkle, and high value. They are also important in many technical applications. However, in terms of chemistry, diamonds consist of only carbon atoms, except impurities. Like diamond, the chemistry of carbon is indeed very interesting and valuable.

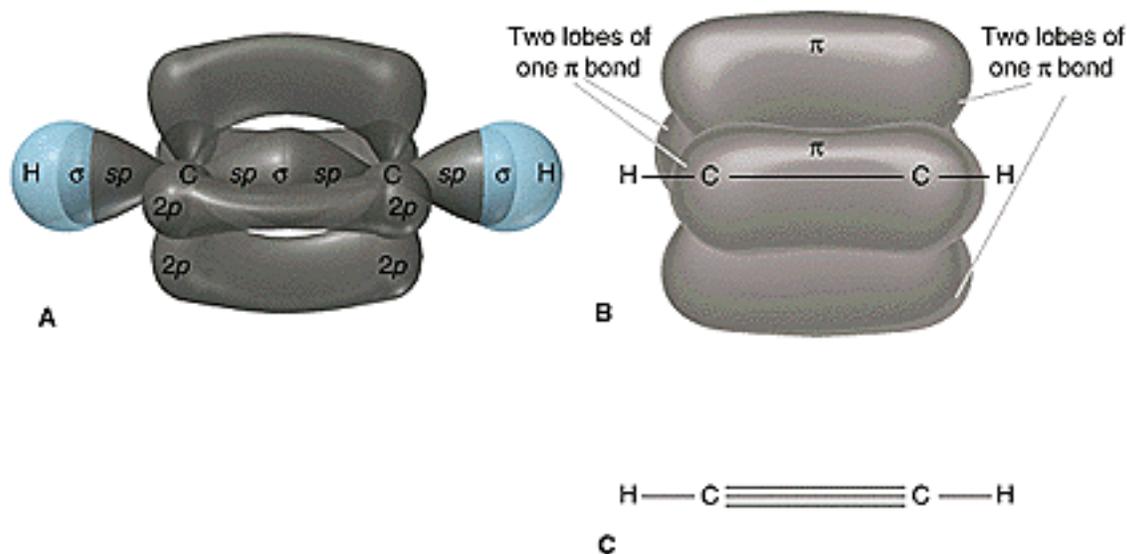


Carbon atoms have the ability to bond to themselves and to other atoms with sp , sp^2 , and sp^3 , [hybrid orbitals](#). This link gives you the basics about the hybrid orbitals, and you are introduced to the various bonding of carbon in this document.

Compounds containing carbon-hydrogen bonds are called organic compounds. May also contain C-C, C=C, C≡C, C-N, C=N, C≡N, C-O, and C=O bonds. Such a variety is due to the ability of carbon to make use of sp , sp^2 , and sp^3 hybrid orbitals for the bonding. There are also various inorganic compounds such as carbon monoxide, carbon dioxide, calcium carbonate, sodium bicarbonate, etc. involving carbon.

Carbon atoms using sp hybrid orbitals.

When sp hybrid orbitals are used for the sigma bond, the two sigma bonds around the carbon is linear. Two other p orbitals are available for pi bonding, and a typical compound is the acetylene or ethyne $\text{HC}\equiv\text{CH}$. The three sigma and two pi bonds of this molecule from [University of Florida: General chemistry](#) is shown below.

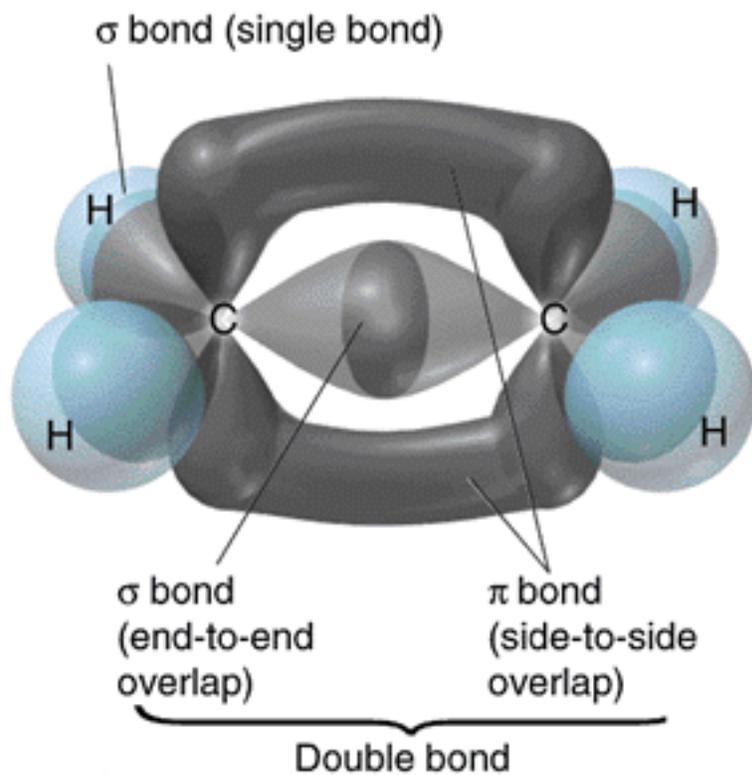


Note that molecules $\text{H-C}\equiv\text{C-H}$, $\text{H-C}\equiv\text{N}$, and $\text{C}\equiv\text{O}$ have the same number of electrons. Bonding in these molecules can be explained by the same theory, and thus their formation is no surprise. The $\text{O}=\text{C}=\text{O}$ molecule is linear, and the carbon atom in this molecule also involve the sp hybrid orbitals. Two pi bonds are also present in this simple molecule. As an exercise, draw a picture to show the two sigma and two pi bonds for this molecule.

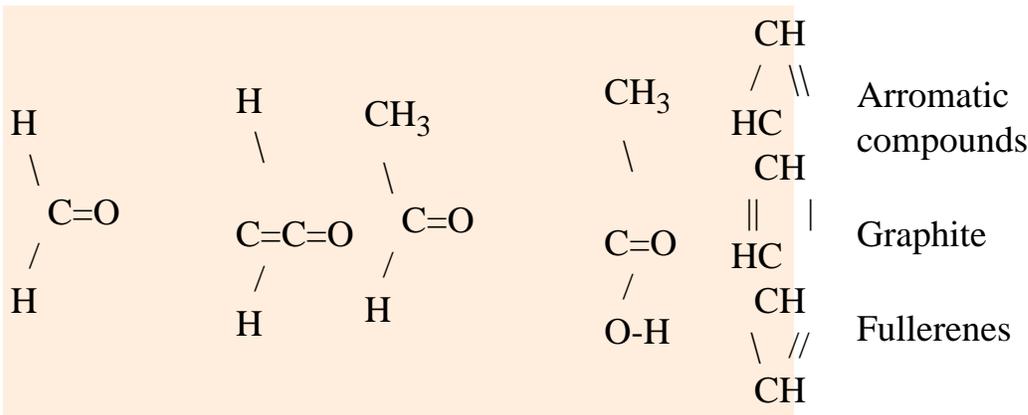
Carbon atoms using sp^2 hybrid orbitals.

When carbon atoms make use of sp^2 hybrid orbitals for sigma bonding, the three bonds lie on the same plane. One such compound is ethene, in which, both carbon atoms make use of sp^2 hybrid orbitals. One of the remaining p orbital for each carbon overlap to form a pi bond. A pi bond consists of two parts where bonding electrons are suppose to be located. A picture depicting the sigma and pi bonds in ethene from the same source as previous picture is shown on the right.

Carbon atoms make use of sp^2 hybrid orbitals not only in ethene, but also in many other type of compounds. The following are some of these compounds:



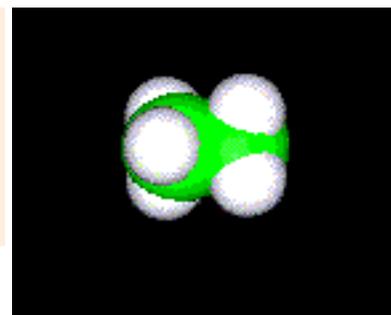
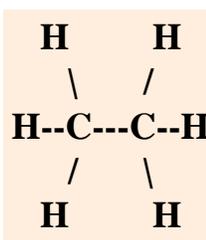
Formaldehyde Ketene Ethylaldehyde Acetic acid Benzene Others



During the lecture on covalent bonding, we can illustrate how atomic orbitals overlap in the formation of bonds. Here, we can only show you the nice picture as a result.

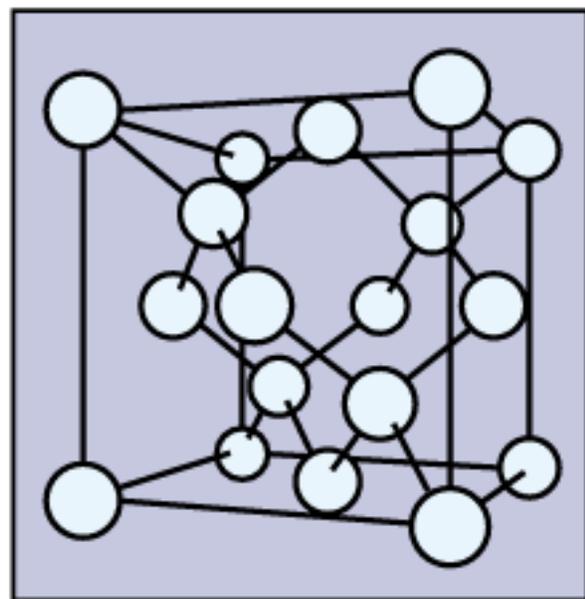
Carbon atoms using sp^3 hybrid orbitals.

In ethane, the carbon atoms use sp^3 hybrid orbitals for the formation of sigma bonds. The four bonds around each C atom point toward the vertices of a regular tetrahedron, and the ideal bond angles are 109.5° . The simplest compound is methane, CH_4 , which is the first member of the alkane family. The next few members are ethane CH_3CH_3 , propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, etc..



Diamond is a crystal form of elemental carbon, and the structure is particularly interesting. In the crystal, every carbon atom is bonded to four other carbon atoms, and the bonds are arranged in a tetrahedral fashion. The bonding, no doubt, is due to the sp^3 hybrid orbitals. The bondlength of 154 pm is the same as the C-C bondlength in ethane, propane and other alkanes.

An idealized single crystal of diamond is a gigantic molecule, because all the atoms are inter-bonded. The bonding has given diamond some very unusual properties. It is the hardest stone, much harder than any thing else in the material world. It is a poor conductor, because all electrons are localized in the chemical bonds. However, diamond is an excellent heat conductor. A stone made of pure carbon is colorless, but the presence of impurities gives it various colors. The index of refraction is very high, and their glitter (sparkle or splendor) has made them the most precious stones.



Comparison of structural features

Some typical bonding features of ethane, ethene, and ethyne are summarized in the table below:

Systematic name	Ethane	Ethene	Ethyne
Hybrid orbitals of C	sp^3	sp^2	sp
Structural formula	$ \begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{H}-\text{C} \cdots \text{C}-\text{H} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H}-\text{C}\equiv\text{C}- \\ \text{H} \end{array} $
C-C Bondlength pm	154	134	120
C-H Bondlength pm	112	110	106
H-C-C bond angle $^\circ$	111	121	180
C-C bond energy kJ/mol	368	611	820
C-H bond energy kJ/mol	410	451	536

As the bond order between carbon atoms increases from 1 to 3 for ethane, ethene, and ethyne, the bond lengths decrease, and the bond energy increases. Note that the bond energies given here are specific for these compounds, and the values may be different from the average values for this type of bonds.

Confidence Building Questions

- What hybrid orbitals are used by the carbon atoms in $\text{HC}\equiv\text{CH}$?

Discussion -

Linear $-\text{C}-$ bonds due to sp hybridized orbitals. This molecule is linear, and it consists of 3 sigma, σ , bonds, and two pi π , bonds. Compare the bonding of this with $\text{C}\equiv\text{O}$, $\text{H}-\text{C}\equiv\text{N}$, $\text{CH}_3-\text{C}\equiv\text{N}$

- **What hybrid orbitals are used by the carbon atoms in $\text{H}_2\text{C}=\text{CH}_2$?**

Discussion -

Planar $\text{C}=\text{C}$ bonds due to sp^2 hybridized orbitals. Another of p orbital is used for the π , π . How many sigma and pi bonds does this molecule have? Do all atoms in this molecule lie on the same plane?

- **What hybrid orbitals are used by the carbon in CH_3CH_3 ?**

Discussion -

Tetrahedral arrangement around C is due to sp^3 hybridized orbitals.

- **What hybrid orbitals are used by the oxygen in $\text{CH}_3\text{CH}_2\text{OH}$?**

Discussion -

Tetrahedral arrangement around C is due to sp^3 hybridized orbitals.

- **Which carbon to carbon bond length is the shortest in the following molecule $\text{CH}_3\text{CCCH}_2\text{CHCHCH}_2\text{OH}$?**

Discussion -

The bond length decreases as the bond order increases.

- **How many carbon atoms make use of sp^2 hybrid orbitals in this molecule $\text{CH}_3\text{CCCH}_2\text{CHCHCH}_2\text{COOH}$?**

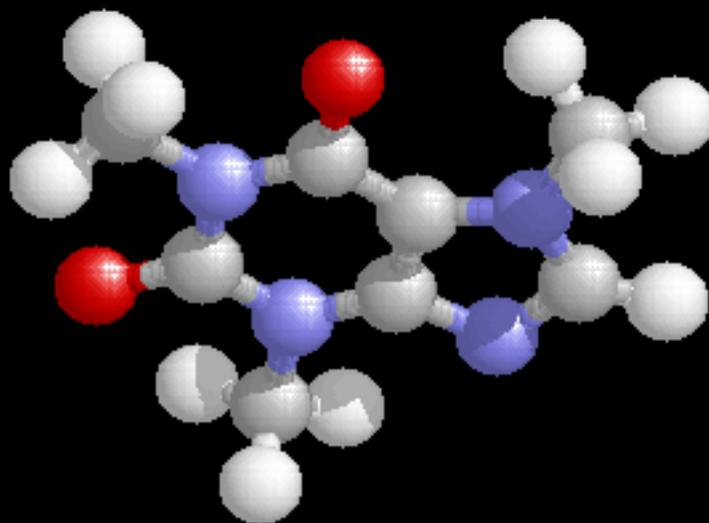
Discussion -

Recognize the type of bonding is important.

- **The molecular formula of caffeine is $C_8H_{10}N_4O_2$, draw a reasonable structure for it.**

Discussion -

The structure is shown below. Can you sketch a bonding structure for caffeine? How many carbon atoms makes use of sp^2 hybrid orbitals?



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