

Chapter 1 – Chemical Bonding & Chemical Structure

Getting Started

If you've downloaded this guide, it means you're getting serious about studying. So do you already have an idea about how you're going to study?

Maybe you thought you would read all of chapter 1 and then try the homework? That sounds good. Or maybe you thought you'd read a little bit, then do some problems from the book, and just keep switching back and forth? That sounds really good. Or ... maybe you thought you would go through the chapter and make a list of all of the important technical terms in bold? That might be good too.

So what point am I trying to make here? Simply this – you should do whatever you think will work. Try something. *Do* something. Anything you *do* will help.

Are some things better to do than others? Of course! But figuring out which study methods work well and which ones don't will take time. And you won't be able to figure anything out if you don't actually *do* something. So just dive in and see what happens.

(FYI - if you can't resist reading professorial advice, read the "idiosyncratic assortment of study tips" that I've posted online. There is a permanent link to this entry at the top of the Study Guide web page.)

Now go study.

What do the study guides contain?

If time permits, I will post a short study guide online for each chapter. I expect to build the study guides around four items.

1. The **Checklist** contains everything that I think you should be able to *do* after you finish studying a chapter.
2. The **Top "10+" Problems** are 10-15 end-of-chapter problems spanning all of the topics in the chapter. If your time is limited, work the problems on this list, but if you have more time, work more problems for practice and depth. (Note: I expect that you will be working many of the in-chapter problems as you read so I generally won't list these in the Top 10.)
3. **Additional Readings** alert you to sources of information outside of your textbook. I have not listed read-

ings from *inside* your textbook because I normally expect you to read the entire chapter.

4. Finally, there will often be a **Supplement** that contains comments on material that I have found especially tricky. Material that I expect you to memorize will also be placed here.

Checklist

When you have finished studying Chapter 1, you should be able to:¹

1. State the number of valence electrons on the following atoms: H, Li, Na, K, Mg, B, Al, C, Si, N, P, O, S, F, Cl, Br, I
2. Draw and interpret Lewis structures
 - a. Use bond lengths to predict bond orders, and *vice versa*
 - b. Use VSEPR to predict bond angles
3. Identify and compare polar covalent bonds, ionic bonds, and covalent bonds using electronegativity trends and/or potential maps²
4. Make qualitative dipole moment predictions
5. Draw and interpret resonance structures
6. Describe an atom's electron configuration using the atomic orbital model
 - a. Draw cartoons of atomic orbitals and label the orbitals using orbital quantum numbers
 - b. Locate nodal surfaces on your cartoons
 - c. Apply the aufbau principle, the Pauli exclusion principle, and Hund's rules
7. Describe a bond's electron configuration using the molecular orbital model
 - a. Identify sp^3 hybridized atoms
 - i) Draw orbital cartoons of sp^3 hybrid orbitals showing their directionality and nodal surfaces

¹ "Be able to" usually assumes independent work, i.e., working without a book, notes, web page, data table, or help from a friend. The knowledge you need should be in your head and ready for use.

² "Potential map" is my label for "electrostatic potential maps" or EPM.

- b. Identify atomic (hybrid) orbitals on neighboring atoms that can engage in sigma overlap
- c. Draw an orbital interaction diagram showing
 - i) relevant atomic (hybrid) orbitals, their occupancies, and relative energies
 - ii) bonding and antibonding orbitals, their occupancies and relative energies
- d. Draw orbital cartoons of sigma bonding and antibonding orbitals.
 - i) Locate nodal surfaces on your cartoons
- e. Correlate bond length, bond strength, and bond electron configuration

Top 12 Problems for Chapter 1

All of these problems are drawn from the *Additional Problems* located at the end of the chapter 1. Since the problems come from the same chapter, I have decided to save space by referring to problem 1.25 as '25'. If a problem contains several parts, I may indicate a specific part as in '25a'.

The top 12 for chapter 1 are **23, 25, 27, 28, 31cf, 32, 34, 35, 42, 43, 45, 46**

Additional Readings

ROCO stands for Reed Organic Chemistry Online, a collection of essays that I have posted online for chemistry students. You can find the link to ROCO at the top of our class home page. Here are some ROCO readings that might prove helpful:

- *Lewis structures*
- *Electron density*
- *Electrostatic potentials* (I recommend reading *Electron density* first)
- *Resonance* (read the ones marked "revisions planned" at your own risk)

Supplement

VSEPR

Your book makes one small (and rather common) error when talking about VSEPR. The repulsion between electron pairs is not mainly due to electrostatic interactions

although that plays a role. Rather, the proponents of VSEPR claim electron pair repulsion is due something called "Pauli repulsion", that is, repulsion that is a consequence of the Pauli exclusion principle.

The Pauli exclusion principle is often expressed this way: *two electrons with the same spin cannot occupy the same orbital*. However, the principle can be generalized to: two electrons with the same spin cannot occupy *overlapping* orbitals. This means that same spin electrons must avoid each other, and avoidance looks just like repulsion, so we refer to this avoidance that is rooted in the Pauli exclusion principle as "Pauli repulsion".

If you're still with me, try to picture the electron spins found in two electron *pairs*. Each pair contains one spin-up electron and one spin-down electron. The pairs must avoid each because each pair contains a spin-up electron (and also a spin-down electron). So we expect to see Pauli repulsion between electron *pairs*. Hence, VSEPR.

Valence electrons and chemical bonds

When Lewis says a covalent bond requires 'electron sharing', it evokes a nice picture, but it leaves a lot of questions unanswered. What is about electron sharing that draws two atoms together? Why is it that two hydrogens can profitably share electrons, but two heliums cannot?

The answer to these questions and others lies in quantum mechanics. Unfortunately, a proper treatment of electron behavior using quantum mechanics lies far beyond the material covered in this course. If we are going to make some headway with these questions, we will have to base our answers on some simpler *models* of electron behavior that can still capture the essence of this mysterious quantum mechanics subject.

Chemists have developed several simplified models of electron behavior and each has something to recommend it for student use. Therefore, every textbook author must choose the model that he or she thinks is best. Loudon has chosen a molecular orbital (MO) model that he applies to each bond in a molecule. This bond-specific version of the MO model is sometimes called the 'bond orbital model' or 'localized molecular orbital model', but I will follow Loudon's practice and just call it the 'molecular orbital model'.³

The MO model has much in common with the atomic orbital (AO) model of atoms that you studied back in intro-

³ Other MO models exist. For example, instead of building orbitals for individual bonds, we could build orbitals that encompass the entire molecule. This is the approach followed by many computer programs. It is also a powerful conceptual approach for dealing with resonance hybrids.

ductory chemistry. Both models imagine that electrons in a chemical system (an atom or a bond) can choose from a set of orbitals of different energies. The lowest energy state for the system is obtained by placing the electrons in the orbital of lowest energy (*aufbau principle*). A maximum of two electrons can occupy an orbital (*Pauli exclusion principle*) so if a system contains more than two electrons, several low energy orbitals are occupied. The distribution of electrons in these orbitals is called the system's *electron configuration*.

So far, so good, but what do the molecular orbitals of a bond look like? Well, it turns out that each MO looks like a combination of two atomic orbitals, one from each atom (Loudon Figures 1.13 & 1.14 & p. 39). It is traditional to refer to these atomic orbital combinations as "superpositions", a word that I favor because it (correctly) implies that the atomic orbitals overlap in the same region of space.

Unfortunately, this is where things start to get tangled up. I am going to quickly map out a few important ideas and you should challenge me to explain them to you.

Directionality. Sigma bonding and antibonding orbitals are aligned with the axis containing the two nuclei and have cylindrical symmetry about this axis. (Figure 1.15)

Overlap. A bonding MO is more stable than its atomic orbital pieces *only if the atomic orbitals overlap*. (The same statement applies to antibonding MOs except you need to replace "more" with "less".) Overlap depends on the distance between atoms and the shapes of the interacting orbitals.

Orbital energy match. A bonding MO is more stable than its atomic orbital pieces *only if these pieces have similar energies*. (The same statement applies to antibonding MOs except that you need to replace "more" with "less".)

sp³ hybridization and sp³ hybrid orbitals. sp³ hybrid orbitals are an alternative description of how electrons behave in certain atoms. Paradoxically, we only invoke these hybrid orbitals when discussing how the atom bonds to other atoms.

A hybrid orbital is similar to a molecular orbital in that it is a superposition of atomic orbitals. The difference is that molecular orbitals involve a superposition of AO on *different* atoms, while hybrid orbitals involve a superposition of AO on the *same* atom.

The properties of a hybrid orbital (direction, nodes, energy, %s character, %p character) are determined by the atomic orbitals that go into its construction. In the case of an sp³ hybrid orbital, we make the hybrid orbital by combining 25% of an s valence orbital and 75% of a p orbital. This process is repeated *four* times to make *four* new sp³ orbi-

tals that point in different directions (Figures 1.16d and 1.17)⁴ and we refer to the atom as "sp³ hybridized".

It is important to realize that the four sp³ hybrid orbitals are a package deal. If we invoke sp³ hybridization for an atom, we completely toss out the standard valence AO model and replace it with a new hybrid orbital model. This still gives the atom four valence orbitals, but they are now hybrid orbitals. The other (core) atomic orbitals are not affected. (The top figure on p. 39 shows an orbital pattern in which a core 1s AO is combined with four valence sp³ hybrid orbitals.)

The number of orbitals is conserved when we mix, combine, or superposition orbitals. For reasons of convenience, chemists often prefer to describe electron behavior with one set of orbitals instead of another. We might replace combinations of atomic orbitals with molecular orbitals, or we might replace some atomic orbitals with some hybrid orbitals. Whatever our motivation, mixing (combining, superpositioning) conserves the number of orbitals in the system. That is, the original *N* orbitals are replaced by *N* new combinations.

Two examples illustrate this idea. When we combine 4 valence atomic orbitals on carbon, we replace them with 4 hybrid orbitals (see diagram on p. 39). Similarly, when we combine 2 1s atomic orbitals on neighboring hydrogen atoms, we replace them with 2 molecular orbitals, one bonding and one antibonding (see Figure 1.14).

⁴ Interested students might want to see the algebraic formulas for converting standard atomic orbitals into sp³ hybrid orbitals. The mixing procedure and formulas are described in "A Simple Method for Generating Sets of Orthonormal Hybrid Atomic Orbitals", C-Y Hsu and M. Orchin, *Journal of Chemical Education*, **1973**, 50(2), 114-118. A hard copy of this journal article can be found in the Reed library. Electronic copies can be downloaded from the Journal's web site.