Faculty of Science

Unit 3:
Molecules

CHEM 1503
Chemical Bonding and
Organic Chemistry

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Overview

In this unit, we will consider the factors involved in the formation of molecules from atoms—the concept of chemical bonding. We will also examine shapes of molecules, methods of predicting these shapes, and the relationship of molecular shape and properties. Use this overview to gain an idea of the scope of Unit 3. Then, after working through the material in the unit and in your textbook, it would be a good idea to reread this overview to help you summarize the material.

Before you begin, there is one point that requires emphasis here (and again throughout the unit). While working through this unit you will be working with conceptual models. These models are used by chemists to help explain observed facts. The models are not exactly like real molecules, but at times you will find yourself believing they are. Remember, chemical bonding is not the same as putting sticks and balls together. Nor is it the same as drawing Lewis structures and MO diagrams, or deducing VSEPR angles. You must learn to deal with the abstractions of chemical bonding, and the unit commentary will help you to do this.

What exactly is a **chemical bond**? Is it a "thing" that exists, just because we can draw it? No. A chemical bond is an *effect*. All atoms have some attraction for other atoms. But a stable "bond" exists only if this attractive energy exceeds the energy associated with random thermal motion.

A chemical bond forms when electrons spend most of their time between two nuclei. Electrons are the "glue" that holds the nuclei of atoms together. If enough electrons can be fitted together into the right regions of space, then the atoms will "stick together." This simple explanation is all that is needed to account for the phenomenon of bonding, and it applies to both ionic and covalent bonding.

Different kinds of atoms attract electrons to their nuclei to different degrees. In a compound such as LiF or NaCl, the electrons that are shared between the metal and the halogen atom spend most of their time closer to the halogen atom. Such a bond is said to be *polar* or to have *ionic character*. The effect is similar to what you would expect if the interacting atoms were oppositely charged ions. Why do bonds form between some pairs of atoms and not others? There is no simple, definite answer for every possible case. That is because the behaviour of electrons is more complex when more than one atom is involved. Bonding often depends on the balance of a number of competing factors. However, there are several very useful models that possess remarkable predictive powers as long as they are valid. Unfortunately, the simpler the model, the more limited is the range of validity.

G. N. Lewis, an American chemist, proposed the **octet model** in 1916. The model states that, in many stable molecules, each atom can be surrounded by as many as eight valence electrons. If there are eight valence electrons, the atom has a "noble gas" configuration. One, two, or three *pairs* of electrons can be said to constitute a bond between any two atoms. You will use this octet rule when you draw Lewis diagrams, but you should remember that there are a number of exceptions to the rule. You will also find that the octet model lacks the sophistication necessary to explain the physical properties of certain molecules. Two more recently defined models are now commonly used to explain bonding.

The Valence Bond (VB) Model

This model assumes that bonding is a consequence of the interaction between electrons in the outer atomic orbitals of two atoms. Bonds form when a pair of these orbitals (and, hence, the electrons contained in them) occupies the same space between the two atoms. Since the atomic orbitals of the isolated atoms do not possess the right energetic or geometric properties for bonding, the valence bond model assumes that electrostatic interaction between the two atoms distorts the atomic orbitals. They become mixtures, or **hybrids**, of conventional atomic orbitals. When two of these hybrid atomic orbitals encompass the same region of space, they are said to "overlap." The geometric properties of these orbitals determine the geometry of the molecule as a whole. The VB model is widely applicable and predicts bond formation, shapes of molecules, and many other bond properties as well. An understanding of the valence bond hybridization model is essential in the study of organic chemistry.

The Molecular Orbital (MO) Model

The MO theory is the more general model. The various orbitals of an isolated *atom* are determined by the central force field of the nucleus. However, the orbitals in a *molecule*, called **molecular orbitals**, result from the more complicated arrangement of positive nuclei in an aggregate of several atoms. These orbitals are related to the molecule as a whole, rather than to the original atoms. Valence electrons are distributed among molecular orbitals according to the same rules that apply to atoms. The MO model provides the most satisfying explanation of why electrons do or do not arrange themselves to form bonds. It is the only model that permits actual numerical calculations of such measurable properties as bond strength. In this unit, you will use the MO model to take a detailed look at bonding in relatively simple molecules where the model can be easily applied without mathematics.

Learning Outcomes

By the end of this unit, you should be able to:

- Describe ionic bonds.

- Explain the concept of electronegativity and its consequences in bonding.

- Draw Lewis structures for molecular and ionic species.

- Calculate formal charges of atoms in molecules and ions.

- Explain the concept of resonance.

- Use bond dissociation energies to calculate reaction enthalpies.

- Use the VSEPR model to deduce molecular geometry of molecules.

- Predict which molecules will possess a dipole moment.

- Use the hybridization method to deduce molecular geometry of molecules.

- Describe sigma (σ) and pi (π) bonds.

- Explain valence bond (VB) and molecular orbital (MO) theories of bonding and the difference between them.

- Draw MO energy level diagrams for the homonuclear diatomic molecules and ions of the first ten elements of the periodic table, and deduce the number of bonds and the paramagnetism of these species.

Ionic Compounds

Lewis Dot Symbols

Study Section 9.1 of your textbook. Note that all representative elements in, for example, group 5A have the same arrangement of Lewis dots showing their valence electrons. Generally, you do not draw Lewis dot structures for transition element atoms since they do not have completely filled inner (*d* orbital) shells.

Formation of Ionic Compounds

Study Section 9.2 of your textbook. Work through Example 9.1 and its practice exercise.

Lattice Energy

Study Section 9.3 of your textbook. You do not have to memorize Coulomb's law. Salts are a class of compounds that form solid crystals. The crystals are usually made up of metals combined with nonmetals (NaCl is the most common example). These crystals have properties that suggest they consist of an extended array of oppositely charged ions. Such an array is called a **lattice**. Because each ion in the crystal is electrostatically attracted to ions of opposite charge, the whole arrangement is held together very tightly. That is why ionic solids usually have very high melting points.

Chemists often say that these crystalline solids are held together by "ionic bonds." Most textbooks discuss ionic bonds and covalent bonds separately. It is important that you understand, however, that *all* chemical bonding is electrostatic in nature, and results from electron sharing between atoms. Electrons move simultaneously between two nuclei, helping to hold them together by electrostatic attraction. **Ionic bonding** represents an extreme case where electrons are much more closely associated with one atom than with the other. Other than this, there is no fundamental difference between *ionic* and *covalent* bonding. However, the distinction is one that has been traditionally made by chemists.

No bond is completely ionic. There is always some electron sharing, and thus some covalent character. The model of ionic solids consisting of ions is a useful approximation, but not an accurate one. Your textbook refers to the "transfer" of electrons, but this is an over-simplification. The salt lithium fluoride, LiF, is considered to be highly ionic (84% ionic character). Experimental evidence shows that, in LiF, the electron that is "lost" by the Li atom resides at an average distance of 0.156 nm from the Li nucleus. In a neutral, gaseous Li atom, the average distance of the same electron is 0.252 nm. Thus, in LiF, the "lost" electron is closer to the Li nucleus than in the isolated Li atom. The electron can only be considered "lost" in the sense that it is more closely associated with the fluorine atom than the lithium atom.

The steps involved in the formation of ions and ion pairs are summarized in Figure 3.1 of this unit. This figure is for solid sodium chloride and is analogous to Figure 9.2 in your textbook where lithium fluoride is used. Such figures are known as **Born-Haber diagrams** or **Born-Haber cycles**.
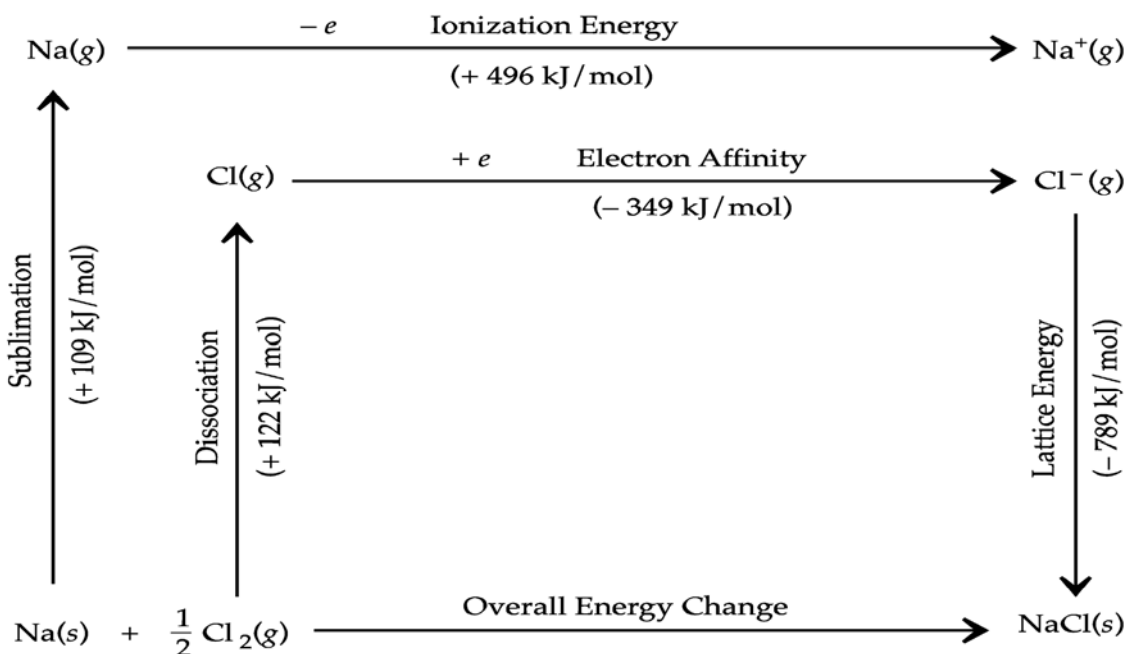
$$Na(g) \xrightarrow[\quad(+496 \text{ kJ/mol})\quad]{-e \quad \text{Ionization Energy}} Na^+(g)$$

$$Cl(g) \xrightarrow[\quad(-349 \text{ kJ/mol})\quad]{+e \quad \text{Electron Affinity}} Cl^-(g)$$

Sublimation (+ 109 kJ/mol)

Dissociation (+ 122 kJ/mol)

Lattice Energy (– 789 kJ/mol)

$$Na(s) + \frac{1}{2}Cl_2(g) \xrightarrow{\text{Overall Energy Change}} NaCl(s)$$

Figure 3.1: Energies involved in the formation of NaCl(s) from elemental Na(s) and gaseous Cl_2. The overall energy change, -411 kJ/mol, is the sum of that in all the processes involved.

Covalent Bonds

Study Section 9.4 in your textbook. Figure 3.2 in this unit shows how the location of the single electron in the simplest possible molecule, H_2^+, determines whether the net force between the two nuclei is attractive or repulsive.

Electronegativity and Bonding

If electrons in a covalent bond are equally shared, the bond is considered to be completely covalent or **nonpolar**. This occurs when both atoms involved in the bond are identical (for example, homonuclear diatomic molecules such as H_2 and Br_2). When the two electrons of the bond are not shared equally, a **polar** bond results.
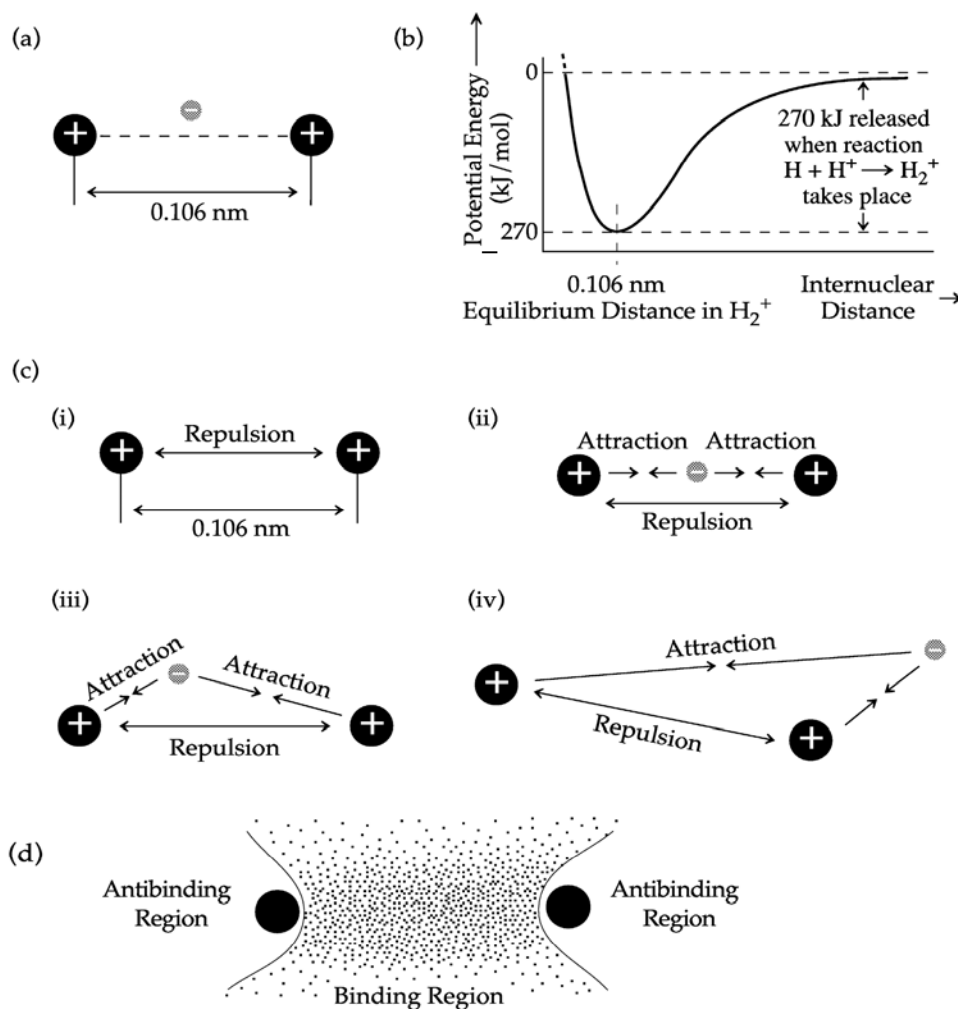
Figure 3.2: Bonding in the simplest molecule, H_2^+.

(a) Although H_2^+ can be thought of as derived from one H^+ and one H atom, the positive charge is associated with the species as a whole—the proton and the H atom have no discrete existence within the H_2^+.

(b) The potential energy curve for the H_2^+ molecule. Note the energy scale. Zero near the top denotes no interaction, while potential energies greater than zero represent repulsion.

(c) Balance between electrostatic attractions (unlike charges) and repulsions (like charges) in the H_2^+ molecule. In (i) two bare protons (H^+) at 0.106 nm repel each other. In (ii) and (iii) an electron has been added, bringing with it *two* electron-proton attraction components that just balance out the repulsion at the equilibrium internuclear distance. In (iv) the electron is no longer in a position to contribute to the binding of the two nuclei, but actually helps to force them apart.

(d)   Since H_2^+ is known to be a stable molecule, the electron must spend most of its time in the binding region (the shaded area), with its probability most highly concentrated along the internuclear axis. An electron that spends most of its time in the antibinding region is said to occupy an **antibonding orbital**.

Study Section 9.5 in your textbook and make sure you have a thorough understanding of the concept of **electronegativity**. It is the ability of a bonded atom to attract electrons to itself. Ionization energy and electron affinity can be measured directly, but electronegativity cannot. It is a relative value, assigned to atoms depending on how they behave in various bonds. The most common set of assignments is known as the **Pauling electronegativities**. You can find these in Figure 9.5 of your textbook. You do not need to memorize these values, but you should know that fluorine is the most electronegative element, followed by oxygen and then chlorine. Metals have low electronegativities. Low electronegativity can be equated with high **electropositivity**, a metallic property. Note that cesium and francium are the most metallic elements listed. It is important for you to realize that electronegativity values are assigned and not directly measured. Pauling could have assigned a number other than 4.0 as the electronegativity value of fluorine; then all the electronegativities of the other elements would be different. However, this electronegativity value of fluorine is now widely accepted.

Electronegativity differences between two atoms in a bond give an indication of the bond polarity. Your textbook says that a difference of 2.0 or more between the electronegativities of two atoms is associated with the formation of ionic compounds. The value of 2.0 here is not absolute. Other textbooks use the difference of 1.7 and above for ionic formation, so you can see that this rule is not a chemical rule, but rather, a general guide. If the electronegativity difference between two atoms is less than about 0.5, the compound behaves as if there were no electronegativity difference at all. Electronegativity is an important concept and you will often use it in your study of chemistry. Now do Example 9.2 from your textbook and its practice exercise.

Lewis Structures

Lewis structures are an important tool for describing the structure, the bonding, and the shape of molecules.

The Octet Rule

Study Section 9.6 in your textbook and learn how to draw Lewis structures for species (molecules and ions) that obey the octet rule. It is very important to learn and practise the four steps for drawing Lewis structures listed in your textbook as they form the basis of understanding later concepts and ideas in this unit. Here are some additional tips to help you draw these structures:

1.   Note that a single atom in a formula is usually the central atom surrounded by the other atoms, for example CH_4, PCl_3, PCl_5, and NO_3^-. At this point of your chemical education, if the geometry is not obvious, it will be given to you.

2.   Use the periodic table to determine the total number of valence electrons for all atoms in the species. If the species is ionic, then add one electron for each negative charge and subtract one electron for each positive charge.

3.   Assign electrons in pairs. Each dash represents a pair of shared electrons known as a bonding pair (or a bond pair). An electron pair assigned to an atom (and not shared as in a bond) is designated as ":" and is known as a lone pair.

4.   Note that two or three pairs of electrons shared between atoms (i.e., = or ≡) represent double bonds and triple bonds, respectively.

Again, the best way to learn to draw Lewis diagrams is to do some examples and practise. With this in mind, work through the following problems.

Problem: Write a Lewis structure for carbon tetrachloride, CCl_4.

Solution: Where there is a single atom in the formula (usually the least electronegative atom), you can assume that it is the central atom unless told otherwise. So the skeleton formula is:

$$
\begin{array}{ccc}
 & Cl & \\
Cl & C & Cl \\
 & Cl & \\
\end{array}
$$
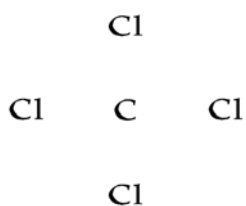
The total number of valence electrons is 32. (Carbon has 4, and each of the 4 chlorines has 7. That is, $4 + 4(7) = 4 + 28 = 32$.) Now assign bond pairs:

$$
\begin{array}{c}
\text{Cl} \\
| \\
\text{Cl} - \text{C} - \text{Cl} \\
| \\
\text{Cl}
\end{array}
$$
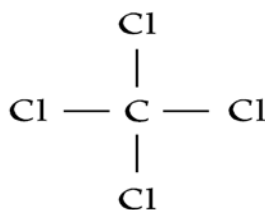
This partial structure has now used up 8 electrons (as 4 bond pairs). This leaves 32 − 8 = 24 electrons still to be distributed. Begin by assigning lone pairs of electrons around the chlorine atoms, so that each chlorine obeys the octet rule and the remaining 24 electrons are arranged as shown:

$$
\begin{array}{c}
:\ddot{\text{Cl}}: \\
| \\
:\ddot{\text{Cl}} - \text{C} - \ddot{\text{Cl}}: \\
| \\
:\ddot{\text{Cl}}:
\end{array}
$$
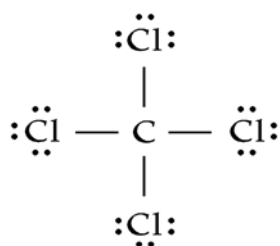
In summary, 12 lone pairs + 4 bond pairs = 16 electron pairs or 32 electrons, with all atoms obeying the octet rule, including the central carbon atom.

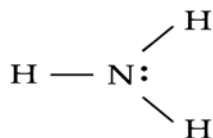**Problem:** Draw the Lewis structure for ammonia, NH_3.

Solution: Assume that the lone nitrogen is the central atom.

$$
\begin{array}{ccc}
 & & \text{H} \\
\text{H} & \text{N} & \\
 & & \text{H}
\end{array}
$$
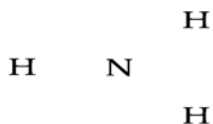
The total number of valence electrons is 8 (5 from nitrogen and 1 from each of 3 hydrogens). Now assign bond pairs:

$$
\text{H} - \text{N} \diagdown^{\text{H}}_{\text{H}}
$$
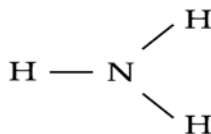
This partial structure has used up 6 electrons (as 3 bond pairs). This leaves 8 − 6 = 2 electrons still to be distributed. The 3 hydrogens are exceptions since they have the same electron configuration as helium and only require 2 electrons to complete their valence shell—the "duet" rule. So the remaining 2 electrons are assigned to the nitrogen, as a lone pair, to complete its octet as shown:
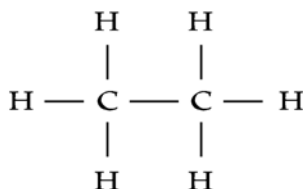
H
/
H — N:
\
H

Problem: Draw the Lewis structure for ethane, C_2H_6.

Solution: Since hydrogen can bond to only one other atom to complete its duet, the two carbons must be bonded to each other, giving a skeleton formula:

```
      H    H

 H    C — C    H

      H    H
```
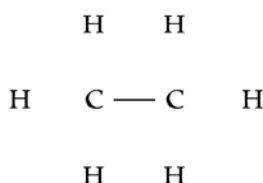
The total number of valence electrons is 14 as there are 4 from each carbon and 1 from each hydrogen atom: $2(4) + 6(1) = 14$. Now assign bond pairs:

```
      H    H
      |    |
 H — C — C — H
      |    |
      H    H
```

This structure has used up all the 14 electrons (as 7 bond pairs). Each atom satisfies the octet (or duet) rule so the Lewis structure contains all bond pairs and no lone pairs.

Problem: Draw a Lewis structure for ethylene, C_2H_4.

Solution: Again the 2 carbon atoms must be bonded to each other:

```
   H              H

       C — C
   H              H
```
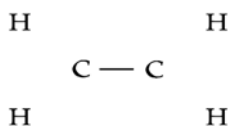
The total number of valence electrons is $2(4) + 4(1) = 12$. Now assign bond pairs:

```
  H\        /H
     C — C
  H/        \H
```
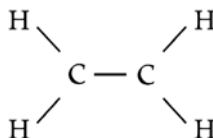
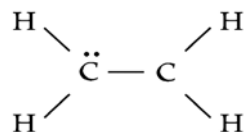This uses up 10 electrons (as 5 bond pairs) and leaves 2 electrons. If these 2 electrons are assigned as a lone pair on one of the carbon atoms,

$$
\begin{array}{ccc}
H & & H \\
\diagdown & & \diagup \\
& \ddot{C} - C & \\
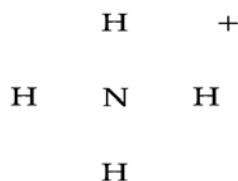\diagup & & \diagdown \\
H & & H
\end{array}
$$

the other carbon atom will not obey the octet rule. You are 2 electrons short of completing the octet. This means that you must use a double bond (i.e., the carbon atoms share 2 pairs of electrons), as shown:

$$
\begin{array}{ccc}
H & & H \\
\diagdown & & \diagup \\
& C = C & \\
\diagup & & \diagdown \\
H & & H
\end{array}
$$
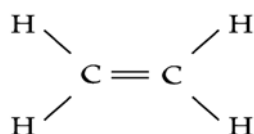
Problem: Draw the Lewis structure for the ammonium ion, NH_4^+.

Solution: Nitrogen is the central atom:

$$
\begin{array}{ccc}
& H & + \\
H & N & H \\
& H &
\end{array}
$$

The total number of valence electrons is 8 (5 from the nitrogen, 1 each from the hydrogen atoms and subtract 1 for the positive charge: $5 + 4(1) - 1 = 8$). Now assign the bond electrons:

$$
\begin{array}{ccc}
& H & + \\
& | & \\
H - & N & - H \\
& | & \\
& H &
\end{array}
$$
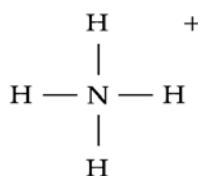
You can see that the 8 valence electrons available are used as 4 bond pairs in this Lewis structure and all our octets and duets are satisfied.

Now work through Examples 9.3, 9.4, and 9.5 from your textbook, and their practice exercises.

Formal Charge and Resonance

Study Sections 9.7 and 9.8 in your textbook. Formal charge can be used to give an approximate picture of the way electrical charge is distributed over a molecule. It is also useful in selecting the most likely of several possible Lewis diagrams for a given compound. Work through Examples 9.6 and 9.7 and their practice exercises. It might help you to remember (informally) how to determine formal charge on atoms in Lewis structures by asking: "Does an atom have more valence electrons (a negative formal charge) or less valence electrons (a positive formal charge) than it started off with?" This can be thought of in equation form as follows:

$$\text{formal charge} = \begin{matrix}\text{number of valence electrons} \\ \text{an atom came with}\end{matrix} - \begin{matrix}\text{number of valence electrons} \\ \text{assigned in our structure}\end{matrix}$$

where the number of valence electrons assigned in our structure is equal to all the lone pairs of electrons on the atom and half the electrons bonded to the atom. So:

$$\text{formal charge} = \begin{matrix}\text{valence} \\ \text{electrons}\end{matrix} - \left(\begin{matrix}2 \text{ for each} \\ \text{lone pair}\end{matrix}\right) - \left(\begin{matrix}1 \text{ for each} \\ \text{bond pair}\end{matrix}\right)$$

If you can draw more than one *correct* Lewis diagram for a molecule or ion, the actual structure is drawn as something between the diagrams. This phenomenon is known as **resonance**. Students often have two incorrect impressions of resonance structures. First, they believe that the molecule is flipping back and forth between contributing structures. This is untrue. The symbol $\longleftrightarrow$ does not indicate that the molecule is switching from one form to the other. Second, they believe that the resonance structure is a mixture of all the contributing structures. This is also untrue. One way to explain resonance is to use the analogy of a mule. A mule is a hybrid of a horse and a donkey. Obviously, a mule does not spend half its life as a donkey and the other half as a horse. Nor does a mule have the head of a horse and the body of a donkey. Rather, it is somewhere between a horse and a donkey. Similarly, a resonance hybrid is somewhere between its contributing structures. For example, the contributing structures of HNO_3 are:

The resonance hybrid is neither of these but something in between that could perhaps be drawn as:
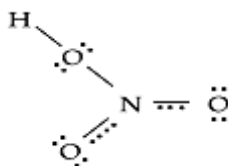
where the ▦ represents a partial double bond or one double bond spread over three atoms. With a structure like this it is not possible to assign all 24 valence electrons exactly.

Remember that resonance does not really occur. It is simply a consequence of the inadequacy of the electron-dot model that requires an electron to be written as a dot in a specific place. In fact, electrons in molecules do not behave as dots, but rather as charge clouds that can extend over a region encompassing several atoms. A more modern approach to this problem is to write "dotted bonds" (just the resonance hybrid) rather than separate contributing resonance structures.

Now work through Example 9.8 from your textbook and its practice exercise.

Exceptions to the Octet Rule

As mentioned earlier, there are a number of cases where the octet rule does not hold (as for hydrogen, for instance). Study Section 9.9 in your textbook. You may be short of electrons to complete an octet, and yet the elements involved (such as hydrogen or the halogens) cannot form multiple bonds. In this case, some octets must be left incomplete.

The atom with the lower electronegativity will have the incomplete octet. Group 3A elements often have incomplete octets when they are in covalent compounds.

Some compounds have more valence electrons than you can use. In such cases, one of the elements in the species can accommodate these extra electrons, either as extra bond pairs or extra lone pairs. Elements that have an atomic number of 14 or greater can have expanded octets to a maximum of 12 electrons (usually 10 or 12 electrons). The explanation for these expanded octets is that such elements may have vacant d orbitals in the valence shell—these are close enough in energy and available for bonding. The elements H to Ne have no d orbitals in the valence shell and cannot have expanded octets. You will learn more about expanded octets later in this unit.

Go over Examples 9.9, 9.10, 9.11, and 9.12 in your textbook, and their practice exercises. Notice the use of formal charge in Example 9.11.

By now you have probably decided that the octet rule is very poorly named. Octet implies 8, and yet for hydrogen and helium the octet rule is satisfied at 2 electrons, and may be satisfied for beryllium at 4, for boron at 6, for phosphorus at 10, and for sulphur at 12. Think of the octet rule as aiming for noble gas configuration rather than for 8 electrons. The word "octet" is used for historical and traditional reasons. You can consider expanded and incomplete octets as terminology rather than as exceptions to an absolute rule.

At this point, you should be able to draw Lewis structures for simple molecules. Sometimes students are so busy learning rules for drawing structures that they forget a simple fact—rules are simply tools that chemists use to understand the relationship between bonding and molecular properties. The following examples should help you see how Lewis structures are used. These examples also show the distinction between stability and reactivity.

1. Draw the Lewis structure for HF. Note that the octet rule applies to the F, but the H atom "seeks" an He configuration (a duet).

2. The hydroxyl molecule (OH) has the following Lewis structure:

    $$\text{H} \text{---} \ddot{\underset{\displaystyle \cdot}{\text{O}}}\,\text{:}$$
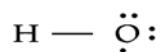
    It is highly reactive since it has an unpaired electron. This molecule can react with an H atom to form H_2O, or with another OH to form hydrogen peroxide, H_2O_2. Molecules or atoms with unpaired electrons are often known as **radicals** or **free radicals**.

3. The molecules CH, CH_2, and CH_3 are unstable. You can deduce this because you can draw Lewis structures with electron pairs between the carbon and each hydrogen.
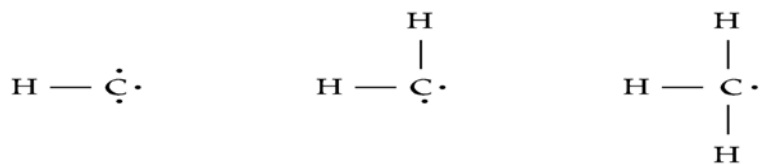
    However, these species are highly reactive. They cannot exist by themselves since they react with themselves. Methane, CH_4, is stable but unreactive. There are no unpaired electrons in CH_4.

4.   In O_2, CO_2, and N_2, the octet rule leads to multiple electron pairs. Practise drawing their Lewis structures and see that you can interpret this as multiple bonds. The experimental evidence suggests that such bonds are stronger than "single bonds," so the interpretation seems valid. The more electrons there are between the nuclei, the lower the potential energy and the more stable the resulting molecule.

In this unit, we spend quite a bit of time on Lewis structures. However, you should be aware that there are a number of shortcomings in the model. The diagram for O_2 represents the electrons as paired up, but experimental evidence shows that there are two unpaired electrons in this molecule. You cannot write satisfactory electron dot structures for a number of stable molecules (e.g., O_2 and HF_2^-). However, you can write correct Lewis structures for nonexistent molecules (e.g., O_4, FO_3^-, and NO_4^-). The Lewis model is not always sophisticated enough to correlate molecular properties with structure, but it helps us along the road to understanding bonding in molecules.

Strength of Covalent Bonds

Study Section 9.10 in your textbook. Be sure that you understand why bond dissociation energies for diatomic molecules are given to more significant figures (in Table 9.4 of your textbook) than for the average bond energies. Work through Examples 9.13 and 9.14, and their practice exercises.

Use the summary at the end of Chapter 9 to ensure that you know the basic concepts explained there.

Molecular Geometry

Study the part of Section 10.1 of your textbook that deals with molecular geometry. You must know the five geometric shapes discussed here and the bond angles associated with them. It may take a little time to be able to visualize the three-dimensional tetrahedral, trigonal bipyramidal, and octahedral shapes. Just ask yourself the question, "How do I arrange 2 (or 3, 4, 5, or 6) lines leading away from one point so that all the lines form a maximum angle away from each other?" You should then see that two lines are at an angle of 180°, giving a straight line. You can see this in Figure 3.3a of this unit.

In Figure 3.3b, three lines are arranged to make an angle of 120°. This shape is known as **trigonal planar**. When you make an arrangement of four lines at equal angles from each other, you must begin to visualize in three dimensions. The four

lines lead from a point at the centre of a regular tetrahedron as shown in Figure 3.3c. The angle formed by these lines is 109.5°, known as the **tetrahedral angle**; the overall shape is **tetrahedral**. The only case where you do not find equal angles is when you have five lines to arrange from a point. You just have to learn that the resulting shape, shown in Figure 3.3d, is called a **trigonal bipyramid**. You can imagine this shape as something like two tetrahedrons joined at their base. The lines radiate from a point in the middle of the central triangle. Three **equatorial** lines form a triangular plane with angle of 120°. There are two **axial** lines, one above this plane and one below, with angles of 90° to the three equatorial lines. When you have six lines from a point, the angles between the lines are all 90° or 180° and the shape is **octahedral**, as shown in Figure 3.3e. The octahedron has four equatorial lines and two axial lines. If you rotate the octahedron, then two other lines will become the axial lines.
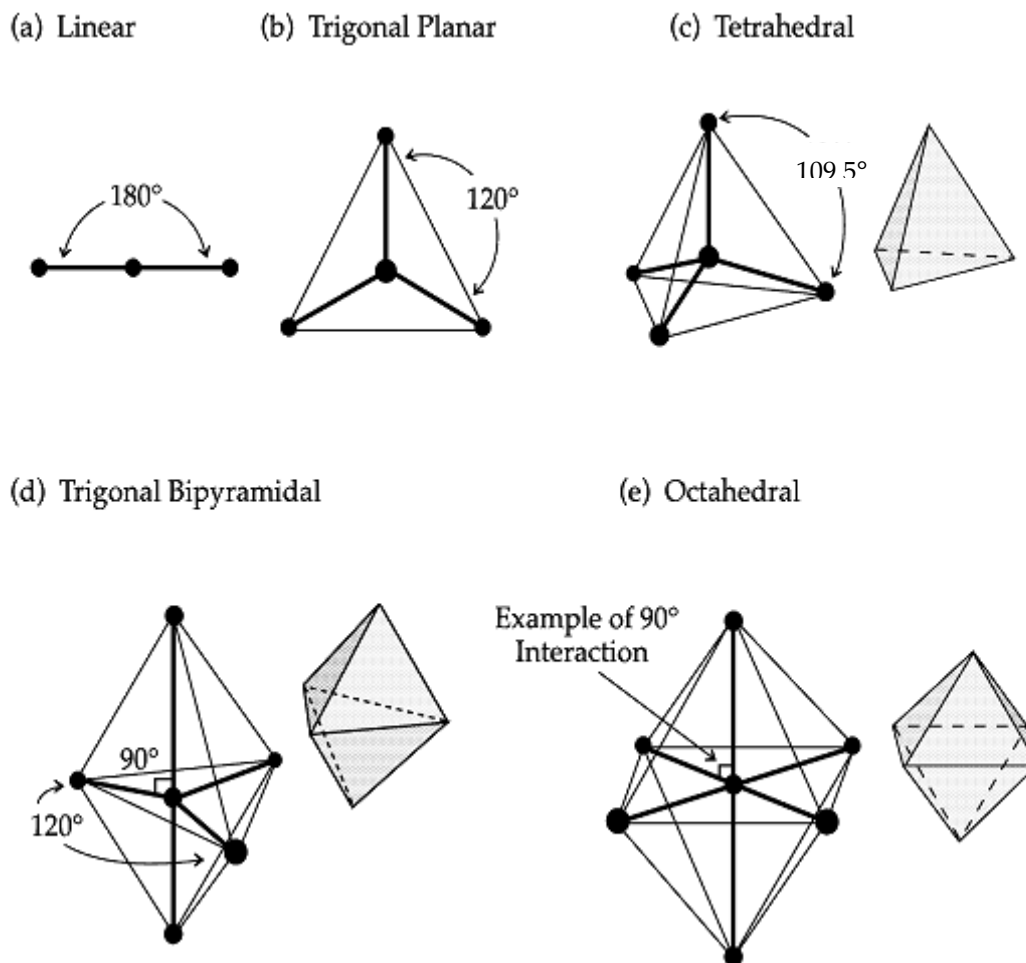
(a) Linear   (b) Trigonal Planar   (c) Tetrahedral

180°   120°   109.5°

(d) Trigonal Bipyramidal   (e) Octahedral

90°   Example of 90°
Interaction

120°

Figure 3.3: Ideal geometric shapes

    a.   linear

    b.   trigonal planar

    c.   tetrahedral

    d.   trigonal bipyramidal

    e.   octahedral. In both (d) and (e) there are 90° interactions between bond pairs.
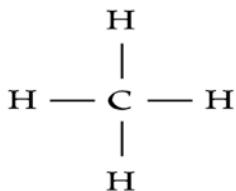
At this stage, if you have a molecular model kit, you should make models of these five ideal geometries. (A simple model kit can be made using soft candies and toothpicks!)
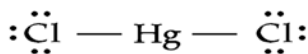
The VSEPR Model

Study the part of Section 10.1 in your textbook that deals with the VSEPR model. Read over the whole section first, then go through it again using Example 10.1 to help you understand how to use the VSEPR approach. The **VSEPR model** relies on the principle that *total repulsion between the valence shell electron pairs around the central atom of a molecule should be minimized.*

Remember that for the purposes of VSEPR, *each multiple bond counts as one bond pair.* Now practise determining the number of electron pairs around the central atom of the following species drawn as Lewis structures.
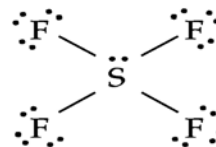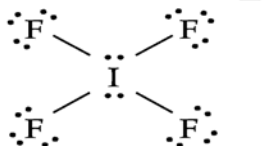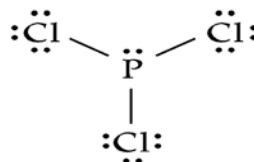
a)

$$H - C - H$$ (with H above and H below the central C)

b)

$$:\ddot{Cl} - Hg - \ddot{Cl}:$$

c)

(structure with S central atom bonded to four F atoms with lone pairs)

d)

(structure with I central atom bonded to four F atoms, bracketed with negative charge)

e)

(structure with P central atom bonded to three Cl atoms)

The answers are: (a) 4; (b) 2; (c) 5; (d) 6; and (e) 4. (a) has 4 bond pairs (or atoms) and no lone pairs around the central C atom. In (b), there are 2 bond pairs and no lone pairs around the central Hg atom. (c) has 4 F atoms and, therefore, 4 bond pairs in addition to the one lone pair around the central S atom. Thus, $4 + 1 = 5$. In (d), there are 4 bond pairs and 2 lone pairs around the central I atom and $4 + 2 = 6$. In (e), there are 3 bond pairs and one lone pair around the central P atom and $3 + 1 = 4$.

When the number of electron pairs around the central atom is made up from bond pairs and lone pairs, you have to consider the difference in repulsions between lone pairs and bond pairs. Note that, because the lone pair "electron cloud" spreads out in space relative to a bond pair of electrons:

repulsions between one lone pair and another lone pair	>	repulsions between a lone pair and a bond pair	>	repulsions between one bond pair and another bond pair

Your textbook uses the terms "lone pair" and "nonbonding pair" interchangeably. You should understand that, although the presence of lone pairs helps to determine the structure of the molecule, its final actual shape is measured by the position of the atoms and, therefore, of the bond pairs. The VSEPR model predicts the directions in which the various bonding and nonbonding orbitals project out from the central atom. Since the nonbonding orbitals have no atoms at the other end, the molecule itself has a less complex shape. A water molecule demonstrates this point. You can consider the oxygen atom as being at the centre of a regular tetrahedron with two bond pairs pointing towards two of the corners of the tetrahedron, and the two lone pairs pointing towards the other two corners. However, the H_2O molecule is not tetrahedral since the shape is measured from where the atoms are and not where the lone pairs are. Consequently, the water molecule is bent as shown in Table 10.2 and Figure 10.1 of your textbook.

In some cases, more than one geometric structure seems possible. If the five electron pairs come from four bond pairs and one lone pair as in the SF_4 molecule, then the trigonal bipyramidal shape can be modified as shown in Figure 3.4 of this unit. What you have to do is to work out which of the two possible arrangements, Figure 3.4b or 3.4c, minimizes the total repulsion between electron pairs in the molecule.

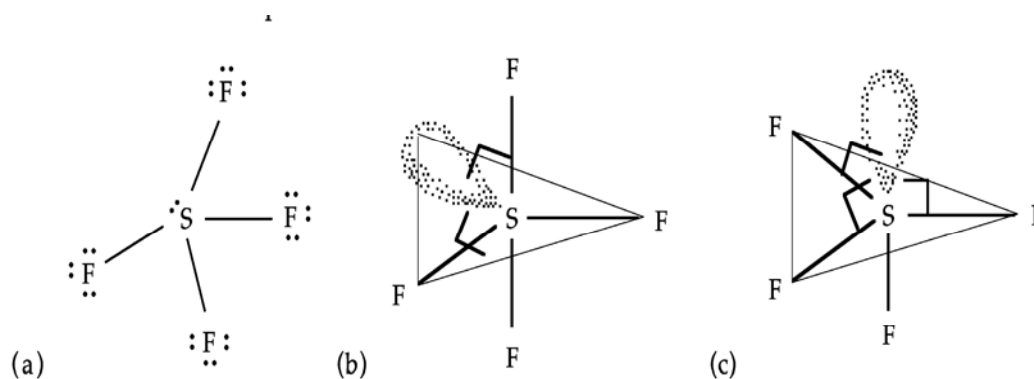**Figure 3.4:** VSEPR model on the SF_4 molecule.

 a. Lewis structure of SF_4.

 b. Arrangement where the lone pair is in the equatorial position.

 c. Arrangement where the lone pair is in the axial position. 90° repulsions are shown as right angles: **L.**

Since there is only one lone pair in SF_4, you do not have any lone pair/lone pair repulsions. But you do have lone pair/bond pair repulsions, and these are greater than bond pair/bond pair repulsions. Now take a look at the structure in Figure 3.4b. The lone pair is in the equatorial position, and there are two lone pair/bond pair repulsions at 90°. (A 90° repulsion occurs when the angle between two bond pairs, or between a bond pair and a lone pair, or between two lone pairs, is a right angle.) Again, in Figure 3.4c, where the lone pair is in the axial position, there are three lone pair/bond pair repulsions at 90°. Since only 90° repulsions need be considered, you can predict that 3.4b has the smaller number of 90° lone pair/bond pair repulsions; therefore, it should be the favoured structure of SF_4. Experimental evidence confirms this prediction; the SF_4 molecular shape is known as a **distorted tetrahedron** (or see-saw.)

If the five electron pairs are due to three bond pairs and two lone pairs, you can apply the VSEPR model to predict the structure of a molecule such as ClF_3. Figure 3.5 in this unit shows the Lewis structure of ClF_3 and its possible molecular geometries. Structure 3.5b has a 90° lone pair/lone pair repulsion. Since you are trying to minimize such repulsions, you can dismiss the structure in 3.5b. Structure 3.5c has six lone pair/bond pair repulsions at 90° (three above the plane of the triangle and three below). Therefore, it is less stable than 3.5d, where there are only four lone pair/bond pair repulsions at 90° (two above the plane of the triangle and two below). Consequently, you predict that the molecular geometry of ClF_3 is T-shaped, as shown in Figure 3.5d. This prediction agrees with the experimentally observed geometry of ClF_3.
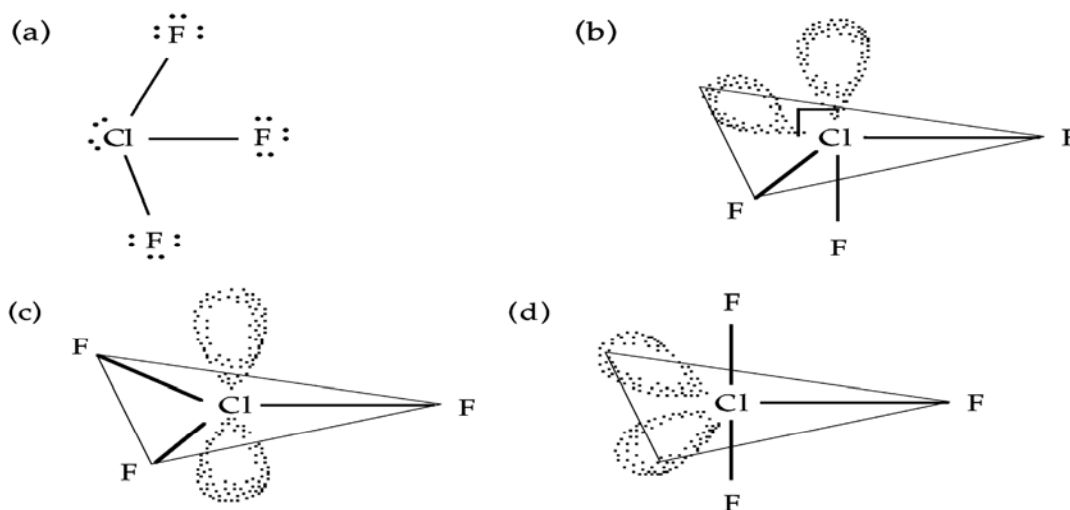

Figure 3.5: VSEPR model on the ClF_3 molecule

a. Lewis structure of ClF_3.

b. Arrangement of bond pairs and lone pairs with one axial and one equatorial lone pair. This arrangement has a 90° lone pair/lone pair interaction.

c. Arrangement with axial lone pairs.

d. Arrangement with equatorial lone pairs. This has the least repulsive interactions at 90° of any of these structures.

The I_3^- ion is an example of five electron pairs from two bond pairs and three lone pairs. Figure 3.6 in this unit shows a Lewis structure of I_3^- and a molecular structure (see 3.6b). Any other arrangement of the three lone pairs and two bond pairs yields a 90° lone pair/lone pair repulsion as in 3.6c. The structure in 3.6b is the only possible arrangement where there are no 90° lone pair/lone pair repulsions. Therefore, it is predicted to be the shape of I_3^-. Experimental evidence confirms that the structure of I_3^- is linear.
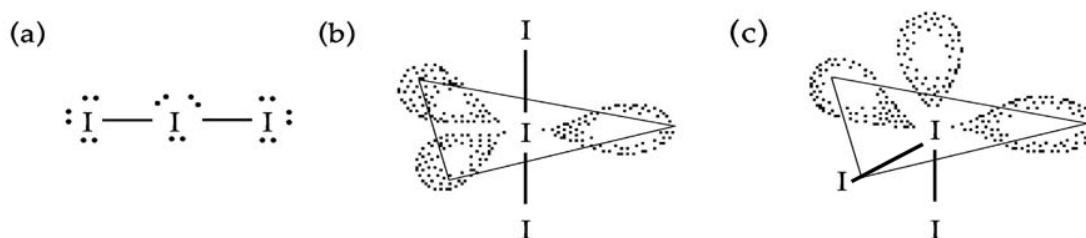
Figure 3.6: VSEPR model on the I_3^- ion

a. Lewis structure of the I_3^- ion.

b. Actual molecular structure of I_3^-. All three lone pairs are equatorial and there are no 90° lone pair/lone pair repulsions.

c. Arrangement with two equatorial lone pairs and one axial lone pair. This ion would have two 90° lone pair/lone pair repulsions.

Table 3.1: Molecular geometry as a function of the distribution of electron pairs.

Number of electron pairs around central atom	Number of bond pairs	Number of lone pairs	Shape of orbitals	Expected configuration of bonded neighbours and unshared pairs		Example
2	2	0	Linear		Linear	$H-C\equiv C-H$
3	3	0	Trigonal planar		Trigonal planar	BCl_3
3	2	1			Bent	SO_2
4	4	0	Tetrahedral		Tetrahedral	CH_4
4	3	1			Trigonal pyramidal	NH_3
4	2	2			Bent	H_2O
5	5	0	Trigonal bipyramidal		Trigonal bipyramidal	PCl_5
5	4	1			Distorted tetrahedron (or See-saw)	SF_4
5	3	2			T-shaped	BrF_3
5	2	3			Linear	I_3^-
6	6	0	Octahedral		Octahedral	SF_6
6	5	1			Square pyramidal	BrF_5
6	4	2			Square planar	XeF_4

(Summary of the VSEPR model.)

You now have to consider the molecular shape of molecules where the number of electron pairs around the central atom is 6. The final molecular shapes are given in Table 3.1 in this unit, but you should try to work out the reasoning behind a prediction of these shapes. This will give you an idea of whether you can apply the VSEPR model by yourself.

Here is a summary of the steps you use when predicting molecular shape:

1. Draw the Lewis structure for the molecule. Obey the octet rule if possible, but remember that you can expand the valence shell of the central atom when the atomic number is 14 or greater.

2. Determine the number of bond pairs and lone pairs around the central atom. Remember that a multiple bond counts as only one bond pair. Select the appropriate arrangement of electron pairs (for 2, the arrangement is linear; for 3, it is trigonal planar; for 4, it is tetrahedral; for 5, it is trigonal bipyramidal; and for 6, it is octahedral).

3. Locate the lone pairs around the central atom so that the repulsions between lone pairs and lone pairs, and between lone pairs and bond pairs, are minimized. You need only consider 90° repulsions and concentrate on minimizing lone pair/bond pair interactions. (There cannot be any 90° lone pair/lone pair structures.) If there are no lone pairs, then of course the geometry of the molecule fits the ideal case.

Now try this process in the following problem. The answers are given in Table 3.1 in this unit, but you should try to make the appropriate VSEPR deductions yourself and then work through the solution before looking up the answer.

Problem: Use the VSEPR model to predict the molecular structure of (a) BrF_5 and (b) XeF_4.

Solution:
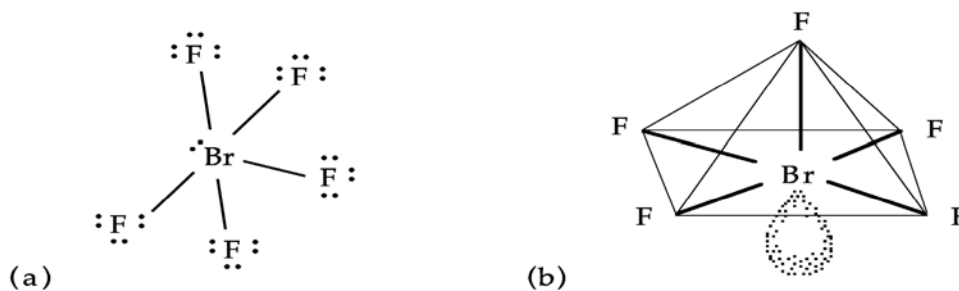
Figure 3.7 (a) Lewis diagram for BrF_5.

(b) Only possible arrangement of 5 bond pairs and 1 lone pair. This gives a square pyramidal geometry to BrF_5.

a. First draw the Lewis structure for BrF_5. There are 7 valence electrons
    from Br and $5 \times 7 = 35$ valence electrons from the F atoms. This gives a
    total of $7 + 35 = 42$ electrons which are arranged as shown in Figure 3.7a in
    this unit. Note that the central Br atom has an expanded octet (5 bond
    pairs and 1 lone pair = 12 electrons). This configuration is allowable for Br
    since its atomic number is greater than 14. The number of electron pairs
    for the central Br atom is 6 (5 bond pairs and 1 lone pair). These 6 valence
    shell electron pairs have an octahedral arrangement. It does not matter
    where you put the lone pair; the molecular structure will always be that
    shown in Figure 3.7b, a shape known as square pyramidal. This agrees
    with information shown in Table 3.1 in this unit.
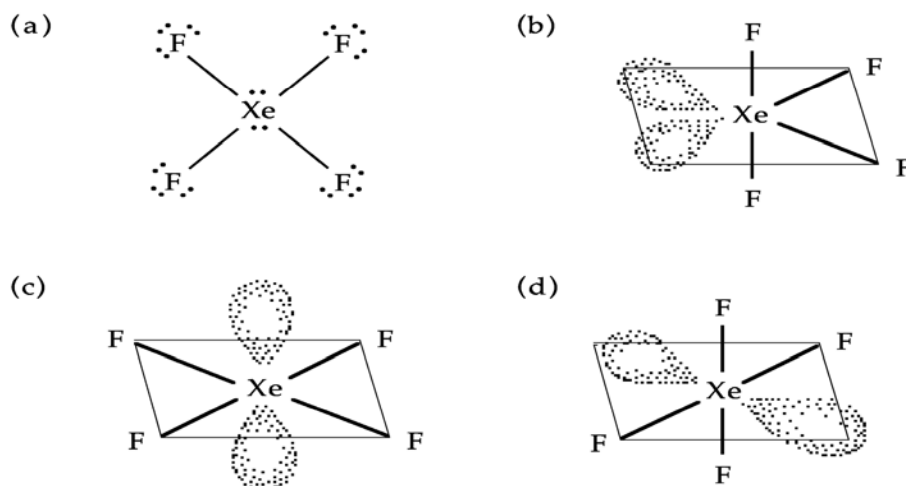
Figure 3.8: VSEPR model on the XeF_4 molecule

a. Lewis diagram of XeF_4.

b. Arrangement where the two lone pairs are at an angle of 90°. Since this is
    the worst possible arrangement for minimizing repulsions, this structure
    can be eliminated.

c. Arrangement where the lone pairs are at 180°. This is the correct
    structure.

d. This structure is equivalent to that shown in 3.8c.

First draw the Lewis structure for XeF_4. Xe contributes 8 valence electrons and the F atoms contribute $4 \times 7 = 28$ for a total of $8 + 28 = 36$. These are arranged as shown in Figure 3.8a. Note that the central atom, Xe, has an expanded octet. The number of electron pairs for the central Xe is 6, from 4 bond pairs and 2 lone pairs. Thus, the basic arrangement for the valence shell electron pairs is octahedral. You can now choose where to put the 2 lone pairs. To minimize lone pair/lone pair repulsions, you should not place them at 90°. This eliminates the structure shown in Figure 3.8b. If the lone pairs are at an angle of 180° from each other, as shown in Figure 3.8c, the lone pair/lone pair repulsion is minimized. Therefore, you can predict that XeF_4 has the structure known as square planar. Experimental observations confirm that the molecular geometry of XeF_4 is square planar. This geometry agrees with Table 3.1 in the unit for 6 electron pairs (4 bond pairs and 2 lone pairs). You should note that the structure in 3.8d is the same as 3.8c, it has just been turned 90°. If you do not understand this idea, try making a model of XeF_4 with your model kit. You should then see that, when you turn it around, 3.8d becomes 3.8c.

Now try Example 10.1 from your textbook and its practice exercise. You will eventually need to know the shapes summarized for you in Table 3.1 of this unit. If you first apply the VSEPR model to a number of different molecules and ions, and you understand why you can predict a particular shape, you will find the memorization process fairly straightforward.

Dipole Moments

Study Section 10.2 of your textbook. You do not need to know the details about measuring dipole moments, but you do need to be able to predict whether or not a molecule is polar, that is, whether it possesses a dipole moment. When deciding whether a molecule is **polar**, consider two conditions:

- Does the molecule have polar bonds?

- Is the geometric shape of the molecule such that the bond moments and/or lone pairs cancel one another?

Now apply these two criteria to the molecules given in Example 10.2 in your textbook and its practice exercise.

Valence Bond Theory

Study Section 10.3 in your textbook. Look back at Figure 3.2 in this unit; it is a more detailed version of Figure 10.5 in your textbook. Notice that the minimum potential energy point corresponds to the bond length. **Valence bond theory** says that bonds are formed when an atomic orbital on one atom overlaps with an atomic orbital on another atom. Generally, there is one electron in each atomic orbital involved in the bond, thus giving two electrons in the bond. However, if an atomic orbital containing two electrons overlaps with an atomic orbital containing no electrons, the result is still a two-electron bond, known as a **coordinate covalent bond**. Although the two electrons of the coordinate covalent bond come from the same atom, the actual bond is no different from other covalent bonds.

Hybridization of Atomic Orbitals

Study Section 10.4 in your textbook. Hybridization is another method of predicting molecular geometry. VSEPR predicts only the final geometry, while the hybridization theory also tries to explain how the bonding occurs. The result of applying the hybridization model will be the same as if you used the VSEPR model, but the method of arriving at the prediction involves modifying the atomic orbitals to form hybrid orbitals. The atoms are thought to retain their atomic orbitals, but these orbitals are distorted as a result of interaction. This results in mixing different types of atomic orbitals, such as s and p, to form hybrid atomic orbitals.

Note that hybrid orbitals cannot be considered *real*—they are merely part of a model. However, you can justify using the model because it can predict a large number of molecular structures. First go through this section in the textbook so that you have some idea about the hybridization method. Then work through the following descriptions of the different hybridized orbitals.

*sp*³ Hybrid Orbitals

One way to understand why chemists developed the theory of hybridization is to consider the ground state electronic configuration of the carbon atom: $1s^2\ 2s^2\ 2p^2$. The valence electrons are the $2s^2\ 2p^2$ electrons.

You can see this in Figure 3.9a in this unit, where only the valence electrons are represented on the energy level diagram. Normally, covalent bonding requires the overlap of two atomic orbitals, each containing one electron. As shown in Figure 3.9a, there would be only two orbitals available for bonding (the two $2p$ orbitals with electrons) if bonding occurred when the atom is in this ground state. Your conclusion should be that carbon atoms form two bonds at 90° from each other.

But it can be shown experimentally that carbon can form four bonds at approximately 109.5° from each other. Therefore, a bonding state of the carbon atom is postulated where there are four electrons, one in each of four equal energy orbitals. This is shown in the bonding energy level diagram for carbon in Figure 3.9b. Here, the four valence shell orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$) have been combined then divided into four equal energy orbitals. This process is known as **hybridization**, and each resulting hybrid orbital is known as an *sp*³ **hybrid orbital**. Since there are four of them, they can each overlap with atomic orbitals of other atoms to form four bonds. These are of equal energy, so they form equal energy bonds in a compound such as CH_4. The hybrid orbitals and, therefore, the bonds are directional. They form 109.5° angles and give a tetrahedral geometry. You should note that it is the orbitals that are considered to be hybridized, not the electrons. The electrons are distributed among the hybridized orbitals.

(a)

$$\underbrace{\overset{1}{—}\quad\overset{1}{—}\quad—}_{2p}$$

$$\underset{2s}{\overset{1\downarrow}{—}}$$

E

(b)

- - - - - - - - - - - - - - - Original p level

$$\underset{sp^3}{\overset{1}{—}}\quad\underset{sp^3}{\overset{1}{—}}\quad\underset{sp^3}{\overset{1}{—}}\quad\underset{sp^3}{\overset{1}{—}}\quad\updownarrow 1$$

$$\downarrow 3$$

- - - - - - - - - - - - - - - Original s level

E

(c)

109.5°
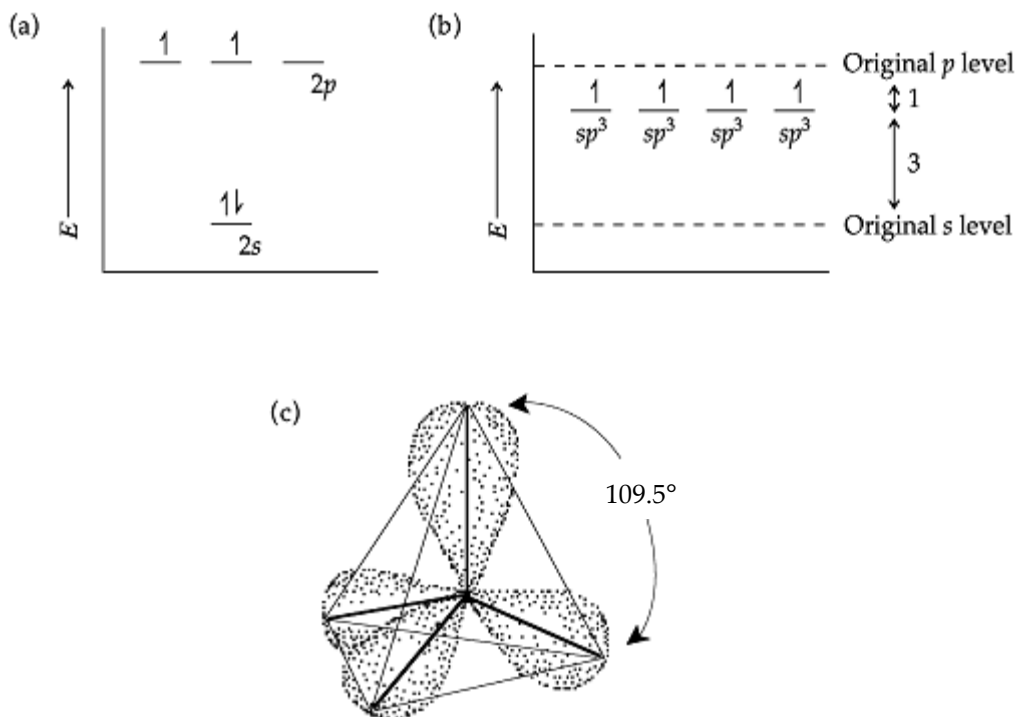
Figure 3.9: sp^3 hybridization of the carbon atom in methane, CH_4

    a.   Energy level diagram of the ground state of the carbon atom. Only the valence electrons are shown.

    b.   Energy level diagram of the bonding (hybridized) state of the carbon atom showing four equal energy sp^3 hybrid orbitals. Note that the sp^3 hybrid orbitals are at an energy level between the original $2s$ and $2p$ levels in the same 1:3 ratio as the one-s : three-p mixture in the hybridization.

    c.   Representation of the four sp^3 hybrid atomic orbitals of carbon, each pointing towards the corner of a regular tetrahedron.

You might now find it helpful to relate the VSEPR and hybridization methods. If the central atom has four electron pairs, then its hybridization is sp^3 and you can deduce the molecular geometry of the molecule. Since the number of electron pairs includes both lone pairs and bond pairs, the hybridization of N in NH_3 and of O in H_2O is sp^3 in both cases. Figure 3.10 in this unit shows the ground state and the bonding state energy level diagrams for N and O in these compounds. One of the sp^3 hybrid orbitals in NH_3 contains two electrons and is therefore a lone pair. The other three orbitals have one electron each and will form bonds. The lone pair hybrid orbital points to one of the corners of a regular tetrahedron and the overall shape of NH_3 is

trigonal pyramidal. Similarly, two of the sp^3 hybrid orbitals of O in H_2O are fully occupied, leaving the other two orbitals available for bonding. This gives the water molecule a bent shape.

(a)

$\underline{1} \quad \underline{1} \quad \underline{1}$
$2p$

$\underline{1\downarrow}$
$2s$

E

(b)

Lone pair

$\underline{1\downarrow} \quad \underline{1} \quad \underline{1} \quad \underline{1}$
$sp^3 \quad sp^3 \quad sp^3 \quad sp^3$

E

(c)

$H \quad N \quad H$
H

(d)

$\underline{1\downarrow} \quad \underline{1} \quad \underline{1}$
$2p$

$\underline{1\downarrow}$
$2s$

E

(e)

Lone pair
Lone pair

$\underline{1\downarrow} \quad \underline{1\downarrow} \quad \underline{1} \quad \underline{1}$
$sp^3 \quad sp^3 \quad sp^3 \quad sp^3$

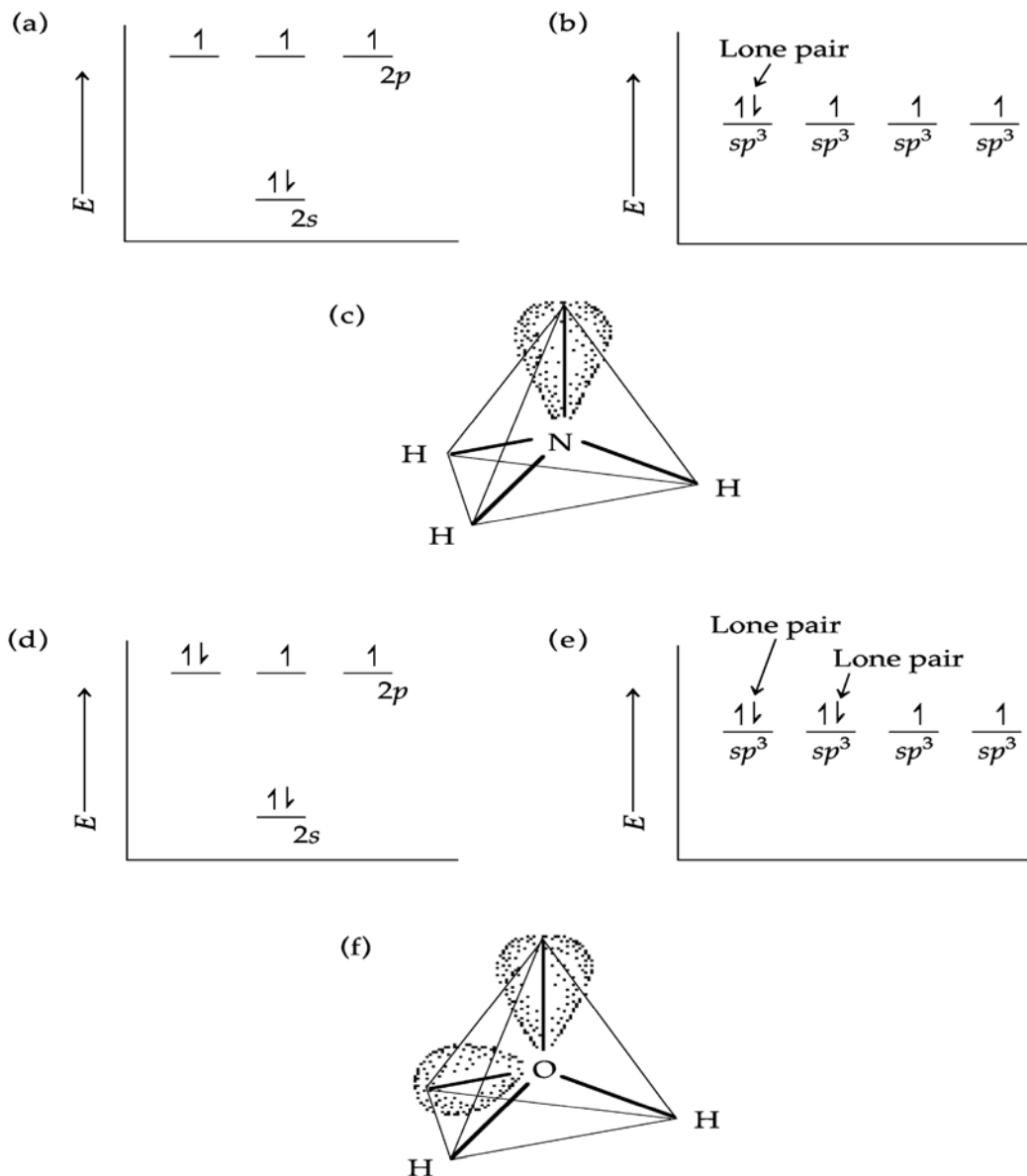E

(f)

O
H
H

Figure 3.10: sp^3 hybridization in NH_3 and H_2O.

   (a) Energy level diagram of the ground state of the nitrogen atom.

   (b) Energy level diagram of the bonding (hybridized) state of the nitrogen atom in NH_3. Two of the five valence electrons occupy the same sp^3 orbital, forming a lone pair.

(c) Representation of the NH_3 molecule showing three bond pairs and one lone pair.

(d) Energy level diagram of the ground state of the oxygen atom.

(e) Energy level diagram of the bonding (hybridized) state of oxygen in H_2O.

(f) Representation of the H_2O molecule. Note the two lone pairs pointing towards the corners of the tetrahedron. The overall molecular shape is said to be "bent."

These examples also demonstrate the inadequacy of the hybridization model. You have to use a "fudge factor" to account for the fact that the bond angles in these molecules are not exactly the 109.5° of the true tetrahedral angle. The bond angle in H_2O is experimentally found to be 104.5° and in NH_3 is 107°. Chemists explain this by saying that the sp^3 hybridization is incomplete. For example, instead of 25% s-character and 75% p-character (our 1:3 ratio seen earlier), the observed shape of the NH_3 molecule corresponds to 7% s-character and 93% p-character.

To summarize sp^3 hybridization, you can assign it to any atom that has 4 pairs of electrons around the central atom (4 bond pairs and 0 lone pairs, 3 bond pairs and 1 lone pair, or 2 bond pairs and 2 lone pairs).

sp^2 Hybrid Orbitals

There are two categories where you can predict sp^2 **hybridization**. The first is when there is an incomplete octet of six electrons around the central atom. The second is when there is a double bond to the central atom. Figure 3.11 in this unit shows the energy level diagrams of the ground and bonding (hybridization) states of B in BF_3. The Lewis structure shows that boron has an incomplete octet (our first category). There are only three valence electrons in boron ($2s^2\ 2p^1$), so only two of the $2p$ orbitals and the one $2s$ orbital are involved in the hybridization. This leaves one unoccupied p orbital. An orbital is only a volume in space where an electron may exist, so an unoccupied orbital is empty space and does not affect hybridization or geometry. We will see the second category, double bonds, later in this unit.

(a)

(b) $2p$ $2s$

(c) Unused p orbital

Original p level

sp^2 sp^2 sp^2

Original s level

(d) 120° 120° 120°
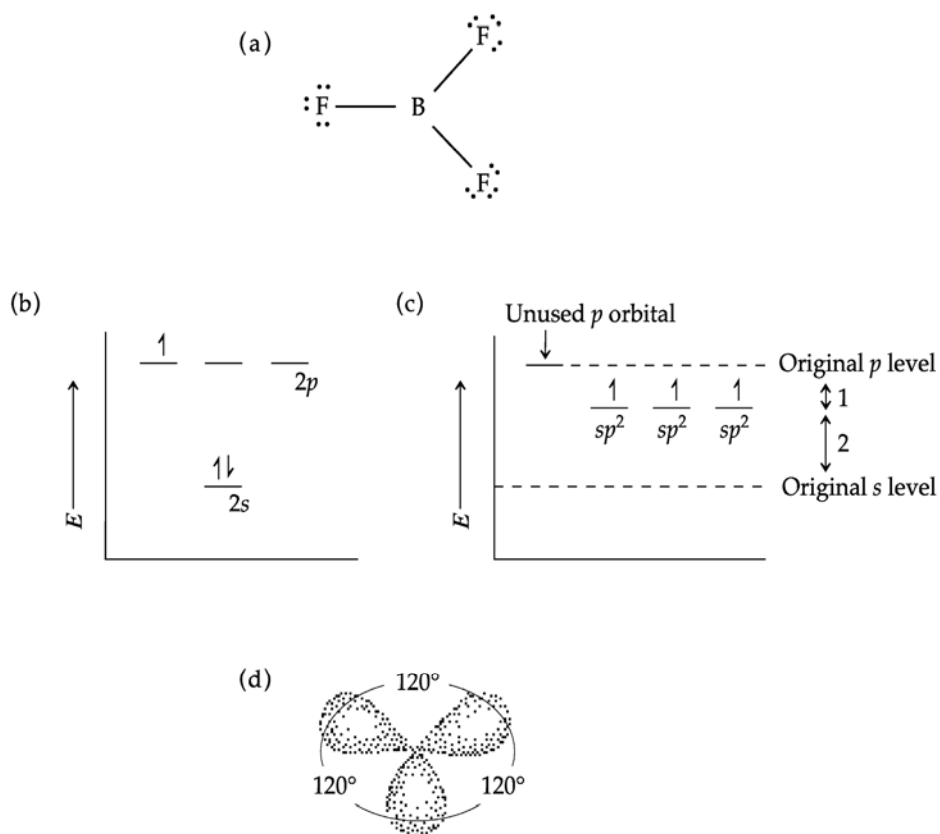
Figure 3.11: sp^2 hybridization in BF_3.

(a) Lewis structure of BF_3.

(b) Energy level diagram of the ground state of the boron atom.

(c) Energy level diagram of the bonding (hybridized) state of boron in BF_3. One of the vacant $2p$ orbitals is not included in the hybridization to form three sp^2 hybrid orbitals. Note that the sp^2 energy level is a 1:2 ratio between the s and the p levels.

(d) The arrangement of the three sp^2 hybrid orbitals at 120° to each other.

sp Hybrid Orbitals

This type of hybridization occurs when the central atom has an incomplete octet of four electrons, as in $BeCl_2$ shown in Figure 3.12 in this unit. It also occurs in compounds with a triple bond. In both of these cases, *sp* hybridization leads to linear geometry with a bond angle of 180°.

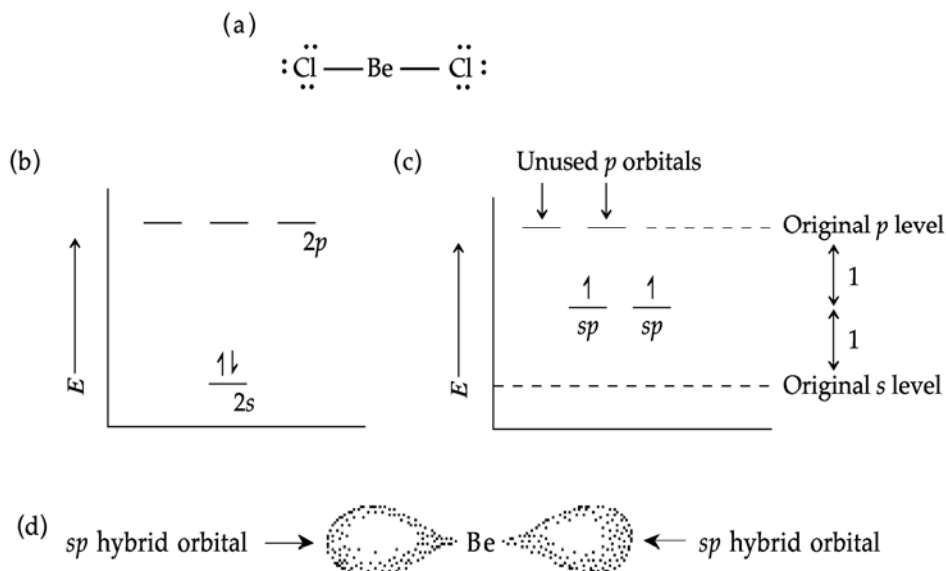**Figure 3.12:** *sp* hybridization in $BeCl_2$.

(a) Lewis structure of $BeCl_2$.

(b) Energy level diagram of the ground state of the Be atom showing two valence electrons.

(c) Energy level diagram of the bonding (hybridized) state of the Be atom in $BeCl_2$.

(d) Representation of the two *sp* orbitals of Be before overlap with the *p* orbitals of chlorine to form $BeCl_2$.

sp^3d Hybrid Orbitals

The hybridization model explains why some atoms have an expanded octet. PCl_5 has five bonds to the central atom as shown in Figure 3.13a in this unit. If you consider the energy level diagram of the valence electrons of phosphorus shown in Figure 3.13b, you see that there are five valence electrons in four orbitals. If you use one of the vacant $3d$ orbitals for hybridization, you end up with five orbitals; each is known as sp^3d and each contains one electron (Figure 3.13c). These hybrid orbitals are arranged at angles of 90° and 120°. The end result, once these hybrid orbitals overlap to give bonds, is a trigonal bipyramidal–shaped molecule. If there are more than five valence electrons on the central atom (for example, ClF_3 as in Figure 3.13e), some of the sp^3d hybrid orbitals are occupied by lone pairs. This corresponds to the VSEPR result shown earlier in this unit in Figure 3.5.

Figure 3.13: sp^3d hybridization.

    (a) Lewis structure of PCl_5.

    (b) Energy level diagram of the ground state of the phosphorous atom.

(c) Energy level diagram of the bonding (hybridized) state of the phosphorus atom in PCl_5. One of the d orbitals has been included in the hybridization.

(d) Representation of the five sp^3d hybrid orbitals of phosphorus.

(e) Lewis structure of ClF_3.

(f) Energy level diagram of the ground state of the chlorine atom.

(g) Energy level diagram of the bonding (hybridized) state of chlorine in ClF_3.

(h) Representation of the molecule of ClF_3 showing the two lone pairs occupying equatorial positions.

sp³d² Hybrid Orbitals

Molecules such as SF_6 have six electron pairs around the central atom and use two *d* orbitals in their hybridization. Figure 3.14 in this unit shows the appropriate energy level diagrams for the central S atom of SF_6. This molecule has bond angles of 90° and the geometry is octahedral. Table 3.2 in this unit expands the previous VSEPR table to show the hybridizations of the central atoms for different numbers of pairs of electrons around the central atom.

Work through Examples 10.3 and 10.4 from your textbook and their practice exercises.
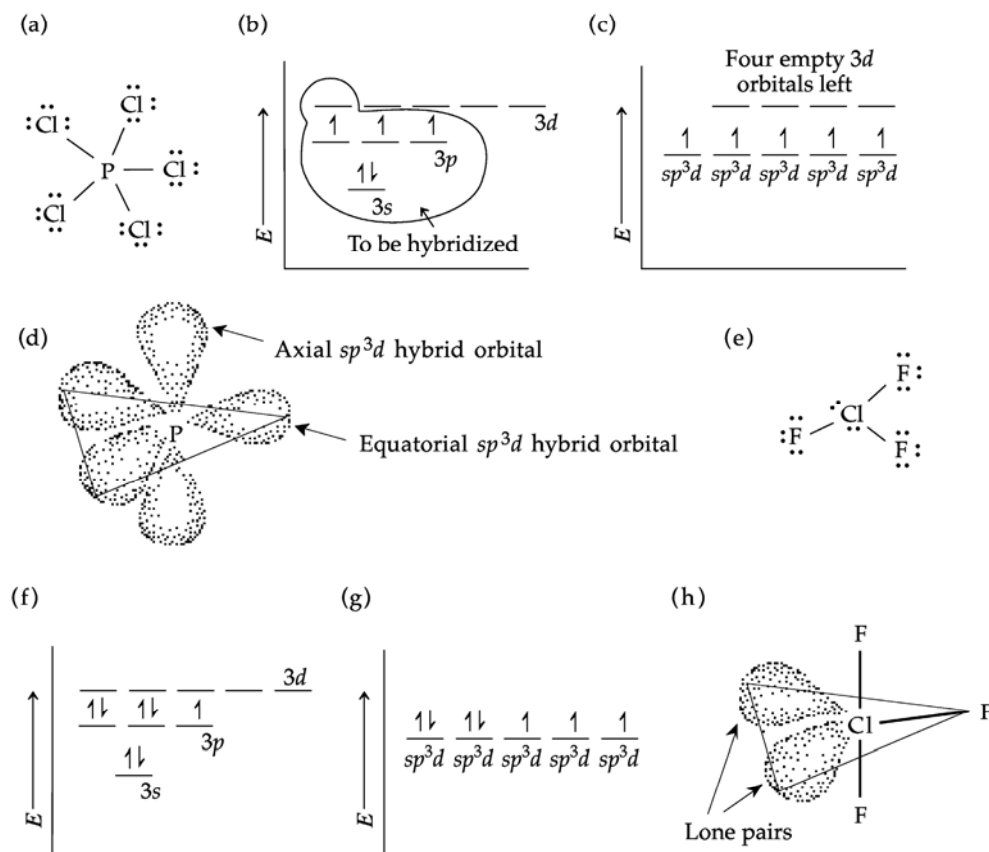
(a)

(b)

(c)

(d)
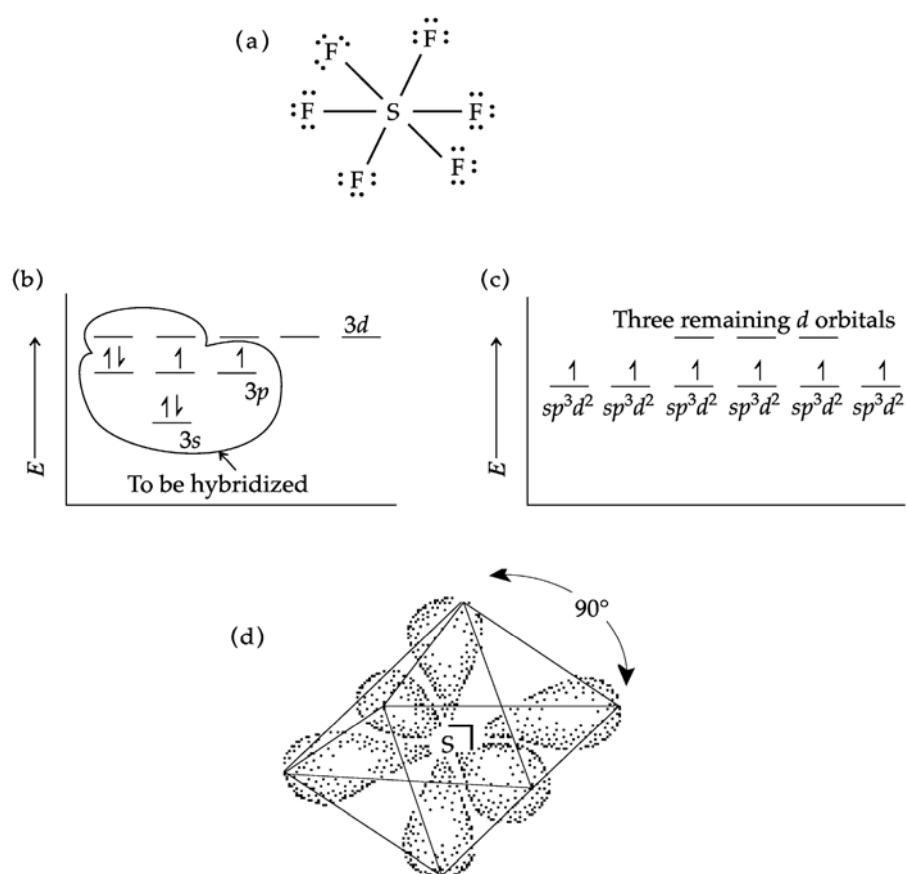
Figure 3.14: *sp³d²* hybridization.

    (a) Lewis structure of SF_6.

    (b) Energy level diagram of the ground state of the sulphur atom.

    (c) Energy level diagram of the bonding (hybridization) state of sulphur in SF_6. Two of the *d* orbitals have been included in the hybridization.

    (d) Representation of the six *sp³d²* hybrid orbitals of sulphur.

Table 3.2: Relationship between the VSEPR model and hybridization.

Number of electron pairs around central atom	Hybridization of the central atom	Molecular shape	Examples
2	sp	Linear	$BeCl_2$, $H–C{\equiv}C–H$
3	sp^2	Trigonal planar	BCl_3, $H_2C{=}CH_2$
		Bent	SO_2
4	sp^3	Tetrahedral	CH_4
		Trigonal pyramidal	NH_3
		Bent	H_2O
5	sp^3d	Trigonal bipyramidal	PCl_5
		Distorted tetrahedron (or See-saw)	SF_4
		T-shaped	BrF_3
		Linear	I_3^-
6	sp^3d^2	Octahedral	SF_6
		Square pyramidal	BrF_5
		Square planar	XeF_4

Note: Remember that *hybridization is something chemists do, not something atoms do!* Hybridization is a method used by chemists to explain structures that result from bonding.

Multiple Bonding

Study Section 10.5 in your textbook. **Bonds** occupy the volume around the internuclear axis. There is only one internuclear axis (i.e., the imaginary line drawn as the shortest distance between the two nuclei involved in the bond), so there can be only one bonding orbital along this **line of centres**. This is an important point. The way we achieve **double** and **triple bonds** is as follows:

double bond: one sigma (σ) bond and one pi (π) bond

triple bond: one sigma (σ) bond and two pi (π) bonds.

The representations of a double bond as = and a triple bond as ≡ are misleading. These symbols could be misinterpreted as representing two or three equal parts to each bond. The use of = or ≡ is not intended to say anything about the actual composition of these multiple bonds. **Sigma bonds** are always formed from a maximum overlap of the contributing atomic orbitals such as *s*, *p*, *d*, or hybrid orbitals. Except for the spherical *s* orbitals, these other atomic orbitals are directional; therefore, maximum overlap means head-on overlap to form the σ bond.

Pi bonds normally do not form unless there is also a σ bond present. Thus, if two atoms are joined by a single bond, that bond must be a σ bond. A π bond is only present as part of a multiple bond. It cannot occupy the space around the internuclear axis. Pi bonds are formed from only one type of atomic orbital and only in one specific way. Figure 3.15 in this unit shows π bond formation from the *sideways overlap of parallel* p *orbitals*. In the formation of these multiple bonds, each atom supplies one electron for each bonding molecular orbital. There are no coordinate covalent π bonds. The material that you have just covered on σ and π bonds, what they are and how they are formed, is very important. You must know (i.e., understand and memorize) the details described.
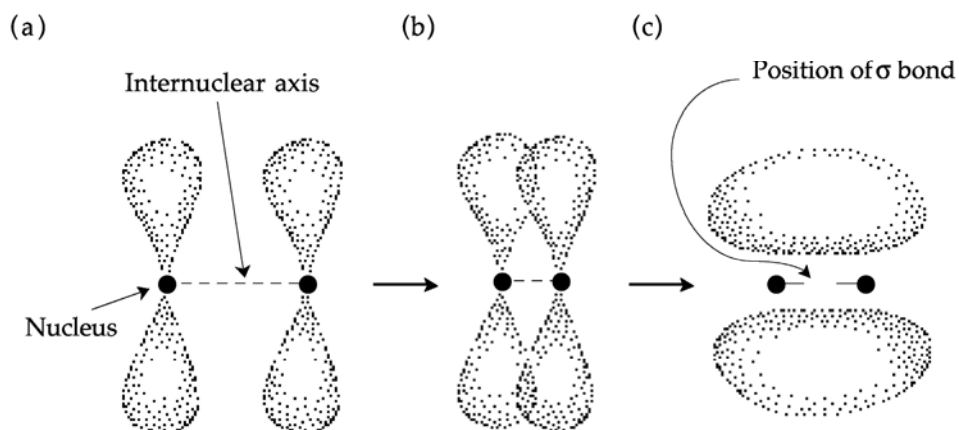
Figure 3.15: Formation of a π bond.

(a) Two parallel *p* orbitals. For clarity, the σ bonds have been left out of this diagram.

(b) Sideways overlap of the *p* orbitals.

(c) Formation of the π bond. Note that the π bond has two lobes, one above and one below the internuclear axis.

In ethene, C_2H_4, there is a double bond between the two carbon atoms as shown in the Lewis structure in Figure 3.16a. Again, I must emphasize an important point. Although σ bonds are made from a variety of atomic orbital overlaps (for example, *s/s*, *s/p*, *sp³/s*, *sp³/sp³*, etc.), there is only one way to make a π bond. *Pi bonds are formed from the sideways overlap of two parallel p orbitals.* If a compound contains a π bond, then the *p* orbitals from which it came must remain unhybridized. This is shown graphically in Figure 3.16b and c. On each carbon atom, one of the two *p* orbitals containing an electron is reserved for π bonding. The remaining orbitals, two 2*p* and one 2*s*, hybridize to give the three *sp²* orbitals. Figure 3.16d in this unit shows a diagrammatic representation of the bonding orbitals of $H_2C=CH_2$.

(a)

(b)

(c)
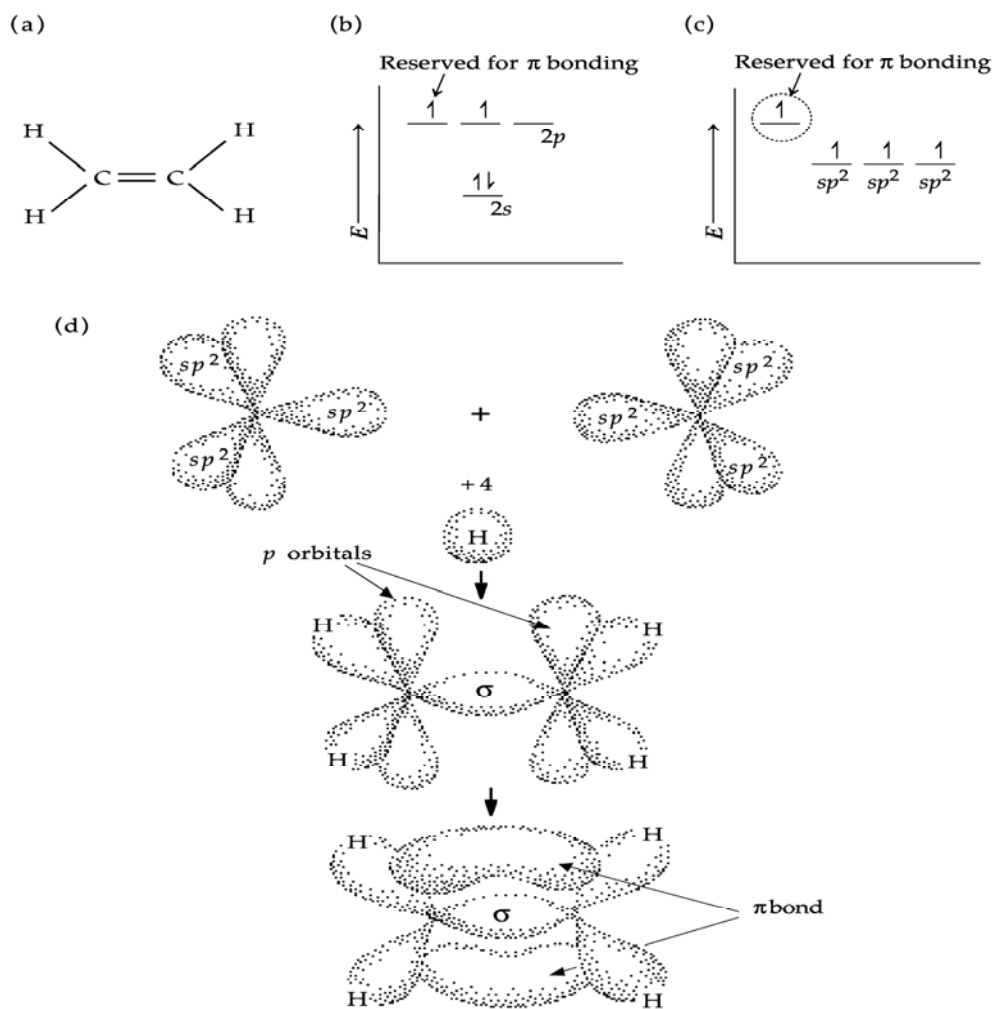
Figure 3.16: sp^2 hybridization in C_2H_4.

(a) Lewis structure of C_2H_4.

(b) Energy level diagram of the ground state of the carbon atom. To form a π bond, one of the p orbitals containing an electron must remain unhybridized.

(c) Energy level diagram of the bonding (hybridized) state of the carbon atom(s) in C_2H_4.

(d) Representation of the orbitals of the two sp^2 hybridized carbon atoms and the four hydrogen s orbitals that form $H_2C=CH_2$. Note that the one π bond formed from the two unhybridized p orbitals has two lobes.

Note that when the π bond is formed, it has two lobes; one lobe of the π bond is above the plane of the C–C bond and the other lobe is below. The net result of sp^2 hybridization in C_2H_4 should be a planar geometry with bond angles of 120°.

Measurements on the C_2H_4 molecule confirm this prediction. Experiments show that rotation is not possible around the carbon-carbon double bond in C_2H_4, as it is around the carbon-carbon single bond. Rotation would destroy the orbital overlap of the π bond. This gives experimental support for the picture of a π bond as being asymmetric around the internuclear axis. Now try Example 10.5 from your textbook and its practice exercise.

In the case of C_2H_2, where there is a triple bond, *two p* orbitals on each carbon atom must be reserved for the two π bonds. A triple bond consists of four lobes, two for each π bond. You can think of these four lobes as overlapping each other and forming a hollow cylinder of bonding (see Figure 3.17e in this unit).

(a)

(b)

Reserved for π bonding

(c)

Reserved for π bonding

$H—C\equiv C—H$

$2p$

- - - Original p level

sp sp

$2s$

Original s level

(d)

sp hybrid orbitals
overlap to form
σ bond

+

+2

H

σ bond

H   H

π

π

H   σ   H

π

π

(e)

Other π bond
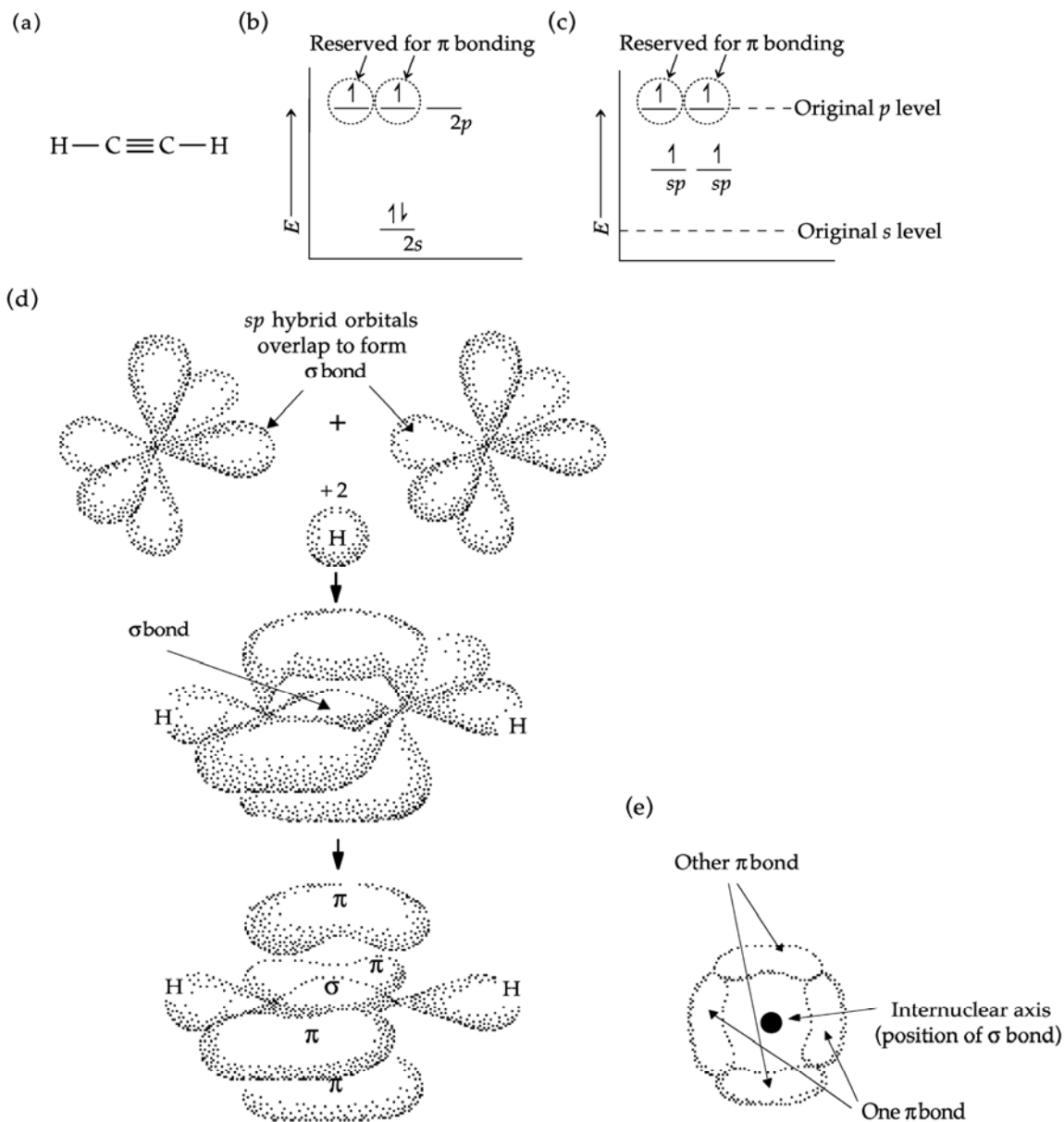
Internuclear axis
(position of σ bond)

One π bond

Figure 3.17: *sp* hybridization in C_2H_2.

(a) Lewis structure of C_2H_2.

(b) Energy level diagram of the ground state of the carbon atom.

(c) Energy level diagram of the bonding (hybridized) state of the carbon atoms in C_2H_2. Note that two *p* orbitals, each with an electron, remain unhybridized.

(d) Representation of the bonding orbitals' overlap of two *sp* hybridized carbon atoms and *s* orbitals of two hydrogen atoms. Two π bonds (each with two lobes) are formed: one in front of and behind the σ bond, and the other above and below the σ bond.

(e) A cross-section through the triple bond showing the cylinder of π bonding.

Noble Gas Compounds

Chemists use the hybridization method to explain why some noble gases form compounds. The very first noble gas compound, $XePtF_6$, was synthesized in 1962 by Neil Bartlett in the Chemistry Department at the University of British Columbia. Make sure that you can draw Lewis structures of molecules such as XeF_2 and XeF_4, and can deduce that the number of electron pairs around Xe is five and six, respectively. Then establish that the shapes of these molecules are linear and square planar (see Table 3.2 in this unit). If you draw an energy level diagram for Xe, you can see that in the ground state it looks as if there are no orbitals available for bonding. Figure 3.18 in this unit shows that hybridization involving one *d* orbital (XeF_2) or two *d* orbitals (XeF_4) allows for bonding via sp^3d or sp^3d^2 hybrid orbitals.

Problem: XeF_4 is known to exist as a square planar molecule with bond angles of 90°. Would you expect NeF_4 to exist?

Solution: The central atom Xe in XeF_4 uses two *d* orbitals to expand its valence shell to six electron pairs (two lone pairs and four bond pairs). Ne valence electrons are in the $n = 2$ energy level where there are no *d* orbitals. The next available orbitals are in the $n = 3$ level. This level differs too greatly in energy to allow hybridization with the $n = 2$ level. Consequently, no sp^3d^2 (or sp^3d) hybridization is possible and Ne will not form compounds.

(a)   (b)   (c)

$$:\overset{..}{\underset{..}{F}}— Xe —\overset{..}{\underset{..}{F}}:$$

(b)
5d
↑↓ ↑↓ ↑↓
5p
↑↓
5s

(c)
Empty 5d
↑↓ ↑↓ ↑↓ ↑ ↑
sp^3d
hybrid
orbitals

(d)   (e)   (f)

(d)
F
Lone pair
Xe
Bond pair
F

(e)
Empty 5d
↑↓ ↑↓ ↑ ↑ ↑ ↑
sp^3d^2 hybrid orbitals

(f)
Lone pair
F   F
Xe
F   F
Bond pair
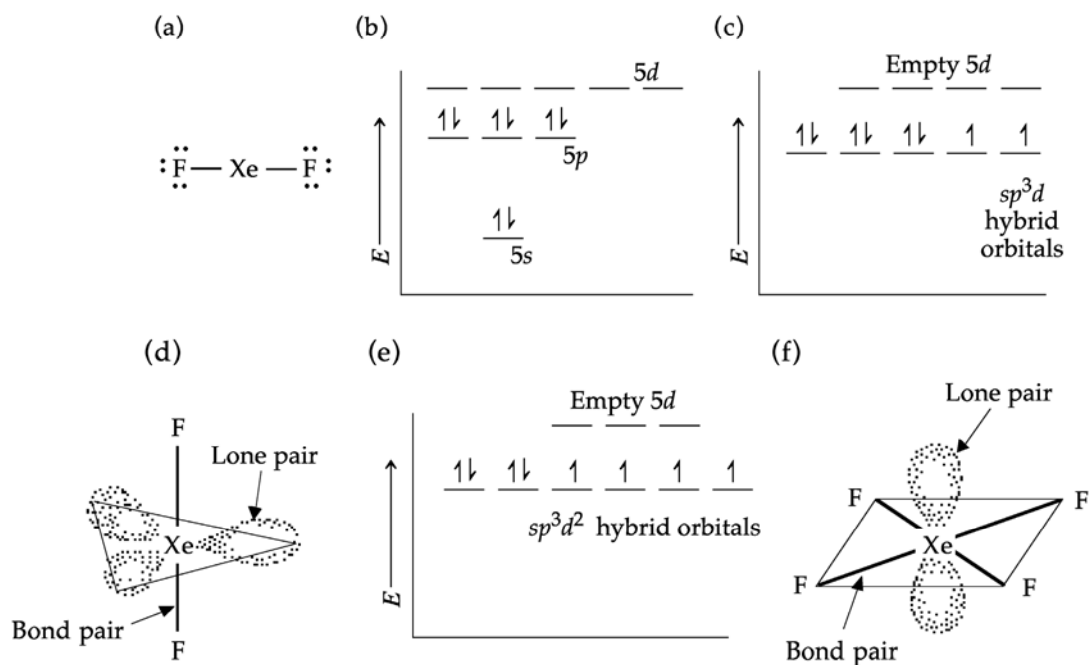
Figure 3.18: Hybridization in XeF_2 and XeF_4.

(a) Lewis structure of XeF_2.

(b) Energy level diagram of the ground state of the Xe atom.

(c) Energy level diagram of the bonding state of Xe in XeF_2 showing sp^3d hybridization.

(d) Representation of the XeF_2 molecule showing three lone pairs in the equatorial positions. This is the only arrangement where there are no 90° lone pair/lone pair repulsions. It gives a linear molecule.

(e) Energy level diagram of the bonding state of Xe in XeF_4 showing sp^3d^2 hybridization.

(f) Representation of the XeF_4 molecule with the lone pairs at 180°. This gives a square planar molecule.

Molecular Orbital Theory

Bonding and Antibonding Orbitals

So far you have considered molecules using the **valence bond (VB) model**. According to this method, when two atoms approach each other, their atomic orbitals interact. This interaction may result in distortion and the formation of hybrid orbitals, but the orbitals involved are still basically the atomic orbitals of the two bonded atoms. This is what you have been doing when you draw Lewis structures—you put lone pair electrons on the individual atoms. The valence bond approach is fairly simple and can be used effectively for molecules with more than two atoms.

There is another method, known as the **molecular orbital (MO) model**, where the molecule is treated as one entity. We saw that various atomic orbitals are the result of an interaction between wavelike electron clouds and a central positive force field. Molecular orbitals result from a similar interaction between the positive nuclei of two (or more) atoms.

Study Section 10.6 of your textbook. You will probably have no difficulty in visualizing a **bonding molecular orbital**. This is just a more sophisticated way of saying a *bond*. However, the idea of an **antibonding molecular orbital** often mystifies students. How can there be an *antibond*? The electron waves that define orbitals, like other kinds of waves, may combine to reinforce or to oppose each other. When the atomic orbitals of two atoms begin to overlap, both kinds of combination occur. The reinforced combination creates a molecular orbital where the electrons can spend most of their time between nuclei. The resulting *bonding orbital* has a lower potential energy compared to the two original, non-interacting atomic orbitals. The interfering combination creates a molecular orbital where electrons cannot contribute to bonding because they are in the wrong locations. These electrons tend to destabilize the molecule. The potential energy of this orbital is higher than that of the original atomic orbitals and is therefore referred to as an *antibonding orbital*.

An antibonding orbital has an energy level as much above the original orbital, the atomic orbital, as the bonding orbital is below. The antibonding orbital works *against* forming a bond as much as the bonding orbital works towards forming a bond. Electrons in an antibonding orbital are on the outside of the two nuclei, pulling the atoms apart, rather than holding them together as do the electrons in a bonding orbital. The net result of a filled bonding orbital and a filled antibonding orbital is no bond. The filled antibonding orbital cancels out the filled bonding orbital.

Molecular orbitals follow the same orbital rules as atomic orbitals. There is a maximum of two electrons per molecular orbital. These two electrons have opposite spins. In most cases, you can assume that each atom in the bond donates an electron to the molecular orbital. In other cases, both electrons come from one of the atoms in the bond; this gives a coordinate-covalent bond.

There are two kinds of **symmetry** found in bonding molecular orbitals (that is, in bonds). The first is uniformly distributed about a centre point, or about a line of centres, between two atoms. These are **sigma (σ) orbitals** or **bonds**. The second is half on one side and half on the other side of an atom. These are **pi (π) orbitals** or **bonds**. You should know the following rules of combination; they are dictated by symmetry considerations:

1.   Two atomic *s* orbitals (for example, on two H atoms) combine to form a pair of molecular orbitals having the same symmetry. That is, a sigma bonding (σ) and a sigma antibonding (σ*) orbital are formed.

2.   Two directional atomic orbitals that combine end-to-end are still symmetrical about the line of centres between the two atoms. Therefore, they also form a pair of sigma orbitals. If, for example, one atom with an *s* orbital interacts with another atom with a *p* orbital, the overlap is still symmetric around the line of centres. In this case, a pair of sigma orbitals also forms.

3.   Two adjacent atoms have two sets of *p* orbitals parallel to each other. Since the two halves of each orbital are on opposite sides of the line of centres between the atoms, the resulting molecular orbitals possess this same symmetry. Pi (π) orbitals result.

There are only two types of molecular bonding orbitals: σ and π. Their corresponding antibonding orbitals are known as σ* and π* (sigma star and pi star, respectively). It is important that you know how these bonds are formed and when they occur. To discuss the chemical properties of molecules, you must know something about bond types.

Electron Configuration of Molecules

Study Section 10.7 of your textbook. The MO model is more complicated than a simple VB approach because you must consider multi-centre interaction. However, the MO theory provides a more complete view of a molecule. In this course, you will use the MO method only for simple, homonuclear diatomic molecules such as H_2, Li_2, and F_2. The MO approach explains observed properties that cannot be explained by a simple VB approach.

Energy level diagrams for homonuclear diatomic molecules usually show both the orbitals of atoms that form the molecule, as well as the resulting molecular orbitals. Figure 3.19 in this unit is an energy level diagram for an H_2 molecule.
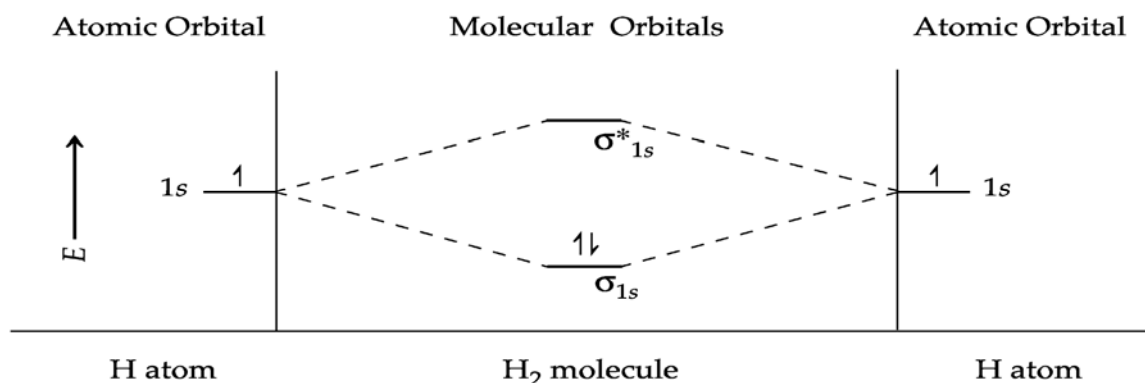

Figure 3.19: MO diagram for H_2. The energy level diagram shows separate atoms and combined atoms (molecules). Note that the two electrons in the σ_{1s} orbital have opposite spins.

In the same way you can write an electronic configuration for an atom or an ion, you can now write an electronic configuration for simple molecules or molecular ions. For example, the electronic configurations of H_2 and He_2 are:

$$H_2 \qquad \sigma_{1s}^2$$

$$He_2 \qquad \sigma_{1s}^2 \quad \sigma_{1s}^{*2}$$
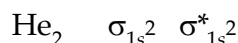
Be sure that you can write the electronic configurations for H_2^+ and He_2^+. Figure 3.20 in this unit shows energy level diagrams for Li_2 and Be_2.

Figure 3.20: MO diagrams for Li_2 and Be_2.
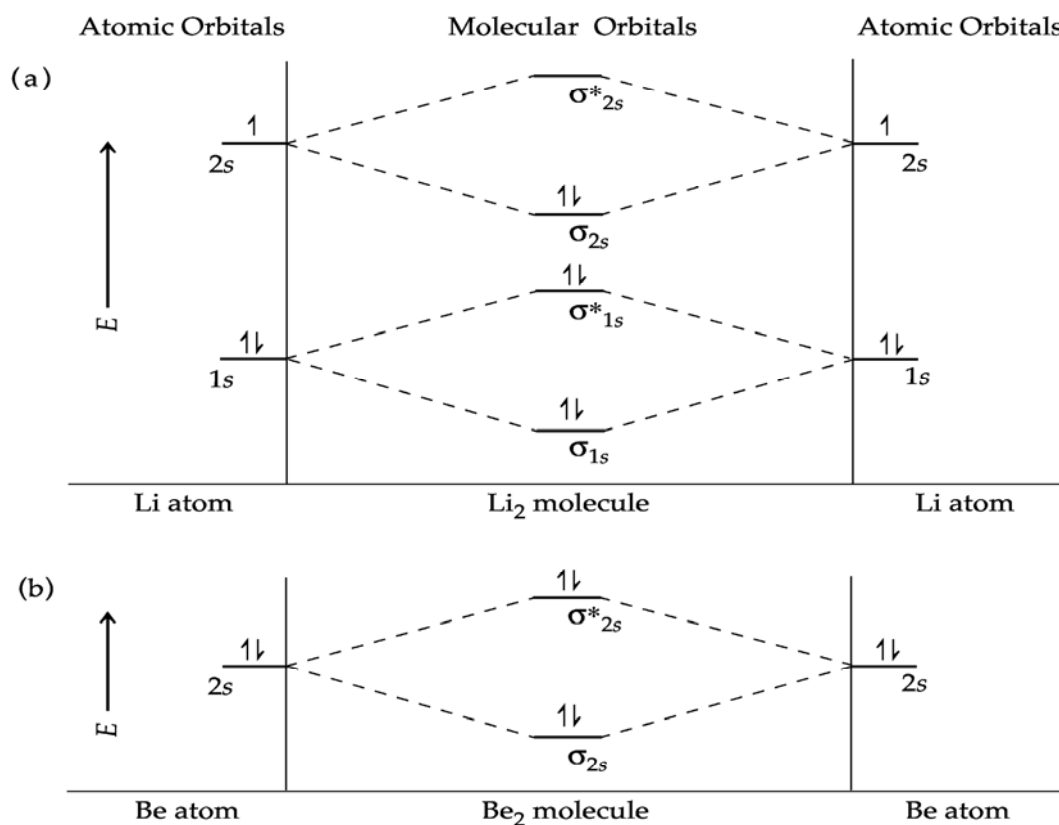
(a) For the Li_2 molecule, all the occupied energy levels are shown. The filled bonding orbital (σ_{1s}) is cancelled out by the filled antibonding orbital (σ^*_{1s}), leaving the filled bonding σ_{2s} orbital.

(b) For the Be_2 molecule, only the MO energy levels for the valence electrons are shown. In the nonvalence shells, the filled bonding orbital (σ_{1s}) is cancelled out by the filled antibonding orbital (σ^*_{1s}). Generally, you need only draw the MO energy levels for the valence electrons.

Now draw energy level diagrams for Li_2^+ and Be_2^+ and write electronic configurations for all of these species. You can work out the *bond order* in the molecular species using:

$$\text{bond order} = \frac{1}{2}(\text{bonding electrons} - \text{antibonding electrons})$$

If the number of bonds (or the bond order) is zero, then the molecule is unstable. This explains why Li_2 has been found experimentally (bond order of one), but Be_2 has not (bond order of zero). Such an explanation is not possible using the simple valence bond theory.

Table 3.3: Experimental physical data from some simple diatomic molecules.

Molecule	Bond energy (in kJ/mole)	Bond length (in picometres, pm)	Bond order (or # bonds)
H_2^+	270	106	$\frac{1}{2}$
H_2	436	25	1
He_2^+	301	108	$\frac{1}{2}$
He_2	0.08	–	0
Li_2	105	267	1
LiH	243	161	1

Table 3.3 in this unit shows bond dissociation energies, bond lengths, and bond orders of some simple molecules. A molecule is much more stable than the pieces (atoms, or atoms and ions) that comprise it. This is shown by the bond dissociation energies listed in Table 3.3. The data in this table will help you to visualize and understand some of the fundamental ideas that follow. **Note:** 1 pm = 10^{-12} m.

Why is the bond in H_2 not twice as strong as the bond, bound by only a single electron, in H_2^+? The answer is that in H_2, there is electron-electron repulsion. Nevertheless, the bond in H_2 is the strongest two-electron bond known. The small size of an H atom permits the two electrons to penetrate very close to the two nuclei.

More electrons do not imply stronger bonding. You can confirm this if you compare He_2^+ and He_2. He_2 has one more electron in an antibonding orbital. This reduces the bond dissociation energy to 0.08 kJ, a value typical of weak intermolecular attractions, but not of a bond.

The radius of the 2s orbital of Li is 252 pm. However, the measured bond length is 267 pm in Li_2. Therefore, it is apparent that there are more electrons closer to more nuclei in the molecule than in the separated atoms. This is, of course, why the molecule forms in the first place. You should now be able to see how you can correlate the MO model with experimental measurements.

Figure 3.21 in this unit shows energy level diagrams for the B_2, C_2, and N_2 molecules. Just as you learned that the order of the energy levels of atomic orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, and so on, you now have to learn the order of molecular orbital energy levels for B_2, C_2, and N_2. It is σ_{1s}, σ^*_{1s}, σ_{2s}, σ^*_{2s}, π_{2p}, π_{2p}, σ_{2p}, π^*_{2p}, π^*_{2p}, σ^*_{2p}. The two π_{2p} orbitals are at the same energy level (degenerate) as are the two π^*_{2p} orbitals. If you want to indicate that different p orbitals are involved, you can label the molecular orbitals as σ_{2p_x}, π_{2p_y}, and π_{2p_z} as has been done in Figure 3.21. Referring to this figure, write out the electronic configurations of B_2, C_2, and N_2. Then calculate the number of bonds in each of these species. You can then try drawing an energy level diagram, calculating the number of bonds, and writing electronic configurations for ionic species such as N_2^+ or C_2^-. You will find that these species have an odd number of electrons (in fact, the equivalent of 2.5 bonds in the C_2^- molecular ion). The idea of a half bond makes little sense according to the VB theory, but is quite acceptable according to the MO theory. A half bond signifies a molecular orbital that is occupied by only one electron.
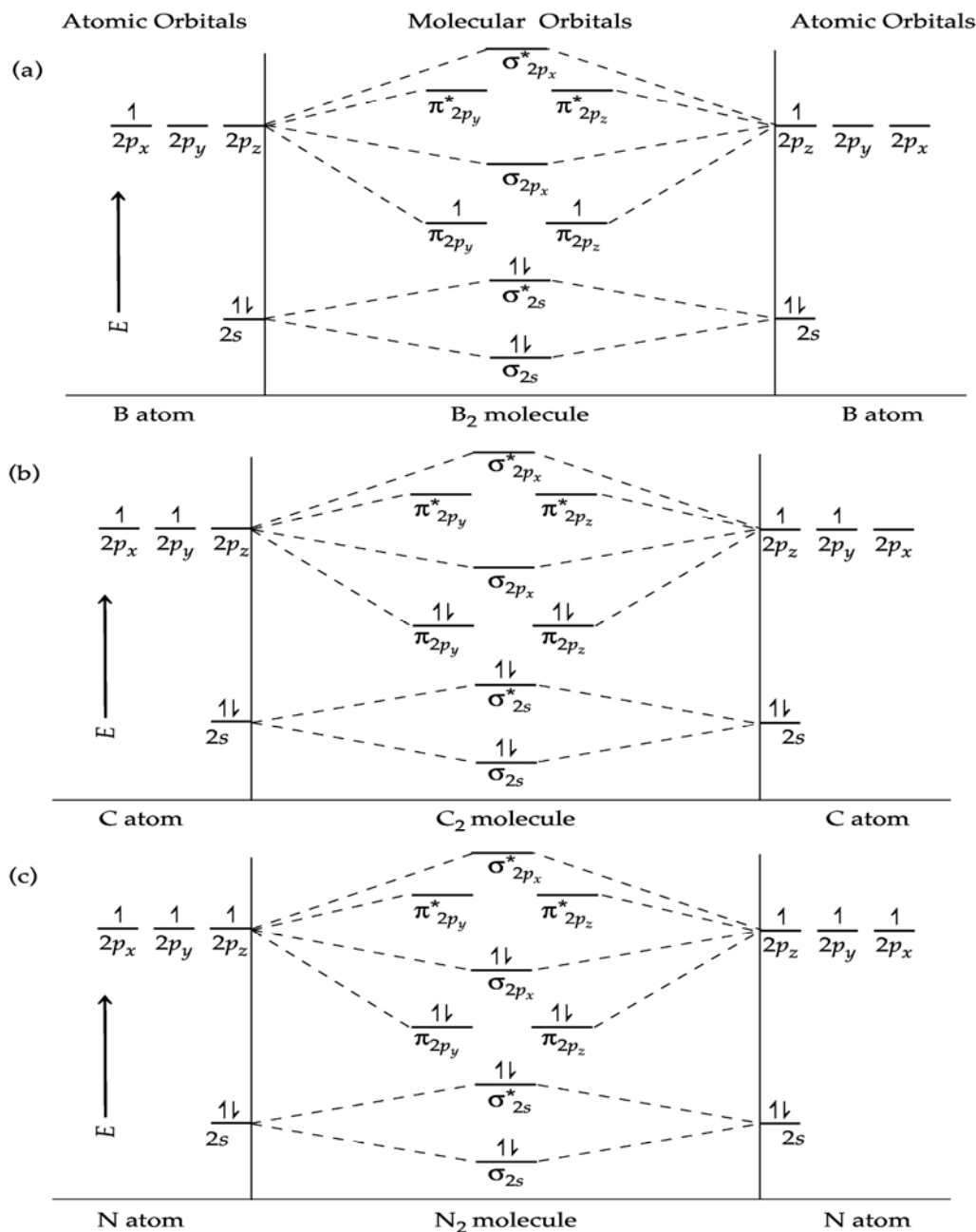
Figure 3.21: MO diagrams for B_2, C_2, and N_2.

a. The B_2 molecule.

b. The C_2 molecule.

c. The N_2 molecule. Only valence shell electrons are shown. The Aufbau principle and Hund's rule are followed. Note that for B_2, C_2, and N_2, the two-fold degenerate π_{2p} orbitals are lower in energy than the σ_{2p} orbital.

The remaining three, second-row, homonuclear diatomic molecules are shown in Figure 3.22 in this unit. In some textbooks, you may find that there is a slightly different molecular orbital energy level order for these species; the σ_{2p} is lower in energy than the doubly degenerate π_{2p} orbitals. But in this course, you should use the order given in your textbook. Now try Example 10.6 in your textbook and its practice exercise. For more practice, you may also want to try the following problem.

Problem: For each of the species F_2^+ and F_2^-:

    a.   Draw an energy level diagram.

    b.   Give an electron configuration.

    c.   Determine the bond order.

    d.   Are these ions paramagnetic or diamagnetic?

Solution:

    a.   For F_2^+, as in Figure 3.22b with only one electron in one of the π^*_{2p} orbitals.

        For F_2^-, as in Figure 3.22b with an additional electron in the σ^*_{2p} orbital.

    b.   For F_2^+: $\sigma_{1s}^2\ \sigma^*_{1s}{}^2\ \sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \pi_{2p}^2\ \pi_{2p}^2\ \sigma_{2p}^2\ \pi^*_{2p}{}^2\ \pi^*_{2p}{}^1$

        For F_2^-: $\sigma_{1s}^2\ \sigma^*_{1s}{}^2\ \sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \pi_{2p}^2\ \pi_{2p}^2\ \sigma_{2p}^2\ \pi^*_{2p}{}^2\ \pi^*_{2p}{}^2\ \sigma^*_{2p}{}^1$

    c.   For F_2^+, the bond order is 1.5.

        For F_2^-, the bond order is 0.5.

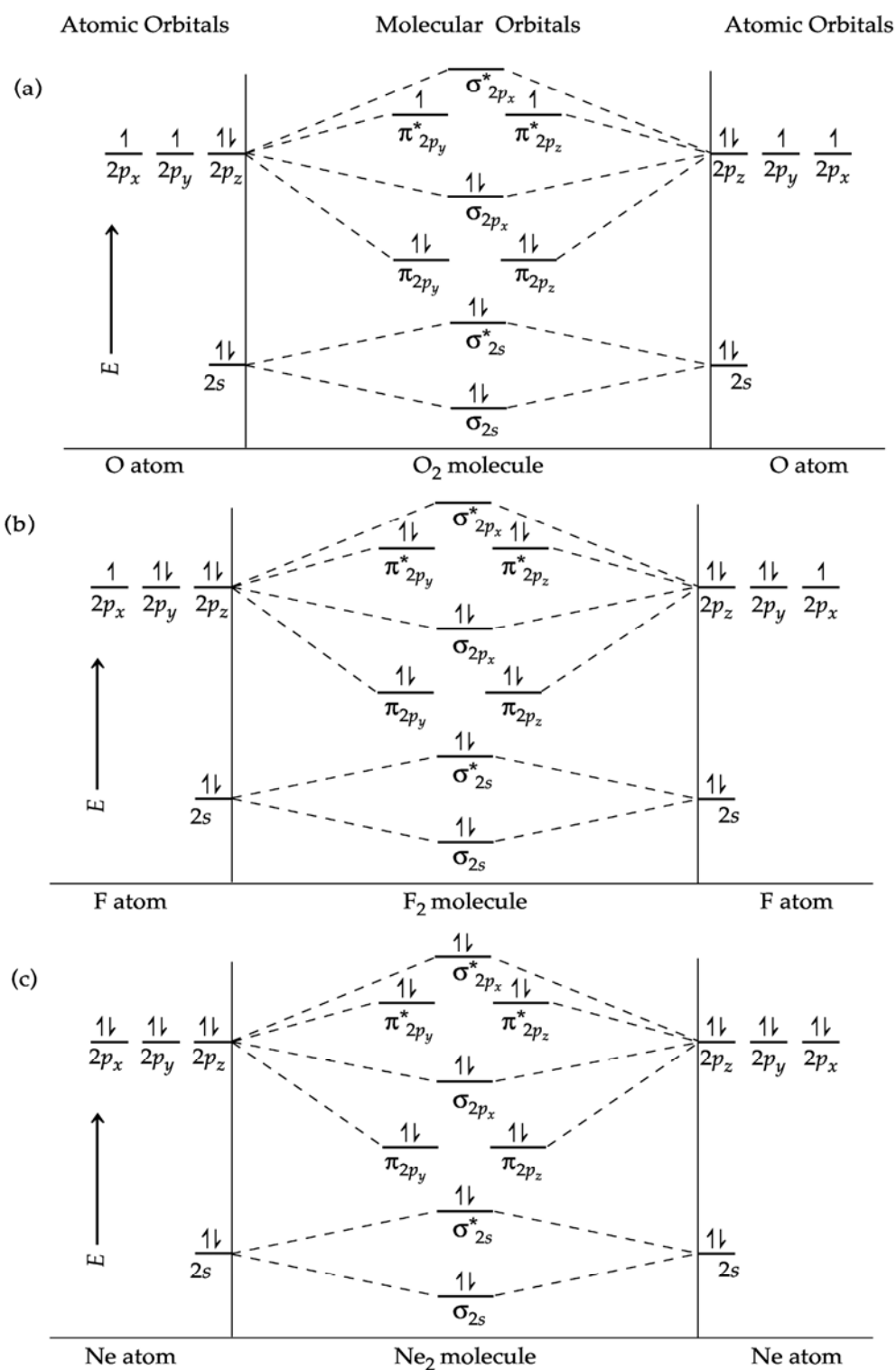   d.   Both have one unpaired electron, so both are paramagnetic.

Figure 3.22: MO diagrams for O_2, F_2, and Ne_2.

(a) The O_2 molecule. (b) The F_2 molecule. (c) The Ne_2 molecule.

The simple VB method of drawing B_2 and O_2 gives the following Lewis structures:

$$:B \!-\! B: \qquad\qquad :\ddot{O} \!=\! \ddot{O}:$$

Although these representations give the correct bonding order, neither of them show that both B_2 and O_2 are paramagnetic. (See Unit 2 and also Section 7.8 of your textbook for a review of magnetic properties and paramagnetism.) Experimentally, it can be shown that each B_2 and O_2 molecule has two unpaired electrons. There is no way that Lewis structures can show this. The following structures are *not* correct:

$$:O \!=\! O: \qquad\qquad \cdot\dot{O} \!=\! \dot{O}\cdot$$

Just because you cannot write an experimentally correct Lewis structure does not mean that the VB method is not useful. It simply tells you that the VB method is not sophisticated enough to indicate the correct paramagnetic details in Lewis structures. Using the MO approach, you can draw *two* MO assignments for O_2. In one, the electrons are paired in one of the two π^* orbitals and, in the other, each π^* orbital contains one electron. When the two electrons are in the same orbital (known as the singlet state of O_2), there is a greater associated electron-electron repulsion than in the so-called triplet state of O_2 where these two electrons occupy separate π^* orbitals. Actual measurements show that the singlet state of O_2 is 92 kJ/mol higher in energy than the triplet form. This is the basis for applying Hund's rule to these molecular energy level diagrams. Molecules and atoms can exist in various states, although under normal circumstances the most stable state is the only one significantly populated. Singlet oxygen is chemically important. It is highly reactive, can be formed in chemical and photochemical reactions, and has been implicated in carcinogenesis and photochemical smog formation. If you consider the energy level diagrams of O_2 and B_2 that you have drawn, you should see why these molecules are paramagnetic. The most stable state in each involves unpaired electrons in two degenerate energy levels. These are the π_{2p} level in B_2 and the π_{2p}^* level in O_2.

Delocalized Molecular Orbitals

The MO model becomes more complicated when you consider heteronuclear diatomic molecules and polyatomic molecules. Study Section 10.8 in your textbook. Take special note of the example of the benzene molecule. Its properties are consistent with both the VB resonance picture and the MO picture of a closed ring of π bonds.

Use the summary at the end of Chapter 10 to help you review the important concepts covered here.

Self-Assessment

Having reached the end of this unit, you should now be able to:

- Describe ionic bonds.

- Explain the concept of electronegativity and its consequences in bonding.

- Draw Lewis structures for molecular and ionic species.

- Calculate formal charges of atoms in molecules and ions.

- Explain the concept of resonance.

- Use bond dissociation energies to calculate reaction enthalpies.

- Use the VSEPR model to deduce molecular geometry of molecules.

- Predict which molecules will possess a dipole moment.

- Use the hybridization method to deduce molecular geometry of molecules.

- Describe sigma (σ) and pi (π) bonds.

- Explain valence bond (VB) and molecular orbital (MO) theories of bonding and the difference between them.

- Draw MO energy level diagrams for the homonuclear diatomic molecules and ions of the first ten elements of the periodic table, and deduce the number of bonds and the paramagnetism of these species.

Practice Exercise 3

Finish working through Unit 3 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in Unit 3 is integrated throughout the practice exercise. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can start the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 3. If you feel that you need more practice, go to the Suggested Supplementary Exercises that follow.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar examples given in the textbook and in this unit. If your attempt is serious, you will learn a lot more from the worked.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for all even-numbered problems are given in the *Student Solutions Manual*, by B. J. Cruickshank and Raymond Chang. Some of the even-numbered exercises at the end of the chapter have their answers in the back of the textbook. If you decide to try the odd-numbered problems and need help, consult your Open Learning Faculty Member.

Important: You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 9:

9.18, 9.20, 9.26, 9.38, 9.44, 9.48, 9.52, 9.54, 9.56, 9.62, 9.64, 9.66, 9.72(a), 9.74, 9.76, 9.78, 9.80, 9.86, 9.90, 9.92, 9.96, 9.98, 9.102, 9.106

From Chapter 10:

10.8, 10.10, 10.14, 10.22, 10.24, 10.34, 10.36, 10.38, 10.40, 10.42, 10.44, 10.52, 10.54, 10.58, 10.68, 10.70, 10.74, 10.78, 10.80, 10.82, 10.84, 10.86, 10.88, 10.92, 10.96

Assignment 3

Now refer to your *Assignments* and complete Assignment 3. Consult your Course Guide for the week this assignment is due.

You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form.

Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.