SUMMARY OF SIMPLE CHEMICAL BONDING THEORY **Chemistry BC2001x**

1. **Metallic bonding** results when the relatively loose valence electrons of metal atoms are shared among all the metal atoms in a solid or liquid sample.

The metal atoms may all be the same, if the substance is an element, for example Mg, Al, Fe, Cu, or they may be different, if the sample is an intermetallic compound of a definite stoichiometry, for example Ag_3Sn, or is an alloy of two or more metals with an allowed range of composition, for example brass, bronze, pewter, solder, dental amalgams, coinage and jewelry alloys.

2. **Ionic bonding** in a solid results from the net electrostatic attraction between regular ordered arrays of positively charged cations (+ ions) and negatively charged anions (− ions).

Metals can form monatomic cations: M^+ for the alkali metals; M^{2+} for the alkaline earth metals; characteristic unique or multiple possible cations for other metals, for example Al^{3+}, Sc^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^+, Cu^{2+}, Ag^+, Ce^{3+}, Ce^{4+}, Pb^{2+}. Exception: Hg(I) forms the diatomic cation Hg_2^{2+}. Nonmetals can form monatomic anions: X^- for halogens and H; X^{2-} for chalcogens; N^{3-}, P^{3-}. The only common nonmetal cations are the polyatomic NH_4^+ and H_3O^+ (written H^+ for short).

There are many polyatomic molecular anions, for example NO_3^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, $Cr_2O_7^{2-}$. In polyatomic cations or anions, atoms are held together by covalent (shared electron pair) bonds. The charge on a polyatomic ion resides on the ion as a whole. Cations lose electrons from the valence shell, anions add electrons to the valence shell, corresponding to the charge on the ion.

Memorize the names, formulas, and charges of all the common monatomic and polyatomic ions.

When ionic solids dissolve in water, they generally *dissociate*: the cations and anions separate and move about more or less independently in the solution, each surrounded by water molecules.

3. **Covalent bonding** in a molecule or in a molecular ion results from sharing of electron pairs.

A shared electron pair forms a covalent chemical bond, as in H_2. Covalent bonding in molecules and molecular ions composed entirely of nonmetal elements follows patterns summarized in the procedure for drawing *Lewis structures*, which are governed by the *octet rule*, except for H.

For H and He, 2 electrons constitute a stable filled valence shell. For all the other nonmetal elements, eight electrons constitute a stable filled valence shell. This is called the *octet rule*.

Covalent chemical bonding and Lewis structures

The requirements for a satisfactory Lewis molecular structure are very simple: the structure must have (1) the correct number of valence electrons, and (2) each atoms associated with an octet of electrons (except H, which has two). [Helium, He, is not include here, since it does not form stable molecules.] This is accomplished by putting the valence electrons in combinations of bonds (shared electron pairs) and lone pairs (not shared). There are many different ways to go about finding such structures: there is no one correct method. The method given in your textbook is simple and direct; the procedure below is equivalent. You may have learned a different method in an earlier chemistry course; if it works for you and finds correct structures, use it! Some books tell you to start with each atom with its valence electrons, and then draw lines between unpaired electrons to form bonds and create octets. Often a useful approach, this does not always work without moving pairs of electrons: example: CO. **Remember that electrons are equivalent**.

Suggested procedure for drawing Lewis structures

(1) Start by counting valence electrons (**always do this step, whatever method you use!**)

a) The number of valence electrons for each atom is found from the element's column in the periodic table.

Examples: H 1; B 3; C, Si 4; N, P 5; O, S 6; F, Cl, Br, I 7

b) In a neutral molecule, the total number of valence electrons is the sum for all atoms

Examples: CH_4: 4 + 4(1) = 8; H_2O: 2(1) + 8 = 10; N_2O: 2(5) + 6 = 16

c) In a covalently bonded molecular **ion**, the net **charge** must be considered in the total count. Add one valence electron for each negative charge on the ion; remove one valence electron for each positive charge on the ion.

Examples: SO_4^{2-} [6 +4(6) **+2** = 32] PO_4^{3-} [5 +4(6) **+3** = 32] NH_4^+ [5 +4(1) **–1** = 8]

(2) Decide what atom is connected to what, which atom is in the center, etc. This is sometimes stated, sometimes implied by the formula; for example, in SO_4^{2-}, S is in the middle, with bonds to each O. You are not assuming geometry, just topology. Use this to write symbols for each atom.

(3) Draw a single line, implying a shared electron pair, between all bonded atom pairs. Count how many electrons you have used (two per bond).

(4) Starting from the outside, and working around the molecule, add lone pairs to each atom to complete the octets. (Each H atom is connected to another atom with a bond, so H's are automatically ok.) If your molecule contains halogens, complete their octets first. Stop when you have used up your valence electrons. If all octets are complete, you are done.

Examples: CH_4 NH_3 H_2O HF CCl_4 CH_2Cl_2 PCl_3 ICl HOOH P_4

(5) If you run out of electrons before completing all octets, the molecule has **multiple bonds**. Two shared pairs of electrons constitute a **double** bond; three shared pairs of electrons constitute a **triple** bond. Move a lone pair from an atom with a filled octet (not a halogen) to be shared with an adjacent atom that needs electrons to complete its octet. Continue forming multiple bonds until you have satisfied the octet rule for each atom. Rewrite the completed structure, using lines to indicate bonds**. Check that the final structure has the correct number of valence electrons. (Do this for any method)**.

Examples: O_2 N_2 CO_2 HCN H_2CO F_2CCF_2 HCCH CO CN^-

(6) When there are multiple bonds, it is sometimes possible to draw two or more equivalent Lewis structures, each satisfying all the rules of valence electron octet theory. These structures are called **"resonance" structures**. When drawing resonance structures, the positions of the atoms may never change; only the electrons.

Examples: SO_2 NO_3^- CH_3COO^- C_6H_6 CO_3^{2-} SO_3

The implication of multiple resonance forms is a limitation of Lewis theory. Molecules and ions have only **one** stable structure, but the theory is inadequate to describe it with a single diagram. In such substances, electron pairs are **delocalized.** Bonding pairs may be shared among more than two atoms, and lone pairs may reside on more than one atom, while in standard Lewis structures bonding pairs are between two specific atoms, lone pairs localized on one atom. If we think of the true structure as a weighted "average" of the Lewis structures, with weights determined by relative stability of the structures, this picture of the bonding is in reasonable accord with observations.

Simple Lewis theory accounts for essentially all bonding in organic compounds (molecules made of C, H, N, O, plus the halogens F, Cl, Br, I, and S and P) and in many other molecules as well.

Some texts instruct you to determine the **formal charge** on each atom after writing Lewis structures. This is an optional step, not essential to drawing Lewis structures. It is useful in deciding which resonance structures make a larger contribution to the actual average structure.

Several classes of **exceptions or extensions to Lewis theory** exist. In such molecules or ions, one cannot draw any Lewis structures that simultaneously satisfy the octet rule and have all bonding electrons in pairs localized between two atoms and all nonbonding electrons in lone pair groups. In increasing order of importance, the classes of exceptions are as follows.

(1) **Odd-electron molecules,** for example NO, NO_2, and ClO_2. A few such molecules exist, plus more complicated nitrogen-containing odd-electron organic molecules, called *free radicals*. In such molecules, the central atom has 7 atoms in its Lewis structure or resonance structures.

(2) Molecules or ions with **electron-deficient atoms**, for example BeH_2; diborane, B_2H_6; a large number of other boranes (compounds of B with H), and many other compounds of boron. In many compounds of B, bonds form sharing two electrons among 3 (or more) atoms.

(3) Molecules or ions containing atoms with apparently **excess electrons in the valence shells**, for example, PCl_5, SF_6, IF_7, XeF_2, I_3^-. There are two different, formally adequate ways to extend Lewis theory to explain how all the bonds in these molecules are formed. Deciding which approach is better depends on the results of more sophisticated quantitative theories.

    (a) Allow more than 8 electrons to surround a central atom. An octet is never exceeded in atoms B through Ne, but can be in P, S, Cl, and nonmetal atoms in the longer rows of the periodic table. This approach allows 8, 10, 12, or 14 valence electrons to surround a central atom.

    Lewis structures in expanded valence shell molecules still draw covalent bonds as shared electron pairs localized between atoms, and unshared electrons as lone pairs on single atoms.

    (b) Keep the octet rule, but allow delocalized bonding pairs and lone pairs as necessary. Write formal structures, including resonance structures, allowing split bonding pairs: one electron in one bond to the central atom and one electron in another bond to the central atom represents a bonding electron pair shared among those three atoms. One lone electron on a peripheral atom and one lone electron on another peripheral atom represents a lone electron pair shared between those two atoms.

(4) **Transition metal covalent compounds and complexes**. The octet rule applies fairly well to most covalent compounds of elements in the ***p*** block of the periodic table (columns 13-18), including the metal elements in that block. All these elements have either no ***d*** electrons or have completely filled ***d*** electron shells, which would include the elements Zn, Cd, and Hg. These ***p*** block elements all have valence shells with an effective maximum of 8 electrons. This is not true for the transition metal elements (columns 3-12) with incompletely filled ***d*** electron shells. For these elements, we must consider a much larger valence shell, in general one capable of holding a maximum of 18 electrons altogether, occasionally even more.

Molecular geometry: the valence shell electron pair repulsion (VSEPR) model

The geometry of covalent molecules can be derived from their Lewis electron-dot structures.

The most stable molecular shape has the lowest total energy. Electrons shared in a bond between two atoms have lower energies than they would on separated atoms. In a covalent molecule, a shared pair of electrons in a single bond (two shared pairs in a double bond, three shared pairs in a triple bond) is confined more or less to the space between the bonded atoms. A lone pair is confined to a limited region on an atom, and points away from it in some particular direction.

Electrons repel each other. The magnitude of electron-electron repulsion in covalent molecules depends on the molecular geometry. Both bonded electron pairs and lone electron pairs in the valence shell of any atom will try to get as far away from each other as possible. A covalent molecule can thus minimize its total energy by adopting the **geometry that achieves minimum electron-electron repulsion**, while at the same time retaining the maximum bonding consistent with simple Lewis theory. That is the whole VSEPR theory of molecular geometry in a nutshell.

In the valence shell electron pair repulsion model, multiple bonds between a pair of atoms are treated in the same way as single bonds. One more observation completes this simple picture. Lone pairs take up somewhat more space than bonding pairs, and thus exert slightly greater repulsive forces than bonding pairs. This has the effects shown in the table below.

Molecular geometry means the relative locations and arrangement in space of the **nuclei** of a molecule or a molecular ion. Molecular geometry is determined by the geometry of the valence electron pairs, including any lone pairs, so the geometry of the nuclei and the electrons need not be the same. For all the different possible numbers of valence electron pairs, whether bonded or lone, we have tabulated the geometry that minimizes electron-electron repulsion in each case. The assumption that atoms can somehow rearrange their valence electrons to do this is correct.

The tables below illustrate geometries around an individual atom. In a complex molecule, exactly the same principles are applied to each atom in the molecule that has bonds to two or more other atoms, one by one, to build up the entire molecular geometry. Complex molecules may have relatively rigid, fixed geometries, or there may remain some degree of flexibility, still consistent with all the rules given here.

Diatomic molecules are not tabulated: in geometry two points determine a line, so **diatomics are by definition linear. Examples**: F_2, HF, CO, OCl^-.

Notations in the tables (pages 7-8): Formula Type and AX_n refer to the immediate chemical surroundings of atom A in a molecule, bonded to n other atoms X. Atoms X may be the same or different. Molecular geometry can also refer to the geometry of a fragment.

B = number of bonding groups (sets of electron pair bonds between two atoms) around atom A. Note that a bond between atoms (single, double, or triple) counts as one bonding group. **B is the same as the subscript in AX_n,** so B is also the number of atoms bound to A.

L = number of lone electron pairs on atom A.

N = number of substituents on atom A: bonded atoms plus lone pairs: **N = B + L**. Some books, for example Brown and LeMay, call this the number of electron domains.

The first table facilitates seeing how molecular shapes are derived from a common electron-pair geometry (same N) as atoms are replaced by lone pairs (increasing L). Note that when L=0, the framework (electron pair) and molecular geometries are the same. The second table facilitates comparing geometries of each fragment type (AX_n) as the number of lone pairs (L) increases.

VSEPR

Framework Geometry. The basic idea of VSEPR is that the number of substituents N (bonded atoms plus lone pairs) determines the framework geometry: the location of the substituents. There are only five important possibilities. Note that when there is an octet around an atom, only N = 2, 3, or 4 are possible. N=5 and 6 apply when there is an expanded valence shell.

N	framework geometry	Angles between substituents
2	linear	180°
3	planar, trigonal	120°
4	tetrahedral	109°27′
5	trigonal bipyramidal	120° around equator, 90° to poles, 180° between poles
6	octahedral	90° adjacent, 180° across

Be sure you have a clear mental image of each of these framework geometries and their angles. Pictures are on the following page.

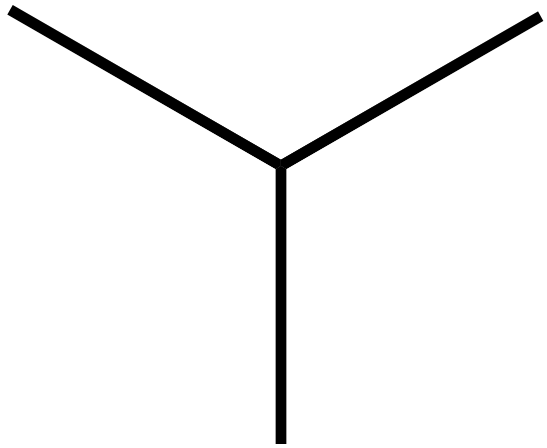
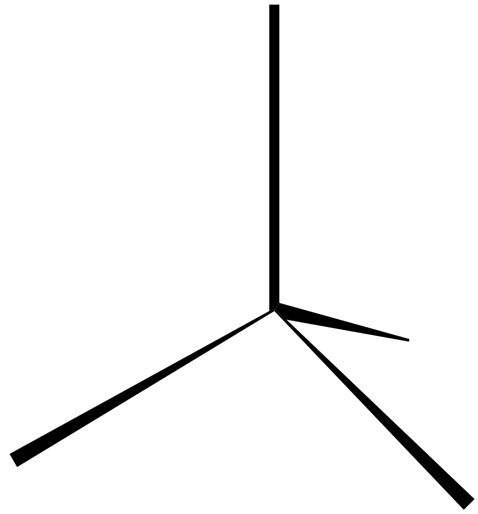
Molecular Geometry describes the location of the nuclei of atoms, not lone pairs. Thus when there are lone pairs, molecular geometry differs from framework geometry. The location of the atoms and angles between them is still is determined by the framework geometry, but different words must be used to describe the molecule. For example, SO_2 has N=3 (framework: planar trigonal), but there is one lone pair on the central S atom. The O atoms occupy the two other sites on the trigonal framework. The molecule is **bent**, with an approximate 120° angle. Note that it is not useful to describe a triatomic molecule as planar: three points are always planar --- they define a plane --- so no information is conveyed by saying that it is planar. With four or more atoms, planarity is an issue. Experimentally, it is observed that when lone pairs are present, the bond angles are often a bit less that predicted by the framework geometry, so it is said that the lone pairs take up more room. The bond angle in SO_2 is 118.8°, slightly less than 120°.

It is essential that you understand and can predict any molecular geometries when N = 2, 3, and 4, as well as the framework geometries for N = 5 and 6. N = 5 and 6 with L > 0 are less common in the molecules you will encounter in this course. They are included in the tables below for completeness.

In the chart below are the molecular shapes that arise from framework geometries combined with lone pairs for N = 3 and 4. Examples for N= 5 and 6 are given in the tables that follow.

N	L	molecular shape	bond angles	example
3	1	bent	~120°	SO_2
4	1	trigonal pyramid	~109°	NH_3
4	2	bent	~109°	H_2O

There are several good web-based VSEPR tutorials that help you to visualize the 3D geometry. Consult the course web page for links.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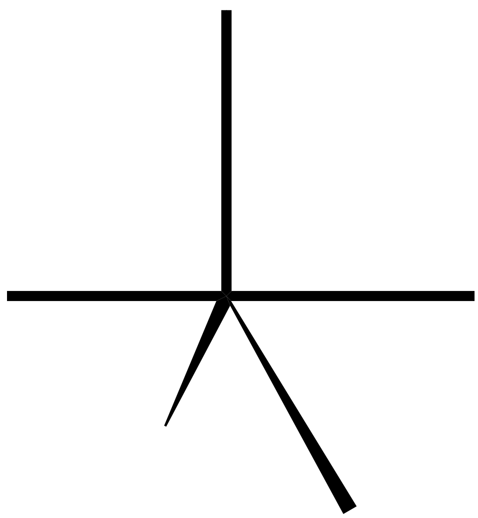	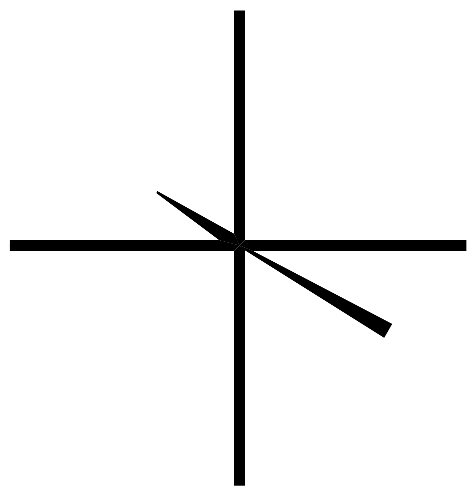
trigonal bipyramidal	octohedredral

This method can be used to predict bond angles in molecules where more than one atom is bonded to several others. One proceeds stepwise, describing the geometry around each center. Example: methanol has the formula CH_3OH. Both the C and the O have multiple attachments. At the C center, N = 4 and L = 0, so the bonds (three to H and one to O) are arranged tetrahedrally. The O center has two bonds (one to C and one to H) and two lone pairs. Again N = 4, with a tetrahedral framework. This tells us that the C–O–H bond angle is approximately 109°; a little less, since lone pairs take up more space. There is no simple word to describe the overall geometry, but a picture is useful.