ORBITALS and MOLECULAR REPRESENTATION

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

by
DR. STEPHEN THOMPSON
MR. JOE STALEY
ORBITALS AND MOLECULAR REPRESENTATION

CONTENTS

2 Atomic Orbitals (n = 1)
3 Atomic Orbitals (n = 2)
4 Atomic orbitals (n = 3)
5 Hybrid Atomic Orbitals (sp)
6 Hybrid Atomic orbitals (sp²)
7 Hybrid Atomic Orbitals (sp²)
8 Hybrid Atomic Orbitals (sp³)
9 Overlapping Orbitals (Bonding And Antibonding)
10 Orbital Pictures For H And H₂
11 Difluorine
12 Carbon Orbitals (Methane And Ethane)
13 Carbon Orbitals (Ethene)
14 Carbon Orbitals (Ethene)
15 Carbon Orbitals (Ethyne)
16 Carbon Orbitals (Ethyne)
17 Carbon Orbitals (Benzene)
18 Carbon Orbitals (Benzene)
19 Several Representations Of Molecules
20 Several Representations Of Benzene
21 Representations Of Molecules
22 Representations Of Molecules
23 Representations Of Molecules
ORBITALS AND MOLECULAR REPRESENTATION

ATOMIC ORBITALS

While Lewis diagrams and energy level structures can show connectivity and energy relationships of molecules, they do not show the shape of the molecules. For this we need to picture atomic and molecular orbitals.

\[n = 1\]

\[l = 0\]

The picture above shows the spherically symmetric 1s orbital in the ‘green’ phase. Sometimes it is more convenient not to show the phase, in which case we can use a greyed representation, as shown below.

We denote the phase of the wave function by color, using light red for one phase and green for the opposite phase. Many books assign these phases plus or minus signs but the only real meaning is that they are opposite. Neither phase is plus or minus anything on its own but they are only opposite to each other. Sometimes when we are not concerned with phase we will draw the orbitals as a slightly reddish gray.

It is also possible to show the orbital as a simple loop.

And if you are drawing his by hand, the loop does not have to be an exact circle.

As we proceed developing atomic and molecular orbitals we will show various forms of representation.

\[n = 2\]

\[l = 0\]

Here are some boxes for you to practice drawing s orbitals in, although you do not really need boxes.

You can draw the two loops for 2s in the box below.
ATOMIC ORBITALS

l = 1

This is an accurate representation of a 2p_x orbital.

This is a common picture of a p_x orbital.

This simplified p_x orbital is often useful.

A hand drawn version does not have to be exact.

We can combine all three p orbitals in a three dimensional display.

Use these axes to draw all three p orbitals.
ATOMIC ORBITALS

\[ n = 3 \]

\[ l = 0 \]

3s

\[ l = 1 \]

3p_x

3p_y

3p_z

\[ l = 2 \]

3d_{xy}

3d_{xz}

3d_{yz}

3d_{x^2-y^2}

3d_z^2
HYBRID ATOMIC ORBITALS

**sp**

sp orbitals are a combination, or hybrid, of an s and a p orbital. In addition there will be two remaining unhybridized p orbitals orthogonal to each other and to the line joining the two hybrid sp orbitals.

You will also see these orbitals in greyscale, without phases. We use reddish grey for unhybridized orbitals and plain grey for hybridized orbitals.

We can also draw these orbitals as simplified loops.

An sp hybridized atom uses one s and one p orbital to make two sp hybrid orbitals; there are two remaining p orbitals.

Next we show the phase pictures of combining the sp hybrid orbitals with first one and then both of the remaining p orbitals.

NOTE: When we write 2 x sp we mean two instances of sp and when we write 2p we mean one instance of a 2p orbital.
**HYBRID ATOMIC ORBITALS**

**sp²**

sp² hybrid orbitals are formed when one 2s orbital combines or hybridizes with two 2p orbitals in the shapes and arrangement shown.

In greyscale:

You will often see a simple presentation of the sp² orbitals. The important points to know about are that the three bonds are in a plane and that they are 120° apart.

You can also draw the sp² hybrid orbital as simple loops.

Draw the loop version of the trigonal set of sp² orbitals in the box at right.

The pictures below are trigonal views of sp². Trigonal means arranged in triangular form in a plane.
**ORBITALS AND MOLECULAR REPRESENTATION**

**HYBRID ATOMIC ORBITALS**

$sp^2$

In addition to the trigonal set of hybridized orbitals there is a remaining 2p orbital that will point above and below the trigonal plane.

First we show the phase orbitals.

![Planar view of sp$^2$](image1)

$+$

![2p](image2)

$\equiv$

![sp$^2$ + 2p](image3)

Here we show the grayscale.

![Grayscale representation](image4)
**HYBRID ATOMIC ORBITALS**

**sp³**

sp³ orbitals are formed by the hybridization of a 2s orbital and three 2p orbitals.

**ORBITALS AND MOLECULAR REPRESENTATION**

sp³ orbitals have a tetrahedral structure.
OVERLAPPING ORBITALS

Chemical bonds are formed from the overlapping of atomic orbitals having the same phase.

**Bonding Orbitals**

- \( s + s \sigma \)
- \( s + p \sigma \)
- \( p + p \sigma \)
- \( p + p \pi \)

**Antibonding Orbitals**

- \( s - s \sigma^* \)
- \( s - p \sigma^* \)
- \( p - p \sigma^* \)
- \( p - p \pi^* \)

Overlapping orbitals of opposite phase form antibonding orbitals.
We can also make orbital energy levels for molecules.
ORBITALS AND MOLECULAR REPRESENTATION

DIFLUORINE

In picture 1 we show the molecular orbital structure of F$_2$. In picture 2 we show the overlapping p orbitals, which form the bond between the two fluorine atoms, in red and green gradients.

The dashed lines show the remaining p orbitals which do not take part in the bonding.

Construct the molecular orbital diagram for dichlorine.

Showing the p orbitals.

Showing the s and p orbitals.
METHANE AND ETHANE

In methane and ethane, all of the bonds are σ-bonds, which means that they are formed by orbitals overlapping along a direct line between the nuclei of the two bonding atoms.

**Color conventions:**
Hydrogen atoms are shown in gray.
Hybrid atomic orbitals are shown in blue and yellow.
Atomic p orbitals are shown in red and green.

**Greyscale Conventions:**
Hybrid orbitals are shown in grey.
Unhybridized atomic orbitals are shown in reddish-grey.
Picture 3 shows the sigma bond formed by overlapping sp\(^2\) orbitals between the two carbon atoms of ethene. The other sp\(^2\) orbitals are shown in dashed outline.

Picture 4 shows the \(\pi\) bond between the p orbitals of the carbon atoms. The pi bond is the overlap of the two red spheres and is actually coming out of the plane of the paper.

Picture 5 is similar to picture 4 but rotated 90\(^\circ\) around the \(\sigma\) bond, so that the overlapping p orbitals which form the \(\pi\) bond are shown with the red phase above the \(\sigma\) bond and with the green phase below.
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

ETHENE $C_2H_4$

Ethene from above the trigonal plane. The carbon atoms and orbitals are shown.

Ethene from above the trigonal plane with the hydrogen atoms shown. The bond angles and relative bond lengths are correct.

Ethene in the trigonal plane.
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

ETHYNE $\text{C}_2\text{H}_2$

This drawing shows the sigma bond between two carbon atoms.

In this drawing we have added a pi bond to the ethyne.

We have added the other pi bond which, as it needs to be orthogonal to both the first pi bond and to the sigma bond, must be imagined as coming out of the paper.
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

ETHYNE $\text{C}_2\text{H}_2$

Ethyne in the trigonal plane, but with the hydrogen atoms added.

Unlike ethene, ethyne has the same form and appearance when rotated $90^\circ$ around the C-C axis.

12

13
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

BENZENE $\text{C}_6\text{H}_6$

The sigma bond ring of benzene.

The sigma bond ring of benzene with the additional sp$^2$ orbitals.

This is the ring of $\sigma$ bonds whose orbitals are shown in picture 15.

This is a former representation of the resonance structure of benzene.

This is a contemporary representation of the resonance structure of benzene.
To which we have now added the pi orbitals above the ring.

Benzene carbon orbitals viewed from the side.

Adding the hydrogen atoms to picture 16 we view benzene from above, complete.

This picture illustrates the delocalization of the six 2p electrons in the benzene molecule. These six electrons are shared collectively among all six of the carbon atoms.

Benzene from the side, complete with hydrogen atoms.
SEVERAL REPRESENTATIONS OF MOLECULES

METHANE \( \text{CH}_4 \)

ETHANE \( \text{C}_2\text{H}_6 \)

ETHENE \( \text{C}_2\text{H}_4 \)

ETHYNE \( \text{C}_2\text{H}_2 \)

ORBITALS AND MOLECULAR REPRESENTATION
SEVERAL REPRESENTATIONS OF BENZENE

BENZENE \( \text{C}_6\text{H}_6 \)

Benzene showing all orbitals

Benzene textbook \( \sigma \) bonds

Benzene textbook \( \sigma \) and \( \pi \) bonds from the side

Benzene space filling

Benzene ball and stick

Benzene structural carbon ring

Benzene structural carbon ring and hydrogens

140 nm

110 nm
You can easily draw orbitals, bonds and molecules.

**Start by drawing a circle, like this:**

![Circle](image1)

This is an s orbital.

**Now draw one circle above another one, like this:**

![Two circles tangent](image2)

This is a p orbital.

When two s orbitals from different atoms overlap, this is called a $\sigma$ (sigma) bond.

![Two overlapping circles](image3)

You draw two overlapping circles in the box below. This is a $\sigma$ bond.

When an s and a p orbital overlap, this is a $\sigma$ bond.

![S and p overlap](image4)

You can draw the s and p overlap.
**ORBITALS AND MOLECULAR REPRESENTATION**

**REPRESENTATIONS OF MOLECULES**

**DINITROGEN** $N_2$

- Textbook orbitals
- Structural
- Space filling
- Ball and stick

All bonding orbitals

**DIOXYGEN** $O_2$

- Structural
- Space filling
- Ball and stick

For clarity, only the orbitals which form the $\pi$ bonds are shown.

**SIMPLIFIED ORBITALS**

We have shown molecular pictures which are as accurate as possible, however such orbitals are difficult to draw by hand. But a simplified version of them is easy to draw and shows much about molecular structure and bonding.

- an $s$ orbital
- a $p_x$ orbital
- a $p_y$ orbital
- a $p_z$ orbital

All three $p$ orbitals

**Draw the bonding orbitals for:**

- $H_2O$
- $NH_3$
- CO
- $CO_2$
There are three orthogonal p orbitals. They can be drawn like this.

Two p orbitals (on different atoms) in the same direction can overlap forming a $\pi$ (pi) bond.

You can draw hybrid orbitals like this:

You draw an sp hybridized atom in the box below.

You draw an sp$^2$ hybridized atom.