Chapter 2. Molecular Structure and Bonding
Lewis structures: a review
Lewis Theory
3.1 The octet rule
All elements except hydrogen (hydrogen have a duet of electrons) have octet of electrons once they from ions and covalent compounds.
The Lewis dot symbols for atoms and ions shows how many electrons are need for a atom to fill the octet. Normally there are octet of electrons on most monoatomic ions
Basic rules drawing Lewis dot symbols:
1. Draw the atomic symbol.
2. Treat each side as a box that can hold up to two electrons.
3. Count the electrons in the valence shell.
Start filling box - don’t make pairs unless you need to.

Lewis symbols of second period elements

Elements try to complete their valence shell to achieve noble-gas electron configurations. The stability of noble/inert gases must be due to their filled valence shell. Elements either loose/gain or share electrons for this purpose. Electron transfer is associated with the formation of ionic compounds. Covalent compounds are formed when electrons are shared between atoms.
A Lewis symbol is a symbol in which the electrons in the valence shell of an atom or simple ion are represented by dots placed around the letter symbol of the element. Each dot represents one electron.

<table>
<thead>
<tr>
<th>Element</th>
<th>Lewis Dot Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1s(^1) H \cdot</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1s(^2) 2s(^2) 2p(^4) \cdot \cdot \cdot</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^5) \cdot \cdot \cdot \cdot \cdot</td>
</tr>
<tr>
<td>Chloride ion</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) \cdot \cdot \cdot</td>
</tr>
</tbody>
</table>

A covalent bond is a chemical bond formed by the sharing of a pair of electrons between two atoms.
The Lewis structure of a covalent compound or polyatomic ion shows how the valence electrons are arranged among the atoms in the molecule to show the connectivity of the atoms.
Instead of using two dots to indicate the two electrons that comprise the covalent bond, a line is substituted for the two dots that represent the two electrons.

Below is shown the Lewis structure for water. Two hydrogens (H) are separately covalently bonded to the central oxygen (O) atom. The bonding electrons are indicated by the dashes between the oxygen (O) and each hydrogen (H) and the other two pairs of electrons that constitute oxygen's octet, are called non-bonding electrons as they are not involved in a covalent bond.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{S} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{S} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{S} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Rules for getting Lewis Structures

1. Determine whether the compound is covalent or ionic. If covalent, treat the entire molecule. If ionic, treat each ion separately. Compounds of low electronegativity metals with high electronegativity nonmetals (ΔEN 1.6) are ionic as are compounds of metals with polyatomic anions. For a monoatomic ion, the electronic configuration of the ion represents the correct Lewis structure. For compounds containing complex ions, you must learn to recognize the formulas of cations and anions.
2. Determine the total number of valence electrons available to the molecule or ion by:
(a) summing the valence electrons of all the atoms in the unit and
(b) adding one electron for each net negative charge or subtracting one electron for each net positive charge. Then divide the total number of available electrons by 2 to obtain the number of electron pairs (E.P.) available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) in the following manner until all available pairs have been distributed:
(a) One pair between the central atom and each ligand atom.
(b) Three more pairs on each outer atom (except hydrogen, which has no additional pairs), yielding 4 E.P. (i.e., an octet) around each ligand atom when the bonding pair is included in the count.
(c) Remaining electron pairs (if any) on the central atom.

**Types of Electrons Pairs**

**Bond pair**: electron pair shared between two atoms.

**Lone pair**: electron pair found on a single atom.

**Molecules obeying the octet rule.**
In many molecules, each atom (except hydrogen) is surrounded by eight bonding or lone-pair electrons. There is a special stability associated with this configuration. Examples are water, ammonia and methane.

![Lewis structure of N2H4](image)

The ground state (g.s.) configuration of N has three unpaired electrons. Each hydrogen atom has one. No rearrangement is necessary to make the three N-H bonds. Be sure to mark the lone pair on the Lewis diagram.

![Lewis structure of CCl4](image)

The ground state of carbon has only two unpaired electrons, but it is necessary to make four bonds to the hydrogens. The solution, in this case, is to promote a 2s electron to the empty p orbital. Then four bonds can be made. SiH4 has the same Lewis Structure as CH4 since Si and C are in the same group.

**Lewis structure of CCl4**
i) Valence electrons: 4 (from one carbon) + 28 (7 from each chlorine) = 32 = \textbf{16 electron pairs}

ii) Central atom

iii) Octet on C is already complete iv). Count electrons

\[
4 \times 3 \text{ lone pairs} = 12 \text{ pairs} \\
4 \times 4 \text{ bond pairs} = 4 \text{ pairs}
\]

\textbf{16 electron pairs}

Lewis Structure of CCl\textsubscript{4}, CF\textsubscript{4} and CBr\textsubscript{4} have similar structures.

\textbf{Lewis Structure of PCl\textsubscript{3}}

i) Valence electrons: 5 + 3 \times 7 = 26 (13 pairs)

ii) Central atom is P

iii) Connect to terminal atoms to central atom

vi) Give octet to P and give octets to Cl

v) Count electron pairs:

\[
3 \text{ bond pairs} = 3 \text{ pairs} \\
1 + 3 \times 3 = 10 \text{ lone pairs} = 10 \text{ pairs} \\
\]

\textbf{16 electron pairs}

NF\textsubscript{3} and NCl\textsubscript{3} have similar Lewis Structures.

\textbf{Molecules with multiple bonds:}

\textbf{Examples: Consider carbon dioxide CO\textsubscript{2}}

1. The first step in drawing Lewis structures is to determine the number of electrons to be used to connect the atoms. This is done by simply adding up the number of valence electrons of the atoms in the molecule.

carbon (C) has four valence electrons x 1 carbon = 4 \text{ e}^{-} \\
oxygen (O) has six valence electrons x 2 oxygens = 12 \text{ e}^{-} \\
There are a total of 16 \text{ e}^{-} to be placed in the Lewis structure.

1. Connect the central atom to the other atoms in the molecule with single bonds.

\[
\text{Carbon is the central atom, the two oxygens are bound to it and electrons are added to fulfill the octets of the outer atoms.} \\
\text{O} \text{--C--O}
\]
2. Complete the valence shell of the outer atoms in the molecule.

\[ \ddots \overset{\text{C}}{\text{C}} \overset{\ddots}{\text{O}} \]

3. Place any remaining electrons on the central atom.

There are no more electrons available in this example.

4. If the valence shell of the central atom is complete, you have drawn an acceptable Lewis structure.

Carbon is electron deficient - it only has four electrons around it. This is not an acceptable Lewis structure.

5. If the valence shell of the central atom is not complete, use a lone pair on one of the outer atoms to form a double bond between that outer atom and the central atom. Continue this process of making multiple bonds between the outer atoms and the central atom until the valence shell of the central atom is complete.

The central atom is still electron deficient, so share another pair.

The best Lewis structure that can be drawn for carbon dioxide is:

\[ \ddots \overset{\text{C}}{\text{C}} \overset{\ddots}{\text{O}} \]

Lewis Structure of nitrosyl chloride NOCl

Setting up the bonding in this molecule is straight forward. Note the lone pairs, especially the one on the nitrogen.

Neutral nitrogen has 3 unpaired electrons, while one negatively charged oxygen and two neutral ones would have 5 unpaired electrons between them. You must move one electron from nitrogen to a neutral oxygen to get the configurations shown. Notice the formal charges marked where they belong on the Lewis structure.
**Bond Order and Bond Length**

The **bond order** is equal to the number of bonds between two atoms.

\[
\text{Bond Order (BO)} = \text{# bonds between two atoms}
\]

The **bond length** is the distance between those two atoms. The greater the number of electrons between two atoms, the closer the atoms can be brought towards one another, and the shorter the bond.

The BO is an indication of the bond length, the greater the bond order, the shorter the bond.

**Formal charge**

Formal charge is an accounting procedure. It allows chemists to determine the location of charge in a molecule as well as compare how good a Lewis structure might be. The formula for calculating formal charge is shown below:

\[
\text{Formal Charge} = \text{# valence } \sigma - (\text{# non-bonding } \sigma + \frac{1}{2} \text{ # bonding } \sigma)
\]

Consider the molecule \( \text{H}_2\text{CO}_2 \). There are two possible Lewis structures for this molecule. Each has the same number of bonds. We can determine which is better by determining which has the least formal charge. It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure. There are two possible Lewis structures for this molecule. Each has the same number of bonds. We can determine which is better by determining which has the least formal charge. It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure. The two possible Lewis structures are shown below. They are connected by a double headed arrow and placed in brackets. The non-zero formal charge on any atoms in the molecule have been written near the atom.
Electron deficient molecules: atoms have less than octet of electrons
Do not have enough electrons to satisfy the octet rule. Simple examples are beryllium hydride and boron trichloride:

**Lewis Structure of BeCl$_2$**
Beryllium, an element of the second column of the periodic classification, has for electronical configuration: $\text{[He]}$ 2$s^2$. It has two single bonds with two atoms in BeCl$_2$.

Berillium do not have a octet, therefore, BeCl$_2$ is an electron deficient compound. Be has only four electrons. BeCl$_2$ violate octet rule.

**Lewis Structure of BCl$_3$**
The boron must be in a suitable valence state to bind to the three chlorines. In the molecule the boron is associated with only six electrons. Much of the chemistry of this molecule and others like it is connected with the resulting strong electrophilic nature. Other examples include the boron hydrides...
such as diborane and alkyl-lithium, beryllium and aluminum compounds, which will be described later.

**Lewis Structure of BF$_3$**

1. **fill octet to fluorene first**
   \[
   \ce{F-B-F} \quad \rightarrow \quad \ce{\text{F}B\text{F}}
   \]
   \(F\) is the most electronegative

   i) Count total valence electrons: \(3 + 3 \times 7 = 24\) (12 electron pairs)
   ii) Central atom is B
   iii) Connect central atom terminal atoms:
   iv) 3 bonds pairs on B.
   3 lone pairs on 3F
   \(3 + 3 \times 3 = 12\) pairs

   Boron do not have a octet, therfore, BF$_3$ is an electron deficient compound. BF$_3$ violate octet rule.

   ![Lewis Structure of BF$_3$](image)

**Lewis Structure of BH$_3$**

Similarly BH$_3$ has the Lewis Structure:

![Lewis Structure of BH$_3$](image)

B has on 3 electron pairs. BH$_3$ violates octet rule. It exists as diborane B$_2$H$_6$

**Lewis Structure of AlCl$_3$**

Similarly AlCl$_3$ has the Lewis Structure:
Al has only 3 electron pairs. AlCl$_3$ also violates octet rule and exists as a dimer Al$_2$Cl$_6$.

**Atoms having odd numbers of electrons.**

**Example, nitrogen dioxide NO$_2$.**

Total of 17 valence electrons are present.

24 electrons would be needed to satisfy the valencies independently.

$24 - 17 = 7$. The odd number of electrons is a signal that there will be a place where we would normally expect to find another electron. When you have some experience with these situations, you probably will have no problem in assigning the Lewis structure directly. If this is a problem for you, the easiest way to treat these is to assume that we have one extra valence electron to begin with and remove that electron at the end. In this case, it means drawing the Lewis diagram for NO$_2^-$.

For NO$_2^-$ the answer to question 1 is 18 valence electrons and the answer to 3 become 6 electrons, or 3 bonds.

We draw one N-O single bond and one N=O double bond in order to achieve the correct number of bonds.

For NO$_2^-$ there will be 12 electrons left to make into nonbonding pairs that can be assigned as shown in the picture below. This will give octets at each atom. To derive the Lewis structure for NO$_2$, the neutral molecule, we must then remove one electron from NO$_2^-$. The choice preferred is to remove the electron from the lone pair that resides on the least electronegative atom. Since N is less electronegative than O, we will take the electron from the N lone pair.

The Lewis diagram for NO$_2$ is consistent with its reaction chemistry. NO$_2$ undergoes a dimerization (two molecules joining to form one) which gives N$_2$O$_4$. The structure of N$_2$O$_4$ is simple two NO$_2$ molecules joined to form an N-N bond by pairing the odd electrons.

**Molecules with expanded valence shells: Hypervalent compounds** occur for central atoms beyond period 2. Such atoms often have more than their octet. Examples are phosphorus trichloride, chlorine trifluoride and xenon difluoride:
Chlorine in its ground state has only one unpaired electron. In order to form the three required bonds, valence bond theory requires the promotion of an electron to an empty d-orbital to form the valence state shown. While it is customary to invoke a valence state using some d-orbitals to rationalize the bonding, there is an alternative approach which is best described using molecular orbital theory.

**Lewis Structure of SF₆**

i) Count total valence electrons: 6 + 6 x 7 = 48 (24 pairs)

ii) S is the central atom; sulfur already have excess of 4 electrons to octet

iii) fill octet to F's

iv) count electrons:

S - 6 bond pairs = 6
6F - 3 x 6 lone pairs = 18
24 pairs

Sulfur violates octet rule, is an exception to octet rule having more than eight electrons on S. S has 12 electrons.

**Lewis Structure of PCl₅**

i) Count the total valence electrons: 5 + 5 x 7 = 40 (20 pairs)

ii) P is the central atom:

iii) P already have 5 electron pairs then give octets to Cl's

iv) count electron pairs.

5 pairs on P = 5
5 x 3 pairs on Cl = 15
20 electron pairs
AsCl₅ have similar structure. PCl₅ and AsCl₅ violates octet rule having 10 electrons on P and As.

**Resonance Structures**

There are a number of compounds and polyatomic ions that cannot be written using one single structure. This was known even back to the early beginnings of structural chemistry in the mid-1850s. These substances must be described in terms of "intermediate" structures, possessing non-integral bonds such as one and one-half bonds or one and one-third bonds.

For example, certain molecules it is necessary to draw several Lewis structures (resonance structures) to adequately describe the structures of the molecules: Examples are CO₃²⁻, NO₃⁻, NO₂⁻

**Resonance Lewis Structures of CO₃²⁻:**

i) valence electrons: 4 + 3 x 6 + 2(negative charge) = 24 (12 pairs)

ii) central atom is carbon

iii) fill octet to C; fill octet to O

One oxygen does not have an octet. Share lone pair on C with the oxygens. The double bond could be on any other oxygen atoms.

\[
\begin{align*}
\text{[O=C-O]}^2- & \quad \leftrightarrow \quad \text{[O=C-O]}^2- & \quad \leftrightarrow \quad \text{[O=C-O]}^2-
\end{align*}
\]

Therefore, there are three resonance structures for CO₃²⁻ ion

**Resonance Lewis Structures of NO₃⁻:**

i) valence electrons: 5 + 3 x 6 + 1(negative charge) = 24 (12 pairs)

iii) N is the central atom:
iii) Fill octet to N; Fill octet to Os

one oxygen has only 6 electrons
share lone pair on N with the oxygen
The double bond could be on any other oxygen atoms. Therefore, there are three resonance structures for the NO$_3^-$ ion.

Resonance Lewis Structure of NO$_2^-$

i) valence electrons:

\[
5 + 2 \times 6 + 1(\text{negative charge}) = 18 \,(9 \text{ pairs})
\]

ii) central atom is nitrogen.

iii) Fill octet to N; Fill octet to O
one oxygen has only six electrons
share lone pair on N with oxygen.
The double bond could be on any of the two oxygen atoms. Therefore, there are two resonance structures for NO$_2^-$ ion.

Resonance Lewis Structure of PO$_4^{3-}$

Resonance structures of Benzene Ring
Any compound with the benzene ring is an aromatic compound. Since the benzene ring looks very much like a triene (alkene with three double bonds), it should be expected that its properties would be like one, but it is not. It does not undergo the addition reactions that alkenes do, and it is unusually stable to oxidizing agents. The reason why is because the benzene ring is a resonance structure. When one Lewis Structure fails to explain the bonding and properties of molecule have to draw more structures.

3.2 Structure and bond properties

3.3 The VSEPR model

Valence Shell Electron Pair Repulsion is a simple but effective model for predicting molecular geometry. VSEPR assumes a molecule adopts the geometry that minimizes the repulsive force among a given number of electron pairs.

Applying VSEPR

Draw the Lewis structure of the molecule.
Count the number of electron pairs around the central atom. Multiple bonds count as one electron pair.
The arrangement of electron pairs that minimizes repulsion is called the electron-pair geometry.
The arrangement of atoms is called the molecular geometry.

Electron-Pair Geometries

Basic Geometry. Once a Lewis structure of a molecule has been constructed, a basic geometry
can be inferred for each non-terminal atom in a molecule by counting the number of objects surrounding it. An "object" is a lone-pair or a bonded atom (regardless of the bond order - single, double, triple or fractional).

<table>
<thead>
<tr>
<th>Objects</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>Linear</td>
<td>Trigonal planar</td>
<td>Tetrahedral</td>
<td>Trigonal bipyramidal</td>
<td>Octahedral</td>
<td>Pentagonal bipyramid</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>#E.P.s</th>
<th>Geometry</th>
<th>#E.P.s</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>5</td>
<td>Trigonal bipyramidal</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal Planar</td>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Some Basic Geometries

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Lewis Structure</th>
<th>EP Geometry</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>O=C=O</td>
<td>2 - Linear</td>
<td>180°</td>
</tr>
<tr>
<td>SO₂</td>
<td>S=O=S</td>
<td>3 - Trigonal Planar</td>
<td>120°</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>[O=C=O]^⁻</td>
<td>3 - Trigonal Planar</td>
<td>120°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Lewis Structure</th>
<th>EP Geometry</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>H–C≡H</td>
<td>4 - Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>NH₃</td>
<td>H–N–H</td>
<td>4 - Tetrahedral</td>
<td>109.5°</td>
</tr>
</tbody>
</table>
Refinements to molecular geometry. The details of the predicted geometry can be further refined by considering what the objects are more carefully. Is another atom bound by a single bond or higher bond order? Is the bond polar? What about the difference between a lone pair and a bond pair? The table below shows how these questions and others can be answered.

<table>
<thead>
<tr>
<th>Lone pair - Lone pair</th>
<th>Lone pair-bond pair</th>
<th>Bond pair-bond pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>Largest Repulsion</td>
<td>Lone Pairs</td>
<td>Multiple or shorter bonds or bonds polarized towards the centre atom</td>
</tr>
<tr>
<td>Medium Repulsion</td>
<td>Normal single bonds</td>
<td></td>
</tr>
<tr>
<td>Smallest Repulsion</td>
<td>Longer single bonds and bonds polarized away from the central atom</td>
<td></td>
</tr>
</tbody>
</table>

Polarity of Molecules

The "charge distribution" of a molecule is determined by

- The shape of the molecule
- The polarity of its bonds

A Polar Molecule:

- The center of the overall negative charge on the molecule does not coincide with the center of overall positive charge on the molecule
- The molecule can be oriented such that one end has a net negative charge and the other a net positive charge, i.e. the molecule is a dipole

A Nonpolar molecule

- Has no charges on the opposite ends of the molecule
- Or, has charges of the same sign on the opposite ends of the molecule
- Molecule is not a dipole

Any diatomic molecule with a polar bond is a polar molecule (dipole)
Polar molecules align themselves:

- in an electric field
- with respect to one another
- with respect to ions

The degree of polarity of a molecule is described by its *dipole moment*, \( \mu = Q \cdot r \)

where

- \( Q \) equals the charge on either end of the dipole
- \( r \) is the distance between the charges

*the greater the distance or the higher the charge, the greater the magnitude of the dipole*

Dipole moments are generally reported in **Debye** units

1 debye = 3.33 x 10^{-30} coulomb meters (C m)

Example: H-Cl a **covalent polar** compound

- The H-Cl bond distance is 1.27Å
- +1 and -1 charges in a dipole produce 1.60 x 10^{-19} C

\[
\mu = Qr = (1.60 \times 10^{-19} \text{ C})(1.27 \times 10^{-10} \text{ m}) = 2.03 \times 10^{-29} \text{ C m}
\]

The actual dipole of H-Cl is **1.08 debye**. The reason for this is that the compound is covalent and not ionic, thus the charges of the dipole are less than +1, and -1 (values expected for a fully ionic compound)
Although the bond length is increasing, the dipole is decreasing as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the charge at the ends of the dipole).

The Polarity of Polyatomic Molecules

- Each polar bond in a polyatomic molecule will have an associated dipole
- The overall dipole of the molecule will be the sum of the individual dipoles

Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles

ABn molecules and non-polar geometries
For AB_n molecules, where the central atom A is surrounded by identical atoms for B, there a certain molecular geometries which result in no effective dipole, regardless of how polar the individual bonds may be. These geometries are:
Valence bond theory
Valence Bond Theory: Assumes that covalent bonds are formed when atomic orbitals (with electrons) on different atoms overlap and the electrons are shared. The atomic orbitals can be the original atomic orbitals of the atoms, but often the geometry of these orbitals is such that effective overlap cannot occur in the known geometry of the molecule. Under these circumstances, the atomic orbitals on an atom can reconfigure themselves into a different configuration, and the reconfigured orbitals are said to be hybridized. This theory is similar to molecular orbital theory which is concerned with the formation of covalent bonds. The difference being molecular orbitals are formed by empty atomic orbitals and later electrons are filled into them.

The Valence Electrons and Valence Shell Orbitals
The valence shell orbitals of an atom are taken to be the ns, np and nd orbitals where n is the number of the period of the element. The valence electrons are the electrons contained in these orbitals.

- Filled (n-1)d orbitals are considered part of the core of electrons which do not contribute to bonding.
Regardless of what you might expect from the filling order, only the nd orbitals are used (if necessary) to form an excited valence state because the (n+1)s orbital is spherical and therefore not very useful for forming directed hybrids.
Hybridization of atomic orbitals

Orbital hybridization was proposed in the 1930's to explain the geometry of polyatomic molecules. Covalent bonding was presumed to arise due to the overlap of atomic orbitals and the sharing of electron pairs. However, the known geometries of even simple covalent molecules like methane could not be correctly predicted by the Wave Mechanical Model, and the theory needed modification. Linus Pauling in 1931 showed mathematically that an s orbital and three p orbitals can combine (or hybridize) to form four equivalent atomic orbitals called sp³ hybrids. The rationale was that by expending energy to "reshuffle" electrons away from their normal atomic orbitals into hybridized orbitals prior to bonding, bonding could occur at less hindered angles. This allowed more effective orbital overlaps, better separation of bonding electron pairs, and produced more stable molecules.

The method of handling this in valence bond theory is via the mixing of the basic atomic orbitals mathematically to form hybrid orbitals pointing in the required directions. This mixing is achieved mathematically by taking linear combinations of the atomic orbitals as indicated below:

**Linear sp hybrids**. These are composed of the valence shell s-orbital and one of the three p-orbitals. The other two p-orbitals remain unhybridized and may hold lone pairs or participate in \( \pi \)-bonding. The two equivalent sp hybrid orbitals point at 180° to each other and their formation is depicted graphically and mathematically below:

The diagram below shows the 2s and 2pₓ orbitals superimposed in the same space before hybridization. The colours represent the relative signs of \( \psi \). The signs/colors for the 2p orbital would be reversed by the negative sign in first equation which follows the diagram:

\[
\psi_1 = \frac{1}{\sqrt{2}} \psi_s - \frac{1}{\sqrt{2}} \psi_p
\]

\[
\psi_2 = \frac{1}{\sqrt{2}} \psi_s + \frac{1}{\sqrt{2}} \psi_p
\]

The hybrids corresponding to two the equations above are shown separately for clarity below. Where the blue outer part of the 2s orbital combines with the red part of the 2p orbital there is destructive interference and only the little red knob is left. Where both orbitals are blue the main part of the hybrid is formed. Remember, the negative sign in the first equation causes the signs/colors of the p-orbital to be reversed and the hybrid on the left results. The other results from the second equation:
Two bonds could then be formed by overlap with each of the two sp-hybrid orbitals. The two unaffected p orbitals are still present, located perpendicular to each other and perpendicular to the line of the sp-hybrid orbitals. These p orbitals were available for sideways overlap to form two pi bonds, as in acetylene (or ethyne) shown below. In the case of acetylene, both carbons in the carbon-carbon triple bond are sp-hybridized.

**Linear sp Hybridization**

Acetylene or ethyne $\text{C}_2\text{H}_2$

$\sigma$ bonds
\[ \pi \text{ bonds} \]

**Trigonal sp\(^2\) hybrids.** These are composed of the valence shell s-orbital and two of the p-orbitals, say the \(p_x\) and \(p_y\) to produce a set of hybrids directed in the xy plane at 120° to each other. The \(p_z\) orbital will be left to hold a lone pair or participate in \(\pi\)-bonding. The diagram below shows the 2s, 2p\(_x\) and 2p\(_y\) orbitals superimposed in the same space before hybridization. They are combined to form the hybrids according to the equations which follow the diagram:

\[
\begin{align*}
\psi_1 &= \frac{1}{\sqrt{3}}\psi_s + \frac{1}{\sqrt{6}}\psi_{px} + \frac{1}{\sqrt{2}}\psi_{py} \\
\psi_2 &= \frac{1}{\sqrt{3}}\psi_s + \frac{1}{\sqrt{6}}\psi_{px} - \frac{1}{\sqrt{2}}\psi_{py} \\
\psi_3 &= \frac{1}{\sqrt{3}}\psi_s - \frac{2}{\sqrt{6}}\psi_{px}
\end{align*}
\]

Below, the hybrids corresponding to the three equations above are shown separately (in order from top to bottom):
In the diagrams below, the trio of hybrids are superimposed in the same space as they should be. Two diagrams are shown: On the left the antinodes are shown transparent. The small knob of each hybrid is buried deeply. The right hand diagram shows the equivalent hybrid enclosure surfaces and hides the internal structure. Note the "three-fold" symmetry:
sp$^2$ hybridization was postulated for the possibility of an s orbital hybridizing with two p orbitals:

Three bonds could then be formed by overlap with each of the three sp$^2$-hybrid orbitals. The unaffected p orbital is perpendicular to the plane of the three sp$^2$-hybrid orbitals, available for sideways overlap to form a pi bond, or, in molecules like boron trifluoride (shown below), the p orbital is left empty.

**Ethylene or ethyene C$_2$H$_4$**

**σ bonds**
**π bonds**

**Tetrahedral sp³ hybrids.** These are composed of the valence shell s-orbital and all three p-orbitals. The diagram below shows these superimposed in the same space before hybridization. They are combined according to the equations which appear below the diagram:

\[
\psi_1 = \frac{1}{\sqrt{4}}\psi_s + \frac{1}{\sqrt{4}}\psi_{px} + \frac{1}{\sqrt{4}}\psi_{py} + \frac{1}{\sqrt{4}}\psi_{pz}
\]
\[
\psi_2 = \frac{1}{\sqrt{4}}\psi_s - \frac{1}{\sqrt{4}}\psi_{px} + \frac{1}{\sqrt{4}}\psi_{py} + \frac{1}{\sqrt{4}}\psi_{pz}
\]
\[
\psi_3 = \frac{1}{\sqrt{4}}\psi_s - \frac{1}{\sqrt{4}}\psi_{px} - \frac{1}{\sqrt{4}}\psi_{py} + \frac{1}{\sqrt{4}}\psi_{pz}
\]
\[
\psi_4 = \frac{1}{\sqrt{4}}\psi_s - \frac{1}{\sqrt{4}}\psi_{px} + \frac{1}{\sqrt{4}}\psi_{py} - \frac{1}{\sqrt{4}}\psi_{pz}
\]

Below, the hybrids corresponding to the four equations above are shown separately (in order, left to right and top to bottom):
In the diagrams below, the quartet of hybrids are superimposed in the same space as they should be. Two diagrams are shown: On the left the antinodes are shown transparent. Again, the small knob of each hybrid is buried deeply. The right hand diagram shows the equivalent hybrid enclosure surfaces and hides the internal structure. Note the tetrahedral symmetry of the group:
Notes on the equations: Each component atomic orbital must be "shared out" completely between the hybrids which leads to the condition that the sum of the squares of the coefficients for a particular atomic orbital add to one. In addition, individual hybrid orbitals must be "normalized", that is, the probability of an electron occupying one of them somewhere must be 1. This leads to the condition that the sum of the squares of the coefficients in one of the formulae must also add to 1.

In order to produce angles which differ from the ideal values, the equations are modified. Increasing the ratio of p to s character in any subset will decrease the appropriate inter-hybrid angles. These sp³-hybridized orbitals were centered about the nucleus, pointing toward the corners of a regular tetrahedron.

Four bonds could then be formed by overlap with each of the four sp³-hybrid orbitals. The resulting molecule would have a tetrahedral shape around this sp³-hybridized atom. This fit the known geometry and bond characteristics of methane (shown below).
Trigonal bipyramidal $sp^3d$ hybrids. These are composed of the valence s-orbital, all the p-orbitals and one of the d-orbitals (normally, the $d_{z^2}$ or one of the two in the xy plane i.e. $d_{xy}$ or $d_{x^2-y^2}$). The choice depends on the atoms involved so it is not possible to write down a unique set of equations like those above.) The remaining d-orbitals could be involved in $\pi$-bonding.

Octahedral $sp^3d^2$ hybrids. These are composed of the valence s-orbital, the three p-orbitals and two d-orbitals (normally the $d_{z^2}$ and one of the two in the xy plane.) The remaining d-orbitals can participate in $\pi$-bonding.
### Linear Molecular Geometry

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX₂</td>
<td>Central atom sp hybridized</td>
</tr>
<tr>
<td>HCN, CO₂</td>
<td></td>
</tr>
<tr>
<td>AX₂E₃</td>
<td>Central atom sp³d hybridized</td>
</tr>
<tr>
<td>I⁻</td>
<td></td>
</tr>
</tbody>
</table>

#### Hybridization in CO₂

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ bonds</td>
<td><img src="image" alt="σ bonds" /></td>
</tr>
<tr>
<td>π bonds</td>
<td><img src="image" alt="π bonds" /></td>
</tr>
</tbody>
</table>
### Trigonal Planar Molecular Geometry

| AX₃ | Central atom sp² hybridized NO₃⁻ |

### Bent Molecular Geometry

| AX₂E₁ | Central atom sp² hybridized NO₂⁻ |
| AX₂E₂ | Central atom sp³ hybridized H₂O |

### Tetrahedral Molecular Geometry

| AX₄ | Central atom sp³ hybridized single bonds CH₄ |
| AX₄ | Central atom sp³ hybridized double bonds ClO₄⁻ |

### Trigonal Pyramidal

| AX₃E₁ | Central atom sp³ hybridized single bonds NH₃ |
| AX₃E₁ | Central atom sp³ hybridized single and double bonds ClFO₂ |

### Trigonal Bipyramidal Molecular Geometry

| AX₅ |  | AX₅ |
Central atom sp$^3$d hybridized

<table>
<thead>
<tr>
<th>Single bonds only</th>
<th>Single and double bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PCl}_5$</td>
<td>$\text{ClO}_2\text{F}_3$</td>
</tr>
</tbody>
</table>

**Seesaw Molecular Geometry**

<table>
<thead>
<tr>
<th>$\text{AX}_4\text{E}_1$</th>
<th>Central atom sp$^3$d hybridized</th>
</tr>
</thead>
<tbody>
<tr>
<td>One Lone Pair in an equatorial hybrid</td>
<td>$\text{IO}_2\text{F}_2^-$</td>
</tr>
</tbody>
</table>

Central atom sp$^3$ hybridized

Doen met eers hibridisasie en dan die mol geometrie

<table>
<thead>
<tr>
<th>Molecular Geometry</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>$\text{AX}_2$ sp, or $\text{AX}_2\text{E}_3$ sp$^3$d</td>
</tr>
</tbody>
</table>

### 3.5 Homonuclear diatomic molecules

### 3.4 The hydrogen molecule

A bond between two atoms is formed when a pair of electrons is shared by two overlapping orbitals, according to the VB theory. For example, in a hydrogen molecule, the two 1s orbitals from each H atoms overlap and share electrons.

![Diagram of H-H bond formation](image)

### 3.6 Polyatomic molecules

In all of the examples given above used as examples for Lewis structures, it was implied that the bonds were formed from two of the basic atomic orbitals. For example, the bonding in ammonia was shown as involving three (mutually perpendicular) 2p orbitals on nitrogen and the 1s orbitals of each hydrogen. (For any one of the bonds $\psi_A$ could be a 2p orbital and $\psi_B$ a 1s orbital in the valence bond theory notes mentioned above.) This simple treatment is clearly not adequate because it predicts a H-N-H bond angles of 90°: the observed angle is 107°.

The method of handling this in valence bond theory is via the mixing of the basic atomic orbitals mathematically to form hybrid orbitals pointing in the required directions. This mixing is achieved mathematically by taking linear combinations of the atomic orbitals as indicated below:

The examples given above are set out again using one more step to include geometry and thus the hybridization of the central atom. Where appropriate the mechanism for $\pi$-bonding is indicated. Comments on distortions from ideal angles are added.
Ammonia - NH₃

The nitrogen is bound to three hydrogen atoms. In addition, there is a lone-pair on N, therefore 4-coordination i.e. tetrahedral geometry (with sp³ hybrids) is predicted. (The molecule is sometimes referred to as pyramidal if the lone-pair is not considered part of the geometry.)

The lone-pair demands more space than the bond pairs so that the H-N-H angles will be less than the ideal 109.5°. The actual experimental value is 107.3°.

The appropriate hybridization is sp³ (but with the lone pair in a hybrid orbital having somewhat greater s character than the other three which are used for the bonds, and which, correspondingly, have slightly higher p character.)

Some related molecules are NF₃ with a bond angle of 102.5° and PH₃ with a bond angle of 93.5°. This latter molecule uses nearly pure 3p orbitals to bind the hydrogens and a nearly pure 3s orbital to house the lone pair. This optimizes the overlap with the H 1s orbitals. Other isoelectronic/isostructural molecule/ions are H₂O⁺ and CH₃⁻.

Methane - CH₄

With four hydrogens bound to carbon and no lone pairs, the structure is predicted to be tetrahedral, and the appropriate hybridization would be sp³.

Some isostructural molecule/ions are BF₄⁻ and NH₄⁺.

Nitrosyl Chloride - NOCl

The nitrogen has three "things" attached: the lone pair, the chlorine and the oxygen. N.B. The oxygen only counts as one "thing" despite the
double bond.) Therefore, the shape is based on trigonal, and disregarding the lone pair, might be called bent or angular. Like COCl₂, the appropriate hybridization, sp² leaves one 2p orbital on nitrogen to form the π bond. This is depicted in the lower diagram on the right.

The hybrid orbitals would all be inequivalent in such a way as to reduce the Cl-N=O angle to make room for the lone-pair and to allow for the differences between bonding orbital sizes on Cl and O.

**Nitrate - NO₃⁻**

The predicted geometry is trigonal because there are three oxygens bound to nitrogen, and no lone-pairs. The appropriate hybridization is sp². The single Lewis structure drawn shows the unhybridized p-orbital of nitrogen interacting with a p-orbital on oxygen to form the π-bond. Molecular orbital theory, see below, treats this situation differently to avoid the need to draw three canonical structures to account for the observed geometry where all angles are 120° and the bond lengths are identical.

**Boron trichloride - BCl₃**

The appropriate hybridization is sp² since the boron is attached to three "things". In certain cases (for example BF₃), π-bonding using the empty boron p-orbital can be invoked. To do this, an electron must be moved from the more electronegative terminal atom to boron. This runs contrary to what one expects from the electronegativities so the exact extent to which this occurs is the subject of some controversy.

**Chlorine Trifluoride - ClF₃**
Because the chlorine carries the three fluorines and two lone pairs, the geometry will be trigonal bipyramidal and the hybridization will be sp$^3$d. Three isomers are possible.

It is highly unfavorable for the lone pairs to be 90° apart which rules one of the three. In order to rationalize the observation that the isomer with both lone pairs in equatorial positions is the observed form, it is necessary to count the number of 90° bond pair - lone pair interactions. The observed isomer (in the box) has four such angles and the isomer with the lone pairs in axial positions has six which is (presumably) less favorable. The molecule might be called T-shaped based on the atomic positions only. The appropriate hybridization would be sp$^3$d where the d orbital will have a greater contribution to the axial hybrids than the equatorial ones.

**A few more examples are:**

**Iodine pentafluoride - IF$_5$**

The five unpaired electrons needed on iodine to bind the fluorines can only be obtained (in the valence bond approximation) by invoking the use of the 5d orbitals. After the bonding with fluorine, the iodine is left with one lone pair, so there are six "things" in all. The geometry will be based on an octahedron, and might be referred to as (square) pyramidal if the lone pair is not counted. The F-I-F angles (basal to apical) will be less than 90° due to the steric influence of the lone pair.

The appropriate hybridization would be sp$^3$d$^2$. By using a molecular orbital approach involving 3-centre 4-electron bonds the use of the d-orbital in understanding the bonding can be avoided, but the predictive value of the valence bond VSEPR approach would be lost.

Some isolectronic/isostructural species are: TeCl$_5^-$ and XeF$_5^+$. 
Carbonyl Chloride (Phosgene) - COCl₂

The two chlorines and the oxygen require four unpaired electrons for bonding on the carbon, i.e. the usual tetravalent excited state. Since there are three "things" on the carbon the predicted shape is trigonal, and the appropriate hybridization is sp². This leaves one unhybridized 2p-orbital on the carbon, and another on the oxygen, to form the π component of the double bond.

It is difficult to predict distortions from the ideal angles because on the one hand the chlorines are larger than the oxygen which would tend to widen the Cl-C-Cl angle, but on the other hand there is a double bond involving the oxygen which would tend to widen the Cl-C=O angles.

Thionyl Chloride - SOC I₂

Unless a canonical structure with charge separation (S⁺ and O⁻) is constructed, the sulphur must form four bonds, one to each of the chlorines and the double bond to oxygen. It is necessary to invoke a valence state using one of the 3d orbitals to do this. Sulphur is attached to four "things": the lone pair, two chlorines and the oxygen, so the shape is based on the tetrahedral geometry, and the structure might be called pyramidal if the lone pair is disregarded.

The hybridization on sulphur for the sigma bonds is sp³, which leaves the d electron available to form the π bond by overlap with one of the oxygen 2p orbitals. This is depicted in the lower diagram on the right. (For clarity, the lone pair is not shown in this diagram.)
Sulphate - SO$_4^{2-}$

If the negative charge on the ion is distributed on two of the oxygen atoms there are six unpaired electrons needed on the sulphur. Promotion of two electrons to the 3d orbitals achieves this. The four oxygens attached to sulphur cause it to adopt a tetrahedral geometry. The appropriate hybridization to account for the $\sigma$ bonds is sp$^3$, leaving the two d orbitals for use forming the $\pi$ bonds. In a full molecular orbital calculation, if the d orbitals really played a part, they would also be hybridized to point in the appropriate directions. The situation is too complicated to attempt to draw meaningful diagrams.

The canonical structures shown at the left correspond to the bonding model described above. It is possible to conceive of other canonical forms where three or four of the oxygen atoms carry a negative charge and the sulphur one or two positive charges. The second of these canonical forms would not require d-orbital involvement.

**Transition Metal Complexes**

It uses "outer orbital" $sp^3d^2$ and "inner orbital" $d^2sp^3$ hybridization to explain the formation of compounds.
Outer orbital hybridization (also called high spin) see the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals, so only the $d_{xz}$, $d_{yz}$, and $d_{yz}$ orbitals are available.

The figure above illustrates inner orbital hybridization (also called low spin).

The Isolobal Analogy

Extension of Valence Bond and Molecular Orbital theory to Complex Molecules: Introduction

Different groups of atoms can give rise to similar shaped fragments. For example, the C-H group and the P atom have 5 electrons and can contribute 3 electrons to a cluster, C-H has 4+1 electrons and uses 2 electrons for the C-H bond, P has 5 electrons and uses 2 electrons for a lone pair.

Both fragments are 3 electrons short of making maximum use of their 4 valence orbitals (s and \(3\times p\)) by achieving an octet. The clusters \(C_4H_4\) or \((CH)_4\) (known as tetrahedrane) and \(P_4\) have the same number of cluster electrons and therefore adopt the same shape:

The organometallic fragment \(Co(CO)_3\) has 15 electrons:

\(Co\) has 9 valence electrons and each CO donates 2e to the metal.

The fragment is 3 electrons short of the stable electron count for an organometallic fragment of eighteen. Eighteen electrons corresponds to making maximum use of the 9 valence orbitals of the transition metal \((s + 3\times p \text{ and } 5\times d)\). It can achieve 18 electrons by sharing 3 electrons to make 3 covalent bonds. The \(Co(CO)_3\) fragment thus has the same requirements as the C-H unit and the P atom. The cluster \([Co(CO)_3]_4\) thus also has the same tetrahedral shape as that shown by \(C_4H_4\) and \(P_4\). It is also possible to swap the three fragments around:

\(B\) and \(C\) are more conventionally thought of as \(\mu^3-P[CoCO]_3\) and \(\eta^3-C_3H_3)Co(CO)_3\) respectively but this hides the structural and electronic links between all these clusters.
The similarity between these fragments and between other groups of fragments has been investigated in detail by Roald Hoffmann. Fragments are deemed to be isolobal if

"the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar"


The isolobal relationship is symbolized by a double-headed arrow with a tear-drop,

\[
\text{CH}_3 \quad \overset{0}{\leftrightarrow} \quad \text{P} \quad \overset{0}{\leftrightarrow} \quad \text{Co(CO)}_3
\]

The isolobal analogy relates the orbitals and bonding in inorganic, organometallic and cluster chemistry to that in organic and main group chemistry. The utility of the isolobal analogy is that one should be able to replace a (transition metal) ML \(_n\) fragment in a molecule with the isolobal (main group) AH \(_n\) fragment, and vice versa, to produce new molecules with very similar bonding.

**Generating isolobal fragments**

Main group fragments can be generated by starting from methane, \(1\) (or any molecule obeying the octet rule). Homolytic cleavage of a C–H bond generates the methyl radical, \(1a\), which has one frontier orbital pointing towards the missing hydrogen with one electron in it. Homolytic cleavage of a second C–H gives methylene, \(1b\), which has too singly occupied hybrids pointing towards the two vacant hydrogen positions. Removal of a third hydrogen gives methine, \(1c\), with three singly occupied hybrids.

\[
\text{H}_3\text{C} \quad \overset{-\text{H}^*}{\rightarrow} \quad \text{H}_2\text{C} \quad \overset{-\text{H}^*}{\rightarrow} \quad \text{H}_1\text{C} \quad \overset{-\text{H}^*}{\rightarrow} \quad \text{H}_0\text{C}
\]

\(1 \quad 1a \quad 1b \quad 1c\)

The transition metal fragments are generated in an analogous way. For example, from the starting point of CrL\(_6\), \(2\), where L is a two electron donor such as CO, (or any molecule obeying the eighteen electron rule such as \(3\)), the fragments \(2a\), \(2b\) and \(2c\) are generated by successive homolytic cleavage of M–L bonds on one octahedral face. As L is a two-electron donor, homolytic cleavage of CrL\(_6\) gives CrL\(_5\)– and L+. To remove the charge, the metal is then replaced by Mn (the element one to the right in the 3d series):
Isolobal scheme

<table>
<thead>
<tr>
<th>8–electron</th>
<th>18–electron</th>
<th>16–electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>H`C−H</td>
<td>L−Cr−L</td>
<td>L−Fe−L</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>H<code>C</code>−</td>
<td>L−Cr−L</td>
<td>L−Fe−L</td>
</tr>
<tr>
<td>1a</td>
<td>2a</td>
<td>4a</td>
</tr>
<tr>
<td>H<code>C</code>−</td>
<td>L−Cr−L</td>
<td>L−Fe−L</td>
</tr>
<tr>
<td>1b</td>
<td>2b</td>
<td>4b</td>
</tr>
</tbody>
</table>

Legend:
- H` represents the hydrogen atom
- L represents a ligand
- M represents a metal
- L` represents a ligand with a lone pair
- Cr` is d^2
- Mn` is d^2
- Fe` is d^2
- Co` is d^2
- Ni` is d^2
As long as the electron count is maintained or consistent changes are made, the metal or main group element can be substituted. Thus,

\[
\begin{align*}
\text{CH}_3 & \quad \text{Me}_3\text{Sn} & \quad \text{Mn}(\text{CO})_5 & \quad \text{Fe}(\text{PPh}_3)_5^+ & \quad \text{Mo}(\text{CO})_5^- \\
\text{CH}_3^+ & \quad \text{BH}_3 & \quad \text{Mn}(\text{CO})_5^+ & \quad \text{Cr}(\text{CO})_5 & \quad \text{Rh}(\text{PPh}_3)_3^+ \\
\text{CH}_3^- & \quad \text{NH}_3 & \quad \text{Mn}(\text{CO})_5^- & \quad \text{Fe}(\text{CO})_5 & \quad \text{Rh}(\text{CO})_5^+
\end{align*}
\]

It should be noted that the main use of the isolobal analogy is in generating alternative fragments in molecules. The geometry of the fragment in a molecule not as an isolated species is important. Thus, CH\textsubscript{3} and BH\textsubscript{3} are considered as pyramidal (not planar) species and Cr(CO)\textsubscript{5} is considered as a square-based pyramid (not trigonal bipyramid).

**Applications of Isolobility**

The isolobal analogy between CH\textsubscript{3} and d\textsuperscript{7} MnL\textsubscript{5} implies similar bonding in the following compounds:

The isolobal relationship of CH\textsubscript{2}, with Fe(CO)\textsubscript{4} generates the compounds illustrated below. The transition metal molecule has been drawn as a metallocyclopropane. A more common description is to consider it as an ethene complexes, (η\textsubscript{2}–C\textsubscript{2}H\textsubscript{4})Fe(CO)\textsubscript{4}. The isolobal relationship shows that cyclopropane itself can be consider as (η\textsubscript{2}–C\textsubscript{2}H\textsubscript{4})CH\textsubscript{2}. 
Modern chemistry has depended upon the use of models of increasing complexity. Atoms can be represented as spheres connected by cylinders or sticks. In order to understand the mechanism of many reactions, Lewis Theory, developed by Robinson and Ingold, can provide a successful answer. Lewis Theory uses curly arrows to denote electron migration during a chemical reaction and has led to a greater understanding of the factors controlling chemical reactions. Pauling with others, developed Resonance Theory, which provided the rationale to an all-embracing orbital theory. The use of "canonical forms" and "resonance hybrids", along with extensive use of curvy arrows has provided the fundamental background to modern organic theory, but for e.g. Diels-Alder and pericyclic reactions, the curly arrow format is not very clear and in some instances the reactions are described as no-mechanism reactions. Woodward and Hoffmann showed that by examining the interaction of the frontier molecular orbitals (i.e. the Highest Occupied, HOMO and Lowest Unoccupied, LUMO) both the regio- and stereospecificity could be accounted for. Woodward and Hoffmann work was assimilated into general organic reaction theory.

3.7 An introduction to the theory of Linear Combination of Atomic Orbitals (LCOA)

A theory which treats bonding as an over lapping of ligand orbitals with those of the central atom.

By summing the original wavefunctions for the bonding orbitals in constituent species, "hybrid" molecular orbitals of the compound can be generated. These new orbitals have an intermediate character between the original $s$, $p$, and $d$ orbitals (if available) in the outer energy level, and produce additional bond sites. The hybridization is named on the basis of the orbitals involved, and the hybrid wavefunction is the (renormalized) sum of the individual wavefunctions, where each addition may be with an arbitrary sign. The composite wavefunctions with differing signs are orthogonal, since
But

$$\int (\psi_1 + \psi_2)(\psi_1 - \psi_2)^* dV = \int (|\psi_1|^2 + \psi_1 \psi_2^* - \psi_1^* \psi_2 - |\psi_2|^2) dV.$$  \hspace{1cm} (1)

But

$$\int \psi_1 \psi_2^* dV = \delta_{1,2},$$  \hspace{1cm} (2)

so

$$\int (\psi_1 + \psi_2)(\psi_1 - \psi_2)^* dV = (1 + 0 + 0 - 1) = 0.$$  \hspace{1cm} (3)

The simplest example is \textit{s}^2-hybridization. There are two possible combinations,

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_{s,1} + \psi_{s,2}) \quad \sigma_{1s}^b$$  \hspace{1cm} (4)

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_{s,1} - \psi_{s,2}) \quad \sigma_{1s}^*,$$  \hspace{1cm} (5)

where the wavefunctions on the right are the solutions to Schrödinger's equation, and the normalization constants are needed so that the hybrid wavefunction is normalized. \(\psi_1\) has the electron density is greatest between the two nuclei. It will therefore bind the nuclei together, and \(\psi_2\) has the electron density greatest on the sides of the nuclei. It will therefore pull the nuclei apart, and is called a bonding molecular orbital. \(\psi_2\) has the electron density greatest on the sides of the nuclei. It will therefore pull the nuclei apart, and is called an antibonding molecular orbital. In some instances, a nonbonding molecular orbital may be generated for which the electron density is uniformly distributed between and on the sides of the nuclei. A measure of the stability of a compound based on the occupancy of its molecular orbitals is given by the body order.

$$[\text{bond order}] \equiv \frac{1}{2} ([\text{#BMO electrons}] - [\text{#ABMO electrons}]).$$

More complicated bonding interactions will involve \textit{s}, \textit{p}, and \textit{d} orbitals. For a homonuclear diatomic compound with hybrid orbitals constructed from \textit{1s, 2s}, and \textit{2p} orbitals, the molecular orbital have the following form.
For heteropolar molecules or more complicated systems, the molecular orbital energy diagram can be quite complex. The molecular orbitals for the CO$_2$ (O$_1$=C=O$_2$) molecules are given by, in order of increasing energy

\[
\begin{align*}
\sigma^b_{2p_x} & \quad \text{(sigma bond)} \\
\pi^b_{2p_y} & \\
\sigma^b_{2p_z} & \\
\sigma^b_{2p_y} & \\
\sigma^b_{2p_z} & \\
\end{align*}
\]

There are 12 electrons in the valence shell, so the levels are filled through the nonbonding orbitals. The compound is therefore stable, with a bond order of 4. For an even more complicated example, consider benzene. For certain compounds, electrons are delocalized. Such compounds have an extremely large number of molecular orbitals. The result, as the number of levels goes to infinity, is a band of bonding orbitals, and band of antibonding orbitals (known as the conduction band, since free electrons will exist here), possibly overlapping or possibly separated by a gap. In metals, the levels overlap, and the bonding orbitals are completely filled. In semiconductors, the levels are separated by a small "forbidden zone." The addition of a small amount of energy will
therefore remove an electron from the filled bonding orbital, through the forbidden zone, and into the conduction band.

Atomic and Molecular Orbitals

By sharing electron, molecules can form bonds, and it is possible to regard the sharing of two electrons by two atoms as constituting a chemical bond. Atoms can share one, two or three electrons (forming single, double and triple bonds).

A hydrogen atom consists of a nucleus (a proton) and an electron. It is not possible to accurately determine the position of the electron, but it is possible to calculate the probability of finding the electron at any point around the nucleus. With a hydrogen atom the probability distribution is spherical around the nucleus and it is possible to draw a spherical boundary surface, inside which there is a 95% possibility of finding the electron. The electron has a fixed energy and a fixed spatial distribution called an orbital. In the helium atom there are two electrons associated with the helium nucleus. The electrons have the same spatial distribution and energy (ie. they occupy the same orbital), but they differ in their spin (Pauli exclusion principle). In general: electrons in atomic nuclei occupy orbitals of fixed energy and spatial distribution, and each orbital only contains a maximum of two electrons with anti-parallel spins.

In physics, periodic phenomena are associated with a "wave equation", and in atomic theory the relevant equation is called the "Schrödinger Equation". The wave equation predicts discrete solutions in one dimension for a particle confined to a box with infinite walls, The solutions can be shown as in the figure below:
$\psi_1 - \psi_4$ represent solutions of increasing energy. In three dimensions, the equation determines the energy and defines the spatial distribution of each electron. Solutions of the wave equations in three-dimensions allows calculation of the "shape" of each orbital. The first five solutions of the wave equation for an electron associated with a proton can be shown in the figure below:

In the hydrogen atom, the 1s atomic orbital has the lowest energy, while the remainder (2s, 2p_x, 2p_y, and 2p_z) are of equal energy (ie. degenerate), but for all other atoms, the 2s atomic orbital is of lower energy than the 2p_x, 2p_y, and 2p_z orbitals, which are degenerate.

In atoms, electrons occupy atomic orbitals, but in molecules they occupy similar molecular orbitals which surround the molecule. The simplest molecule is hydrogen, which can be considered to be made up of two separate protons and electrons. There are two molecular orbitals for hydrogen, the lower energy orbital has its greater electron density between the two nuclei. This is the bonding molecular orbital - and is of lower energy than the two 1s atomic orbitals of hydrogen atoms making this orbital more stable than two separated atomic hydrogen orbitals. The upper molecular orbital has a node in the electronic wave function and the electron density is low between the two positively charged nuclei. The energy of the upper orbital is greater than that of the 1s atomic orbital, and such an orbital is called an antibonding molecular orbital.

Normally, the two electrons in hydrogen occupy the bonding molecular orbital, with anti-parallel spins. If molecular hydrogen is irradiated by ultra-violet (UV) light, the molecule may absorb the energy, and promote one electron into its antibonding orbital ($\sigma^*$), and the atoms will separate. The energy levels in a hydrogen molecule can be represented in a diagram - showing how the two 1s atomic orbitals combine to form two molecular orbitals, one bonding ($\sigma$) and one antibonding ($\sigma^*$). This is shown below - by clicking upon either the $\sigma$ or $\sigma^*$ molecular orbital in the diagram - it will show graphically in a window to the right:
3.8 Homonuclear diatomic molecules

A diatomic hydrogen molecule fills the \( \sigma_{1s}^b \) orbital, and so has a bond order of 1 and is stable.

\[
\begin{align*}
\text{H} + \text{H} & \rightarrow \text{H}_2 \\
1s^1 + 1s^1 & \rightarrow \sigma_{1s}^b
\end{align*}
\]

A diatomic helium molecule fills both the \( \sigma_{1s}^* \) and \( \sigma_{1s}^b \) orbitals, so it has a bond order of zero and is not stable.

\[
\begin{align*}
\text{He} + \text{He} & \rightarrow \text{He}_2 \\
1s^2 + 1s^2 & \rightarrow \sigma_{1s}^*, \sigma_{1s}^b, \sigma_{1s}^*.
\end{align*}
\]

**Diatomic molecules H\(_2\) and He\(_2\)**

The probability plot for \( \Psi_2 \) is also shown in Figure 4. What would be its equation? (The equivalent of equation 3) What do you notice about the electron density between the nuclei as compared to two individual hydrogen atoms simply placed side by side?

Further insight into the bonding of \( H_A \) and \( H_B \) can be obtained by considering the energies of the electrons in \( \Psi_1 \) and \( \Psi_2 \) compared to their energies in the non-interacting atoms. This can be done by plugging the LCAO wave functions for the molecule back into the appropriate Schrödinger equation (just as it can be done for the individual atoms using the atomic wave functions). The results are shown in Figure 5, where \( \Psi_1 \) and \( \Psi_2 \) are sometimes renamed \( \sigma(1s) \) and \( \sigma^*(1s) \), respectively, to indicate the type of molecular orbital and their parentage.
These molecular orbitals are useful for any molecule, or molecule-ion, using only 1s orbitals for bonding. Several possibilities are: \( \text{H}_2^+, \text{H}_2, \text{H}_2^-, \text{He}_2^+, \text{He}_2^- \) and \( \text{He}_2 \). The positive molecule-ions are unstable, but have been detected in the gas phase under high energy conditions. The negative molecule-ions and \( \text{He}_2 \) have not been observed.

**Nitrogen:**
This molecule has ten electrons. The atomic orbitals combine to produce the following molecular orbital diagram:

Here the \( 2\pi_g \) orbital is occupied by two electrons to give a total bond order of three. This corresponds well with the Lewis structure \((\text{N}≡\text{N})\), although the orbital approach tells us that there is one \( \sigma \) and two \( \pi \).
**Oxygen:**
This molecule has twelve electrons, two more than nitrogen - and these extra two are placed in a pair of degenerate \( \pi_g \) orbitals. The atomic orbitals combine to produce the following molecular orbital diagram:

Comparison of the above energy level diagram with that for nitrogen - you can see that the \( 2\sigma_g \) level lies lower than \( \pi_u \). Here, we are starting to fill the anti-bonding orbitals originating from the \( p \) orbital interactions and so the bond order decreases from three to two. The lowest energy arrangement (Hund's rule) - has a single electron, each with parallel spins, in each of the \( \pi_g^x \) and \( \pi_g^y \) orbitals. This produces a paramagnetic molecule, with a double bond and has two unpaired electrons.

### 3.9 Heteronuclear diatomic molecules
If the molecule is heteronuclear, the parent atomic orbitals will have different energy levels. The more easily ionized (less electronegative) atom will have the atomic orbital level closer to \( E = 0 \) in the arrangement depicted below:
The bonding molecular orbital has an energy and a wave function which approximates the more electronegative atom. The antibonding molecular orbital will have an energy and wavefunction which resembles that of the less electronegative atom. As an example, consider the molecule hydrogen chloride. The hydrogen 1s orbital (one electron) would be $\phi_1$ and the chlorine 3p orbital that bonds with it (one electron) will be $\phi_2$. The molecular orbital $\psi$ will look very much like the chlorine 3p orbital and will end up holding both electrons, while the $\psi^*$ orbital will look like the original H 1s orbital and will end up empty. Thus, the molecular orbital theory correctly represents $H^+Cl^-$. (Note that the above is a rather treatment because it ignores the possible involvement of the 3s orbital of Cl.)

**A₂ Molecules**

**Hydrogen Fluoride:**

A simple diatomic molecule is Hydrogen fluoride. There are eight valence electrons which occupy four molecular orbitals. The two highest energy MO's are degenerate, are $\pi$-type and have no electron density associated with the hydrogen atom, *ie.* they are Non-Bonding Orbitals (NBO) and in Lewis Theory are represented as two "Lone Pairs". Another important difference between Hydrogen Fluoride and previous molecules is that the electron density is not equally distributed about the molecule. There is a much greater electron density around the fluorine atom. This is because fluorine is an extremely electronegative element, and in each bonding molecular orbital, fluorine will take a greater share of the electron density.

For the energy diagram and pictorial view of the orbitals - please see below:
3.10 Bond properties in the molecular orbital formalism

**Bond Lengths and Covalent Radii**

There are several points to be made here:

Bond lengths are derived from the sums of covalent radii. The covalent radii can be obtained in the first instance by taking half the length of a homonuclear bond:

- $d_{\text{Cl-Cl}}$ (in Cl$_2$) = 1.988 Å therefore $r_{\text{Cl}} = 0.99$ Å
- $d_{\text{C-C}}$ (in diamond) = 1.54 Å therefore $r_{\text{C}}$ (single bond) = 0.77 Å

Predicted $d_{\text{C-Cl}} = r_{\text{C}}$ (single bond) + $r_{\text{Cl}} = 0.99 + 0.77 = 1.76$ vs actual 1.77 Å

Naturally, the observed bond lengths will vary a little from compound to compound depending on the other atoms bonded to the two participating in the bond under consideration.

The observed bond length will be a function of the bond order for example:

- $d_{\text{N=O}} = 1.10$ Å
- $d_{\text{N=N}} = 1.25$ Å
- $d_{\text{N-N}} = 1.45$ Å

Double- and triple-bond radii are approximately 0.87 and 0.78 times the single-bond radius.

The single-bond covalent radius of an atom is influenced by the type of hybrids that it is using. The more p-character in the hybrid, the larger will be the radius:

- $r_{\text{C}}$(sp$^3$) = 0.77 Å
- $r_{\text{C}}$(sp$^2$) = 0.73 Å
- $r_{\text{C}}$(sp) = 0.70 Å

If the electronegativity of the bound atoms differs substantially, that is the bonds have substantial ionic character, then the bonds will be shorter than predicted by the covalent radii:

In CF$_4$ the C-F bondlength is 1.32 Å (predicted 1.44 Å)
In SiF$_4$ the Si-F bond length is 1.54 Å (predicted 1.81 Å)
In SiF$_4$ some of this shortening is said to involve $\pi$-bonding between empty silicon d-orbital and filled fluorine p-orbitals.

**Overlap of Orbitals**

**Bonding overlap.** All parts of the atomic orbitals which overlap each other have the same sign.
(colour). The electron density is raised in such areas of overlap by $2\psi_1,\psi_2$ relative to the simple sum: $\psi_1^2 + \psi_2^2$ which leads to an attractive component to the interaction between the two atom concerned.

**Antibonding overlap.** All overlapping parts of the atomic orbitals have opposite signs. A node is formed in such regions so the electron density goes to zero at the node. Such molecular orbitals, when occupied by electrons, contribute a repulsive component to the interaction between the two atoms concerned.

**Non-bonding overlap.** If there are some areas of overlap where the signs are the same and others where they are opposite, the net contribution of such a molecular orbital to the interaction between the two atoms would be zero. For this reason such molecular orbital combinations are not constructed.

**The $\sigma,\pi$ and $\delta$ Notation**

The "bottom line" is that a $\sigma$-molecular orbital has no node which passes through all the nuclei involved, a $\pi$-molecular orbital has one such node, and a $\delta$-molecular orbital has two such nodes.

**Molecular orbitals of polyatomic molecules**

3.11 The construction of molecular orbitals

**Orbitals for selected molecules**

This section illustrates pictorially molecular orbitals for several organic and inorganic molecules. If possible - the energy level diagram is included and clicking upon the relevant level will generate the accompanying molecular orbital in the right-hand frame. Please choose from:

3.12 Polyatomic molecules in general

**Saturated molecules**

These are molecules in which all valence electrons are involved in the formation of single bonds. There are no non-bonded lone pairs. These molecules are generally less reactive than either electron-rich or electron-deficient species, with all occupied orbitals having relatively low energies.

**Water:**

In the water molecule the highest occupied orbital, ($1b_1$) is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital ($2a_1$) can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density.
Ammonia:
Ammonia has two pairs of degenerate orbitals, one bonding and one antibonding, and like hydrogen fluoride and water has a non-bonding orbital ($2a_1$). This highest occupied orbital has a lobe pointing away from the three hydrogens, and corresponds to a lone pair orbital localized upon the nitrogen, whereas the three lowest energy MO's lead to the description of the three N-H bonds of the Lewis structure. The lone pair is relatively high in energy, and is responsible for the well known Lewis base properties of ammonia.
The next molecule in the series HF, H₂O and H₃N, is H₄C (methane) - which was discussed earlier - and unlike the other three molecules has no non-bonding orbitals.

**Methane:**
The valence molecular orbitals of methane are delocalized over the entire nuclear skeleton - that is, it is not easy to assign any one orbital to a particular C-H bond. It is possible to see how complex the orbital structure becomes with the increase in energy. Methane has four valence molecular orbitals (bonding), consisting of one orbital with one nodal plane (lowest occupied) and three degenerate (equal energy) orbitals that do have a nodal plane.

For the energy diagram and pictorial view of the orbitals - please see below:
Ethane:
The ethane molecule has fourteen valence electrons occupying seven bonding molecular orbitals. As can be seen from the energy diagram - four of the molecular orbitals occur as degenerate pairs. Like in methane - the molecular orbitals of ethane show increasing nodal structure with increasing orbital energy.
For the energy diagram and pictorial view of the orbitals - please see below:
A Linear Triatomic - BeH₂
The central atom is Be and the ligands are the H's.

The atomic energy levels are shown under Be and 2H in the figure above. Note the hydrogen orbitals are shown to have a lower energy than the beryllium orbitals because the non-metal, hydrogen, is more electronegative (harder to ionize than the metal, Be).

There are two linear combinations of the two hydrogen 1s orbitals:
\[ \psi_1 = \frac{1}{\sqrt{2}}(\psi_{1s_{Ha}} + \psi_{1s_{Hb}}) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}}(\psi_{1s_{Ha}} - \psi_{1s_{Hb}}) \]

- The energy levels that these combinations might have is shown below 2H(combos).
The beryllium 2s orbital is of the correct symmetry to form combinations with \( \psi_1 \) and the Be 2p orbital directed along the internuclear axis (say z) is of the correct symmetry to form combinations with \( \psi_2 \):

\[
\sigma_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_{2\text{Be}}) \quad \text{and} \quad \sigma_3^* = \frac{1}{\sqrt{2}}(\psi_1 - \psi_{2\text{Be}})
\]

\[
\sigma_2 = \frac{1}{\sqrt{2}}(\psi_2 + \psi_{2p\text{Be}}) \quad \text{and} \quad \sigma_4^* = \frac{1}{\sqrt{2}}(\psi_2 - \psi_{2p\text{Be}})
\]

The beryllium 2p\(_x\) and 2p\(_y\) orbitals do not have matching symmetry ligand combinations.

- These molecular orbitals, including the localized 2p\(_x\) and 2p\(_y\) orbitals, are shown under BeH\(_2\) on the energy level diagram.
- As shown on the energy level diagram, the 4 valence electrons are found in \( \sigma_1 \) and \( \sigma_2 \) molecular orbitals which are both bonding 3-centre orbitals. The bond order for one Be-H connection will be:

\[
\text{B.O} = \frac{(# \text{ bonding electrons})}{2}/(\text{# of 2-centre bonds}) = \frac{4}{2}/2 = 1
\]

An Electron Deficient Molecule with Bridging Hydrogen - Diborane, B\(_2\)H\(_6\)

Diborane has the structure shown on the right. At first sight, it seems to have 8 bonds, but between the two boron atoms and the 6 hydrogen atoms, there are only 12 electrons - enough to make only 6 "conventional" 2-centre - 2-electron bonds.

The figure below shows how this situation is handled using molecular orbital theory:
• On the left side of the diagram there is a modified valence bond diagram for the whole molecule. The various orbitals are colour-coded to the structural diagram in the centre of the diagram. Notice that the boron atoms are assigned sp\(^3\) hybridization based on their (predicted) approximately tetrahedral geometry. Although molecular orbital theory could be used to describe the bonding in the whole molecule, and without invoking hybridization in a separate step, here it is only used for the hydrogen bridges.

• The molecular orbital energy level diagram on the right-hand side of the diagram treats only one of the two hydrogen bridges (red or purple). The orbitals used are: one sp\(^3\) hybrid on each boron and the bridging hydrogen's 1s orbital. There are 2 electrons assigned to this system.

• The boron atoms are considered to be ligating hydrogen, so their orbitals are first combined to give two linear combinations:

\[ \psi_1 = \frac{1}{\sqrt{2}}(\psi_{sp}^{3} Ba + \psi_{sp}^{3} Bb) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}}(\psi_{sp}^{3} Ba - \psi_{sp}^{3} Bb) \]

The hydrogen 1s orbital can be combined with \(\psi_1\) yielding a bonding and an antibonding combination. The other ligand combination, \(\psi_2\) is not used.
\[ \sigma = \frac{1}{\sqrt{2}}(\psi_1 + \psi_{1sH}) \quad \text{and} \quad \sigma^* = \frac{1}{\sqrt{2}}(\psi_1 - \psi_{1sH}) \]

- The two electrons end up in the \( \sigma \) orbital delocalized over the entire bridge, i.e. contributing to 2 connections, so the bond order in any one of the B-H bridging bonds is \( \frac{1}{2} \). (The B-H terminal bonds are "normal" 2-electron - 2-centre Lewis bonds.)

**Phosphorus Pentachloride - Without Using Those 3d Orbitals!**

In pure valence bond theory, the bonding in PF\(_5\) requires the use of the 3d orbitals of phosphorus to allow the creation of 5 normal 2-centre - 2-electron bonds. It is possible to avoid this strategy (which has been challenged as unrealistic) by using three-centre bonding described by molecular orbital theory. Valence bond theory accounts for the bonding of the fluorines in equatorial sites by employing sp\(^2\) hybrids on phosphorus. The axial system only is described by molecular orbital theory. The diagram below sets up the situation:

The 2p orbitals oriented along the molecular axis on the two fluorines are first combined:

\[ \psi_1 = \frac{1}{\sqrt{2}}(\psi_{2pFa} + \psi_{2pFb}) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}}(\psi_{2pFa} - \psi_{2pFb}) \]

The diagram below shows the combinations graphically.
The 3p orbital of phosphorus (remaining unhybridized) can be combined with the ligand combination $\psi_1$ to yield a bonding and antibonding combination. The ligand combination, $\psi_2$, remains unused in this simplified treatment.

$$\sigma = \frac{1}{\sqrt{2}}(\psi_1 + \psi_{3pP}) \quad \text{and} \quad \sigma^* = \frac{1}{\sqrt{2}}(\psi_1 - \psi_{3pP})$$

The diagram below shows these combinations graphically.

The diagram below shows the energy levels in the axial orbital system only. There are two electrons in the bonding orbital ($\sigma$) which leads to a bond order of $\frac{1}{2}$; in each phosphorus-fluorine "connection", since the two non-bonding electrons (in $\psi_2$) do not contribute. Therefore, the axial bonds are expected to be weaker than the equatorial bonds. This is supported by the experimental evidence.
3.13 Molecular shape in terms of molecular orbitals

The Delocalized Approach to Bonding: Molecular Orbital Theory

In molecular orbital theory, molecular orbital wavefunctions are constructed by taking linear combinations of atomic orbitals. If there are only two atoms involved, this means the sum and the difference of the atomic orbital wavefunctions. If there are more than two atoms involved, the combinations are formed in a more complicated way, and usually the symmetry properties of the molecular or molecular ion are used to simplify the problem. (Of course, this does not simplify much if the mathematical theory which covers symmetry (group theory) has not been covered!) The first part deals with diatomic species. This is followed by several more complicated sample systems.

Molecules and Ions with double bonds

In molecules where the number of bonding electron pairs exceeds the number of unions between atoms, the extra electrons occupy higher energy molecular orbitals than the orbitals found in molecules where the number of bonding electron pairs equals the number of unions between atoms. These are double bonds, and the orbitals have a nodal plane containing the atoms sharing these \( \pi \)-type orbitals.

Ethene:

The simplest alkene is ethene. Its chemistry is dominated by two \"frontier orbitals\", that is the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). For the ethene orbital energy diagram these are shown as \( \pi_{CC} \) for the HOMO, and \( \pi^*_{CC} \) for the LUMO.

An important property of the ethene molecule, and alkenes in general is the existence of a high barrier to rotation about the C=C which tends to hold the molecule flat.

For the energy diagram and pictorial view of the orbitals - please see below:
Molecules with triple bonds

Ethyne:
For the energy diagram and pictorial view of the orbitals - please see below:
A Trigonal-planar molecule/ion - CO$_3^{2-}$ (or NO$_3^-$ or BF$_3$ which are isoelectronic)

This is a case where the $\sigma$-bonding is usually handled with valence bond theory. If the three-fold axis of the molecule/ion is considered the $z$ axis, the $\sigma$-bond framework involves hybridizing the carbon 2s 2p$_x$, and 2p$_y$ orbitals (sp$^2$) and using them to attach the oxygens by a 2p orbital lying in the molecular plane. This accounts for 6 of the valence electrons.

The $\pi$-bonding molecular orbitals are formed from the carbon and three oxygen 2p$_z$ orbitals and there will be six more electrons to accommodate.

Therefore:

- The central atom is carbon and the ligands are oxygen.
• The atomic orbitals used for the \( \pi \)-bonding system only are shown under C and \( \text{2O}^- \), O in the energy level diagram below (f). The oxygen p-orbitals lie at a lower energy than those of carbon because oxygen is more electronegative. The three oxygen 2p \( _z \) orbitals must form three linear combinations:

\[
\begin{align*}
\psi_1 &= \frac{1}{\sqrt{3}} \psi_{2pz\text{O}_a} + \frac{1}{\sqrt{3}} \psi_{2pz\text{O}_b} + \frac{1}{\sqrt{3}} \psi_{2pz\text{O}_c} \\
\psi_2 &= \frac{1}{\sqrt{2}} \psi_{2pz\text{O}_b} - \frac{1}{\sqrt{2}} \psi_{2pz\text{O}_c} \quad \text{(no contribution from O\text{A})} \\
\psi_3 &= \sqrt{\frac{2}{3}} \psi_{2pz\text{O}_a} - \frac{1}{\sqrt{6}} \psi_{2pz\text{O}_b} - \frac{1}{\sqrt{6}} \psi_{2pz\text{O}_c}
\end{align*}
\]

• The energy level that these combinations would have is shown below \( \text{2O}^- \), O (combos) in the figure below.

• The carbon 2p \( _z \) orbital is of the correct symmetry to combine with \( \psi_1 \).

\[
\begin{align*}
\pi_1 &= \frac{1}{\sqrt{2}} (\psi_1 + \psi_{2pzC}) \\
\pi^* &= \frac{1}{\sqrt{2}} (\psi_1 - \psi_{2pzC})
\end{align*}
\]

This is the only combination involving the carbon so \( \psi_2 \) and \( \psi_3 \) remain non-bonding relabelled as \( \pi_2 \) and \( \pi_3 \).
The resulting molecular orbitals are shown under $\text{CO}_3^{2-}$ on the energy level diagram below.

The 6 electrons occupy $\pi_1$, $\psi_2$ and $\psi_3$ as shown in the energy level diagram. The only bonding $\pi$-orbital, $\pi_1$ contains 2 electrons spread over 4 centres involved in 3 C-O connections. The non-bonding $\psi_2$ and $\psi_3$ orbitals have no contribution. Therefore, the bond order for each carbon-oxygen connection is $1/3$. Do not forget the $\sigma$-bonds which were not included in this scheme.

**Conjugated and aromatic molecules**

$\pi$ bonds in close proximity will often interact. Some of the delocalized molecular orbitals that result will be stabilized, while others will be destabilized. The individual combinations may be polarized, providing an increase in wave function amplitude on some centers at the expense of a decrease in amplitude on others. This gives rise to the possibility of more varied reactivity patterns than are observed for simple alkenes.

Aromatic molecules exhibit a wide range of reactivity patterns toward both electron rich and electron deficient species. These mainly depend on the structures and energies of the frontier $\pi$-type molecular orbitals, the HOMO and LUMO. Except for non-bonded lone pairs, the $\sigma$ framework plays little role in the overall reactivity.

**trans-1,3-Butadiene:**

The energies of the $\pi$-molecular orbitals of conjugated molecules like butadiene, (see below) - occur in pairs, with their energies equal to $(\alpha \pm \chi \beta)$, where $\alpha$ and $\beta$ are constants. For each bonding orbital of and energy $\alpha-\chi \beta$ there is a corresponding antibonding orbital of energy $\alpha+\chi \beta$. The $\pi$-molecular orbitals are extended over the whole molecule.

For butadiene, the $\pi$ manifold contains four electrons, leading to an electronic configuration of $\pi_1^2\pi_2^2$.

For the energy diagram and pictorial view of the $\pi$-molecular orbitals - please see below:
The radicals allyl:

\[
\left\{ \begin{array}{c}
\text{H}_2\text{C} \\
\text{C} \\
\text{CH}_2
\end{array} \right\} \cdot
\]

and pentadienyl:

\[
\left\{ \begin{array}{c}
\text{H}_2\text{C} \\
\text{C} \\
\text{C} \\
\text{H}_2
\end{array} \right\} \cdot
\]

have the same arrangement of \(\pi\)-orbitals, (ie. the occur in pairs of energy \(\alpha \pm \beta\)), but because there is an odd number of carbon atoms in the conjugate chain, there must be a non-bonding orbital with energy \(\alpha = 0\). Also, because of the pairing properties of the \(\pi\)-molecular orbitals of conjugated chains, there will be a node at every alternate carbon atom in the non-bonding orbital. This is important for the unpaired electron of allyl, which will occupy this non-bonding orbital. If an electron is added to the allyl radical to form the anion, the negative charge will appear at the terminal carbon atoms. If the unpaired electron is removed forming the cation, the resulting positive charge is also spread over the terminal carbon atoms.

There are three \(\pi\)-molecular orbitals for allyl, the \(\pi_1\) is bonding, the \(\pi_2\) orbital is non-bonding and the \(\pi_3\) is anti-bonding. In the neutral allyl species - there are a total of seventeen valence electrons - of which three fill the \(\pi\)-orbital manifold. A pictorial representation of the energy diagram for the neutral, cationic and anionic allyl species are shown below - (orbitals are shown only for the cationic species):
In the pentadienyl anion, the negative charge is centred on the carbon atoms in the 1,3 and 5 position - similarly with the positive charge for the cation.

These ions are represented in resonance theory as two or three canonical forms:

The delocalisation of \( \pi \)-electrons is associated with a lowering of the orbital energy. Therefore the total energy of the occupied \( \pi \)-orbitals of butadiene is lower in energy than two isolated ethene-type double bonds.

**Aromatic Molecules**

Further delocalisation of \( \pi \)-electrons occurs in aromatic hydrocarbons. A figure showing the comparative energy levels of the \( \pi \)-orbitals of the cyclic molecules \( \text{C}_n\text{H}_n \), for \( n=3-6 \), is shown below: Aromatic molecules including the prototype molecule, benzene \( \text{C}_6\text{H}_6 \), are also usually considered by separating the \( \sigma \)-bonded system from the \( \pi \)-system:

a. In all cases, the carbon atoms are presumed to be sp\(^2\) hybridized. This leaves one electron in each of the hybrids so each carbon is bonded to its neighbours using two of these hybrid orbitals, and to its hydrogen by the third.
b. The remaining 2p-orbital on each carbon lies perpendicular to the plane of the ring and will contribute to linear combinations resulting in the \( \pi \)-molecular orbitals. If there are \( n \) carbon atoms, then there must be \( n \) \( \pi \)-orbitals formed.

c. The \( \pi \)-molecular orbitals will contain \( n \) electrons minus the charge. For example, for \( \text{C}_3\text{H}_5 \) there will be 6 electrons in the \( \pi \)-orbitals.

d. For the simpler ring systems, it is possible to deduce the relative energy levels of the \( \pi \)-molecular orbitals by a simple "trick" (which comes from something called Hückel theory - the method of forming the linear combinations, which is beyond the scope of this course). Look at the left-hand side of the diagrams below:

e. Draw the polygonal ring "standing" straight up on a single carbon vertex at the bottom. The other corners will be in pairs at the same levels, except perhaps the top one. (See the diagrams below.)

f. Sketch horizontal lines from the corners; one corner goes with one level. The lowest level will always be single, intermediate ones will always be in pairs. At the top, there will be one level for even numbers of carbon atoms or two for odd numbers.

g. There will be enough electrons to fill the bonding levels, which are all those below the centre of the polygon. This will automatically lead to \( 4m + 2 \) electrons, where \( m = 0, 1, 2 \ldots \), which is the rule for aromaticity.

On the right-hand side, the diagrams indicate how the orbitals would look if they are "occupied". Once again, the creation of the linear combinations is beyond the scope of Chem 241, but the results have the following features:

Note that there is always the node in the plane of the ring (shown as a green polygon) which defines them as \( \pi \)-orbitals. This node contains the carbon nuclei. In addition, the orbitals above the lowest have increasing numbers of nodes perpendicular to the rings. In the case of the degenerate pairs, there are the same number of nodes, but they lie 90\(^\circ\), 45\(^\circ\), 30\(^\circ\) etc. apart as you go up. (The highest orbital, for systems with an even number of carbon atoms, is like the original set of p-orbitals with, with alternating phases as you go round the ring.)
In all cyclic polyenes \((C_nH_n)\), the \(\pi\)-molecular orbitals occur in degenerate pairs, except for the lowest \(\pi\)-orbital, and for the cyclic polyenes with even numbers of carbon atoms, the highest \(\pi\)-orbital (see above).

**Tropylium ion: \(C_3H_3^+\)**

**Cyclobutadiene:**

From the cyclic polyene diagram - the square molecule cyclobutadiene \((C_4H_4)\) has four \(\pi\)-orbitals, a bonding orbital \((\pi_1)\), two degenerate non-bonding orbitals \((\pi_2\) and \(\pi_3)\) and an antibonding orbital \((\pi_4)\). Four electrons are placed into these four orbitals; two into the bonding
orbital, and one each with parallel spins into the degenerate non-bonding orbitals (Hund's rule) - see below:

\[ \text{C}_4\text{H}_4^{2+} \]

There is no reason to expect cyclobutadiene to be square, theoretically calculations show an oblong with two double bonds structure has lower energy. Experimentally it is shown that cyclobutadiene acts a very strained cyclo-olefin, rather than as a bi-radical species.

**Cyclopentadiene:**
This molecule is a relatively acidic hydrocarbon, and the anion is formed by the treatment of cyclopentadiene with a strong base. From the cyclic polyene diagram it can be seen that cyclopentadiene has three $\pi$ bonding orbitals which are delocalised over the five carbon atoms. The uppermost $\pi$ bonding orbitals are a degenerate pair, and are the highest occupied molecular orbitals (HOMO's). These orbitals are much higher in energy than those in neutral aromatic species such as benzene, indicating that this anion is far more susceptible to attack by electrophiles. The anion is far more capable of coordinating to transition metals with available empty $d$-orbitals. The anion has six $\pi$-electrons, making the system aromatic. The six electrons are arranged as in the diagram below:

$$C_5H_5; \text{ (cyclopentadienide)}$$
**Benzene:**

Benzene is the archetypal aromatic compound. It has a symmetrical π system and so is not over reactive on any one site. From the cyclic polyene diagram it can be seen that benzene has six π-molecular orbitals, (which contain the six π-electrons), three bonding and three anti-bonding. The upper bonding degenerate pair of orbitals are the HOMO's of benzene. The π orbital manifold, is shown below - but also of interest is that the pattern of the π orbitals is repeated within the σ system. The σ functions - like the π orbitals are delocalized throughout the carbon skeleton.

The six π electrons are arranged as in the diagram below:

\[\text{C}_6\text{H}_6\ (\text{benzene})\]
Bonding in benzene

From the above diagram it can be seen that the lowest lying orbital, $\pi_1$, the orbital coefficients are such that the bonding character between each pair of adjacent carbon atoms is equal. In $\pi_2$ bonding only occurs between atoms C$_2$ and C$_3$ and between C$_5$ and C$_6$ since the coefficients on C$_1$ and C$_4$ are zero. In $\pi_3$, C$_1$, which is bonded to C$_2$ and C$_6$ and C$_4$ is bonded to C$_3$ and C$_5$, there are anti-bonding interactions between C$_2$ and C$_3$ and between C$_5$ and C$_6$. Therefore if we consider the pair of orbitals $\pi_2$ and $\pi_3$ the contribution to the C-C $\pi$ bonding is equal for each bond. Since there are three occupied bonding orbitals and six CC linkages - the $\pi$ bond order is $1/2$. This description is in accord with the two resonating mesomeric forms (or Kekulé structures in a) below in which single and double bond characters alternate around the ring. Conventionally, the diagram in b) is used to show that the six electrons are delocalized around the ring:

a)  

$C_7H_7^+$ (tropyllium) and $C_8H_8^{2+}$

Do them yourself!
The molecular orbital theory of solids

Metallic Bonding

The third major type of chemical bond is the bond between two metal atoms. Metals lose electrons and cannot normally accept them. This means that, in a metallic bond, there are no atoms to accept the electrons. Instead, the electrons are given up to a "sea" of electrons that surrounds the metal atoms. In a way, this is similar to ionic bonding, except that the "ions" are electrons. The attraction between the electrons and the metal ions keeps the metal together. The metals are the most numerous of the elements. About 80 of the 100 or so elements are metals. You know from your own experience something about how metallic atoms bond together. You know that metals have substance and are not easily torn apart. They are ductile and malleable. That means they can be drawn into shapes, like the wire for this paper clip, and their shape can be changed. They conduct heat and electricity. They can be mixed to form alloys. How is it that metallic bonding allows metals to do all these things?

The nature of metals and metallic atoms is that they have loosely held electrons that can be taken away fairly easily. Let's use this idea to create a model of metallic bonding to help us explain these properties. I will use potassium as an example. Its valence electron can be represented by a dot. When packed in a cluster it would look like this (also in example 31 in your workbook). The valence electron is only loosely held and can move to the next atom fairly easily. Each atom has a valence electron nearby but who knows which one belongs to which atom. It doesn't matter as long as there is one nearby.

Metals are held together by delocalized bonds formed from the atomic orbitals of all the atoms in the lattice. The orbitals spread over many atoms and blend into a band of molecular orbitals. The range of energies of these orbitals are closely spaced. The band is composed of as many levels as there are contributing atomic orbitals and each level can hold electrons of opposite spin. The idea that the molecular orbitals of the band of energy levels are spread or delocalized over the atoms of the piece of metal accounts for bonding in metallic solids. This theory of metallic bonding is called the band theory. The band is split into two regions, the upper portion being the empty levels or the antibonding and the lower portion is the filled levels or the bonding orbitals. In a metal the band of energy levels is only partly filled. The highest filled level right before going to the empty level is called the Fermi level. The trend of melting points of the transition metals is based on the electrons in the metal.

Bonding Models for Metals

3.14 Molecular orbital bands

Band Theory of Bonding in Solids

Bonding in solids such as metals, insulators and semiconductors may be understood most effectively by an expansion of simple MO theory to assemblidges of scores of atoms. If we recall, in simple MO theory we assumed that atomic orbitals on two atoms could come together to form bonding and antibonding orbitals.

If we bring three atoms together we can create a string of atoms with bonding that connects all three. Here we have a bonding orbital, an antibonding orbital, and a curious critter called a nonbonding orbital. Essentially a nonbonding orbital is an orbital that neither increases nor decreases the net bonding in the molecule. The important feature here is that three atomic orbitals in must give three molecular orbitals out. The total number of orbitals must remain constant.
Now let's expand these idea by considering combinations of four and ten atoms. As shown below, four atoms (four atomic orbitals) will give four molecular orbitals, two bonding and two antibonding. Notice that the two bonding (and two antibonding) orbitals are not exactly the same energy. The lower bonding orbital is slightly more bonding than the other (and one antibonding orbital is slightly more antibinding than the other). For the ten atoms we'd get a set of five bonding and five antibonding orbitals, each slightly different in energy.
Notice that for n atomic orbitals going into the bond there must be n molecular orbitals produced. If n is even, then there will be n/2 bonding and n/2 antibonding orbitals. If n is uneven there will be a nonbonding orbital.
If we now jump to a huge number of atoms, $n$, where $n$ is perhaps as big as Avogadro’s number, we can see that we’re going to have a huge number of bonding and antibonding orbitals. These orbitals will be so close together in energy that they begin to blur creating bands of bonding and bands of antibonding orbitals. It is the existence of these bands of orbitals that underlie our understanding of the properties of solids.

Notice, by the way, that there is some point at which the properties of an assemblage of atoms makes a transition from separate discrete orbitals (and hence quantum properties like atoms), to bands of orbitals. The technology built upon tiny clusters called nanodots in which groups of atoms with perhaps twenty atoms acts like a quantum object is built upon this concept. By the time one has even a tiny cluster of atoms such as the submicron objects in a computer chip, the properties are best described by band theory.
MO Theory of Solids. Consider a linear chain of \( n \) identical atoms, each bringing in a valence \( s \) orbital for MO formation. If \( n = 2 \), 2 MOs are formed, one bonding and one antibonding. If \( n = 3 \), we obtain 3 MOs, bonding, nonbonding, and antibonding. If we run \( n \) right up to Avogadro's number, we expect to obtain \( N_0 \) MOs, ranging from fully bonding (+++++...) to fully antibonding (+---+---...), with a whole bunch of other MOs between these extremes. This is shown in Figure MO-20. The energy spacing between lowest and highest MOs is determined primarily by the overlap between neighboring atoms, so will stay finite even though the number of atoms in the chain reaches toward the infinite! We thus have a huge number of MOs crammed into a finite energy interval. They will be so close together in energy that they will form, for all practical purposes, a continuous band of energy levels. For this reason the MO theory of solids is often called Band Theory. A very important result of this treatment is that each of the MOs in the band is delocalized over all of the atoms in the chain.

The same ideas apply to a 3-dimensional, close-packed aggregate of atoms. A band of MOs will be formed from each type of valence AO on the atoms. Thus we obtain an \( s \) band, a \( p \) band, a \( d \) band, and so on, as shown in Figure MO-20. All of the MOs are delocalized over all of the atoms in the aggregate, so electrons in them can be considered to be everywhere at once! The highest filled band of MOs is called the valence band; the lowest unfilled band is called the conduction band; and the energy separation between the top of the valence band and the bottom of the conduction band is called the band gap. A partially filled band is simultaneously the valence band and the conduction band, so in this case the band gap is essentially zero.

Now let's apply this picture to understand the electronic nature of the various classes of materials given above.

**A conductor** (which is usually a metal) is a solid with a partially full band, as shown in the Figure. An electron in the highest occupied MO is easily promoted to the next higher empty delocalized MO, where it is then free to roam over the whole solid lattice under the influence of an applied electric field; i.e., the solid conducts electricity due to this facile electron movement. The high reflectivity of metals is also due to the availability of a proliferation of empty MOs above the HOMO. Electrons in the filled MOs of the partially-filled band can absorb and then re-emit light of many wavelengths in making transitions to empty MOs in the band. This gives the metal surface a shiny reflective appearance. An example of a conductor is Na metal. It has an \( s \) band consisting of \( N \) MOs, where \( N \) is the number of Na atoms in the crystal. The band contains \( N \) electrons (one from each Na atom) arrayed in \( N/2 \) pairs. These \( N/2 \) pairs go in the \( N/2 \) bonding MOs, which leaves \( N/2 \) antibonding MOs empty but readily accessible. Thus Na exhibits the characteristic properties of a metal, and is a conductor.

**An insulator** is a solid with a full band and a large band gap, as shown in Figure MO-21. The MOs in the conduction band are so high in energy that they are not thermally populated by the Boltzmann distribution, and there is no conductivity at ordinary temperatures. An example of an insulator is solid carbon in the diamond modification. Diamond consists of a covalently bonded network of carbon atoms (a fcc array of C atoms with more C atoms in half the tetrahedral holes), constructed from sp\(^3\) hybrid orbitals. N carbon atoms contribute \( 4N \) sp\(^3\) hybrids, which overlap strongly to give \( 2N \) bonding MOs and \( 2N \) antibonding MOs which are separated in energy by 5.47 eV from the bonding MOs. The \( 4N \) electrons exactly fill the band of bonding MOs. The antibonding band is not thermally accessible, so diamond does not conduct.
3.15 Semiconduction

A semiconductor is a solid with a full band and a small band gap, as shown in the Figure. There is a small thermal population of the conduction band at normal temperature, hence a small conductivity. For example, silicon has a diamond modification similar to that of carbon, but a band gap of only 1.12 eV, due to poorer overlap of the sp³ hybrids of the larger Si atoms. Since the antibonding band will be occupied to a small extent via the Boltzmann distribution, Si exhibits a small conductivity at room T. The group 4A elements, which have a number of valence electrons equal to twice the number of MOs in the bonding band, are uniquely structured to show semiconductivity. The elements C through Sn all exhibit a diamondlike crystal form, but with a band gap which decreases in magnitude for the larger atoms as orbital overlap becomes weaker. The trend in band gap down family 14 is shown below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Band Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5.47</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
</tr>
<tr>
<td>Ge</td>
<td>0.66</td>
</tr>
<tr>
<td>Sn</td>
<td>0</td>
</tr>
</tbody>
</table>

Thus Si and Ge are semiconductors at room T, and Sn is a conductor. Pure compounds which are electronically analogous to the group 14 elements are also semiconductors. These include the compounds boron nitride, BN, and gallium arsenide, GaAs. Note that these compounds contain one element from group 13 and one element from group 15, in a 1:1 stoichiometric ratio. They thus have exactly the same number of valence electrons as a group 14 element, and will arrange these electrons in a group-14 type band structure. They are often called 3-5 compounds, to indicate that they consist of elements taken from groups 13 and 15. Similarly, 2-6 compounds such as ZnS and CdS (both of which have the zincblende structure, which is analogous to the diamond structure) function as semiconductors. Generally, band gaps vary with position in the periodic table, but tend to decrease with increasing MW of the semiconductor.

The temperature dependence of conductivity is readily understood within the framework of band theory. For a conductor, promotion of electrons is facile within a band at any T. However, As T increases, vibrational motions of the metal atoms in the lattice increases and interferes with the motion of the conducting electrons. The result is a decrease in conductivity as T increases. For a semiconductor, an increase in T causes an exponential increase in the population of the conduction band, because of the Boltzmann distribution. Therefore the conductivity of semiconductors increases dramatically with T. Because an insulator is actually a semiconductor with a large band gap, the conductivity of an insulator should also increase markedly if the temperature is made high enough.

Because of the very large number of atoms that interact in a solid material, the energy levels are so closely spaced that they form bands. The highest energy filled band, which is analogous to the highest occupied molecular orbital in a molecule (HOMO), is called the valence band. The next higher band, which is analogous to the lowest unoccupied molecular orbital (LUMO) in a molecule, is called the conduction band. The energy separation between these bands is called the energy gap, $E_g$. 


The filling of these bands and the size of the energy gap determine if a material is a conductor (a metal), a semiconductor, or an insulator. In metals there is no energy gap between filled and unfilled energy levels. A significant number of electrons are thermally excited into empty levels, creating holes in the filled band. The electrons in a conduction band and the holes in a valence band can move throughout the material, allowing it to easily conduct electricity. In semiconductors $E_g$ is small, but large enough so that a fairly small number of electrons are in the conduction band due to thermal energy, and these materials conduct poorly. In insulators $E_g$ is large so that electrons are not promoted to the conduction band due to thermal energy, and these materials do not conduct electricity.

Three categories of materials may be easily understood by the energy gap between the bonding bands and the antibonding bands. If there is a large gap in energy, the material is called an insulator. If the gap is finite, but small, then the material is a semiconductor, and if there is effectively no gap between the bands, the materials are called conductors. These properties arise because electrons that enter the antibonding band are free to move about the crystal. Such behavior is associated with electrical conduction. To give you an idea of the energies involved, the band gap in diamond is 502 kJ/mol, while that in Si is 100 kJ/mol and that in Ge is 67 kJ/mol. Diamond is an insulator while the other two materials are semiconductors.
3.16 Superconduction

The Discovery of Superconduction

Before the discovery of superconduction, it was already known that cooling a metal increased its conductivity - due to decreased electron-phonon interactions (detailed in the Theory section). After the ‘discovery’ of liquified helium, allowing objects to be cooled to within 4K of absolute zero, it was discovered (by Onnes, 1911) that when mercury was cooled to 4.15K, its resistance suddenly (and unexpectedly) dropped to zero (i.e. it went superconducting).

In 1913, it was discovered that lead went superconducting at 7.2K. It was then 17 years until niobium was found to superconduct at a higher temperature of 9.2K. Onnes also observed that normal conduction characteristics could be restored in the presence of a strong magnetic field.
The Meissner Effect

It was not until 1933 that physicists became aware of the other property of superconductors - perfect diamagnetism. This was when Meissner and Oschenfeld discovered that a superconducting material cooled below its critical temperature in a magnetic field excluded the magnetic flux. This effect has now become known as the Meissner effect (- you can see a QuickTime video of this in action from this link).

Above: The Meissner effect - a superconducting sphere in a constant applied magnetic field excludes the magnetic flux

The limit of external magnetic field strength at which a superconductor can exclude the field is known as the critical field strength, $B_c$.

Type II superconductors have two critical field strengths; $B_{c1}$, above which the field penetrates into the superconductor, and $B_{c2}$, above which superconductivity is destroyed, as per $B_c$ for Type I superconductors.

Theory of Superconduction

Fritz and Heinz London proposed equations to explain the Meissner effect and predict how far a magnetic field could penetrate into a superconductor, but it was not until 1950 that any great theoretical progression was made, with Ginzburg-Landau theory, which explained superconductivity and provided derivation for the London equations.

Ginzburg-Landau theory has been largely superseded by BCS theory, which deals with superconduction in a more microscopic manner. BCS theory was proposed by J. Bardeen, L. Cooper and J. R. Schrieffer in 1957 - it is dealt with in the Theory section. BCS suggests the formation of so-called 'Cooper pairs', and correlates Ginzburg-Landau and London predictions well.
Cooper pair formation - electron-phonon interaction: the electron is attracted to the positive charge density (red glow) created by the first electron distorting the lattice around itself. However, BCS theory does not account well for high temperature superconduction, which is still not fully understood.

High Temperature Superconduction

The highest known temperature at which a material went superconducting increased slowly as scientists found new materials with higher values of $T_c$, but it was in 1986 that a Ba-La-Cu-O system was found to superconduct at 35K - by far the highest then found. This was interesting as BCS theory had predicted a theoretical limit of about 30-40K to $T_c$ (due to thermal vibrations). Soon, materials were found that would superconduct above 77K - the melting point of liquid nitrogen, which is far safer and much less expensive than liquid helium as a refrigerant. Although high temperature superconductors are more useful above 77K, the term technically refers to those materials that superconduct above 30-40K.

In 1994, the record for $T_c$ was 164K, under 30GPa of pressure, for HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$.

**Recommended Questions from Shriver and Atkins:**

"Exercises"

3.1 - 3.5 These are important.
3.6 Important. Ignore the bit about the vapour phase.
3.7 - 3.11 Although not explicitly covered in the course, you should be able to tackle these.
3.12, 3.13 These are important.
3.14 Important. Assume S$_2$ and Cl$_2$ are like their equivalents in the first row.
3.15 Important.
3.16 - 3.28 These are beyond the scope of this course.

"Problems"

3.1 You should be able to answer this.
3.2 You would be able to do this, but in is not explicitly covered in the course.
You should be able to do this by adding on top of to the 1s - 1s interaction, the diagram for the homonuclear diatomic molecules of the first row (which use 2s and 2p interactions).

3.4 - 3.15 These are beyond the scope of this course.

**Some Answers and Questions**

1. What holds molecules together?
2. What are the electrons doing in the molecule?
3. What insight do these considerations give concerning the chemical and physical properties of the molecule?
4. Can we predict existence and structures of molecules?

The first objective is to derive *molecular* orbitals into which we can place all the electrons in the molecule in much the same way as we do for atoms. (Using the Aufbau Principle.) To obtain these molecular orbitals, we use a method called the linear combination of atomic orbitals (LCAO). As the name implies, the molecular orbitals are made by adding or subtracting the atomic orbitals. The simplest example is obtained by considering the hydrogen molecule, H₂, which we write as Hₐ-Hₐ, using the subscripts A and B to label the two atoms. LCAO theory states that one of the molecular orbitals can be written as:

\[ \Psi_1 = c \psi_{1sA} + d \psi_{1sB} \]

The constants c and d are weighting constants indicating the relative amounts of each atomic orbital that will be used. For H₂, where the two hydrogen atoms are equivalent, c = d, and we can replace them by a single "normalizing" constant N:

\[ \Psi_1 = N(\psi_{1sA} + \psi_{1sB}) = (1/\sqrt{2})(\psi_{1sA} + \psi_{1sB}) \ldots (1) \]

(If the probability of finding the electron in such an orbital somewhere in all space is to be equal to 1, N = 1/\sqrt{2}.)

So far we have done nothing difficult, but simply assumed that equation 1 represents our MO. Use the applet to have a look at what this orbital looks like. You can adjust the distance between the nuclei to see what happens as the atomic orbital overlap more and more. Figure 2 gives a rather crude picture of what you should see.

![Figure 2](image-url)
Since $\psi_{1sA}$ and $\psi_{1sB}$ are positive everywhere, their sum must be too. Just as for the atomic orbitals, the value of $\Psi^2$ gives the probability of finding the electron in a small region, or the electron density at a point. This particular orbital is referred to as a bonding molecular orbital for reasons that will shortly be explained.

There is another linear combination that we should have considered according to LCAO theory:

$$\Psi_2 = (1/\sqrt{2}).(\psi_{1sA}-\psi_{1sB}) \quad \ldots \quad (2)$$

Use the applet to have a look at what this combination looks like. Figure 3 shows a crude representation of what you should see. This combination is referred to as antibonding. Whenever we combine two atomic orbitals in a way which produces a change in the sign of $\Psi$ between the two component atomic orbitals, anti-bonding results.

![Figure 3](image.png)

We can better understand the difference between $\Psi_1$ and $\Psi_2$ by examining the electron density or probability. For the bonding combination this is given by:

$$\Psi_1^2 = \frac{1}{2}(\psi_{1sA} + \psi_{1sB})^2 = \frac{1}{2}(\psi_{1sA}^2 + \psi_{1sB}^2 + 2.\psi_{1sA}\psi_{1sB}) \quad \ldots \quad (3)$$

If we compare this to the electron density contribution from two individual hydrogen atoms, $\frac{1}{2}(\psi_{1sA}^2 + \psi_{1sB}^2)$, it is obvious that the electron density has been increased by a amount $\psi_{1sA}\psi_{1sB}$. This effect, which accounts for the bonding because the negatively charged electrons hold the positively charged nuclei together, is illustrated in Figure 4.
Question 1. The probability plot for $\Psi_2^2$ is also shown in Figure 4. What would be its equation? (The equivalent of equation 3) What do you notice about the electron density between the nuclei as compared to two individual hydrogen atoms simply placed side by side?

Further insight into the bonding of $H_A$ and $H_B$ can be obtained by considering the energies of the electrons in $\Psi_1$ and $\Psi_2$ compared to their energies in the non-interacting atoms. This can be done by plugging the LCAO wave functions for the molecule back into the appropriate Schrödinger equation (just as it can be done for the individual atoms using the atomic wave functions). The results are shown in Figure 5, where $\Psi_1$ and $\Psi_2$ are sometimes renamed $\sigma(1s)$ and $\sigma^*(1s)$, respectively, to indicate the type of molecular orbital and their parentage.
These molecular orbitals are useful for any molecule, or molecule-ion, using only 1s orbitals for bonding. Several possibilities are: \( \text{H}_2^+ \), \( \text{H}_2 \), \( \text{H}_2^- \), \( \text{H}_2^{2-} \), \( \text{He}_2^+ \) and \( \text{He}_2 \). The positive molecule-ions are unstable, but have been detected in the gas phase under high energy conditions. The negative molecule-ions and \( \text{He}_2 \) have not been observed.

**Question 2.** Using Figure 5, comment on the observations about the stability of the diatomic species listed above. (Would you expect all the negative molecule-ions to be unstable? Are there other species not listed which might be observed? Your answer should make reference to the electronic configuration and bond orders in these species)

**Second Row : Homonuclear Diatomics**

Second row atoms have 2s and 2p orbitals available for use in bonding. As in the case of two atoms with 1s orbitals interacting, two atoms with 2s orbitals interacting lead to two molecular orbitals called \( \sigma(2s) \) and \( \sigma^*(2s) \).

The symbol \( \sigma \) is used when the molecular orbital has no nodal plane which contains *both* nuclei. For the bonding combination, there is only one region of high electron density between the two nuclei. If there is a single nodal plane containing *both* nuclei, the orbital is of type \( \pi \). In this case, the bonding combination will have two regions of high electron density separated by the node. There are rare cases in certain transition metal compounds, where two nodes per molecular orbital contain both nuclei. These are designated \( \delta \) orbitals.

*In valence bond theory terms, a single bond would have only a \( \sigma \) symmetry bond. A double bond consists of a \( \sigma \) and a \( \pi \) bond, a triple bond would have a \( \sigma \) and two \( \pi \) bonds, and the esoteric quadruple bond has one \( \sigma \), two \( \pi \) and one \( \delta \) combination. In a multiple bond, the various orbitals co-exist in the same region of space between the nuclei. Do not mistake the two regions of overlap of a \( \pi \)-bonding orbital for a double bond!*  

Use the [applet](#) to display the molecular orbitals derived from the 2s atomic orbitals on two atoms.

**Question 3.** Prepare sketches of the \( \sigma(2s) \) and \( \sigma^*(2s) \) orbitals similar to Figures 2 and 3. Do not attempt to copy all shading; just show all the nodes and the phase (sign) of \( \Psi \). Do they differ at all from figures 2 and 3?  
Next use the computer program to display the overlap of two 2px orbitals. (The x axis is taken as the internuclear axis by the computer program.)

**Question 4.** Prepare crude sketches of the resulting orbitals. Which combination, the sum or the difference, corresponds to the bonding combination this time? What would be the names for these orbitals?  
Now use the [applet](#) to examine the molecular orbitals that result from the linear combinations of the 2py orbitals. (Note that the results would be the same for the combinations of 2pz orbitals, which, if you have time you can check by varying the value of \( z \).)
Question 5. Once again prepare simplified sketches of what you see. Give the proper labels for the two combinations, including the * to indicate which is the antibonding orbital. At this point you should have seen all the all the molecular orbitals formed by pairs of 2s and 2p orbitals. We can construct an energy level diagram to illustrate the relative energies of all these molecular orbitals and the atomic orbitals from which they are derived (Figure 6).

Figure 6

Question 6. What is the bond order in Li$_2$ and O$_2$?
What homonuclear molecule-cation and molecule-anion species should have the same bond order as O$_2$? Consider cases between X$_2^{-2}$ and X$_2^{2+}$ where X = Li to Ne. Predict which two second-row elements are unlikely to give a diatomic molecule. Does simple Lewis bonding theory agree with your predictions? Figure 6 does not quite tell the whole story. It can be refined a little by considering some other types of combination. Use the computer program to examine the linear combination of a 2s orbital on one atom with a 2p$_x$ orbital on the other.

Question 7. Again sketch the results. There is no special way to label these combinations, but say if they are of type $\sigma$ or $\pi$, and whether they are bonding or antibonding. Use the computer to form a combination of a 2s orbital on one atom with a 2p$_y$ orbital on the other.

Question 8. Sketch the resulting orbital. Can you classify this orbital as $\sigma$ or $\pi$ and bonding or antibonding? Explain. Go back to the beginning of this section if you are not sure. Your answers to questions 7 and 8 should have convinced you that an LCAO of the type
illustrated in question 7 is a reasonable combination, but that the other combination, described in question 8, is not useful. (Such a combination is called nonbonding.)

The results of including the additional overlap of 2s with 2p orbitals is shown in Figure 7. The main changes are shown in red.

- There is also a little contribution from the 2s orbitals to the most antibonding molecular orbital (at the top of the diagram), and a little contribution by the 2p orbitals to the most bonding molecular orbital (at the bottom).

- The main changes are that the orbital which was labelled $\sigma(2p)$ and was below the $\pi(2p)$ levels is now shown above the $\pi(2P)$ and is now identified as $\sigma^*(2s,2p)$ while what was $\sigma^*(2s)$ has become $\sigma(2s,2p)$.

The difference does not affect our predictions for any of the stable homonuclear diatomic molecules, but it does slightly change our predictions for some of the more exotic species such as $B_2$, which can be detected in boron vapour.

\[
\begin{align*}
\text{E} &= 0 \\
2p_x, 2p_y, 2p_z & \quad \text{and} \quad 2p_x, 2p_y, 2p_z \\
2s & \quad \text{and} \quad 2s \\
\sigma(2s) & \quad \text{and} \quad \sigma(2s) \\
\pi(2p), \pi(2p) & \quad \text{and} \quad \pi(2p), \pi(2p) \\
\sigma^*(2p), \sigma^*(2p) & \quad \text{and} \quad \sigma^*(2p), \sigma^*(2p) \\
\end{align*}
\]

Figure 7

In actual fact the extent of the 2s - 2p interaction changes from $Li_2$ to $F_2$, becoming gradually less important, so that we should use the "improved" diagram (Figure 7) for $Li_2$ to $N_2$ and Figure 6 for $O_2$ $F_2$ (and cations of $Ne_2$). Figure 8 below shows what happens to the molecular orbitals as we cross the period.
**Question 9.** What is the difference for \( B_2 \)?

**Question 10.**
Go back and briefly answer, in the context of the homonuclear diatomic molecules, the four questions which were posed at the beginning of this lab.

Feel free to play with the applet to examine some of the other combinations of atomic orbitals that are possible. Because the projection direction is down the z-axis certain combinations cannot be displayed.