GENERAL CHEMISTRY SECTION II: CHEMICAL BONDING

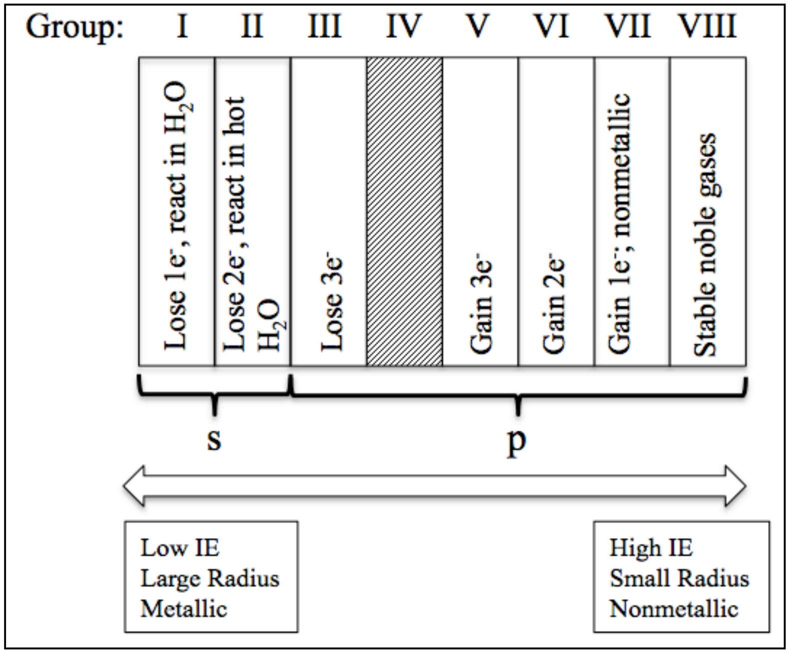
LECTURE 7: AN INTRODUCTION TO THE CHEMICAL BOND

Chapter Summary:

- We use the concept of valence electrons surrounding atoms to create **2-dimensional** structures in which species with **chemical bonds** are **more stable** than **solitary** atoms.
- We base the stability argument for chemical bonds on the generation of species that have achieved **stable noble gas configurations (s^2p^6)**.
- A first kind of bond is **ionic**: electrons are **donated or accepted** to create anions and cations that have **s^2p^6** configurations.
- A second kind of bond is **covalent**: these occur when **non-metal** atoms **share** electrons with one another.
- Many compounds achieve s^2p^6 configurations by sharing electrons in **overlapping p orbits** to form double and triple bonds as well as **resonance** structures.
- Bonds can form even when **s^2p^6** configurations are **not possible** – for example, atoms like boron have 3 valence electrons and usually can form only 3 covalent bonds, with the final molecular bonds having just 6 electrons. Compounds that contain an **odd number** of electrons form **radicals** that can't satisfy the octet rule. **Larger** atoms ($\geq n=3$) have **available d orbits**, able to hold five and six bonds.
- Many compounds can have **multiple Lewis structures** that satisfy the octet rule. It's necessary to evaluate the **formal charge** of atoms in the resonance structure to find the **lowest energy, most stable** structures.
- **Electronegativity** is a measure of the **pull** that an atom has on electrons **in a chemical bond**. Calculation of the **difference in EN** assists in **distinguishing ionic and covalent** character of bonds.
- **Trends** in **bond energy and bond length** can be predicted. Bonds with **multiple** charges are **higher energy and shorter**.

BEFORE WE TAKE ON BONDING: SOME FINAL PERIODIC TABLE TRENDS

As we leave atoms and take on bonding, we need to look at the properties of the **main group** elements, which are those with valence electrons in s and p orbitals:



These main group materials exhibit very **distinct changes by group**. This makes for easy chemistry to teach. Trends are actually present.

Speaking of trends, a new one, **metallic character**, is in the main group elements. The entire **left** side of the table is **metallic**, with Cs being the most metallic. The **right** side is more **nonmetallic**, but as you go **down** the table in each group, metallic character **increases**. There are also some **metalloids** in the p-block of the table; these are nonmetallic elements with metallic properties.

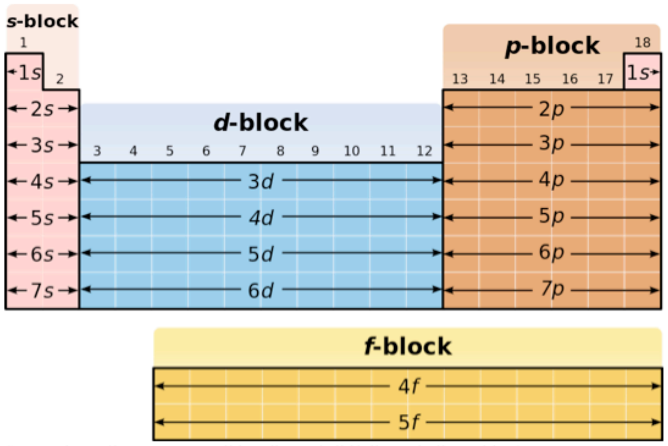
Examples:

- O_2 and S_2 are nonmetal gases.
- Te and Po are metalloids.

TRANSITION METALS

Let's be honest – **d-block elements are a mess**. There are no trends, properties are similar, and they all look like metals. All of this makes them awful to teach in this course.

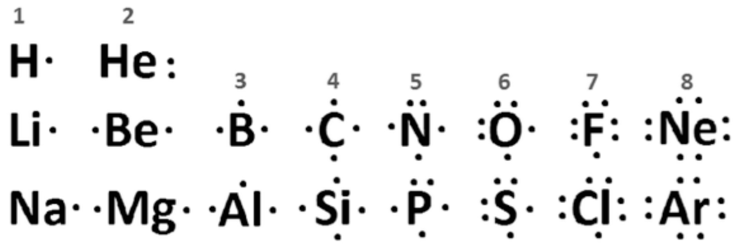
Why are **transition metals** so **similar**? – The electrons in d orbitals are **inner** electrons (i.e., *not* valence; recall: one d orbital has lower energy than the next s orbital). Even still, when a transition metal's number of e^- changes, it's the d orbital electrons that are being changed. So among the transition metals, **valence e^-** are pretty much **constant**, and properties are the same. Can this be a good thing? Well, their **similar atomic radii** let us mix-and-match them to form **alloys** with neat properties, like superconductors. Plus, lots of oxidation numbers mean lots of e^- transfer in biological systems.



Source: https://commons.m.wikimedia.org/wiki/File:Periodic_Table_2.svg

NOW TO BONDING: A COMPARISON OF COVALENT AND IONIC BONDS

Moving on to the big picture! We create **2D Lewis structures** by drawing structures of atoms with their **valence electrons** assigned:

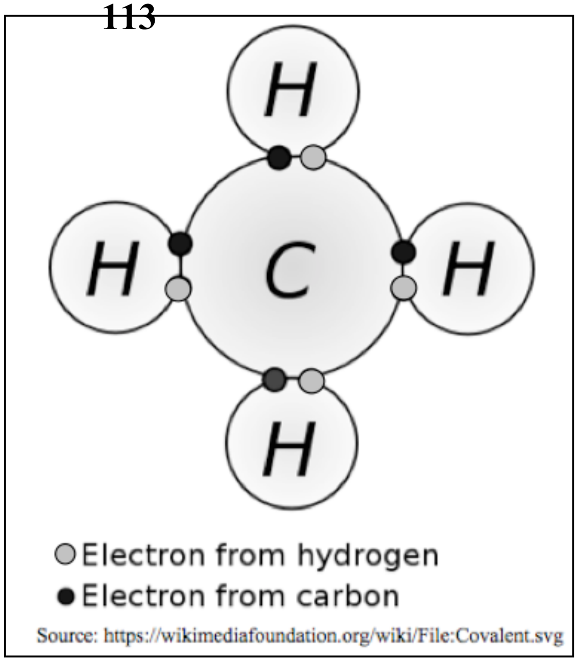


Source: https://wikimediafoundation.org/wiki/File:Lewis_primi_18_elementi.png

Notice that the numbers running along the top are the number of valence electrons.

And mixing and matching to form chemical species in which the **duplet** or **octet** is satisfied.

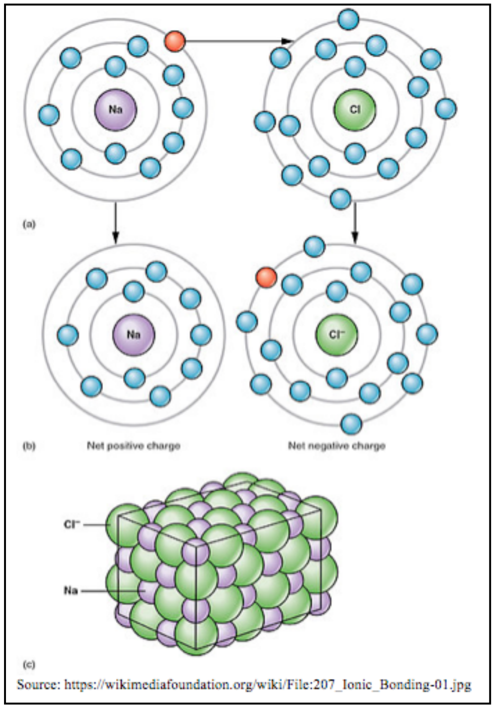
A **bond** is what forms when two electrons are placed in the **same orbital** and the **overall energy** is **lowered**.
There are two kinds of bonds: **ionic** and **covalent** bonds.



Source: https://wikimediafoundation.org/wiki/File:Covalent.svg

<u>Covalent bonds</u> involve electrons being **shared** between two atoms.

<u>Ionic bonds</u> involve a **donation** of electrons from one atom to another.



Source: https://wikimediafoundation.org/wiki/File:207_Ionic_Bonding-01.jpg

<u>ANOTHER PERIODIC TREND: IONIC RADII</u>

Just like the trends we've learned about in previous lectures, **effective nuclear charge** explains **<u>ionic radii</u>**. But there's a complication, because the trend doesn't follow the periodic table, which was built around neutral atoms (with equal numbers of protons and electrons). So to see a smooth trend in ENC – and therefore in ionic radii – we need to rearrange the table in terms of **<u>isoelectronic species</u>**: atoms or ions with the same number of **electrons** (which also means they have the same electronic configurations).

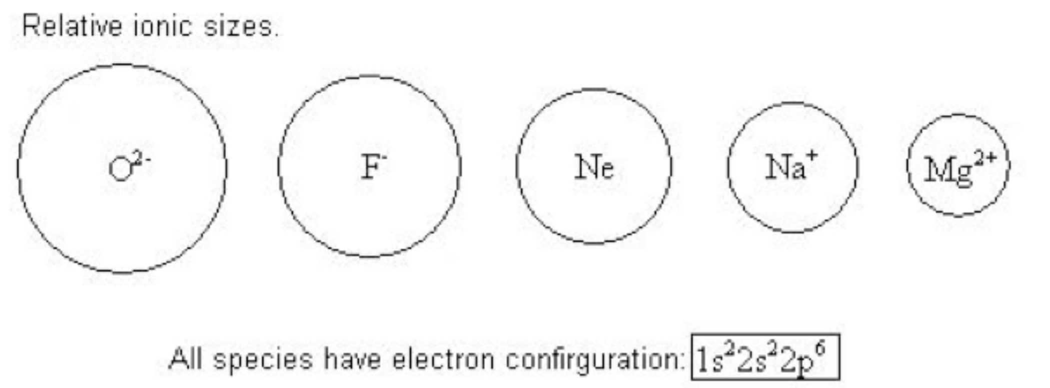
Since isoelectronic species have a certain number of e^-, there is obviously one element with that number of e^- in its neutral form. But the group also has ions that have ended up with that same number, after their neutral form lost or gained e^-. Here's an example where each atom or ion has 10 e^-:

	N^{3-}	O^{2-}	F^{1-}	Ne	Na^{1+}	Mg^{2+}	Al^{3+}
e-	10	10	10	10	10	10	10
p+	7	8	9	10	11	12	13

Smallest ENC
Largest ionic radii

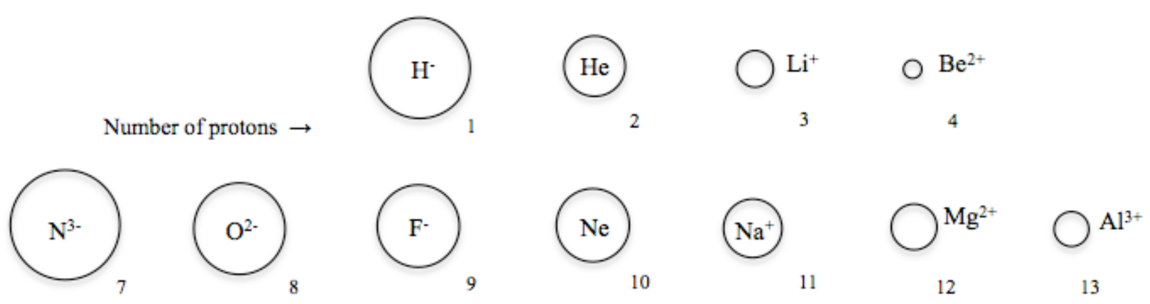
Largest ENC
Smallest ionic radii

Now, since atoms/ions in an isoelectronic species have the same number of electrons but **different numbers of protons**, each will have its own ENC and, consequently, radius size. And there's a trend to these ionic radii – here are some ions from that table, lined up by relative size:



Source: http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Descriptive_Chemistry/Periodic_Trends_of_Elemental_Properties/Periodic_Trends_in_Ionic_Radii

Notice that if you were to put the ions into their respective groups, the order would be: 16 → 17 → 18 (noble gases) → 1 → 2. This mirrors the argument I make in class that an easy way to create an ordered isoelectronic table is to tear the periodic table in half – as in, cut it down the middle and switch the sides, so that group 1 ends up sitting to the right of the noble gases. We also need to move the new right-hand half up by one row, ending up with a table that has Ne ($n = 2$) and Na ($n = 3$) side by side. Here's a picture to help you visualize:



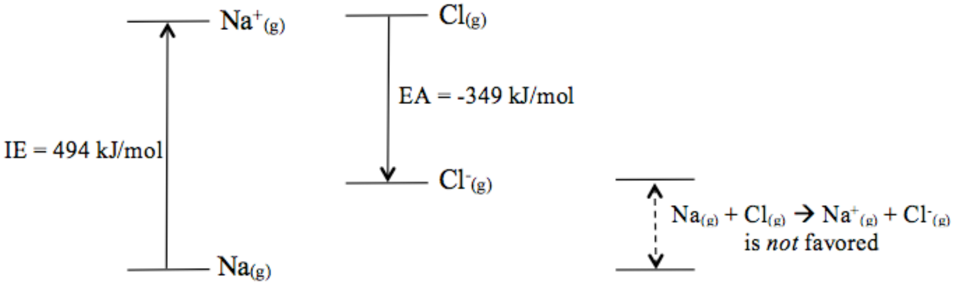
The point of this is to see the ionic radii trend as it goes along the periodic table, so that the ions are ordered by size. It's important to notice that each of the last three graphics shows the exact same ions in the exact same order. It's just that, for that final one, we needed to rearrange the periodic table a little to make that order happen.

THEORY OF IONIC BONDS

Ionic bond formation is often dependent on the phases of the molecules. For example, if we wanted to know whether

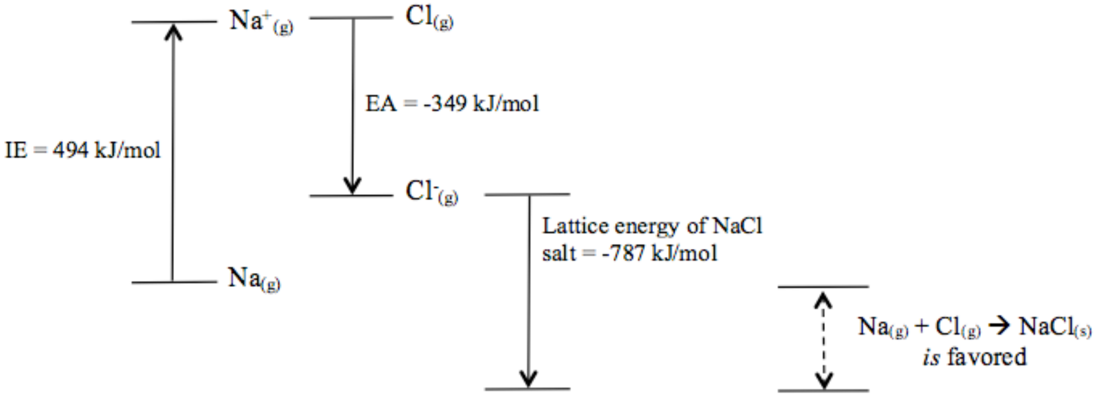
$$Na_{(g)} + Cl_{(g)} \rightarrow Na^{+} \text{ and } Cl^{-}$$

is energetically favored, we could calculate the difference in **ionization energy** of $Na_{(g)}$ and **electron affinity** of $Cl_{(g)}$:



Since $Na_{(g)} + Cl_{(g)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$ requires energy to happen, it's not energetically favored.

But what if our product was a **salt** instead of gas? This means there'd be energy – called **lattice energy** – holding the ions together, due to **Coulombic attraction**:



So our favored reaction turns out to be:

$$Na_{(g)} + Cl_{(g)} \rightarrow NaCl_{(s)}$$

The important thing to note is that even though ion formation is not favored in the **gas** phase, it *is* favored as a **solid** because of all the **Coulombic attraction** present in **salt crystal**.

What kind of **ionic compounds** form? Look at periodic table to see what **combinations** of **electron-donating and electron-accepting groups** can match up – and with what stoichiometry they do – to achieve a **neutral salt**.

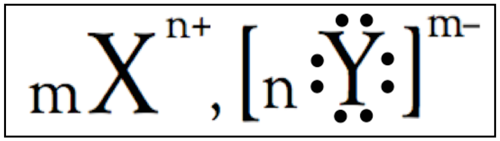
Group	I	II	III	IV	V	VI	VII
Form	$\dot{X}$	$\overset{\cdot}{\underset{\cdot}{X}}$	$\overset{\cdot}{\underset{\cdot}{X}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{X}}\cdot$	$\cdot\overset{\cdot\cdot}{\underset{\cdot}{X}}\cdot$	$\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\cdot$	$\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:$
Elements	Li Na K	Mg Ca Ba	B Al	C Si	N P	O S	F Cl Br

We want to find combinations of X and Y that vield a molecule with 8 electrons.

There are nine possible forms of ionic salts:

Groups to Combine	Cation Form	Anion Form	Salt Form	Example
1 and 7	X^+	Y^-	AB	NaCl
2 and 6	X^{2+}	Y^{2-}	AB	CaO
3 and 5	X^{3+}	Y^{3+}	AB	AlN
1 and 6	$2X^+$	Y^{2-}	A_2B	Na_2O
2 and 7	X^{2+}	$2Y^-$	AB_2	$CaCl_2$
1 and 5	$3X^+$	Y^{3-}	A_3B	Li_3N
3 and 7	X^{3+}	$3Y^-$	AB_3	AlF_3
2 and 5	$3X^{2+}$	$2Y^{3-}$	A_3B_2	Ca_3N_2
3 and 6	$2X^{3+}$	$3Y^{2-}$	A_2B_3	Al_2O_3

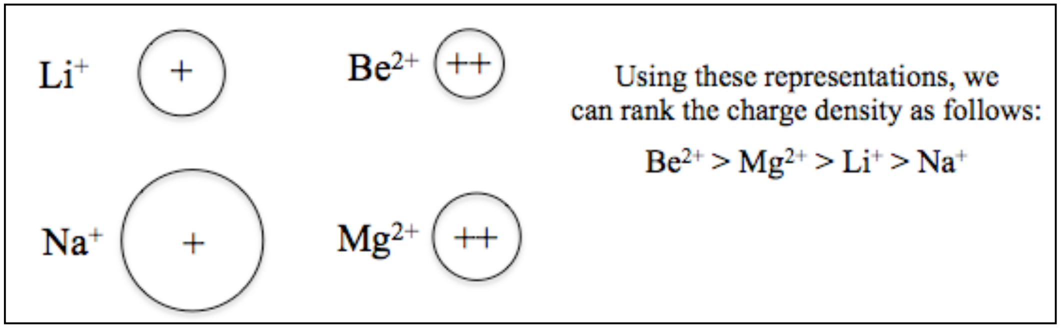
How do we draw structures of ionic bonds? The general Lewis structure of ions is:



$${}_mX^{n+},\ [{}_n:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Y}}:]^{m-}$$

TIME OUT FOR AN ASIDE ON LATTICE ENERGY

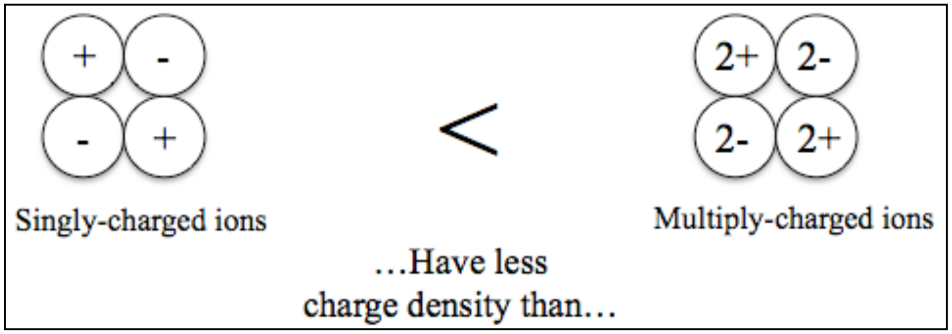
We can develop a reasonable argument with **charge density** considerations that explains the **magnitude** of lattice energy. Consider four ions:



Using these representations, we can rank the charge density as follows:

$Be^{2+} > Mg^{2+} > Li^+ > Na^+$

When we take ions like this and combine them with anions, the **higher the charge density**, the **closer the bonds**, and the **higher the crystal lattice energy**.



Example:

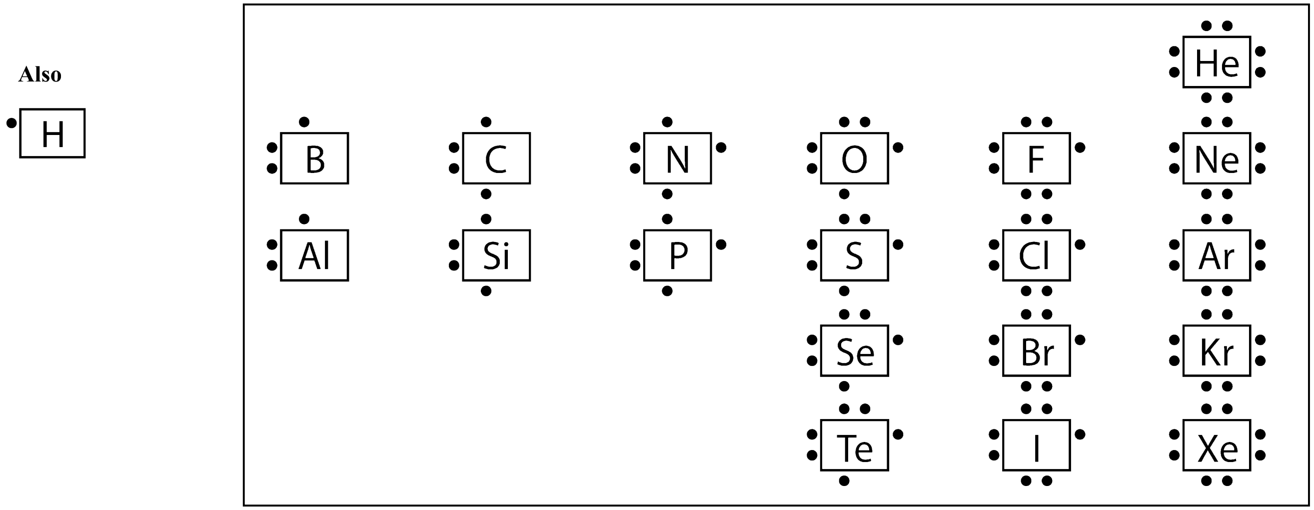
Rank in decreasing order the lattice energies of NaF, $MgCl_2$, KCl.

Solution:

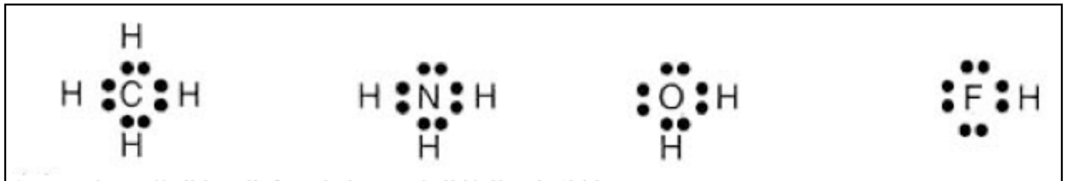
$MgCl_2 > NaF > KCl$ ⟸ $MgCl_2$ has the highest charge density because of its multiply-charged ion (Mg^{2-}). NaF and KCl each have only singly-charged ions, and since NaF is smaller than KCl, KCl has the lower charge density. (Hint: for knowing molecules' size, remember the atomic radius trend.)

LECTURE 8: INTRODUCTION TO COVALENT LEWIS DOT STRUCTURES

In the **upper right** corner of the periodic table are the **nonmetals**. These relatively few atoms have the following Lewis structures:



And we still want to mix and match them to **create filled shells**, like s^2 and s^2p^6. Here are some examples:



Source: https://wikimediafoundation.org/wiki/File:Fig4ld.jpg

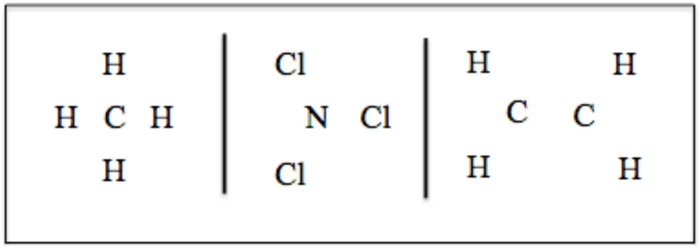
In all cases, **covalent bonds** involve the **sharing** of electrons. **No ions are formed during covalent bonding.**

But there's an important "asterisk" to covalent bonds: though the electrons are shared, they're **not necessarily shared equally** – one atom may tend to "hog" the e^-'s and keep them on its side of the bond. Electronegativity will explain this.

A SYSTEMATIC APPROACH TO DRAWING LEWIS STRUCTURES

Is there a systematic way to build Lewis structures of molecules? Try this:

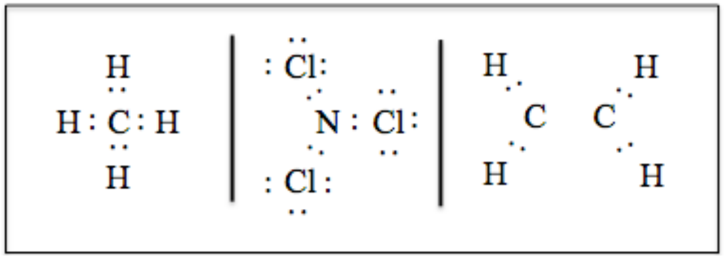
1. Write out the atoms **symmetrically,** with the most **electropositive** in the center:



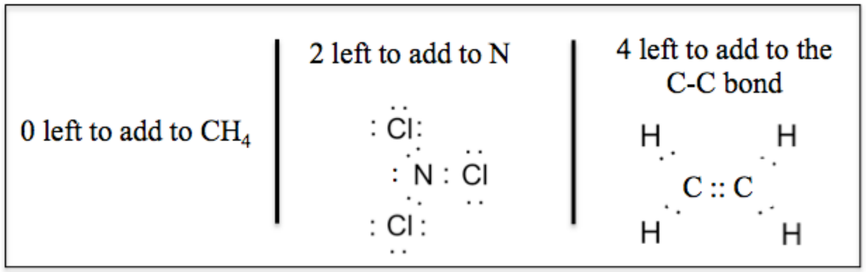
2. Count up the **total** number of **valence electrons** (e.g., hydrogen = 1, carbon = 4, nitrogen = 5):

$CH_4 = 4 + 4(1) = 8$ $NCl_3 = 5 + 3(7) = 26$ $C_2H_4 = 2(4) + 4(1) = 12$

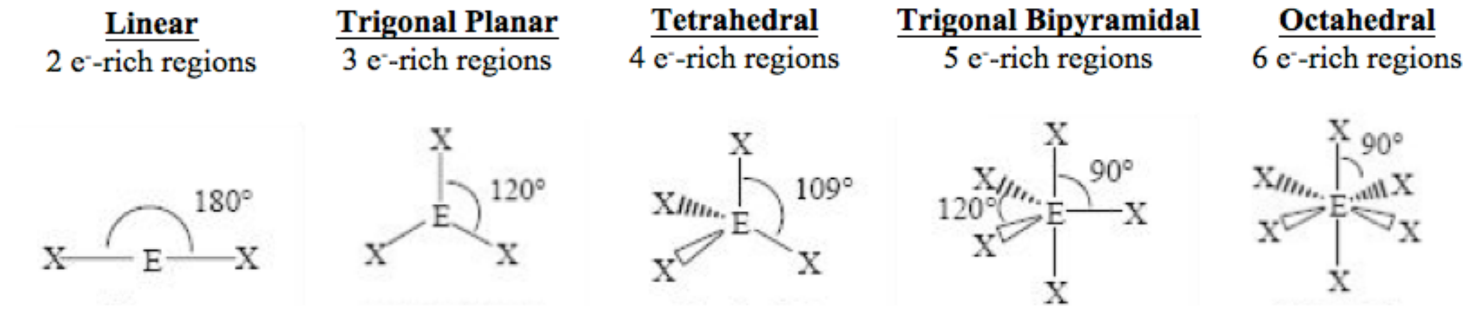
3. Create **octets** and **duplets** for **perimeter atoms**:



4. Put the **remaining e^-'s** around the **central atom**:



Any other helpful hints? Yes – there are a **limited number of shapes** based upon spreading e^- pairs out around the central atom. So know that you need to have an open mind about possible **expanded sizes** to the Lewis structures.

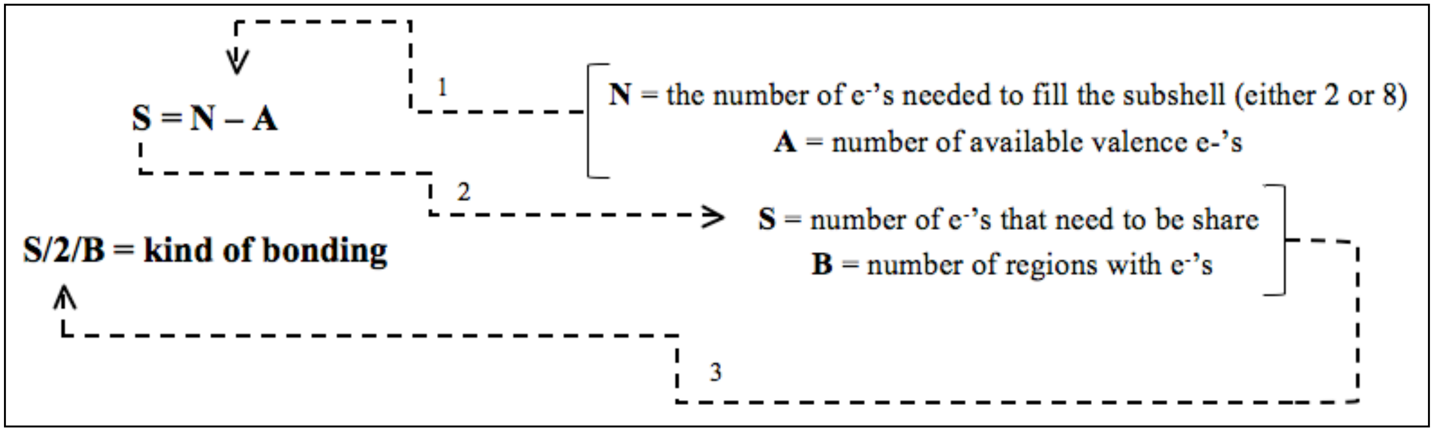


Source: https://wikimediafoundation.org/wiki/File:VSEPR_geometries.PNG

The striped triangles (▨) are bonds on the z-axis (perpendicular to the page); they're pointing away from you, into the page. (Like if you put the pointy end of a nail to this smiley face ☺ and hammered it through the page; the shaft of the nail would be oriented like one of these bonds.)

The white triangles (◁) are bonds that are also on the z-axis, and they are pointing out of the front of the page. (Like if someone did the same nail/hammer thing (see other text box), except from the back of the page; you'd be looking at the pointy end and the nail shaft would be coming out at you on this side of the page, just like one of these bonds.)

Any other help? Yes – there is a simple calculation involving the number of **shared electrons** and number of **bonding sites** that tells you what kind of bonding (i.e., single, double, triple) is there:



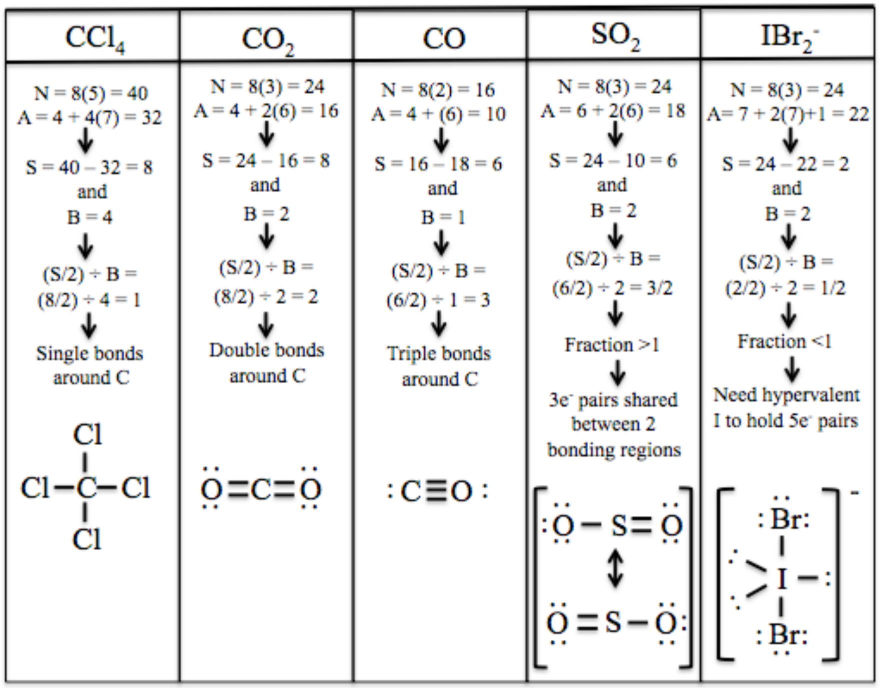
S = N – A

S/2/B = kind of bonding

N = the number of e^-'s needed to fill the subshell (either 2 or 8)
A = number of available valence e-'s

S = number of e^-'s that need to be share
B = number of regions with e^-'s

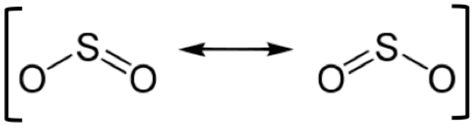
This can be very helpful when it works (when the octet rule is satisfied) but really misleading when it doesn't (when you have hypo- or hypervalent structures that don't satisfy the octet rule). I personally never use it, but, then again, I am a chemistry professor. You might find it a good way to get started on learning this material when you are in doubt about resonance or the number of double or triple bonds.



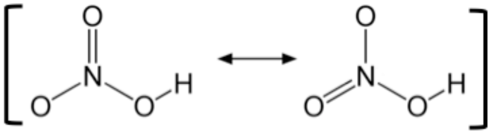
CCl_4	CO_2	CO	SO_2	IBr_2^-
N = 8(5) = 40 A = 4 + 4(7) = 32	N = 8(3) = 24 A = 4 + 2(6) = 16	N = 8(2) = 16 A = 4 + (6) = 10	N = 8(3) = 24 A = 6 + 2(6) = 18	N = 8(3) = 24 A= 7 + 2(7)+1 = 22
↓	↓	↓	↓	↓
S = 40 – 32 = 8 and B = 4	S = 24 – 16 = 8 and B = 2	S = 16 – 18 = 6 and B = 1	S = 24 – 10 = 6 and B = 2	S = 24 – 22 = 2 and B = 2
↓	↓	↓	↓	↓
(S/2) ÷ B = (8/2) ÷ 4 = 1	(S/2) ÷ B = (8/2) ÷ 2 = 2	(S/2) ÷ B = (6/2) ÷ 1 = 3	(S/2) ÷ B = (6/2) ÷ 2 = 3/2	(S/2) ÷ B = (2/2) ÷ 2 = 1/2
↓	↓	↓	↓	↓
Single bonds around C	Double bonds around C	Triple bonds around C	Fraction >1	Fraction <1
			↓	↓
			3e⁻ pairs shared between 2 bonding regions	Need hypervalent I to hold 5e⁻ pairs
Cl Cl–C–Cl Cl	Ö=C=Ö	:C≡O:	[:Ö–S=Ö ↕ Ö=S–Ö:]	[:Br: I :Br:]⁻

EXPLAINING RESONANCE

Drawing Lewis structures lets us explain **resonance**, which is a property of a molecule whose structure has **multiple, equivalent ways** of being drawn. When this happens, we can draw **multiple Lewis structures**. The examples we see most often are when 3 e⁻'s are placed in 2 regions of e⁻'s:

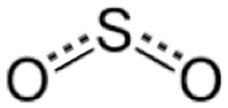


Source: https://wikimediafoundation.org/wiki/File:Sulfurdioxide-resonance.svg

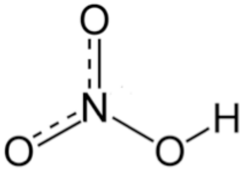


Source: https://wikimediafoundation.org/wiki/File:Nitric-acid-resonance-A.png

Note that when we get lazy, we draw… - - - - - …instead of all the different structures:



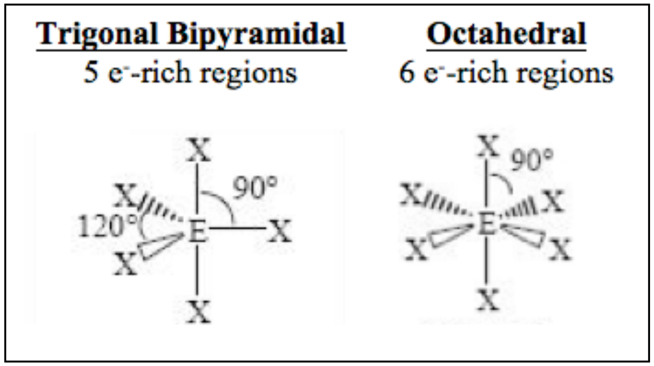
Source:https://wikimediafoundation.org/wiki/File:Sulfurdioxide-resonance.svg



Source:https://wikimediafoundation.org/wiki/File:Nitric-acid-resonance-A.png

HYPERVALENT COMPOUNDS

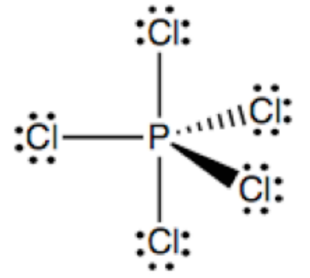
Hypervalent compounds are ones with **5 or 6 electron-rich regions**. They do exist, and they’re nothing to panic about. There are only 2 possible Lewis structures for these:


Trigonal Bipyramidal
5 e^{-}-rich regions

Octahedral
6 e^{-}-rich regions

Example – PCl_5 has 40 valence e^{-}’s to distribute in its Lewis structure.

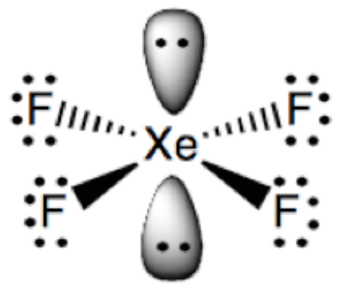
- This structure shows us that **P must accommodate 5 bonds**.



Source: http://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/readings-and-lecture-notes/lecnotes13.pdf

Example – XeF_4 has 36 valence e^{-}’s to distribute in its Lewis structure.

- After we put 32 electrons around the perimeter atoms (the F’s), we still had 4 e^{-}’s to add to our compound. Those were added to the central atom, so it ended up with **6 electron-rich regions** – 4 of them single bonds between Xe and F, and 2 of them **non-bonding electrons** (lone pairs) on Xe.



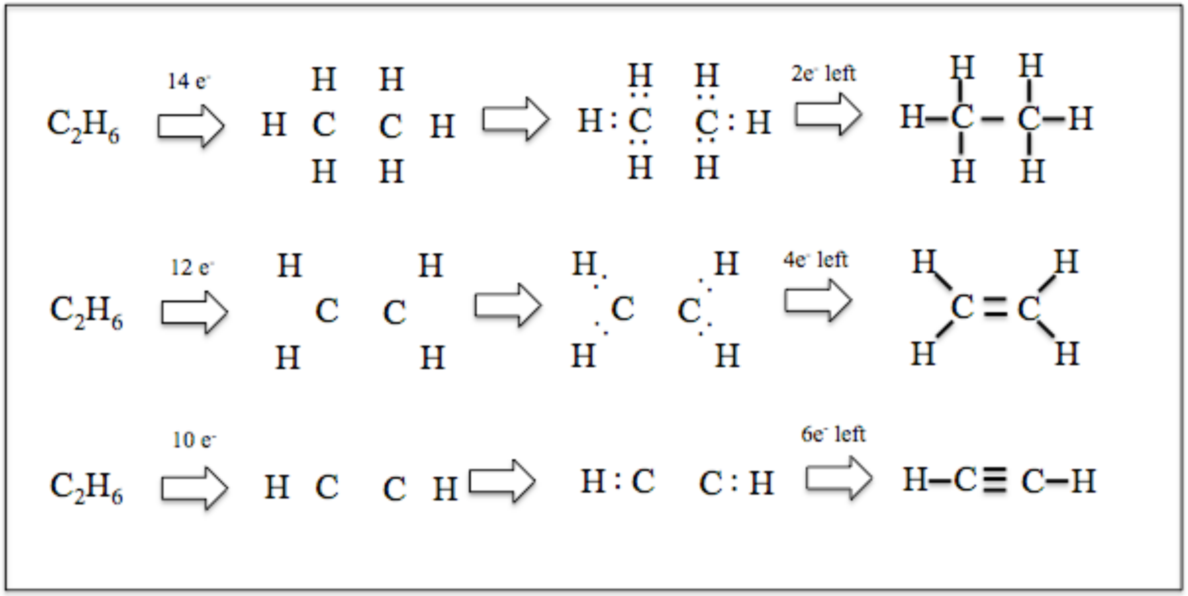
Source: http://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/readings-and-lecture-notes/lecnotes13.pdf

MULTIPLE CENTRAL ATOMS

I'm bored by all these single central atoms. What about molecules with multiple central atoms? How do we draw Lewis structures for those? Well, we draw them just as we drew molecules with a single central atom:

1. Lay out all the atoms.
2. Count the total number of valence electrons.
3. Give the perimeter atoms their valence e⁻'s.
4. Distribute the remaining electrons around the center atoms.

Here are 3 famous examples:



You'll do this for all organic compounds. They almost always end up with 8 e⁻'s around each carbon (as in, its *n* = 2 shell gets filled) and 2 on each hydrogen (its *n* = 1 shell gets filled).

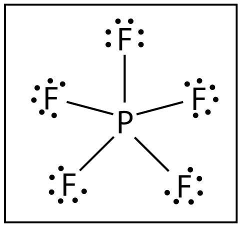
IS THE OCTET/DUPLET RULE ALWAYS FOLLOWED?

A preface in the form of a high school chemistry flashback:

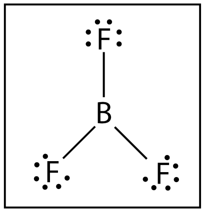
The **octet/duplet rule** says that atoms will **covalently bond** to form molecules in which their **outermost/valence shells** are **filled**. So since $n = 2$ atoms' outermost shell can hold up to 8 electrons, they bond in such a way that gives that shell an **octet** – **a set of 8 electrons** – because a **full valence shell** means a **stable configuration**. The same idea applies to the $n = 1$ atoms (H and He), except that their outermost shell hold up to **2 electrons**, so a full shell has a **duplet**.

Now, back to the question/section title. The answer is no – there are **3 exceptions** to the octet/duplet rule:

- The **hypervalent case** – **more than 8** electrons are around the central atom, like in the cases of SF_6, XeF_4, IBr_2^-, PCl_5, etc. This happens with $n \geq 3$ **atoms**, because they have available **d orbitals**.

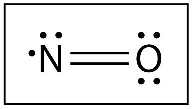


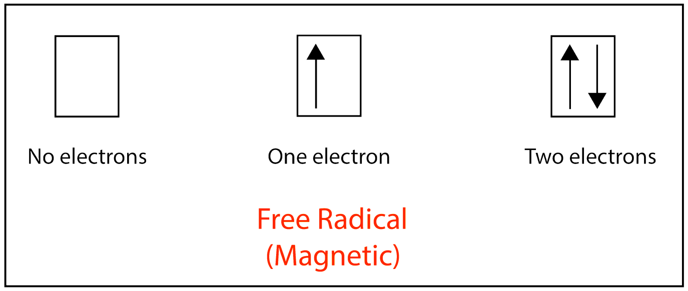
- The **hypovalent case** – **fewer than 8** electrons are around the central atom, like in molecules with B or Be as the central atom. There are too few electrons to form an octet.
  - H has 1 valence e^- → it can use it to form 1 bond.
  - Be has 2 valence e^-'s → it can use them to form 2 bonds.
  - B has 3 valence e^-'s → it can use them to form 3 bonds.



Hint: if you ever see a compound with **boron**, it will be a hypovalent exception to the octet rule.

- The **odd case** – valence shells with an **odd number of electrons** – not all of the electrons can "buddy up," so one **electron pair can't form**. This means that, instead of an "electron pair," there will be one **radical**.



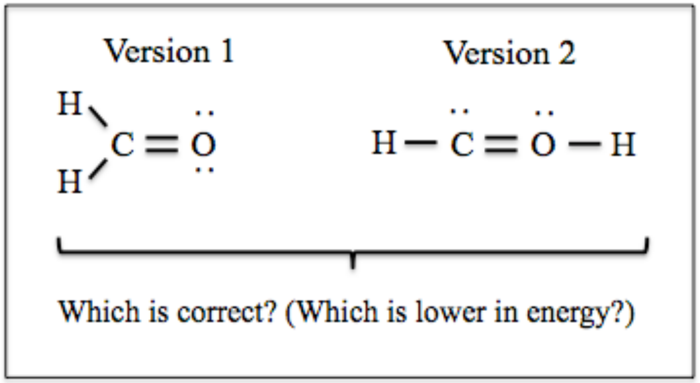


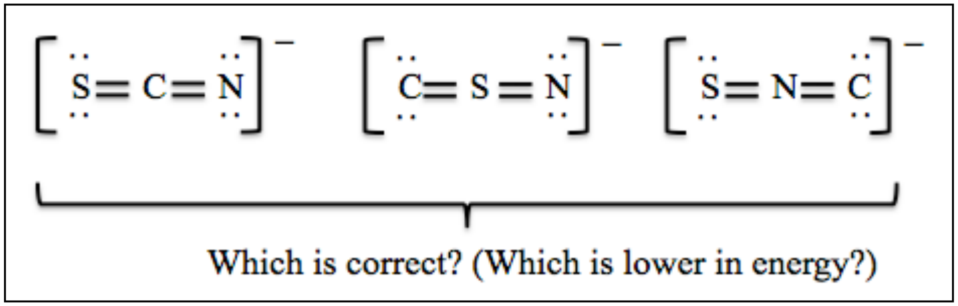
LECTURE 9: MORE SOPHISTICATED IDEAS IN LEWIS DOT STRUCTURES

Can we make things more difficult? Sure!

FORMAL CHARGE

Let's discuss **formal charge**. First, why do it? Consider the following examples of two molecules – CH_2O and SCN^- – that each have multiple Lewis structures fitting our rules:

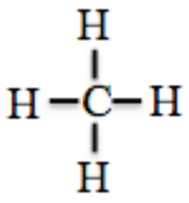




We need to find the **formal charge** of **each atom** to solve this problem. The compound with the **smallest** formal charge values is the **most stable**, which makes it the correct Lewis structure for that molecule. So how do you calculate FC?

Formal charge = (# of the atom's valence e^-'s) - (2e^-'s for every *unbonded* e^--pair + 1e^- from each *bonded* e^--pair)

Let’s assign the formal charges for the atoms in CH_4:

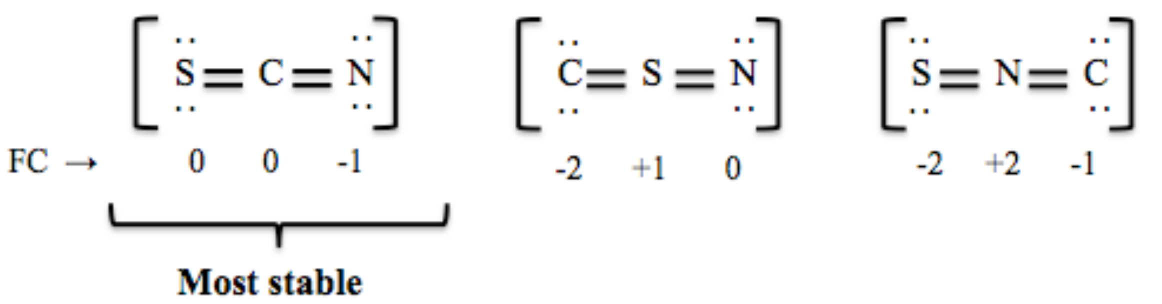


Formal charge → H = (1 valence e^-) – (1 bonded e^-) = 0

Formal charge → C =(4 valence e^-) – (4 bonded e^-) = 0

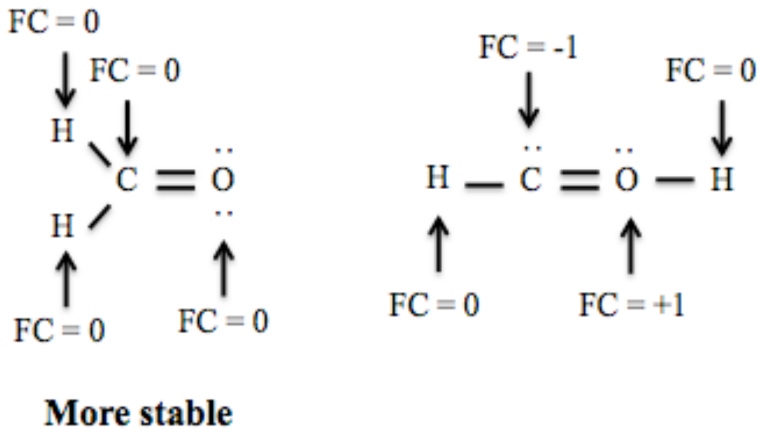
Example:
Which of the following Lewis structures for CH_2O is more stable?

Solution:



Example:
Which of the following Lewis structures for SCN^- is most stable?

Solution:

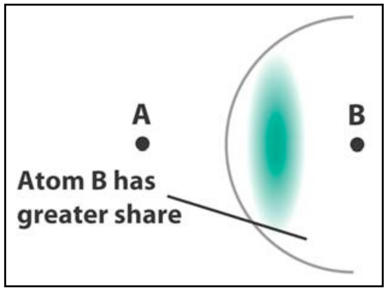


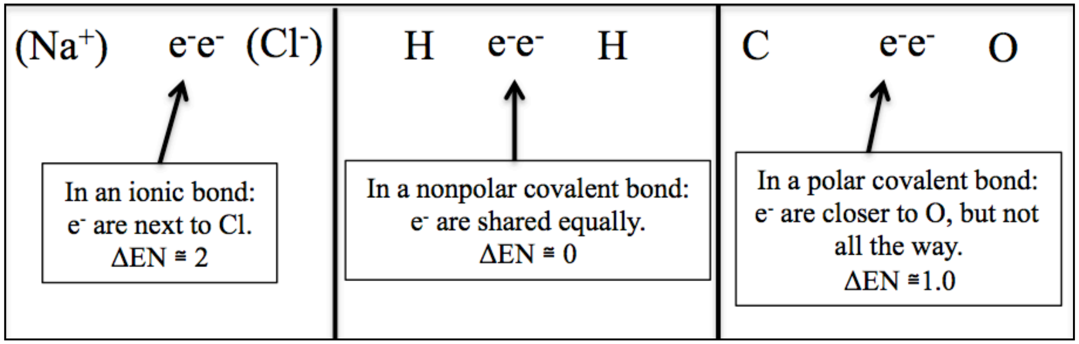
ELECTRONEGATIVITY

How do we distinguish whether a bond is **ionic or covalent**? We can determine this in a quantitative manner using **electronegativity**:

Δ EN < 1.5 is covalent
Δ EN > 1.5 is ionic

But what is EN? **Electronegativity** is a measure of an atom's **pull on electrons**. For the figures below, the atoms on the right side of the bond pull more (have higher EN), and the atoms on the left pull less (have lower EN).



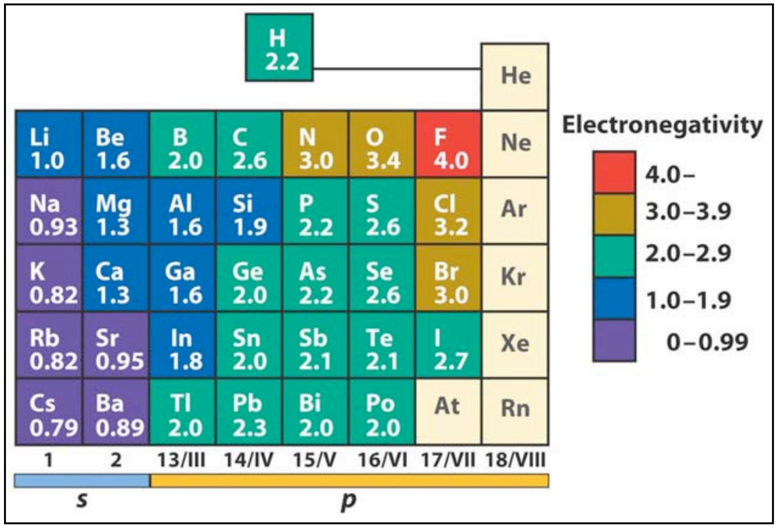


In an ionic bond: e^- are next to Cl. ΔEN ≅ 2

In a nonpolar covalent bond: e^- are shared equally. ΔEN ≅ 0

In a polar covalent bond: e^- are closer to O, but not all the way. ΔEN ≅1.0

So where do these numbers for ΔEN come from? – Both Linus Pauling and Robert Millikan made scales. You'll have to know some elements' EN values (mostly from the second row), but they're easy – here is a rough version that makes them easy to remember in calculations. Starting on the left of the **second row**, assign **Li = 1.0**, and **add 0.5** to each successive element as you move to the right across the table; you should end up with **F = 4.0**. Another (final) element to know is H, which is **H = 2.2**. And that's all there is to it!



1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
			H 2.2				He
Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0	Ne
Na 0.93	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar
K 0.82	Ca 1.3	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 3.0	Kr
Rb 0.82	Sr 0.95	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe
Cs 0.79	Ba 0.89	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At	Rn
s		*p*					

Electronegativity
🟥 4.0–
🟨 3.0–3.9
🟩 2.0–2.9
🟦 1.0–1.9
🟪 0–0.99

Just like other trends, this EN trend can be drawn as a diagonal from the bottom left of the table to the top right. This is also due to effective nuclear charge.

Example:

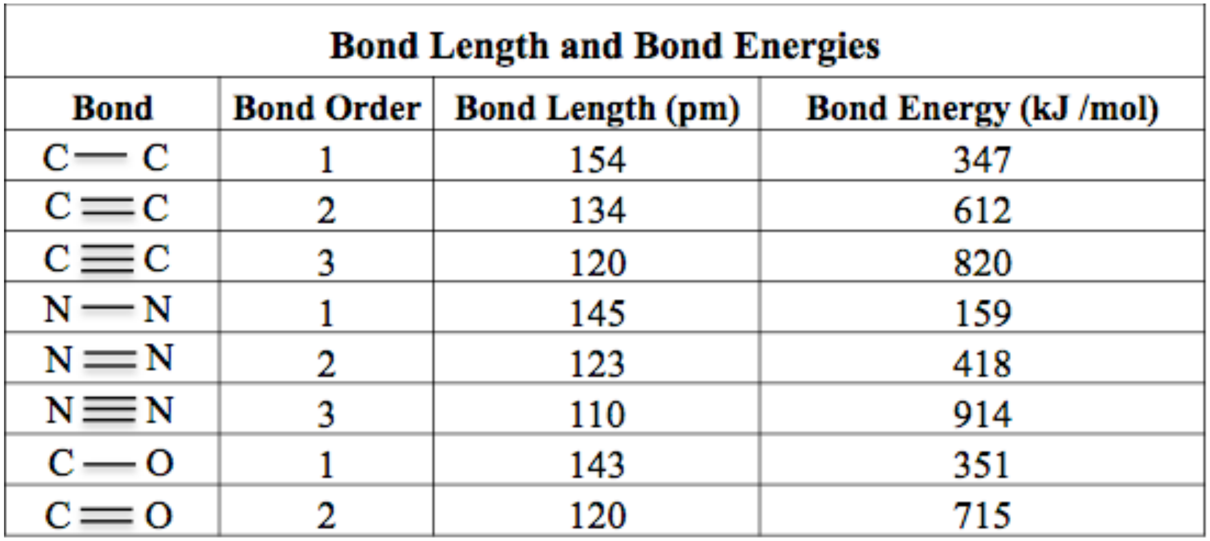
What are the |ΔEN| values for CO, F_2, and Li_2O? What kind of bonds are they?

Solution:

For C–O → |ΔEN| = |2 – 3| = 1.0 → This is a nonpolar covalent bond.
For F–F → |ΔEN| = |4 – 4| = 0 → This is a nonpolar covalent bond.
For Li_2O → |ΔEN| = |1 – 3.5| = 2.5 → This is an ionic bond.

BOND ENERGY AND LENGTH TRENDS

As we add **more bonding** (single, double, triple), the "**glue**" that binds two atoms to one another **increases**. This also means that the **length** of the bond between them **decreases**.



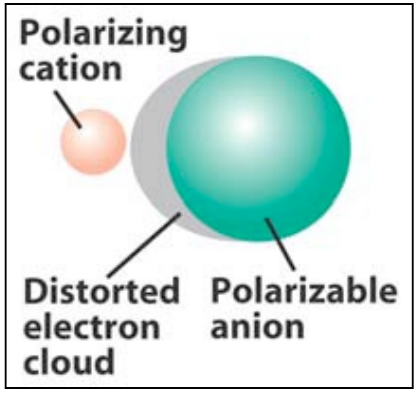
Bond Length and Bond Energies

Bond	Bond Order	Bond Length (pm)	Bond Energy (kJ /mol)
C—C	1	154	347
C=C	2	134	612
C≡C	3	120	820
N—N	1	145	159
N=N	2	123	418
N≡N	3	110	914
C—O	1	143	351
C=O	2	120	715

Type of carbon-carbon bond	Bond length (pm)	Length trend	Bond energy (kJ/mol)	Energy trend
C–C (single bond)	154	Length decreases, bonding increases; **inversely** proportional.	348	Energy increases, bonding increases; **directly** proportional.
C=C (double bond)	134		612	
C≡C (triple bond)	120		837	

POLARIZABILITY

As we travel down the periodic table, **electron density** gets more and more **distorted**. This results in a **decrease** in the ability to form **strong bonds**, hence the tendency for **bond energies** to **go down**.



For example, check out these bond strengths:

HF > HCl > HBr > HI.

Group VII	
HF	543
HCl	419
HBr	354
HI	287

LECTURE 10: TURNING 2D STRUCTURES INTO 3D VSEPR MODELS TO INVESTIGATE POLARITY

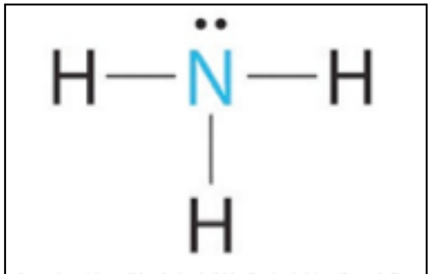
The (Really) Big Picture

In our first lectures on bonding, we dealt in two-dimensions, our chemical structures being well-developed ionic and covalent 2D structures that were based upon simple concepts, like ΔEN and the stability of octet electronic configurations.

Now we'll become more sophisticated as we develop **three-dimensional** structures of covalently bonded compounds. We will use **valence shell electron pair repulsion theory** (**VSEPR**), and we'll devise more satisfactory bonding orbitals based on **valence bond theory** (**VB**). Then we learn about a sophisticated mathematical model for bonding called **molecular orbital theory** (**MO**).

A sneak peek of what's to come – an example of NH_3:

As a Lewis structure:



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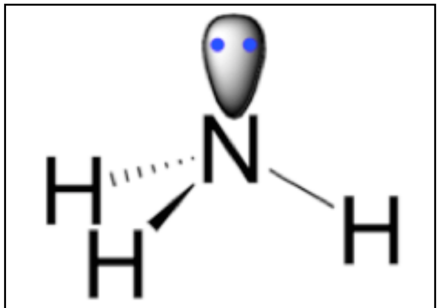
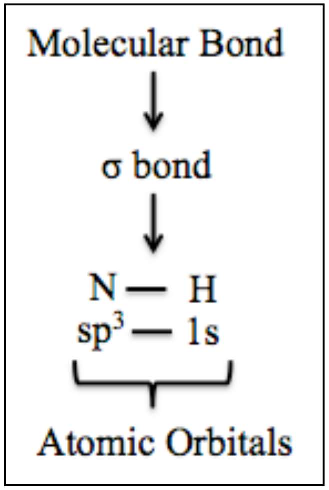
With VSEPR theory:



Source:http://chemwiki.ucdavis.edu/Organic_Chemistry/UMM_chemwiki_project/Organic_Structure_and_Bonding/Valence_bond_theory

With VB theory:



In **VSEPR theory**, the first thing you look for is the **number of regions of electron density**. Regions of e⁻-density can be either a **nonbonding e⁻-pair** or a **bonding e⁻-pair** around an atom. Note that NH_3 has four regions, three of which are bonding and one that's nonbonding.

REGIONS OF ELECTRON DENSITY

The number of **regions of e$^-$-density** tells us **three** important **structural** features:

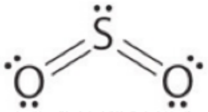
- **Electronic geometry**
  - Example: NH_3 with 4 electron-rich regions → its electronic geometry is **tetrahedral**
- **Bond angles**
  - Example: NH_3 with 4 electron-rich regions → its bond angles are **109.5°**
- **Hybridization**
  - Example: NH_3 with 4 electron-rich regions → its hybridization is **sp^3**

We'll be going over these structural features in the next few lectures.

Examples:

SO_2

Number of e$^-$-rich regions = 3
Electronic geometry = trigonal planar
Bond angles = 120°
Hybridization = sp^2



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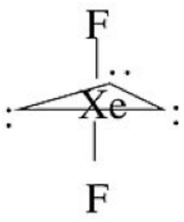
XeF_2

Number of e$^-$-rich regions = 5
Electronic geometry = trigonal pyramidal
Bond angles = 90°, 120°, 180°
Hybridization = sp^{3}d



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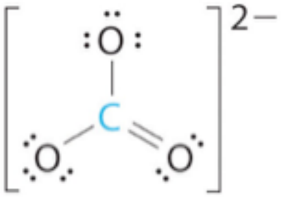
CO_3^{2-}

Number of e$^-$-rich regions = 3
Electronic geometry = trigonal planar
Bond angles = 120°
Hybridization = sp^2



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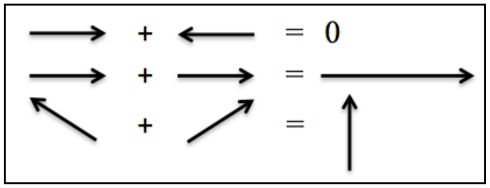
SF_6

Number of e$^-$-rich regions = 6
Electronic geometry = octahedral
Bond angles = 90°, 180°
Hybridization = sp^{3}d^2

Source: http://cnx.org/contents/1a7fcf57-8f3a-430a-a1bf-cdbdea263263@7/Molecular-Structure-and-Polari

IDENTIFYING POLAR AND NONPOLAR COMPOUNDS USING VECTOR ALGEBRA

And now a time-out for a bit of vector math so we can learn about another layer of chemical information: whether a compound is **polar or nonpolar**.

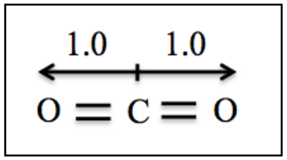


This bit of high school math will be used to **add ΔEN vectors** together. Why? – Because, by definition:

In a **nonpolar** molecule → $\mathbf{\Sigma\Delta EN = 0}$

In a **polar** molecule → $\mathbf{\Sigma\Delta EN \neq 0}$

Example – CO_2:



Find the ΔEN of each bond:

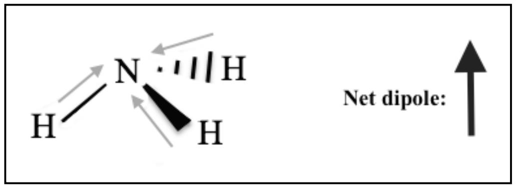
EN of C = 2.5 and EN of O = 3.5 → $\Delta EN = 3.5 - 2.5 = 1.0$

Then sum the two bonds:

$\Sigma\Delta EN = 1.0 + (-1.0) = 0$

Since $\Sigma\Delta EN = 0$, we know CO_2 is nonpolar.

Example – NH_3:



The vectors do not cancel out, so $\Sigma\Delta EN \neq 0$. Therefore, NH_3 is polar.

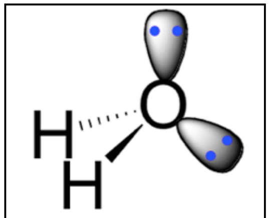
A Famous Example – VSEPR Shows That H_2O Is Polar

As we know, the **Lewis structure** of H_2O looks like this:

$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$

Since there are two O–H vectors going in opposite directions, it seems clear that $\Sigma\Delta EN = 0$, indicating that H_2O is a **nonpolar** molecule.

But showing H_2O in **three dimensions** using **VSEPR**, instead of in two dimensions as a Lewis structure, changes the story:



Source:http://chemwiki.ucdavis.edu/Organic_Chemistry/UMM_chemwiki_project/Organic_Structure_and_Bonding/Valence_bond_theory

It's now clear that **H_2O is a polar molecule**. We will later see that this fact has profound consequences on the chemistry of water solutions.

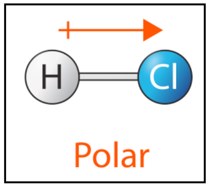
More Examples: Summing ΔEN Vectors

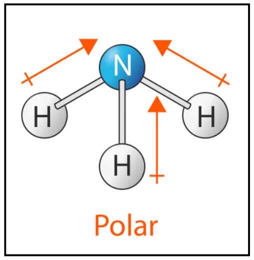
Let's take our previous definitions of polar and nonpolar compounds and make them a bit more interesting:

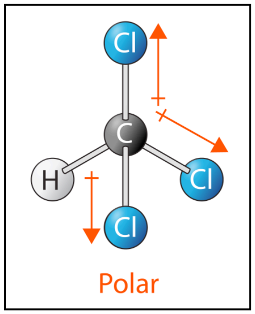
In a **nonpolar** molecule: **$\Sigma\Delta EN = 0$** *or* **non-symmetrical.**

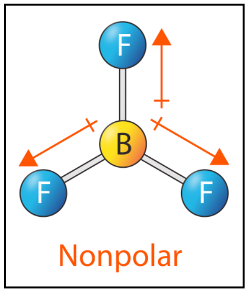
In a **polar** molecule: **$\Sigma\Delta EN \neq 0$** *or* **symmetrical.**

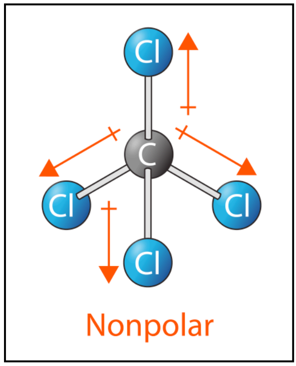
Here are some examples:







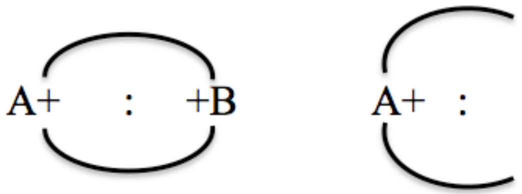




LECTURE 11: AN INTRODUCTION TO VB AND VSEPR THEORY

Now that we can draw 2-dimensional structures using Lewis dot structures, let's move on to doing that in 3 dimensions. How do we do that? By using **valence shell electron pair repulsion (VSEPR) theory.**

VSEPR says that, around any central atom, **electron-rich regions** tend to move and stay **as far away from each other as possible**. But what are electron-rich regions?



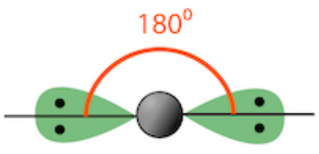
Bonding e^- pair is constrained.

Unbonded e^- pair takes up more space.

→ So in H_2O, the unbonded electrons on O take up more space than the electrons in O-H bonds.

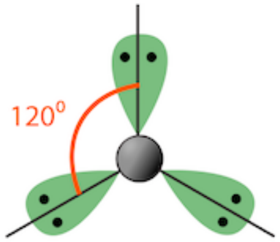
There are 5 "foundational" shapes of VSEPR to consider:

2 electron-rich regions



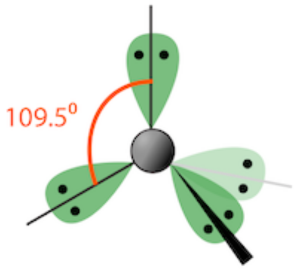
Linear

3 electron-rich regions



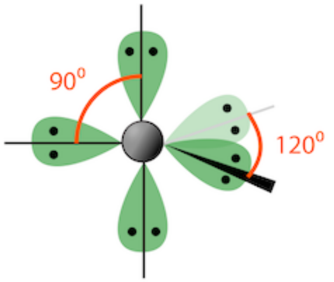
Trigonal Planar

4 electron-rich regions



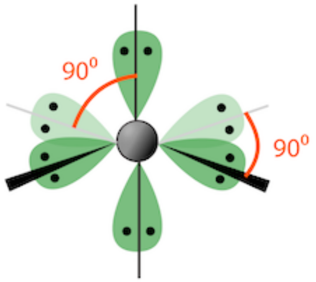
Tetrahedral

5 electron-rich regions



Trigonal Bipyramidal

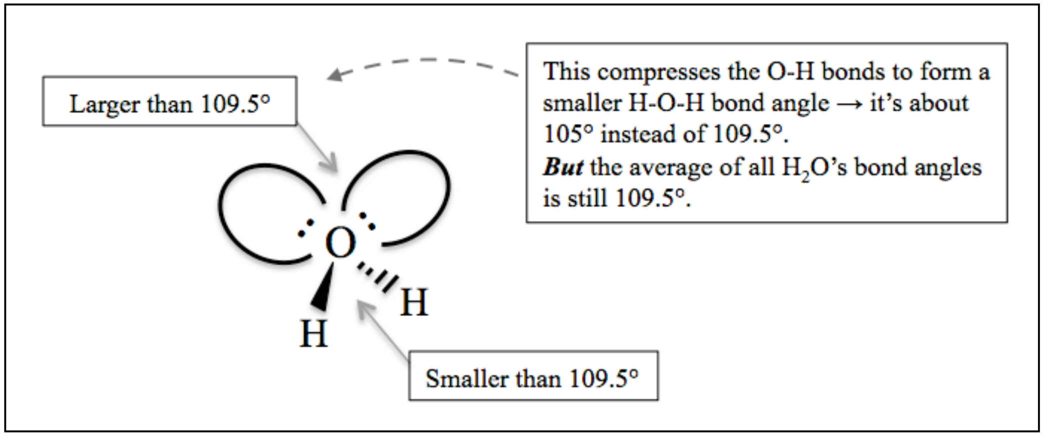
6 electron-rich regions



Octahedral

AN EXCEPTION TO SIMPLE BOND ANGLES

Bonded and unbonded e-pairs are not the same thing. **Bonded e-pairs are constrained by *two* nuclei**, so they take up **less space** (because they're held more tightly and closely to the nuclei) **than if they were constrained by a *single* nucleus**:



This compresses the O-H bonds to form a smaller H-O-H bond angle → it's about 105° instead of 109.5°.
But the average of all H_2O's bond angles is still 109.5°.

A GLIMPSE OF THE NEXT THREE LECTURES

As we finish up our unit on bonding, we'll be learning about some pretty advanced ideas and theories related to (guess what!) chemical bonds. A word of warning: it's going to be important that you keep these concepts straight; they're easy to mix up, and that will not make learning this already-tough stuff any easier. So pay close attention, and follow the sequence. Some names sound confusingly similar but are not the same, such as "molecular geometries" vs. "molecular orbitals" vs. "molecular orbital theory." Of course they're related, but as we teach them, you'll want to keep them in their own compartments; you'll see what I mean when we get there, but you should take my word for it now.

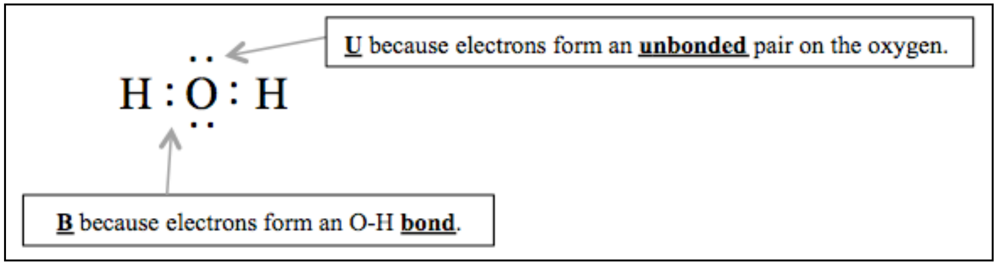
To start you off, here are the main topics gone through in each of the next three lectures:

This lecture's (#11) overarching topic: VSEPR.
    Subtopics – electronic geometries, molecular geometries (pretty hard), multiple central atoms (pretty easy).
Next lecture's (#12) overarching topic: valence bond (VB) theory.
    Subtopics – atomic orbits, molecular orbits (really hard), hybrid orbits (kind of hard).
Next-next lecture's (#13) overarching topic: molecular orbital (MO) theory.

MOLECULAR GEOMETRIES

Before we actually get started here, here's a tip: the next few pages are about both electronic geometries and molecular geometries. Electronic geometries are the simpler, "let's not put *that* much thought into it" version of molecular geometries (but we're learning both, so obviously we are going to put that much thought into it). We'll be talking a lot about both of them for the rest of the chapter, so be sure to keep them straight.

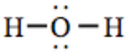
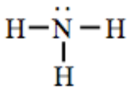
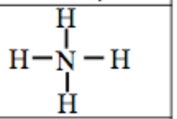
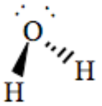
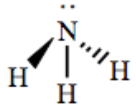
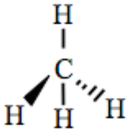
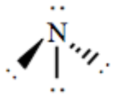
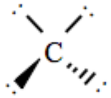
At the beginning of this lecture, we looked briefly at e-rich regions. Now let's think more deeply about them. Check out what happens when you distinguish **bonded (B) e-pairs from unbonded (U) e-pairs**:



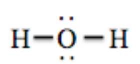
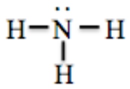
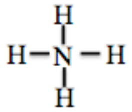
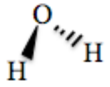
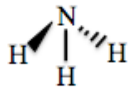
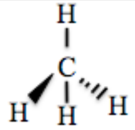
U because electrons form an **unbonded** pair on the oxygen.

B because electrons form an O-H **bond**.

Keeping this in mind, consider three compounds, all with 4 e-rich regions (and therefore tetrahedral):

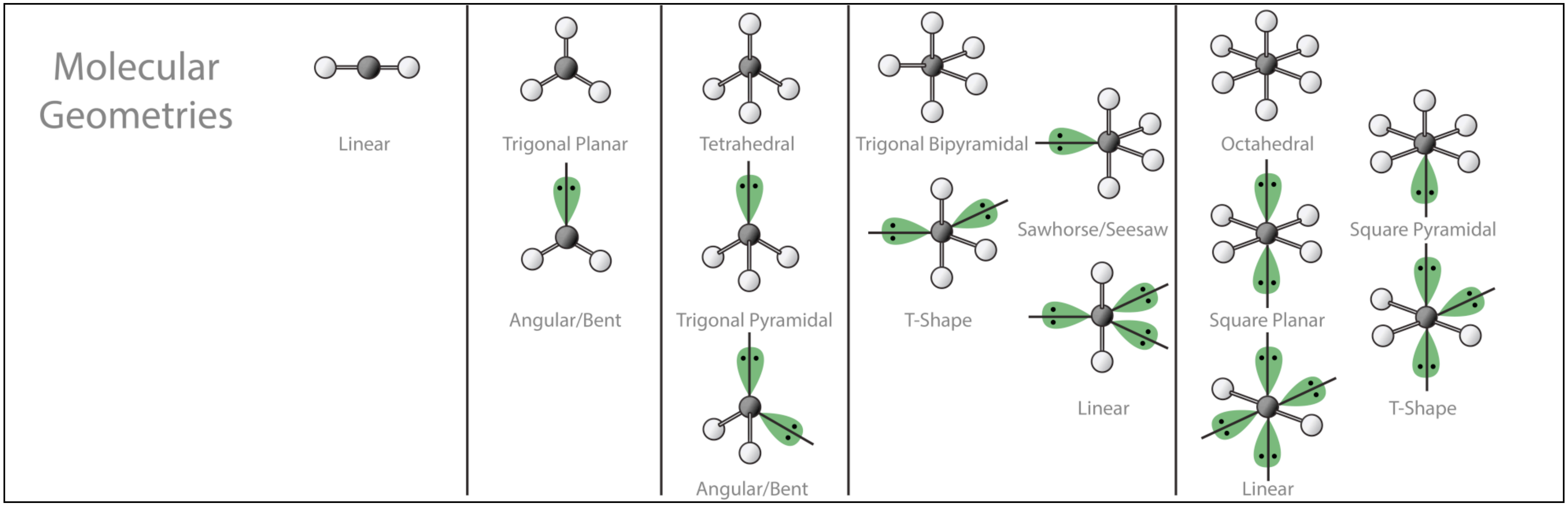
	H_2O	**NH_3**	**CH_4**
In 2D			
In 3D			
# of e-rich regions	4	4	4
Electronic shape			
Electronic geometry	Tetrahedral	Tetrahedral	Tetrahedral
Bond angle	109.5°	109.5°	109.5°
Hybridization	sp^3	sp^3	sp^3

How are they different? – In their numbers of B and U electrons:

	H_2O	NH_3	CH_4
In 2D	 $\mathrm{H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H}$	 $\mathrm{H-\underset{H}{\overset{\cdot\cdot}{N}}-H}$	 $\mathrm{H-\underset{H}{\overset{H}{N}}-H}$
# of B and U electrons	AB_2U_2	AB_3U	AB_4
Drawn without U electrons			
Overall shape			
Molecular geometry	Angular	Pyramidal	Tetrahedral

As you can see, paying attention to whether an e-pair is B or U makes a huge difference when it comes to assigning a molecule's shape. And to put it very generally, that's pretty much the difference between electronic geometries and molecular geometries: electronic geometries are based upon the number of e-rich regions, with no regard for B vs. U pairs; molecular geometries, on the other hand, are based upon the number of e-rich regions, and whether each e-pair is B or U.

There are only 5 electronic geometries; they're the "foundational" VSEPR shapes that we looked at in the beginning of this lecture. There are **15 molecular geometries (5 of which are the electronic geometries)**, but fortunately they have shapes that make sense. Let's take a look at them before going into detail:

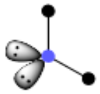
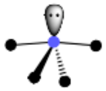
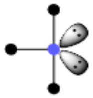
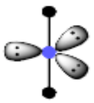


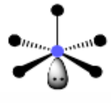
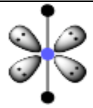
Each line extending from the center atom is an e-rich region. Notice that each e-rich region has either a dark lobe or a light circle at the end of it. The **lobes represent unbonded e-pairs**, and the **circles represent bonded e-pairs**. Most molecules have at least one unbonded pair, but not all of them do – **the 5 that have only bonded electrons are the electronic geometry shapes**. Those are the simplest of the molecular geometries. Also, even molecular geometries with U's are assigned an electronic geometry; it's always the one with the same number of e-rich regions.

Unbonded pairs in a molecule obviously play a major role in determining its shape, but if you looked at a molecule, you wouldn't see the unbonded pairs – just atoms held together by bonding electrons. So the point of molecular geometry is to let you see a molecule's shape after its unbonded pairs have faded out of the image, because that's what you'd really see if you looked at it (as opposed to a frumpy thing with funny lobes).

The next two pages go over the molecular geometries you will need to know. Notes about these tables:

- The **notation "$AB_\#U_\#$"** is what we use to tell the **number of bonded (B) and unbonded (U) electron pairs** in the molecule. So a trigonal pyramidal molecule is AB_3U, and a T-shape can either be AB_3U_2 or AB_3U_3.
- The far right column is for hybridization. You will learn about this in the next lecture, so don't think you should already know it; it was just included for future convenience.

# of e-rich regions	Electronic geometry	$AB_{\#}U_{\#}$	Shape	Molecular geometry	Bond angle	Hybridization
2	Linear	AB_2		Linear	180°	sp
3	Trigonal planar	AB_3		Trigonal planar	120°	sp^2
3		AB_2U		Bent	< 120°	
4	Tetrahedral	AB_4		Tetrahedral	109.5°	sp^3
4		AB_3U		Trigonal pyramidal	< 109.5°	
4		AB_2U_2		Bent	< 109.5°	
5	Square bipyramidal	AB_5		Trigonal bipyramidal	90°, 120°, 180°	dsp^3
5		AB_4U		See-saw	90°, 120°, 180°	
5		AB_3U_2		T-shaped	90°, 180°	
5		AB_2U_3		Linear	180°	

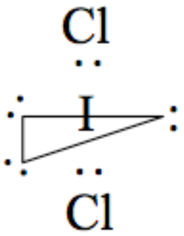
# of e-rich regions	Electronic geometry	$AB_\#U_\#$	Shape	Molecular geometry	Bond angle	Hybridization
6	Octahedral	AB_6		Octahedral	90°, 180°	d^2sp^3
6		AB_5U		Square pyramidal	90°, 180°	
6		AB_4U_2		Square planar	90°	
6		AB_3U_3		T-shaped	90°, 180°	
6		AB_2U4		Linear	180°	

Example:

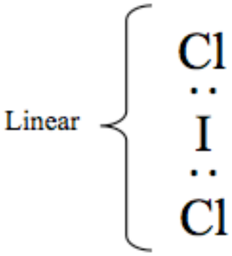
What are the electronic and molecular geometries for ICl_2^-?

Note: ICl_2^- is like I_3^- and has 22 available electrons.

Solution:



Electronic geometry:
5 e-rich regions
→ trigonal bipyramidal



Molecular geometry:
Form AB_2U_3 → linear

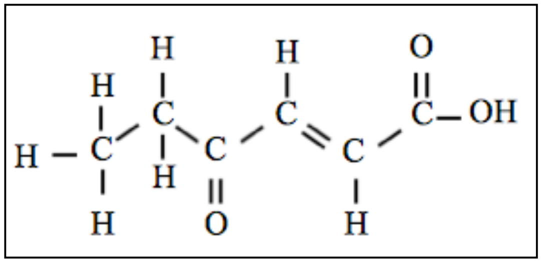
MULTIPLE CENTRAL ATOMS: MUCH SIMPLER THAN YOU MIGHT THINK

Even for molecules with **more than one central atom**, we can assign molecular geometries just as we would for simpler ones. We just look at each central atom individually and count the **number of e-rich regions** around it. So each central atom gets its own molecular geometry.

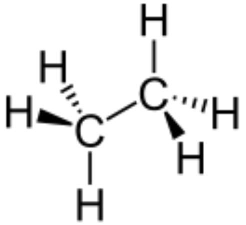
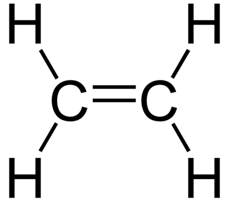
For example, ethane has 2 central atoms (see it in the left column of the table below). Each of them has 4 electron-rich regions, so they're both tetrahedral.

This also applies to large organic molecules, like:

- Tetrahedral C's → 1, 2
- Trigonal C's → 3, 4, 5, 6

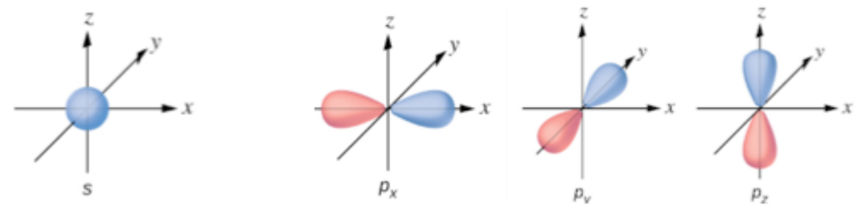


Here are **3 famous molecules with multiple central atoms.** You must know these COLD.

Ethane – C_2H_6	**Ethylene – C_2H_4**	**Acetylene – C_2H_2**
		$H-C\equiv C-H$
Tetrahedral	Trigonal planar	Linear
109.5°	120°	180°
sp^3	sp^2	sp
Sigma bonds: 7 Pi bonds: 0	Sigma bonds: 5 Pi bonds: 1	Sigma bonds: 2 Pi bonds: 2

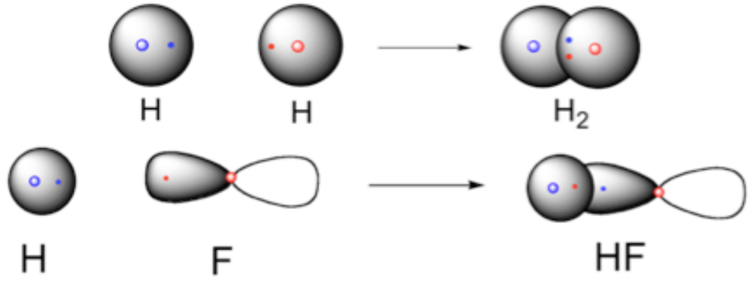
LECTURE 12: USING VB THEORY TO MAKE MO'S FROM AO'S

What is a **bond**? An **overlap of electron-density from 2 atomic orbits (AO's)**. Remember atomic orbits from our electronic configuration days?



Source: http://cnx.org/contents/d66bef54-c39a-4b1c-a9fd-985ac997422e@4/Hybrid-Atomic-Orbitals

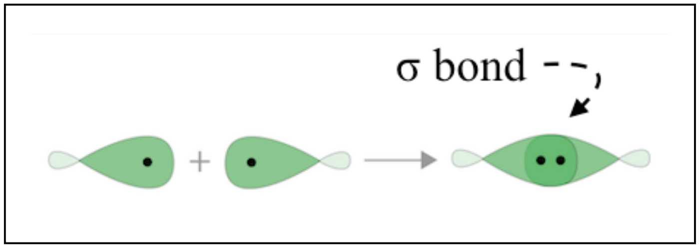
We overlap two atomic orbits to make a **valence bond (VB)**, also called a **molecular orbital (MO)**:

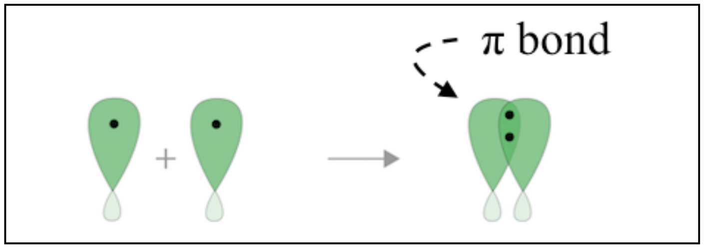


Source:http://chemwiki.ucdavis.edu/@api/deki/files/4538/image213.png?size=bestfit&width=342 &height=93&revision=1

So what are the types of molecular orbitals? There are two: **sigma** and **pi.**

Sigma bonds (σ bonds) occur when the e-density is ***on*** the axis between atoms' nuclei. (Figure on the left.)
Pi bonds (π bonds) occur when the e-density is ***off*** the axis between atoms' nuclei. (Figure on the right.)





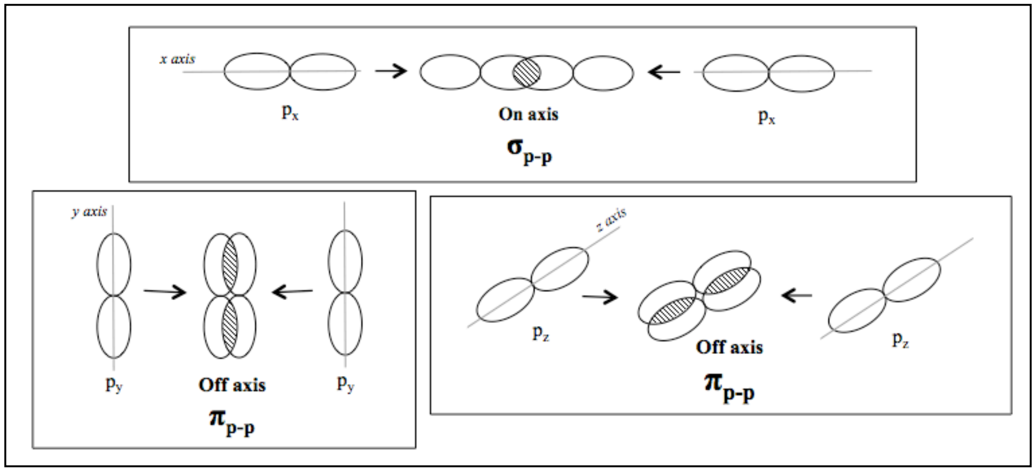
Let’s make some **sigma and pi bonds by mixing s and p atomic orbitals**.

For **sigma bonds**, we need to put the **e-density on the axis** between nuclei, and to do that, we just need our AO’s to meet (and overlap) in the middle. Using s and p orbitals, we can make sigma bonds with three combinations:

Source: https://commons.wikimedia.org/wiki/File:Sigma-bonds-2D.svg

Notice that an s orbit is spherical, there is no way for it to make a bond that *isn’t* on the axis. That means **s orbitals *always* form sigma bonds**, so **MO’s involving an s orbital will *always* be sigma bonds.**

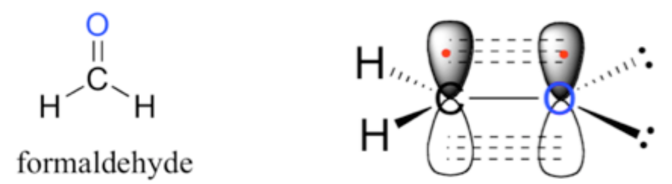
Now onto learning about **pi bonds** by looking at the **three orientations of p orbitals**:



When a **p orbital** is involved in an MO, **one of its orientations will form a σ bond, and the other two will form π bonds**. There are **three cases** in which there are **always π bonds**:

1. **Double bonds**
2. **Triple bonds**
3. **Resonance**

Here is an example of a π bond in the a double bond of CH_2O:



Source:http://chemwiki.ucdavis.edu/@api/deki/files/4538/image213.png?size=bestfit&width=342&height=93&revision=1

To summarize all of that:

The **atomic orbits**:

- **s orbitals** → 1 orientation; sphere shape.
- **p orbitals** → come in sets of 3, each with a different orientation (along x-, y-, or z-axis); lobe shapes.

The **molecular orbits**:

- **Sigma (σ) bonds** → e-densities are on the same axis as nuclei, so bond occurs between them.
  - Form anytime an s orbit is involved → s+s, s+p.
  - Of the 3 p orbits, one will form a σ bond.
- **Pi (π) bonds** → e-densities are off axis of nuclei, so bond appears to hover above and below them.
  - Of the 3 p orbits, two will form π bonds.
  - At least one π bond will always form in double bonds, triple bonds, or resonance.

And that's almost it. Except we need to consider the case where **AO's become hybrid orbitals** (which are types of AO's). AO's exist for all electrons of an atom, but hybrid orbitals are the version **specific to valence electrons**. So instead of the valence e's being secluded in their original orbitals, all of their orbitals get (metaphorically) thrown into a blender. Ultimately, each valence electron ends up with a new **"smoothie" orbital**, made with equal amounts of all original orbitals thrown into it. The **types of hybrid orbits** are:

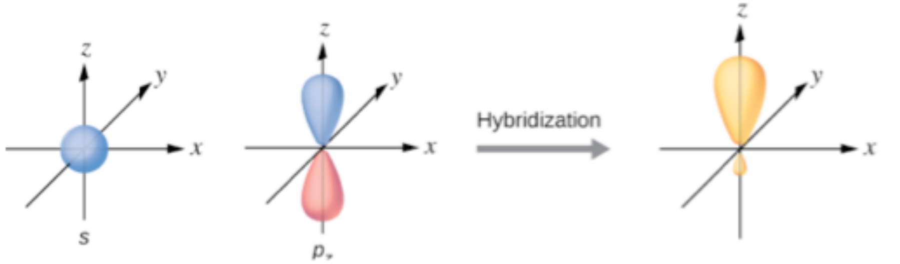
sp **sp^{2}** **sp^{3}** **dsp^{3}** **d^{2}sp^{3}**

And the specific type of hybrid orbit formed depends on which valence AO's were the atom's available ingredients.

Note, happily, that **every hybrid orbit has s character,** which means they all have some e-density along the axis, so:

Every hybrid orbit that forms a valence bond with another atomic orbit makes a sigma, σ, bond.

Plus, the fact that all hybrid orbitals have some s character means they all look the same:

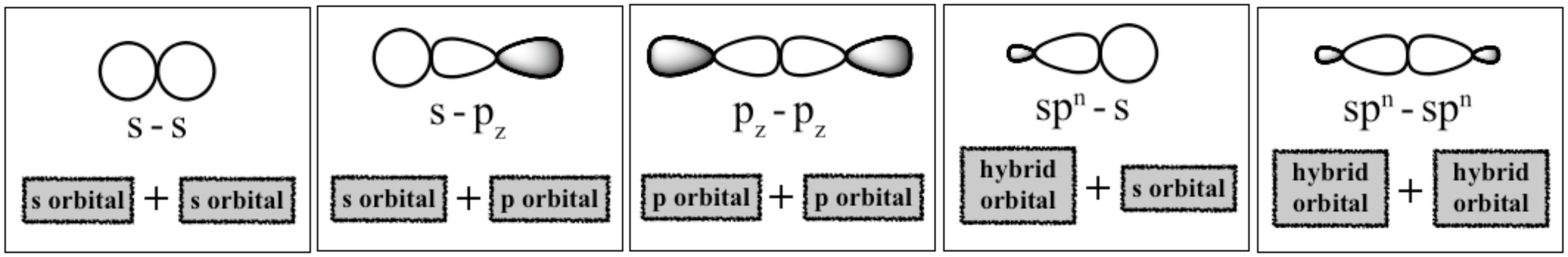


Source: http://cnx.org/contents/d66bef54-c39a-4b1c-a9fd-985ac997422e@4/Hybrid-Atomic-Orbitals

This is how you can picture every hybrid orbit…

Like a pregnant p.

Now that we know about hybrid orbits, let's looks at the ways we can combine AO's to form a sigma bond:

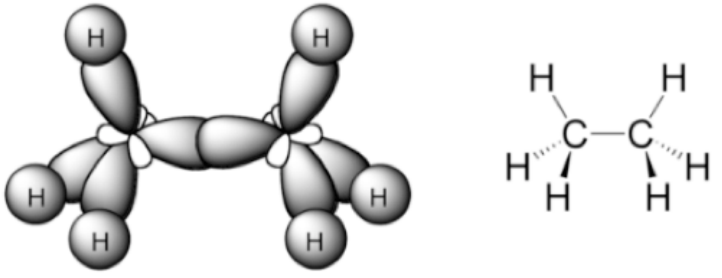


3 EXAMPLES OF ASSIGNING MO'S

Let's practice identifying the sigma and pi bonds – and the AO's that formed them – in C_2H_6, C_2H_4, and C_2H_2.

Example – C_2H_6:

We already know how to figure out a molecule's structure, and we'll use that to determine its MO's. In C_2H_6's case, there are no double bonds, triple bonds, or resonance. C's 4 valence electrons – each in an **sp^3 hybrid orbital** – will bond with H's electrons in their 1s orbitals:

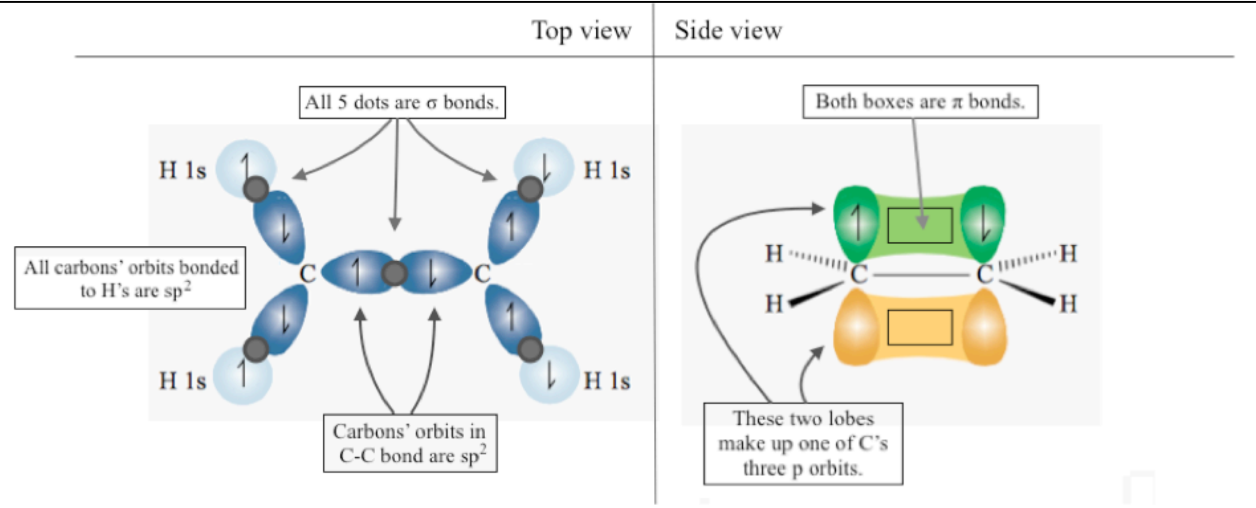


Source: http://chemwiki.ucdavis.edu/Organic_Chemistry/UMM_chemwiki_project/Organic_Structure_and_Bonding/Valence_bond_theory

- All bonds are sigma, so there is a total of **7 σ bonds** → 6 are C-H, and 1 is C-C.
- The **C-H bonds are σ,** made of electrons from H's **1s orbit** and C's **sp^3 hybrid orbit** → Notated: $\sigma_{1s\text{-}sp^3}$
- The **C-C bond is σ,** made of e's from each C's **sp^3 hybrid orbits** → $\sigma_{sp^3\text{-}sp^3}$

Example – C_2H_4:

After we've figured out the structure of C_2H_4, we see that there is a double bond present:



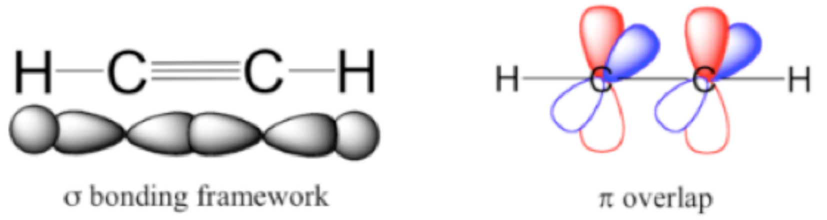
Source: http://ocw.mit.edu/courses/materials-science-and-engineering/3-091sc-introduction-to-solid-state-chemistry-fall-2010/bonding-and-molecules/10.-hybridized-molecular-orbitals-paramagnetism/MIT3_091SCF09_lec10.pdf

- The **C-H bonds are σ**, made of e's from H's **1s orbit** and C's **sp^2 hybrid orbit** → $\boldsymbol{\sigma_{1s\text{-}sp^2}}$
- One of the **C-C bonds is σ**, made of e's from each C's **sp^2 hybrid orbit** → $\boldsymbol{\sigma_{sp^2\text{-}sp^2}}$
- The other **C-C bond is π**, made of e's from each C's leftover **p orbit** → $\boldsymbol{\pi_{2p\text{-}2p}}$

Example – C_2H_2:

Once we know the structure of C_2H_2, we see there is a **triple bond** present in the molecule:

- Both **C-H bonds are σ**, made from H's **1s orbit** and C's **sp hybrid orbit** → $\boldsymbol{\sigma_{1s\text{-}sp}}$
- A **C-C bond is σ**, made from C's **sp hybrid orbits** → $\boldsymbol{\sigma_{sp\text{-}sp}}$
- The other two **C-C bonds are π**, made of e's from the two leftover p orbits of each C → $\boldsymbol{\pi_{2p\text{-}2p}}$



σ bonding framework

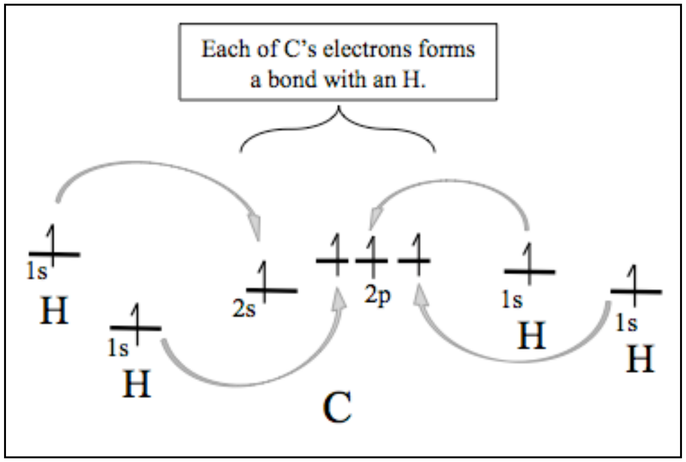
π overlap

Source: http://chemwiki.ucdavis.edu/Organic_Chemistry/UMM_chemwiki_project/Organic_Structure_and_Bonding/Valence_bond_theory

VB THEORY EXPLAINS HYBRIDS

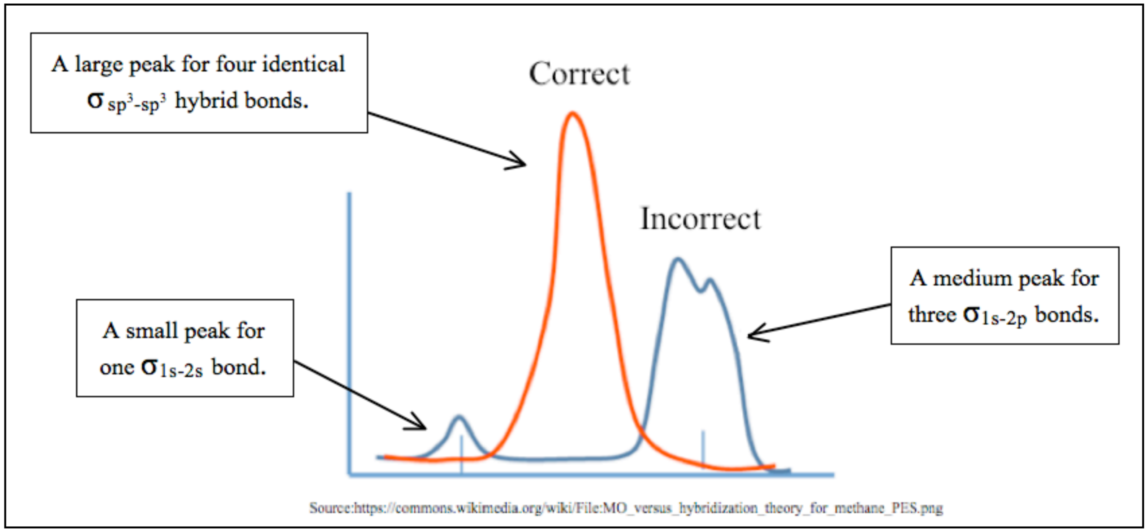
At this point we've learned some stuff about hybrids, but we don't yet know why they form in the first place. Unfortunately, **VB (valence bond) theory is needed to explain that.**

If we didn't know about hybrids, we would think that the molecular orbits in CH_4 were formed like this:


Each of C's electrons forms a bond with an H.

That would mean that CH_4 has 4 sigma bonds. One of the H's would use its 1s electron to bond with the C's 2s electron, and since the C only has a single 2s electron and which has already been put in a bond with H, the remaining 3 H's must bond with C's three 2p electrons.

So there should be 2 different types of bonds → one bond $\sigma_{1s\text{-}2s}$ and the other three $\sigma_{1s\text{-}2p}$. With this thinking, spectroscopy should show 2 peaks, right? **But it doesn't! It shows a single peak:**

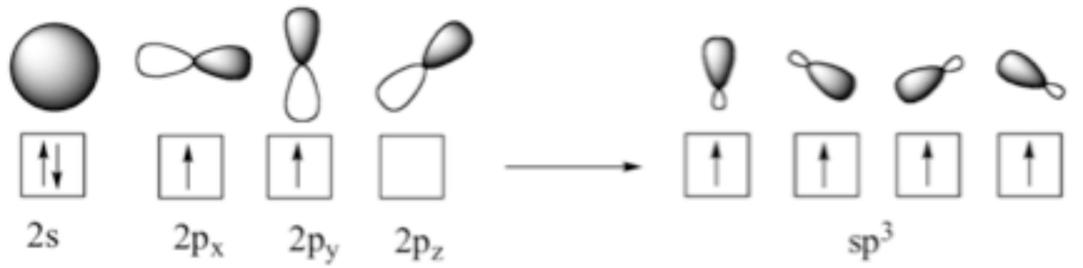

A large peak for four identical $\sigma_{sp^3\text{-}sp^3}$ hybrid bonds.

A small peak for one $\sigma_{1s\text{-}2s}$ bond.

A medium peak for three $\sigma_{1s\text{-}2p}$ bonds.

Source:https://commons.wikimedia.org/wiki/File:MO_versus_hybridization_theory_for_methane_PES.png

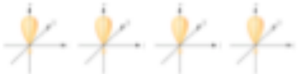
So the 4 bonds must be the same – they must have made all of their orbitals equivalent:



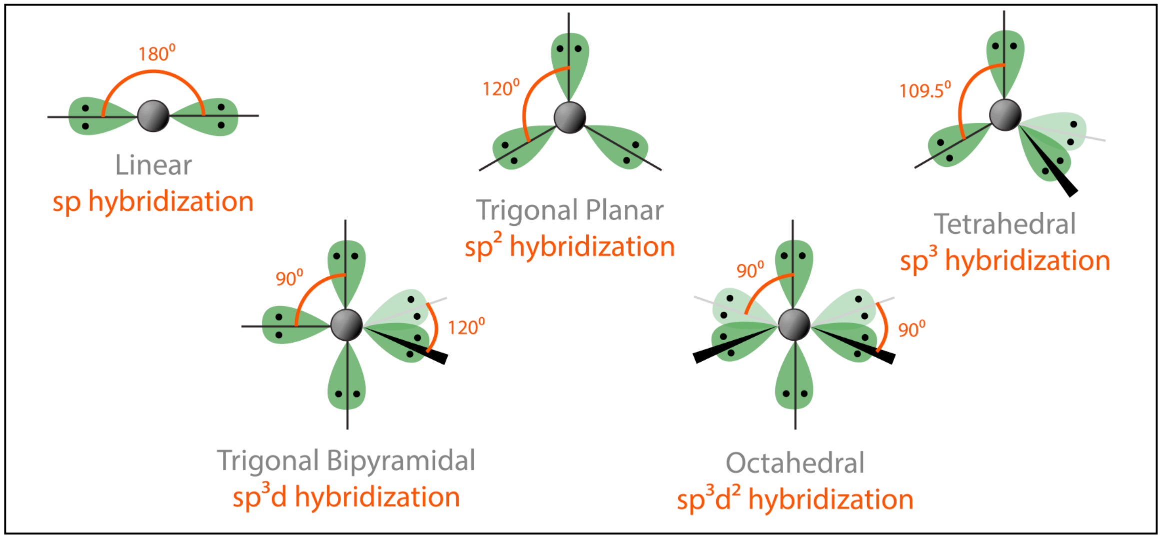
Source:http://chemwiki.ucdavis.edu/@api/deki/files/4538/image213.png?size=bestfit&width=342 &height=93&revision=1

HOW MANY KINDS OF HYBRIDS ORBITALS ARE THERE?

For VSEPR, we learned about determining molecules' shapes based on the number of e-rich regions, and the same idea applies to determining a molecule's hybrid orbitals – **the number of e-rich regions tells you the type (and number) of hybrid orbitals.**

# of e-rich regions	Original AO's	Hybrid orbitals
2	s + p	Two sp orbitals: 
3	s + p + p	Three sp^2 orbitals: 
4	s + p + p + p	Four sp^3 orbitals: 
5	s + p + p + p + d	Five sp^3d orbitals: 
6	s + p + p + p + d + d	Six sp^3d^2 orbitals: 

And in context of electronic geometries:

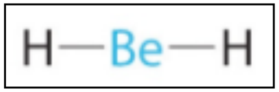


Example:

What is the hybridization of BeH_2?

Solution:

First step is to create Lewis structure (shown to the right).

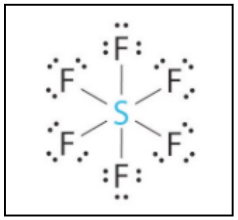


The 2 e-rich regions tell us that there are 2 hybrid orbits, which must have been made with 2 AO's:

One s orbit + **one p** orbit → gives us **two sp hybrid orbits** → BeH_2 has **sp hybridization.**

Example:

What is the hybridization for SF_6?



Solution:

The Lewis structure (to the right) shows 6 e-rich regions, so SF_6 has 6 hybrids, made from 6 AO's:

One s orbit + **three p** orbits + **two d** orbits → makes **six d^2sp^3 hybrid orbits** → it has **d^2sp^3 hybridization.**

LECTURE 13: MOLECULAR ORBITAL THEORY

Chapter Summary

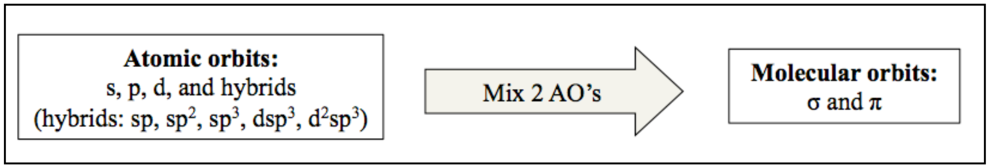
You've probably been learning about chemical bonds for years, but has anyone ever explained to you why bonds come to happen in the first place? Well, we'll learn about that in this lecture, by using **molecular orbital (MO) theory** to see the advantages and disadvantages to certain chemical bonds. Whereas VSEPR and VB focus only on the central atom (and can therefore not explain resonance), MO theory will let us understand more about what a molecular orbit *is*.

MO theory will allow us to:

- Predict the existence of **bonds.**
- Rank bond **energy** and **length.**
- Predict **paramagnetism.**
- Explain **resonance.**

MO theory is complex, so we will look only at the simple case of **diatomic molecules** such as **H_2, O_2, N_2, CO, and HF.**

Recall that bonds are formed from **overlap of electron density** from two **atomic orbitals**. **The bond that is formed is a molecular orbital** and to this point, we have simply called them **σ and π bonds** using **VB theory**.

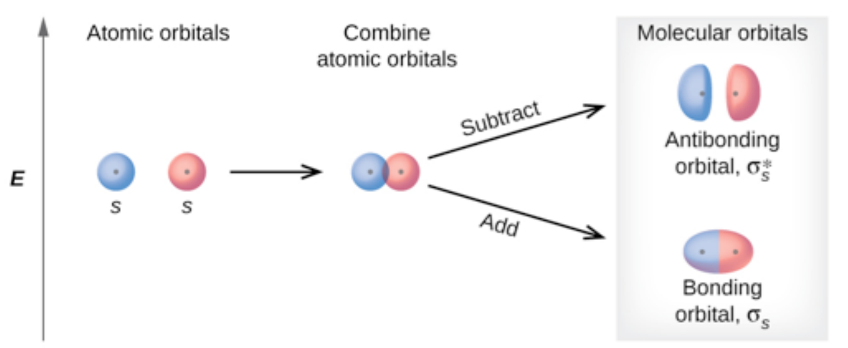


Atomic orbits:
s, p, d, and hybrids
(hybrids: sp, sp^2, sp^3, dsp^3, d^2sp^3)

Mix 2 AO's

Molecular orbits:
σ and π

In contrast, MO theory lets us view bonding in a more sophisticated manner by telling us that when atomic orbits overlap, they can either form an **antibond** or a **bond**:



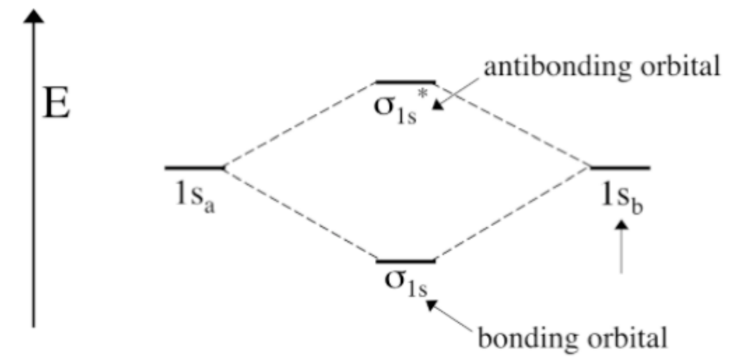
Source: http://cnx.org/contents/337b3f5e-5c32-4f26-bf54-ba278f4ecb6c@5/Molecular-Orbital-Theory

Antibonding occurs if the **MO formed is *higher in energy* than the individual AO's.**
Bonding occurs if the **MO formed is *lower in energy* than the individual AO's.**

We can draw out these antibonding and bonding situations by laying out AO's (which we already know) in a pattern:

Notice that as you go up the diagram, the energy increases.

In these diagrams, you'll notice that almost every other MO line has an **asterisk (*) next to its "σ" or "π"** label. This is used to differentiate bonding from antibonding MO's – an **asterisk indicates antibonding**.



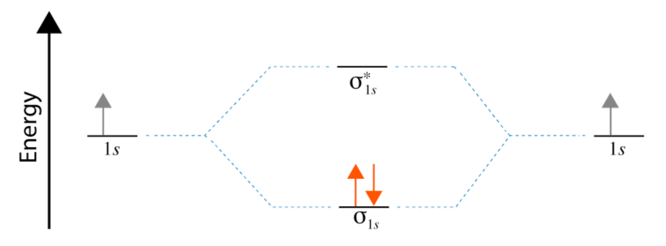
Source: http://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/readings-and-lecture-notes/lecnotes14.pdf

THE TWO SIMPLEST MO THEORY EXAMPLES

Let's check out the MO theory diagrams are for H_2 and He_2.

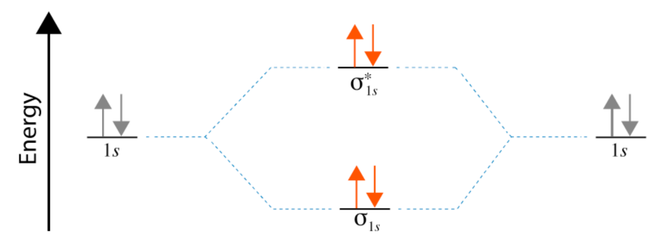
In the case of H_2, we get the figure to the right:

Because the **MO formed is lower in energy** than the individual AO's, this bond is **favorable**, and H_2 forms.



And the diagram for a MO of two helium atoms is to the right:

Unlike in H_2, the bond and antibond cancel each other out, so He_2 doesn't form.



BOND ORDER

A simple way to **determine** from MO theory **whether a bond forms** is by calculating **bond order (b.o.)**, which we do with the following equation:

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

To put it simply, a **bond order of 0 means that no bond will form**, and a **bond order greater than 0 means that a bond will form**. More specifically:

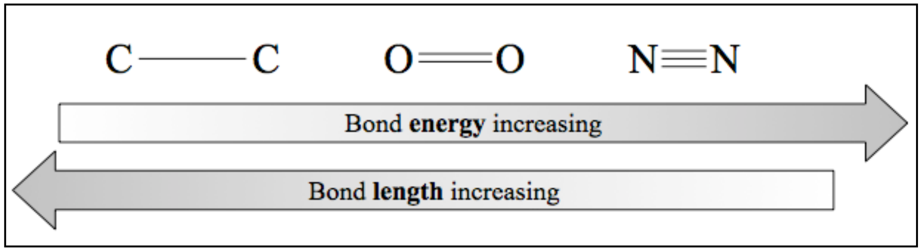
- If **b.o. = 1** → there is a **single bond.**
- If **b.o. = 2** → there is a **double bond.**
- If **b.o. = 3** → there is a **triple bond.**

Now we can apply this to the above examples of H_2 and He_2:

- H_2 → b.o. = (2 – 0) / 2 = 1 → H_2 has a single bond.
- He_2 → b.o. = (2 – 2) / 2 = 0 → He_2 does not exist.

BOND ENERGIES AND LENGTHS

Bond order can also tell us about **bond length and bond energy ranking** – b.o. has an ***indirect* relationship to bond length** and a ***direct* relationship to bond energy**. Here is an example ranking:



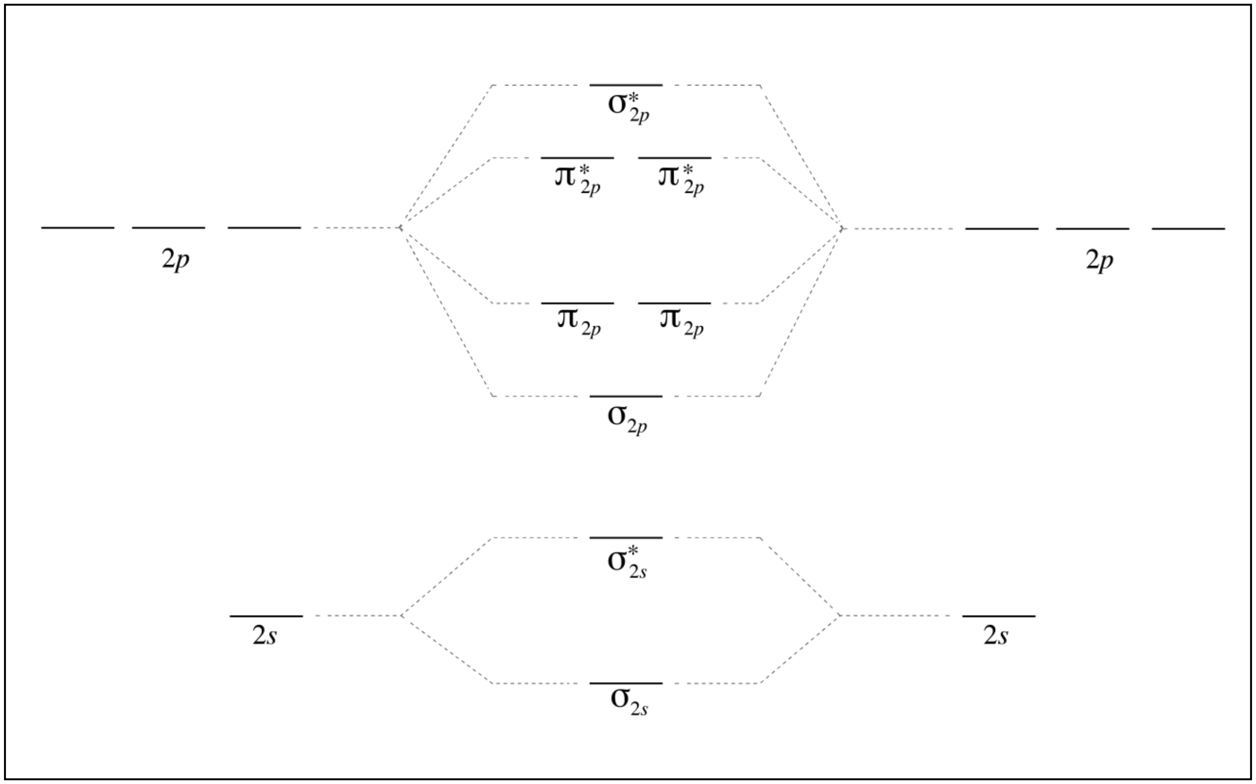
In the case above, N_2's bond has both the highest energy and the shortest length, because its b.o. is the largest.

PARAMAGNETISM

It turns out that **magnets form from unpaired electrons**. This means that any time we draw an AO and MO and see a single, unpaired electron, we are actually looking at a magnet, and we call it **paramagnetism**. This means that molecules in which the **electrons do not pair up** – like B_2 – are paramagnetic. In fact, O_2, which has unpaired electrons in the antibonding π MO's, is experimentally observed to be a magnet.

CREATING MO'S FOR ALL HOMONUCLEAR DIATOMS

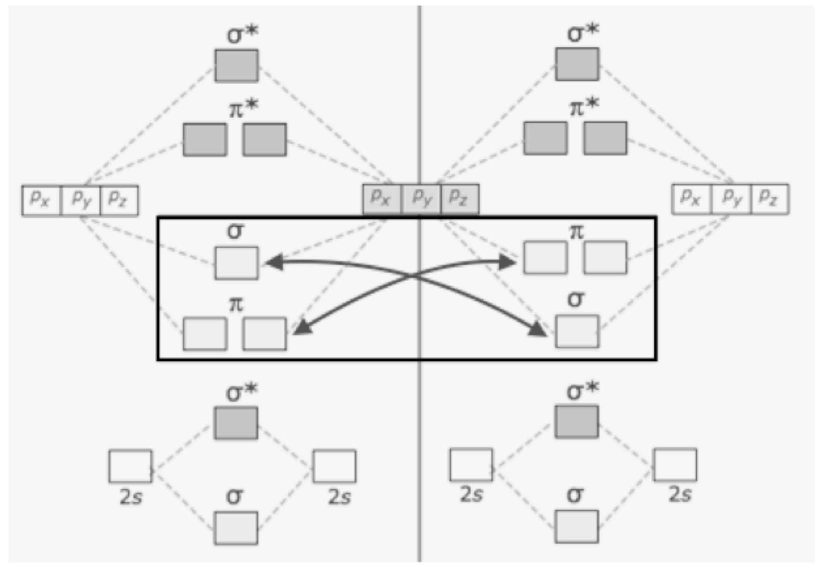
A **homonuclear diatom** is exactly what it sounds like – a molecule made up of two of the same atoms. We're going to learn how to fill in the bonding and antibonding orbitals for all diatoms of the second-row elements. Since this means we'll be working with another energy level (n = 2), we have to expand the MO theory diagram:



Some things to notice about that extended MO energy level chart:

1. **For every AO, there is an MO.**
2. **For every bonding MO, there is an antibonding MO.**
3. The **six 2p AO's make 6 MO's** – **two σ bonds** (one bonding, one antibonding), and **four π bonds** (one bonding and one antibonding for each of the three axes).
4. Just as in VB theory, we see there's **one σ bond for every two π bonds** because there are two axes for π bonds.

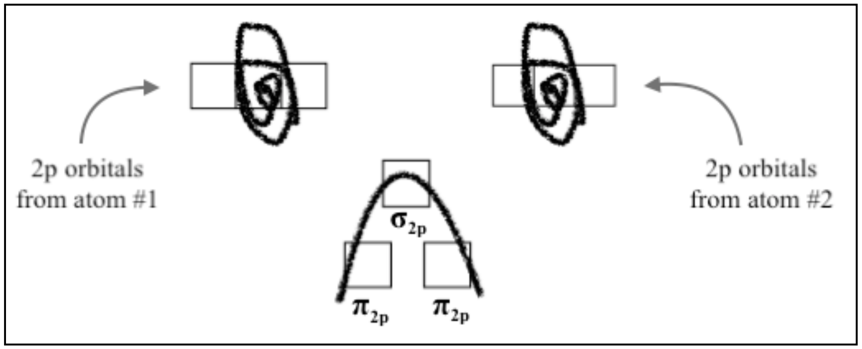
There is one other complication for the second-row diatomic atoms: for the larger ones, the order of MO's change at the top of the energy chart. So for diatoms H_2 through N_2, the MO's are ordered as shown in the left half of the diagram below, and for diatoms O_2 through Ne_2, the MO's are order as shown in the right half:

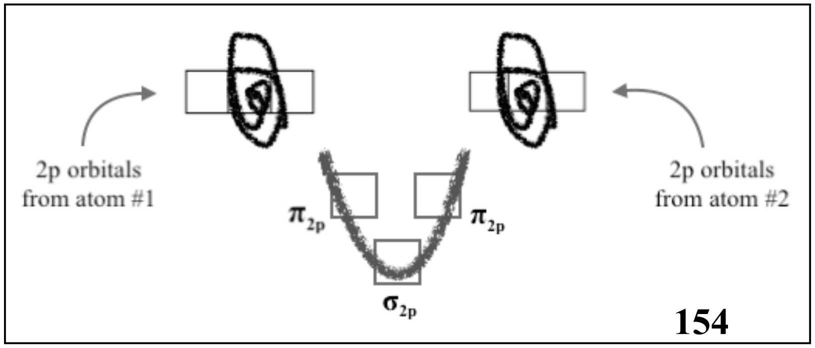


Source:http://chemistry.stackexchange.com/questions/4439/molecular-orbital-theory-predicting-the-stability-of-a-molecule

This order looks like a frowny face.

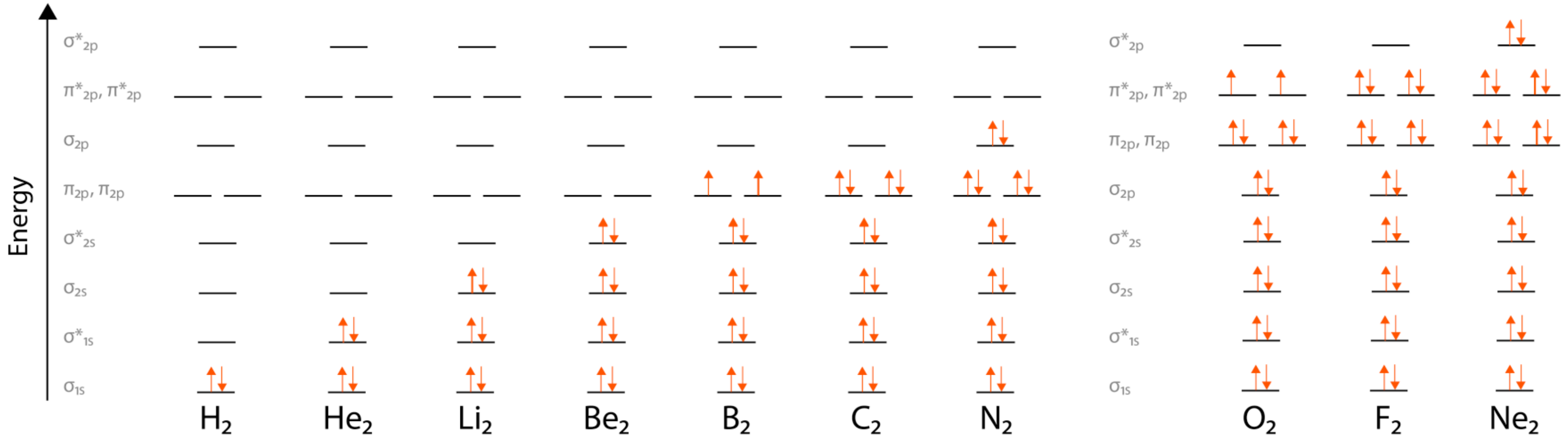
This order looks like a smiley face.





THE GREATEST TABLE EVER

Presented below is a table of MO data for all the second-row homonuclear diatomic molecules. The table presents the **order in which the MO's fill** and also provides experimental data that confirms how the **bond order for each compound corresponds to concepts like magnetism, bond length, and bond energy.** It also shows the reordering of MO's for the larger diatomic compounds. Learn this table cold and you'll be able to handle 90% of MO theory in this class.



	H_2	He_2	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Paramagnetic:	no	no	no	no	yes	no	no	yes	no	no
Bond Order:	1	0	1	0	1	2	3	2	1	0
Bond Length (Å):	0.74	--	2.67	--	1.59	1.31	1.09	1.21	1.43	--
Bond Energy (kJ/mol):	436	--	110	--	270	602	945	498	155	--

HETERONUCLEAR DIATOMS

We'll stick to pretty simple cases of MO's in this class, but there are a few more complex ones we're interested in, like **heteronuclear diatomic compounds**. We won't go into too much depth, but there is something to be learned from simply following the rules for homonuclear cases, adding the total number of AO electrons, and then filling the MO's. For example, CO's 14 total electrons can have MO's formed by following Aufbau, Pauli, Hund, and the MO theory rules above. The energy levels will not be correct, but concepts like bond order and paramagnetism will still apply.