Introduction

This chapter relies heavily on the material in Chapter 2. Make sure you know how to determine atomic configurations and are familiar with the shapes of the s, p and d atomic orbitals. The chapter is divided into two main sections dealing with covalent bonding. In the first part, molecules are treated as having localized two-electron, two-centre bonds, and this section is based on a theory called *valence bond theory*. In the second section, based on another theoretical model called *molecular orbital theory*, certain simple molecules which are not well described by valence bond theory and the class of molecules with delocalized multi-centre bonds are described.

The Valence Electrons and Valence Shell Orbitals

- The following notes do not follow the same order as the text.
- The examples of bonding featuring transition meal compounds which are found in chapter 3 are not covered in this part of the course.
- 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.

The Localized Bond Approach

a. **Lewis Concepts**

The basic concept is the formation of a bond between two atoms or ions by the sharing of two valence electrons. These pairs are called *bonding electrons*. Any pairs of electrons which are not used in bonding are called *lone-pairs*. The diagram which summarizes all this information is called a *Lewis diagram* or *structural formula*. The molecules described in this section are all diamagnetic, that is, they contain no unpaired electrons.

*(Diamagnetic molecules are very very weakly repelled from a magnetic field. Paramagnetic molecules, which contain unpaired electrons, are weakly attracted into a magnetic field. Ferromagnetic materials are often metals and metal alloys and contain unpaired electrons with macroscopic regions where the spins all "point" in the same direction. They are strongly attracted into a magnetic field.)*

The following procedure is used to generate the diagrams you will find below. The next few paragraphs describe certain categories of molecule that you may encounter:

**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.
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.

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.

*Unsaturated molecules* where the number of valence electrons is insufficient to satisfy the octet rule without forming multiple bonds. Examples with one double bond are nitrosyl chloride (NOCl), nitrate and "phosgene" (carbonyl chloride, COCl₂):

Setting up the bonding in this molecule is straightforward. 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.

*Electron deficient molecules* do not have enough electrons to satisfy the octet rule. Simple examples are beryllium hydride and boron trichloride:

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 ones 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.
Molecules with expanded valence shells 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-obital 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. (See below)

1. Pick the central atom.

(Sometimes there may be more than one central atom.)

- Atoms that are present only once in the formula, especially heavy elements and metals, tend to be at the center of the structure.
- Oxygen is often peripheral (I use the word "terminal") and hydrogen almost always is
- Often the formula is written with the central atom first.

2. Write out the valence shell electron configurations for the neutral central atom and the "terminal" atoms in their ground states.

3. If there is a negative charge distribute it among the terminal atoms in the first instance. Bear in mind that all the terminal atoms must make at least one covalent bond with the central atom, so do not create any noble gas configurations on them. Positive charge is best initially assigned by removing electrons from the central atom.

4. The total number of unpaired electrons on the terminal atoms will have to match the number of unpaired electrons on the central atom to account for the bonds and leave no unpaired electrons. If this is not the case, once the first three steps have been carried out, there are two strategies available:

   a. Move electrons between the central atom and the terminal atoms as necessary. Make sure you keep track of the formal charges because you must be specific about their location. Enclosing a Lewis structure in brackets with the charge outside will not do.

   b. If and only if the central atom comes from the second period or below (Na onwards, n=3 and up), electrons can be placed into the nd subshell. (Whether the d orbitals play a significant role in bonding in main group compounds is debatable, but they do help to predict correct structure without invoking canonical structures with unreasonable charge separations.)

Valence-Shell Electron Pair Repulsion (VSEPR) Theory

Note that, in the lectures, this topic will be covered before hybridization, which has little predictive value at the non-mathematical level of Chem 241.

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. (The text calls this number the "occupancy".) An "object" is a lone-pair or a bonded atom (regardless of the bond order (multiplicity)).
Refinements to the 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>Geometry</th>
<th>Largest</th>
<th>Smallest</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lone Pairs</td>
<td>Longer single bonds and bonds polarized away from the central atom</td>
</tr>
<tr>
<td></td>
<td>Multiple or shorter bonds or bonds polarized towards the centre atom</td>
<td>Normal single bonds</td>
</tr>
</tbody>
</table>

a. Resonance

Valence bond theory is designed to provide a mathematical basis for the Lewis electron-pair bond localized between two atoms. There are many molecules and molecule-ions which are not adequately described by a single Lewis structure. In such cases the concept of resonance is invoked. A set of plausible Lewis structures (canonical structures) are averaged to produce a more realistic description of the observed species. Consider the following possible structures for phosphate ion:
The diagram on the right (above) shows a structure which would be the average of the four canonical Lewis structures shown on the same line, however a fifth structure, shown to the left, can be derived without using d-orbitals on phosphorus. Although it involves a greater separation of charge and is therefore a less likely contributor, it is reasonable enough that the true structure might be better modelled by mixing it into the average. Depending on the weighting, the covalent bond order would be reduced and the negative charge on each oxygen would be increased. The phosphorus would carry a fractional positive charge.

Note that any correct canonical structure will predict the same basic geometry for the non-terminal atom(s) even if it is not very realistic in the placement of the electrons, for example the phosphate ion could be drawn with four double bonds and all the negative charge on phosphorus. Such a canonical structure flies in the face of chemical sense which would distribute the negative charge on the more electronegative oxygen atoms. Nevertheless, the predicted structure is still tetrahedral.

b. Lewis Concepts and Valence Bond Theory - Extra Notes

The theory underlying the Lewis electron pair bond concept is valence bond theory. The simplest possible electron pair bond would occur in H₂. It is possible to write down the Schrödinger equation for this molecule:

\[ \frac{d^2\psi}{dx_1^2} + \frac{d^2\psi}{dy_1^2} + \frac{d^2\psi}{dz_1^2} + \frac{d^2\psi}{dx_2^2} + \frac{d^2\psi}{dy_2^2} + \frac{d^2\psi}{dz_2^2} + \left(\frac{8\pi^2m}{\hbar^2}\right)(E - V)\psi = 0 \]

Here \( x_1, y_1 \) and \( z_1 \) are the coordinates of the first electron and \( x_2, y_2, \) and \( z_2 \) the coordinates of the second. The potential energy term expands to:

\[ V = -\frac{e^2}{(1/r_{A1} + 1/r_{A2} + 1/r_{B1} + 1/r_{B2} + 1/r_{12} + 1/r_{AB})} \]

where the nuclei are labelled A and B.

The problem, since this equation cannot be solved analytically, is to find a function \( \psi \) which will give the lowest energy for the molecule. A first approximation might be to use:

\[ \psi_1 = \psi_A(1)\psi_B(2) \]
(Here \( \psi_A(1) \) and \( \psi_B(2) \) would be the 1s orbitals of hydrogen, but, in principle, this mathematical treatment could be adapted for an electron pair bond between any two atoms by using the appropriate atomic or hybrid orbitals.)

This would be appropriate for two widely separated atoms but gives an energy only about 6% of the experimental value when the internuclear distance \( r_{AB} \) is optimized at 0.90 Å, which is also too long contrasted with the experimental value of 0.74 Å. In fact, the function with the electrons exchanged:

\[
\psi_2 = \psi_B(2)\psi_A(1)
\]

is equally reasonable so mathematics requires us to use the linear combinations:

\[
\psi_+ = C_1(\psi_1 + \psi_2) \quad \text{and} \quad \psi_- = C_1(\psi_1 - \psi_2)
\]

The second of these \( \psi_- \) does not yield a minimum, but the first \( \psi_+ \) gives a bond energy which is about 72% of the observed at \( r_{AB} = 0.87 \) Å, so the approximation is getting better.

The final major improvement is to allow for ionic canonical structures \( H_A^+ H_B^- \) and \( H_A^- H_B^+ \). This generates two more terms to be included in the combinations:

\[
\psi_3 = \psi_A(1)\psi_A(2)
\]

\[
\psi_4 = \psi_B(1)\psi_B(2)
\]

then

\[
\psi'_+ = C_2(\psi_1 + \psi_2) + C_3(\psi_3 + \psi_4)
\]

This gives a bond energy 80% of the experimental value at 0.77 Å. Further, (but more abstract) tinkering with the wave function leads to even better results.
Valence Bond Theory Results for H₂

<table>
<thead>
<tr>
<th>Wave Function</th>
<th>Bond Energy</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed</td>
<td>435 kJ mol⁻¹</td>
<td>0.74 Å</td>
</tr>
<tr>
<td>ψ₁</td>
<td>25</td>
<td>0.90</td>
</tr>
<tr>
<td>ψ⁺</td>
<td>301</td>
<td>0.87</td>
</tr>
<tr>
<td>ψ⁻</td>
<td>No minimum</td>
<td>No minimum</td>
</tr>
<tr>
<td>ψ⁺'</td>
<td>335</td>
<td>0.77</td>
</tr>
</tbody>
</table>

**c. Hybridization**

In all of the examples given above, it was implied that the bonds were formed from the two orbitals joined with a line using a calculation similar to the one described for H₂ in the previous section. 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 ψₐ could be a 2p orbital and ψₖ a 1s orbital in the notes above.) This simple treatment is clearly not adequate because it predicts a HNH 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:

**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 π-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 ψ. The signs/colours 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/colours of the p-orbital to be reversed and the hybrid on the left results. The other results from the second equation:

In the diagrams below, the pair 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 one hybrid is buried deeply inside the main part of the other and is not important in bonding. The right hand diagram shows the two equivalent hybrid enclosure surfaces and hides the internal structure.
**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\(^\circ\) to each other. The \(p_z\) orbital will be left to hold a lone pair or participate in π-bonding. The diagram below shows the 2s, 2px and 2py orbitals superimposed in the same space before hybridization. They are combined to form the hybrids according to the equations which follow the diagram:

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

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:
**Tetrahedral sp^3 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:

\[
\begin{align*}
\psi_1 &= \frac{1}{\sqrt{4}} \psi_s + \frac{1}{\sqrt{4}} \psi_{p_x} + \frac{1}{\sqrt{4}} \psi_{p_y} + \frac{1}{\sqrt{4}} \psi_{p_z} \\
\psi_2 &= \frac{1}{\sqrt{4}} \psi_s - \frac{1}{\sqrt{4}} \psi_{p_x} - \frac{1}{\sqrt{4}} \psi_{p_y} + \frac{1}{\sqrt{4}} \psi_{p_z} \\
\psi_3 &= \frac{1}{\sqrt{4}} \psi_s + \frac{1}{\sqrt{4}} \psi_{p_x} - \frac{1}{\sqrt{4}} \psi_{p_y} - \frac{1}{\sqrt{4}} \psi_{p_z} \\
\psi_4 &= \frac{1}{\sqrt{4}} \psi_s - \frac{1}{\sqrt{4}} \psi_{p_x} + \frac{1}{\sqrt{4}} \psi_{p_y} - \frac{1}{\sqrt{4}} \psi_{p_z}
\end{align*}
\]

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.

**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 π-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 π-bonding.

d. **The Examples Revisited**

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 π-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 sp^3 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 sp^3 (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 H₃O⁺ and CH₃⁻.
Methane - CH\textsubscript{4}

With four hydrogens bound to carbon and no lone pairs, the structure is predicted to be tetrahedral, and the appropriate hybridization would be sp\textsuperscript{3}.

Some isostructural molecule/ions are BF\textsubscript{4}\textsuperscript{-} and NH\textsubscript{3}\textsuperscript{+}.

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 COCl\textsubscript{2}, the appropriate hybridization, sp\textsuperscript{2} 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 - NO\textsubscript{3}\textsuperscript{-}

The predicted geometry is trigonal because there are three oxygens bound to nitrogen, and no lone-pairs. The appropriate hybridization is sp\textsuperscript{2}. 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 - BCl$_3$

The appropriate hybridization is sp$^2$ since the boron is attached to three "things". In certain cases (for example BF$_3$), 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 - ClF$_3$

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 sp³d². 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: TeCl₅⁻ and XeF₅⁺.

**Carbonyl Chloride (Phosgene) - COCl₂**

The two chlorines and the oxygen require four unpaired electrons for bonding on the carbon, ie 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 - SOC₁₂**
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 sp$^3$, 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 σ bonds is sp$^3$, leaving the two d orbitals for use forming the π 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.

e. **Bond Lengths and Covalent Radii**

There are several points to be made here:

a. 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:

\[
d_{\text{Cl-Cl}} \text{ (in Cl}_2\text{)} = 1.988 \, \text{Å} \text{ therefore } r_{\text{Cl}} = 0.99 \, \text{Å}
\]
\[
d_{\text{C-C}} \text{ (in diamond)} = 1.54 \, \text{Å} \text{ therefore } r_{\text{C}(\text{single bond})} = 0.77 \, \text{Å}
\]
Predicted \(d_{\text{C-Cl}} = r_{\text{C}(\text{single bond})} + r_{\text{Cl}} = 0.99 + 0.77 = 1.76\) 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.

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

\[
d_{\text{N≡N}} = 1.10 \, \text{Å} \quad d_{\text{N=N}} = 1.25 \, \text{Å} \quad d_{\text{N-N}} = 1.45 \, \text{Å}
\]

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

c. 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:

\[
r_{\text{C}(\text{sp}^3)} = 0.77 \, \text{Å} \quad r_{\text{C}(\text{sp}^2)} = 0.73 \, \text{Å} \quad r_{\text{C}(\text{sp})} = 0.70 \, \text{Å}
\]

d. 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 bond length 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 π-bonding between empty silicon d-orbital and filled fluorine p-orbitals.

f. **Molecular Packing: van der Waals Radii**

This topic was mentioned under atomic properties in Chapter 2.

g. **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, section 3-5 in the text, deals with diatomic species. Section 3-5 treats several more complicated sample systems. **Note:** Dry lab number 4 contains extensive notes relevant to the first of these sections.

**Overlap of Orbitals**

Refer to figure 3-15 in the text and play with the applet (used in dry lab 4) to reproduce the diagrams in the figure. The plus and minus signs of $\psi$ shown in figure 3-15 are represented by red and blue, respectively in the applet's display. Three cases can be considered:

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

This section is covered in the dry lab. 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 $d$-molecular orbital has two such nodes.

**Diatomic molecules H$_2$ and He$_2$**

This section is covered in first part of the dry lab.

**Homonuclear diatomic molecules in general**

This section is mostly covered in the second part of the dry lab. Use the applet to look at the combinations of atomic orbital depicted in text figure 3-21.

**Heteronuclear Diatomic Molecules**

The molecular orbital energy diagram below shows the situation for a homonuclear diatomic combination of two atomic orbitals:
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 $f_1$ and the chlorine 3p orbital that bonds with it (one electron) will be $f_2$. 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 $H^+_1\text{Cl}^-$. The text figure 3-37 shows what might happen for a more complicated situation by comparing $N_2$ with CO. The lines tying each molecular orbital to its atomic parents are omitted for the less important atomic contributor, for example, C 2s is not joined to $\sigma_1$ while O 2s$^\prime$ is not joined to $\sigma_3$. Nevertheless, the ordering of the molecular orbitals and thus the predicted bond orders (triple) are identical for the two molecules.

- **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 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.

**h. Molecular Orbital Theory for Polyatomic Molecules**

Molecular orbital theory can be used to describe the bonding in a molecule completely, including the σ-bonds (see BeH$_2$ below), but often the σ-bonding is described by the valence bond approach including the use of suitable hybridization, and molecular orbital theory is used to describe the π-bonding orbitals (see CO$_3^{2-}$ below).

There are several methods of setting up the molecular orbital description of polyatomic molecules. In the lectures, the method used will be as follows:

**A Linear Triatomic - BeH$_2$**

**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:
To be added (maybe) - an approach to explaining the bonding in compounds with "expanded valence shells" without resorting to the use of d-orbitals by using three-centre 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:

A Trigonal-planar molecule/ion - CO$_3^{2-}$ (or NO$_3^−$ or BF$_3$ which are isoelectronic)
This is a case where the σ-bonding is usually handled with valence bond theory. If the three-fold axis of the molecule/ion is considered the z axis, the σ-bond framework involves hybridizing the carbon 2s 2pₓ and 2pᵧ orbitals (sp²) 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 π-bonding molecular orbitals are formed from the carbon and three oxygen 2p₂ orbitals and there will be six more electrons to accommodate.

Therefore:

a. Separate a central atom from the peripheral atoms bonded to it (ligands).
b. Sketch out the energy levels of the valence orbitals of the central atom and of the ligand atoms.
c. Describe the set of symmetry derived ligand combinations. The derivation of these combinations is beyond the scope of Chem 241, but the results will be shown.
d. Sketch the energy levels of the ligand combinations (which will differ only a little from the atomic levels because the ligands are far apart).
e. Make linear combinations of the suitable atomic orbitals on the central atom with the ligand combinations.
f. Sketch the molecular levels.
g. Distribute the valence electrons according to the aufbau principle and Hund's rule.
h. Work out the bond orders for the equivalent two-centre Lewis style bonds.
i. The central atom is Be and the ligands are the H's.
j. 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.

k. There are two linear combinations of the two hydrogen 1s orbitals:

\[ \psi_1 = \frac{1}{\sqrt{2}}(\psi_{1sH_a} + \psi_{1sH_b}) \] and \[ \psi_2 = \frac{1}{\sqrt{2}}(\psi_{1sH_a} - \psi_{1sH_b}) \]

m. 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 \( \psi_2 \):
The beryllium 2pₓ and 2pᵧ orbitals do not have matching symmetry ligand combinations.

n. These molecular orbitals, including the localized 2pₓ and 2pᵧ orbitals, are shown under BeH₂ on the energy level diagram.

o. As shown on the energy level diagram, the 4 valence electrons electrons are found in σ₁ and σ₂ molecular orbitals which are both bonding 3-centre orbitals.

p. The bond order for one Be-H connection will be:

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

q. 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 sp³ 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.

r. 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 sp³ hybrid on each boron and the bridging hydrogen’s 1s orbital. There are 2 electrons assigned to this system.

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

\[ \psi_1 = \frac{1}{\sqrt{2}}(\psi_{sp³Ba} + \psi_{sp³Bb}) \] and \[ \psi_2 = \frac{1}{\sqrt{2}}(\psi_{sp³Ba} - \psi_{sp³Bb}) \]
t. 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.

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

u. 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\text{bridging} bonds is $\frac{1}{2}$. (The B-H\text{terminal} bonds are "normal" 2-electron - 2-centre Lewis bonds.)

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

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

The diagram below shows the combinations graphically.

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

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

The diagram below show these combinations graphically.
x. The diagram below shows the energy levels in the axial orbital system only. There are two electrons in the bonding orbital (σ) which leads to a bond order of ½ 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.

y. The central atom is carbon and the ligands are oxygen.

z. The atomic orbitals used for the π-bonding system only are shown under C and $2\text{O}^-$, 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.

aa. The three oxygen 2$p_z$ orbitals must form three linear combinations:

$$
\psi_1 = 1/\sqrt{3} \psi_{2p_z}^{\text{Oa}} + 1/\sqrt{3} \psi_{2p_z}^{\text{Ob}} + 1/\sqrt{3} \psi_{2p_z}^{\text{Oc}} \\
\psi_2 = 1/\sqrt{2} \psi_{2p_z}^{\text{Ob}} - 1/\sqrt{2} \psi_{2p_z}^{\text{Oc}} \text{ (no contribution from O}_A) \\
\psi_3 = \sqrt{2/3} \psi_{2p_z}^{\text{Oa}} - 1/\sqrt{6} \psi_{2p_z}^{\text{Ob}} - 1/\sqrt{6} \psi_{2p_z}^{\text{Oc}}
$$
ab. The energy level that these combinations would have is shown below $2O^-$, O (combos) in the figure below.

ac. The carbon $2p_z$ orbital is of the correct symmetry to combine with $\psi_1$.

$$\pi_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_{2p_zC})$$

$$\pi^* = \frac{1}{\sqrt{2}}(\psi_1 - \psi_{2p_zC})$$

This is the only combination involving the carbon so $\psi_2$ and $\psi_3$ remain non-bonding relabelled as $\pi_2$ and $\pi_3$.

ad. The resulting molecular orbitals are shown under $\text{CO}_3^{2-}$ on the energy level diagram below.
ae. 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.

Aromatic Molecules

This section is not in the textbook.

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 $\text{C}_5\text{H}_5^-$ 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:

i. 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.)

ii. 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.

iii. 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.
e. 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.)

$\text{C}_3\text{H}_3^+$

$\text{C}_4\text{H}_4^{2+}$

$\text{C}_5\text{H}_5^- \text{ (cyclopentadienide)}$
C₆H₆ (benzene)
C\textsubscript{7}H\textsubscript{7}\textsuperscript{+} (tropyllium) and C\textsubscript{8}H\textsubscript{8}\textsuperscript{2+}

Do them yourself!

**Bonding in Metals** This material is covered in the notes for [Chemistry 242](#), the wet lab about semiconductors and (briefly) in the text (Chapter 8, pages 249 - 251)

**Recommended Questions from the Text:**

"Study Questions"

"A. Review"

1. Relate these parameters to the "electron density" in the region of overlap.

2 - 7. You should be able to do all these.

8, 9. Use figure 3-26.

10 - 13. You should be able to do these.

14. This question requires rather a long answer, but you should be able to do it.

15, 16. You should be able to answer these.

17. Your answer should include the answer to 16.

18. A very important question. Make sure you can answer it.

19. This question is about van der Waals' radii and actually rather too tricky unless you are really keen!

20. Another important question. Make sure you can answer it.

21. The answer is given in the text is a bit simplistic. It is better just to accept figure 3-26 as the way it is!

"Additional Exercises"

1, 2. You should be able to tackle these.

3, 4. Important questions. Make sure you can answer them.

5. The structure is similar to diborane, that is there are bridging chlorines, but this molecule is not electron deficient. Valence bond theory can deal with it.

6 - 11. More important questions which you must be able to do.

12. You should be able to do this.
Don't bother. You should know the geometry, but hybridization is less useful in describing transition metal complexes bonding. See chapter 23.

A bit too difficult for this course.

You should be able to answer parts (b) (Does the central atom achieve at least an octet?), (c) and (d).

You should be able to answer this.

Another that you must be able to do.

You should be able to do part (a).