Lecture 2

General Chemistry Review

Pease read chapter 1 of White for this week

- Periodic table & electronic configurations.
- Periodic properties: ionic radius, electron negativity, 1st ionization potential
- Covalent & ionic bonding
- Hybridization and molecular orbitals

Background-Elements and Atoms

These are all terms you should already be familiar with:

atom - smallest sub-divisible unit of matter that retains unique chemical properties. Composed of electrons, protons and neutrons.

element - a fundamental building block of matter defined by a specific number of protons in an atomic nucleus. All atoms of an element have the same number of protons.

isotope - different "flavors" of an element that have different numbers of neutrons in their nucleus (thus, they have different atomic masses).

radioactive isotope - isotope that decays away radioactively due to an unstable nuclear configuration.

stable isotope - one that does not decay radioactively.

molecule - a multi-atom material held together by chemical bonds.

compound - a multi-element molecule.

ion - an atom or molecule that has gained or lost one or more valence or bonding electrons, giving it electronic charge.

valence - the outermost electron shell of an atom.

The Periodic Chart and Periodic Properties

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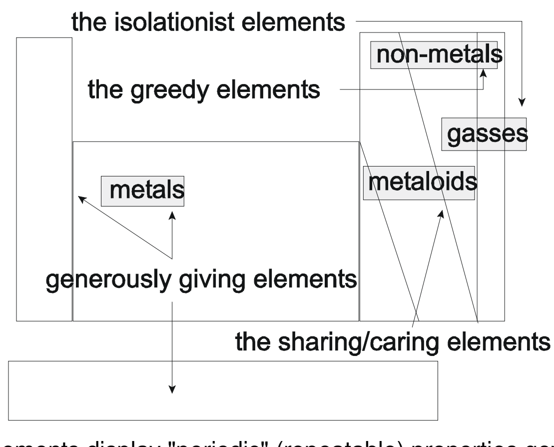
The Periodic Chart of the Elements ala Ken



The chemical elements display "periodic" (repeatable) properties governed by valence electron configurations.

The **Periodic Chart** is a 2d map of the elements that reflects their periodic behavior. There are many ways to draw the Chart but all are set up to classify like-chemistry elements. If you can read the map you will be able to predict an element's behavior in a range of environments.

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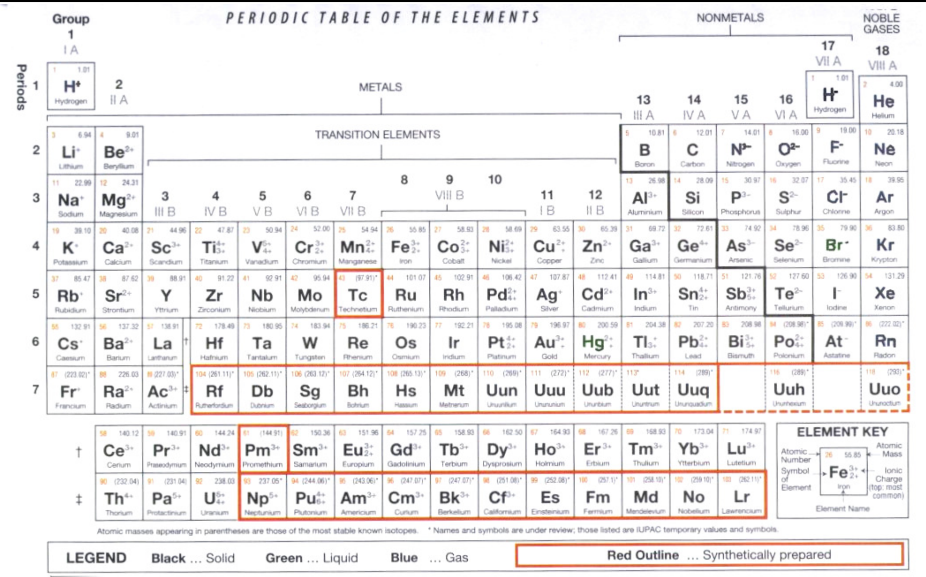


Each element is defined by the number of protons in the nucleus, which in turn determines the number of electrons in a neutral atom. Electronic configuration determines chemical reactivity.

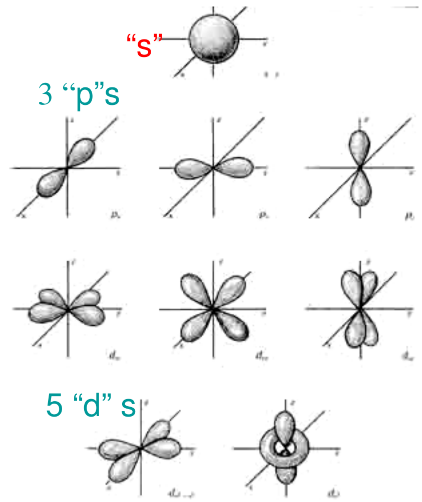
The importance of electrons

Elements that form the columns of the periodic table behave similarly largely because they have similar electron configurations.

Outer most electrons are the most important in chemistry because these are more readily lost and/or shared.

In contrast, inner electrons are tightly bound to the nucleus by electrostatic forces.

Atomic orbitals



- Are a means of describing the likely spatial distribution of electrons about a nucleus.
- 2 electrons "fill" an orbital
- "s" orbitals are spherically symmetric; "p"s are pairs of "lobes" of electron density; d & f orbitals are geometrically more complex
- Orbital geometry (and hybrids thereof) play a huge role in setting molecular geometry

Note: the 14 "f"s are not shown

No 2 electrons can share a quantum number in an atom. There is a progression of quantum numbers and corresponding orbitals

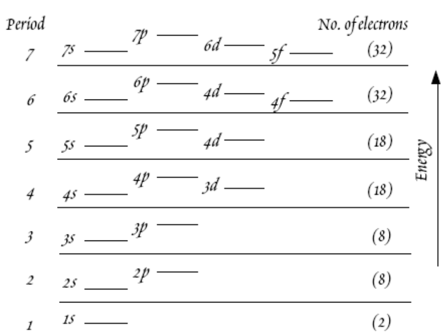


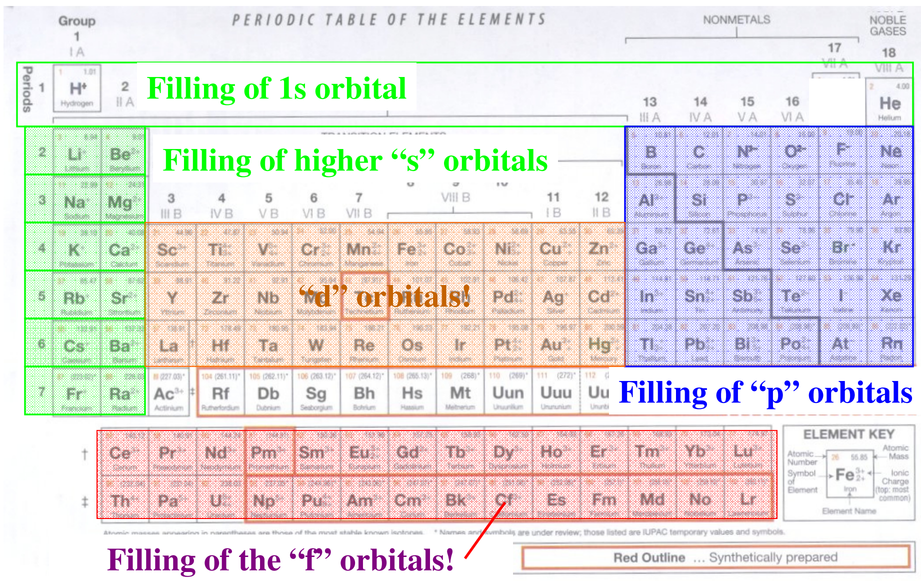
Table 4.1 Quantum Numbers and Orbitals of the Hydrogen Atom

Quantum numbers				
n	*l*	*m*	*s*	*Type of orbital*
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2s
2	1	0	$+\frac{1}{2}, -\frac{1}{2}$	2p
2	1	1	$+\frac{1}{2}, -\frac{1}{2}$	2p
2	1	−1	$+\frac{1}{2}, -\frac{1}{2}$	2p
3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	3s
3	1	0	$+\frac{1}{2}, -\frac{1}{2}$	3p
3	1	1	$+\frac{1}{2}, -\frac{1}{2}$	3p
3	1	−1	$+\frac{1}{2}, -\frac{1}{2}$	3p
3	2	0	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	1	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	−1	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	2	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	−2	$+\frac{1}{2}, -\frac{1}{2}$	3d
			etc.	

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s,
4d, 5p, 6s, 4f, 5d, 6p, 7s, 6d

Aufbau Principle Simplified

- Low energy orbital fills 1st.
- electrons distribute among orbitals to minimize total energy of atom.
- Electron configurations w/ full or half-full orbitals are "preferred" because they are more stable.



Filled orbital assignment shorthand notation:
Ne = $1s^2\ 2s^2\ 2p^6$ and Ar = $[Ne]2s^2\ 3s^2\ 3p^6$.

Please review these Periodic Properties from your course in Introductory Chemistry

1. Atomic radius:

►Radii of the elements increase down a column

decrease across a row (left to right).

2. Ion size (ionic radius)

a positive atomic ion is generally smaller than the neutral atom

a negative atomic ion is larger than the neutral atom.

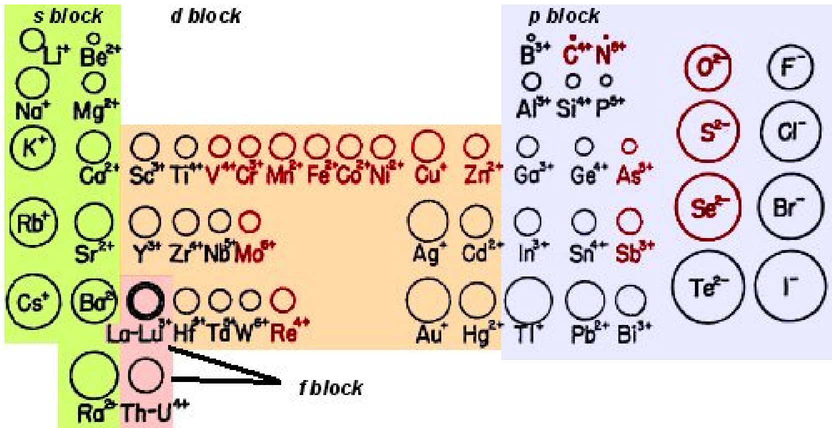
Atoms contract as they become positive ions because the "pull" of the positively charged nucleus is "felt" by fewer electrons than in a neutral atom.

► Like neutral atoms, radii of ions at a given charge increase down a column.

► An *iso-electronic series* contracts with increasing atomic mass: $Li^{+}\rightarrow Be^{+2}\rightarrow B^{+3}\rightarrow C^{+4}\rightarrow N^{+5}\rightarrow O^{+6}\rightarrow F^{+7}$ =big →small ions

Schematic representation of ionic radius of some common ions in common ionization state.

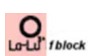
Remember: many elements have more than one stable “valance”.



Elements lettered in red have active “redox” chemistry in nature = important for environmental behavior.

Remember: oxidation = loss of electrons; reduction = gaining electrons.

Why does size matter?



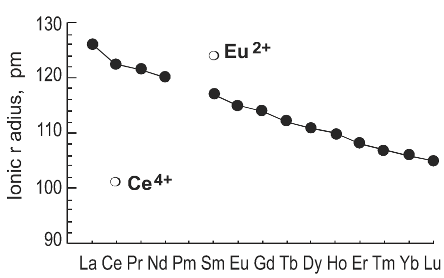


Figure 7.5. Ionic radii of the lanthanide rare earth elements (3+ state except where noted). Promethium (Pm) has no isotope with a half-life longer than 5 years.

modified from White, Geochemistry

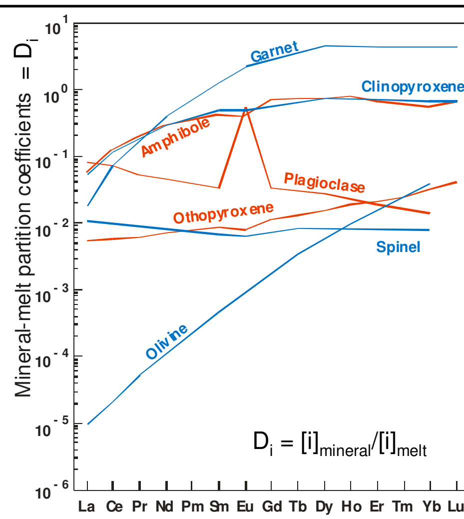
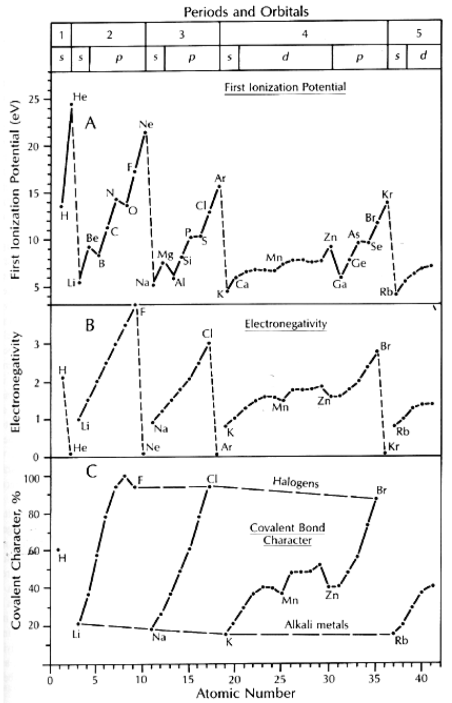


Figure 7.15. Rare earth mineral-melt partition coefficients for mafic magmas. Data from Table 7.5. from: White, Geochemistry



Periodicity is also clear in several other important measures.

These three describe how the elements “feel” about valence electrons.

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3. Ionization and Ionization Energy (aka ionization potential):

Ionization is the removal or addition of one or more electron(s) from a neutral atom or molecule, making a charged (ionized) species.

IE measures how easy or hard it is to remove an electron from an element or ion.

Energies of filled electronic orbitals give rise to common oxidation states for individual elements.

Electronic structure determines ionic charge and IE.

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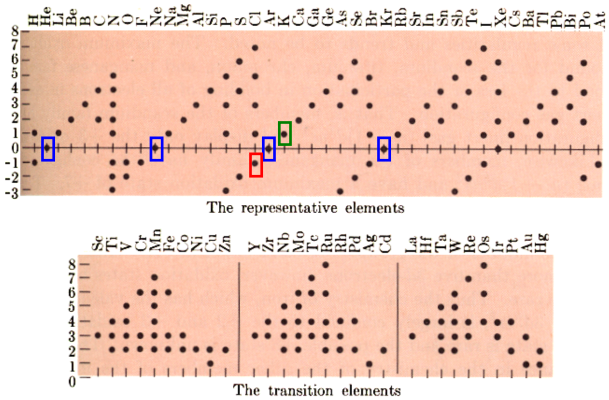


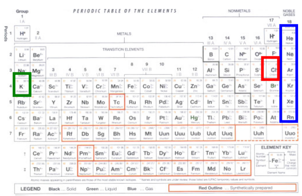


FIG. 13.3

The common oxidation states of the representative elements and transition metals plotted as a function of atomic number *from Mahan, 1975*

►noble gasses have filled valence shells. They rarely ionize (except Xe).

►the element Cl = [Ne]$2s^2$ $3s^2$ $3p^5$ will acquire 1 extra electron to become Cl^- = [Ar] configuration.

► the element K = [Ar]$4s^1$ will lose an electron and also attain an [Ar] electronic configuration (K^+ = [Ar]).

In general, halogens like Cl all make singly charged negative ions and alkali metals like K all make singly charged positive ions for this very reason.

Low IP High IP

But use caution with a generalization like this, because other factors come to bear

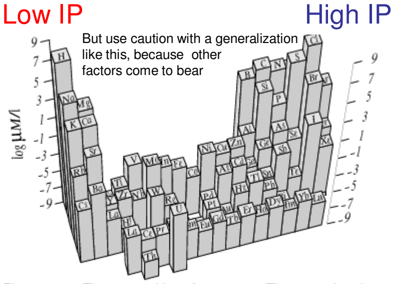
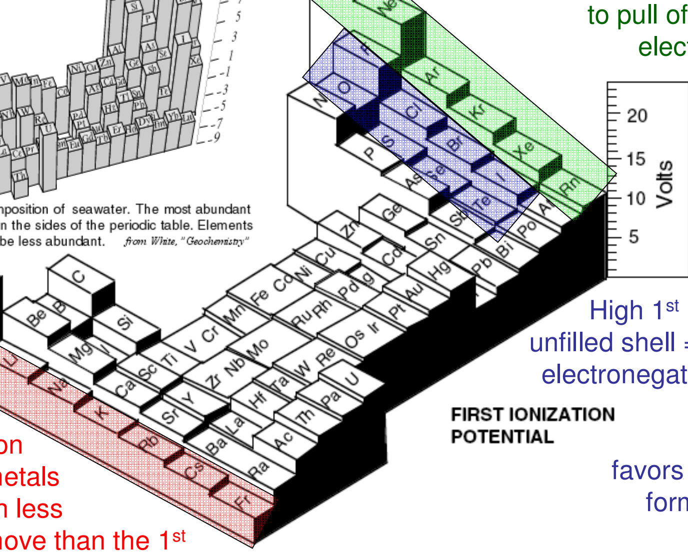


Figure 15.5. The composition of seawater. The most abundant elements are those on the sides of the periodic table. Elements in the interior tend to be less abundant. *from White, "Geochemistry"*

Noble gas: filled shell - lots of energy required to pull off an electron



High 1st IP but unfilled shell = high electronegativity = favors anion formation

The 1st electron of the alkali metals requires much less energy to remove than the 1st electron of atoms to the right of it.

4. Electronegativity

A measure of an atom's desire to gain an electron, forming a negative ion. Atoms can be classified in terms of their electron affinities with respect to their peers in the periodic chart as:

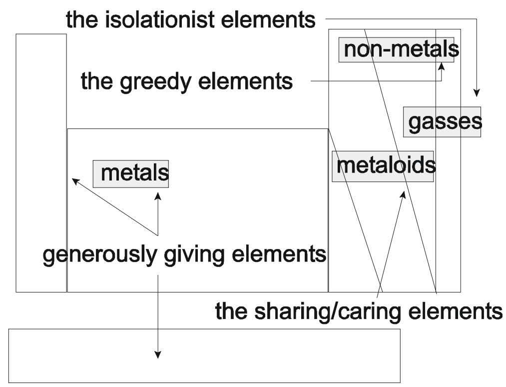
a. donors ("generously giving" and "sharing/caring")

Low electronegativity = mostly or entirely empty valence shell= conductor = metal (gives up electrons easily)

b. acceptors ("greedy")

high electronegativity = mostly or entirely filled valence shell = insulator = non-metal

c. inert ("isolationists").



Electronegativity ≥ 2.5 is a quasi chemical dividing line for the very "greedy elements", but element near that boundary (like C and N) don't always behave a certain way in the presence of other chemical elements.

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.5	Br 2.8	K
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.2	At 2.2	Rd
Fr 0.7	Ra 0.9	Ac 1.1															

La 1.0	Ce 1.0	Pr 1.0	Nd 1.0	Pm 1.0	Sm 1.0	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.2	Yb 1.2	Lu 1.2
Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np 1.4	Pu 1.4									

Figure 1.5. Electronegativities of the elements.

Chemical Bonds

<u>Background - Chemical Bonds</u>
Bonds allow multiple elements to form *molecules.*

Lewis dot configurations
are useful for predicting ionization behavior during the formation of some compounds, but they only work rigorously for s + p block electrons.

Lewis dot configurations for molecular bonding are based upon an element's desire to ultimately attain some sort of noble gas (filled shell) configuration, e.g., He:, :Ne:, :Ar:

where • represents an e^- and : represents an e^- pair.

Each element brings some # of valence electrons in s and p orbitals to a compound that combine to form a *Lewis dot product* containing noble gas configurations around all the elements (2 or 8 electrons, = He or other noble gasses)

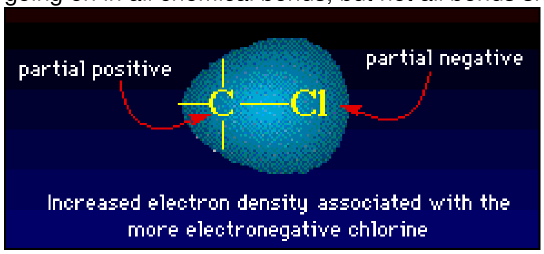
H has 1electron = H•
C has 4electrons = •Ċ• [same as Si], etc..
N has 5electrons = •N̈• [same as P], etc..
O has 6electrons = •Ö: [same as S], etc..

We can use lewis dot product logic to demonstrate why H_2O is a more common and stable combination of elements than other H and O combinations such as HO_2. O has e^- structure like Ne, each H has e^- structure like He.

H• + H• + •Ö: ⟶ H:Ö:H

5. Bond Character

There is e- sharing going on in all chemical bonds, but not all bonds share e- equally.



Two end members:

☞ *Pure Covalent Bond* = exact same electronegativity of two bonded atoms

☞ *Pure Ionic Bond* = largest possible electronegativity difference of two bonded atoms

A spectrum of bond characters exists based on the electronegativity difference of the two bonded atoms.

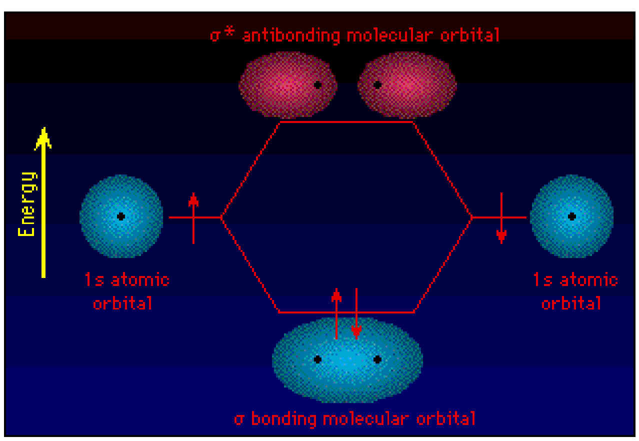
☞ If difference is < 50% maximum, *bond is more covalent.*

☞ If difference is > 50% maximum, *bond is more ionic.*

Because ionically-bonded solids ("salts") and covalently-bonded solids (quartz, octane, etc..) behave differently in H_2O and air, bond character is very useful in determining how a compound will behave in a particular environment.

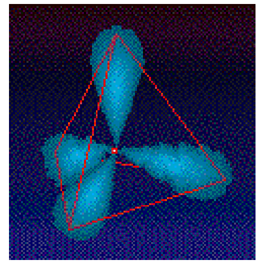
Bond orbitals

Atomic orbitals combine and "hybridize" to make bonding and non-bonding orbitals that define electron density between atoms.



http://chipo.chem.uic.edu/web1/ocol/SB/1-2.htm

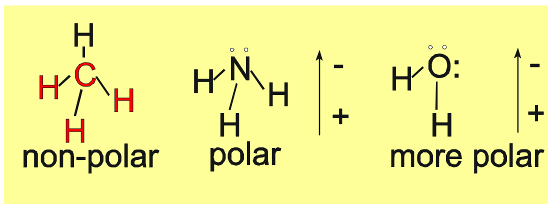
sp^3 hybridization



This simplest combo includes all 3 p orbitals and the s orbital of a valence. This mix produces 4 equal sp^3 orbitals in tetrahedral coordination (angle of 109.5° between each bond). Methane, CH_4, and the $[SiO_4]$ unit in silicate minerals have this geometry.

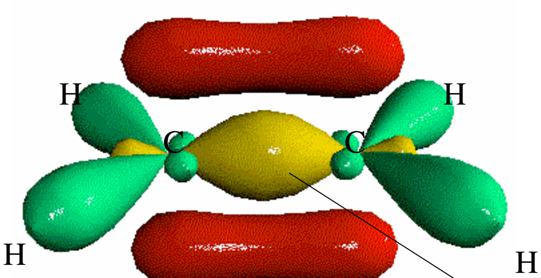
In molecules with one sp^3 bonding orbital containing an electron pair rather than a bond (such as ammonia, H_3N:), the lone pair causes the 3 bonds to contract somewhat to an angle of 107.3°.

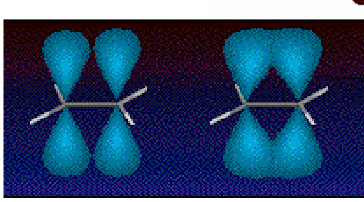
The case is more severe for water, with two e^- pairs and the H-O-H bond angle reduces further to 104°. This makes water (and ammonia) *polar* molecules as charge is not evenly distributed about them and methane *non polar* as charge is symmetrically distributed about it.



Another hybrid type is sp^2 (planar geometry). It involves 1 s orbital and 2 p orbitals, leaving one unhybridized p orbital to do something else.

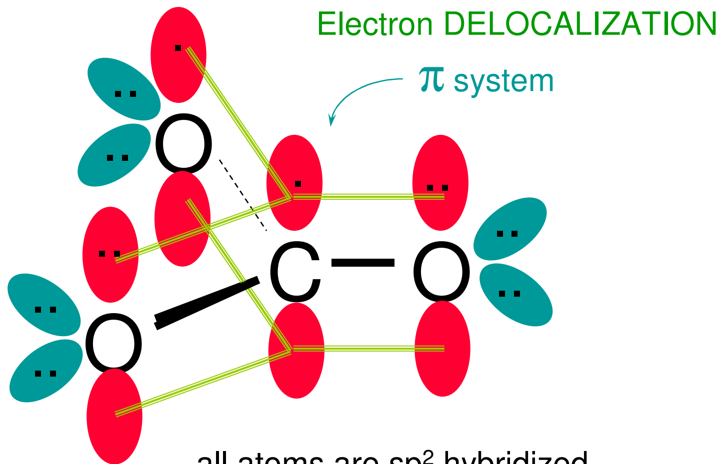
This is common in carbon-carbon double bonds in molecules like C_2H_4, ethene: The primary (σ) bond is from an sp^2 + sp^2 molecular hybrid (in yellow) and a second bond forms from the unhybridized p-orbitals out of the plane of the molecule (also called a π bond), shown in red.





Forming the π bond hybrid from 2 p orbitals on neighboring atoms

Another example:
sp^2 hybridization in the carbonate anion = CO_3^{2-}

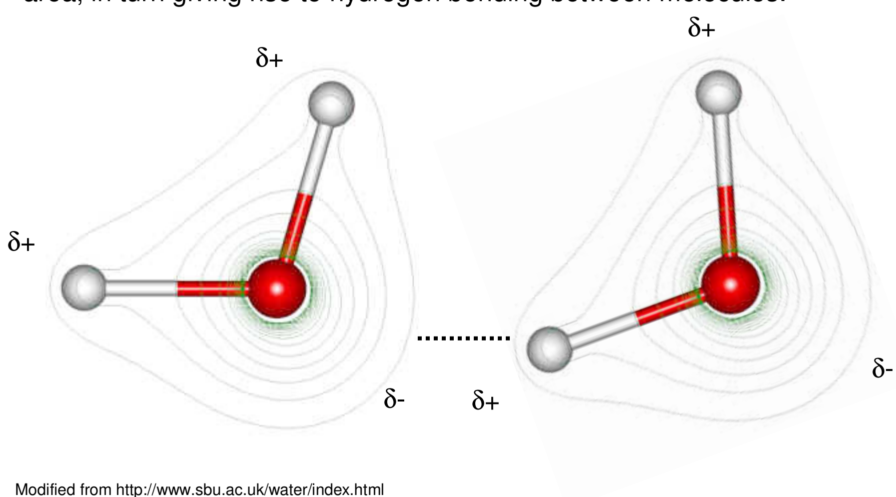


all atoms are sp^2 hybridized

www.chem.wwu.edu/harvey/Chemistry-351/Chapter-6.ppt

Other bonding interactions

Average electron density around oxygen in H_2O is 10 times greater than around the hydrogen atoms. This nearly completely exposes the “naked” protons of the H atoms, giving the molecule a partial positive charge in this area, in turn giving rise to hydrogen bonding between molecules.



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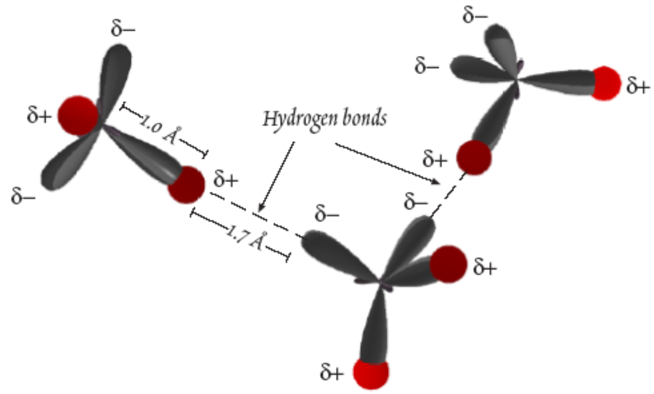

Figure 1.8. Hydrogen bonding between water molecules. Hydogen positions shown as red; sp^3 hybrid orbitals in oxygen shown as dark gray. The δ+ and δ− indicate partial positive and negative charges respectively.

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