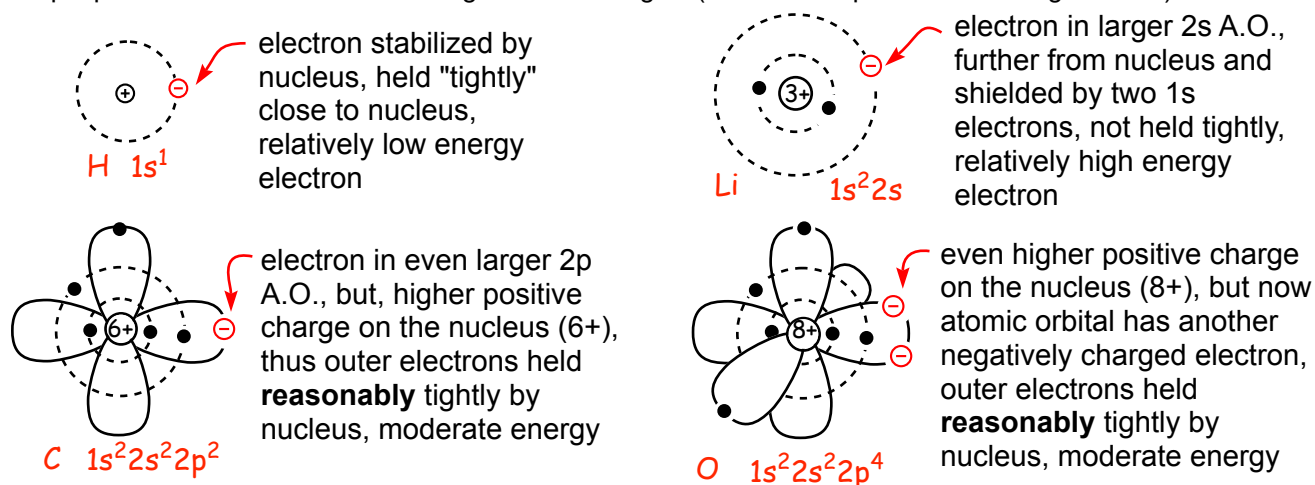


1 Energies of Electrons in Atoms and Molecules

- **Bonding, structure, shape** and **reactions** of organic molecules are determined **primarily** by the **energies** of the electrons in **atomic** and **molecular orbitals**.
- In organic chemistry we use **models**, generally the most useful model is the simplest one that explains what we are trying to understand, in this case the relative energies of electrons.
- Here we introduce a simple model that summarizes the basic factors that determine electron energies in atoms. Later we will develop more sophisticated models for orbitals and bonding to understand electron energies.

1.1 Energies of Electrons in Atomic Orbitals

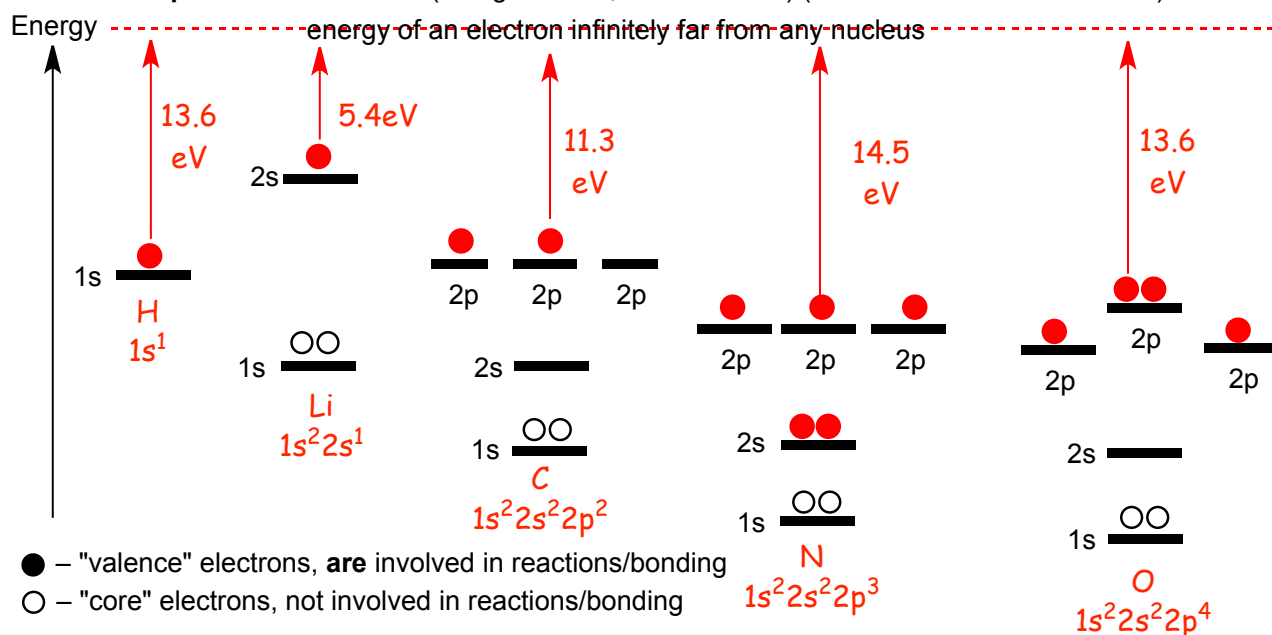
- Simple pictures of the factors controlling electron energies (better descriptions are coming later.....)



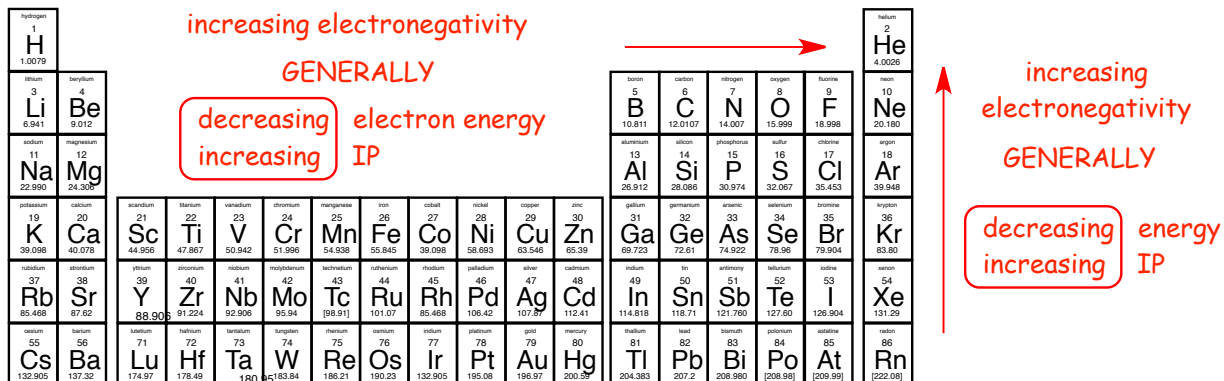
1.2 Quantitative Energies of Electrons in Atoms

- Quantitative information about the relative energies of electrons is obtained from measurements of **ionization Energies** (IEs), or **ionization Potentials** (IPs).
- The **first ionization energy/potential** is the energy required to **completely remove one electron**, the highest energy electron, from an atom or molecule, we are interested mainly in the energies of these highest energy electrons since these are the ones that are involved in chemical reactions, when we talk about I.P. we are always talking about the **first ionization potential** or first ionization energy.
- **Higher energy electrons** in an atom **require less energy** to remove, they have **smaller ionization potentials**.

First ionization potentials for atoms: (energies in eV, electron Volts) (don't memorize the numbers!).

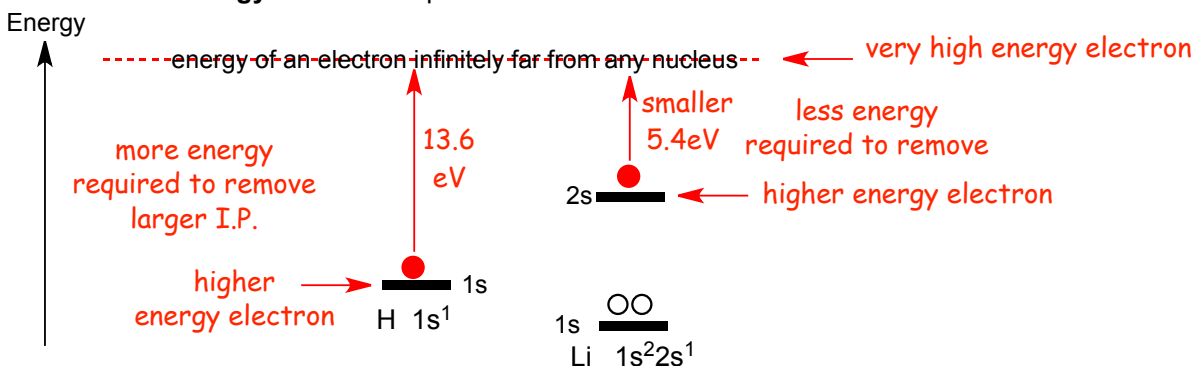


- **Valence electrons** are in the outer shell, **they are highest in energy and get involved in bonding.**
- **Core electrons** are in the inner shells, they are not involved in bonding.
- Electrons are lower in energy when they are in an atomic orbital because they are negatively charged and they are stabilized by the positively charged nucleus.
- Electrons that are held "less tightly" by the nucleus are **high** in energy, and thus require less energy to remove from an atom, and thus have a **low IP.**
- **Many factors influence atomic I.P.s,** (orbital size, nuclear charge, orbital occupancy, etc.), which looks intimidating at first, **however, a detailed understanding of these factors is not necessary at this point.**
- What you **should know** at this point is that I.P. **increases** (electron energy **decreases**) roughly with increasing electronegativity (i.e., left to right across the periodic table and from bottom to top, going up the periodic table)



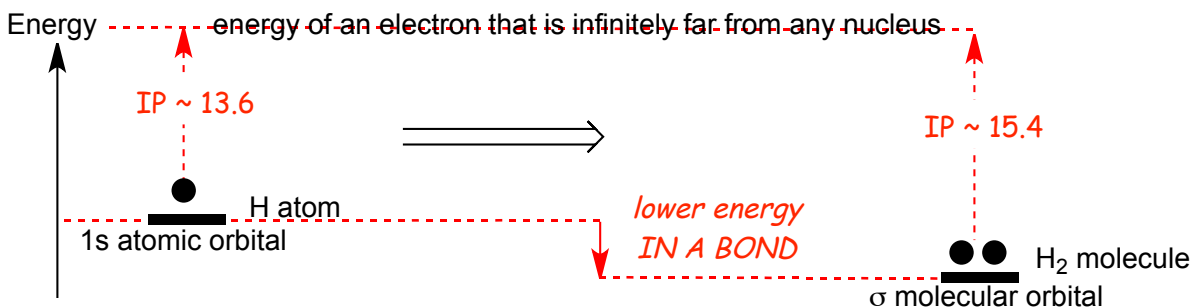
Understanding the Connection Between Ionization Potential/Energy and Electron Energy:

- The ionization energy is the energy required to ionize an atom, it is thus a measure of the energy of the electron that is removed from the atom.
- An electron removed from an atom/molecule has very high energy because it is not stabilized by any nuclei.
- If the **energy** of an electron in an atom is **low**, then **more energy is required to remove** the it from the atom to bring it to the very high energy state when it is not associated with any atom, the energy required to ionize is large, **the ionization energy or ionization potential is large.**
- If the **energy** of an electron in an atom is **high**, then **less energy is required to remove** the it from the atom to bring it to the very high energy state when it is not associated with any atom, the energy required to ionize is large, **the ionization energy or ionization potential is smaller.**

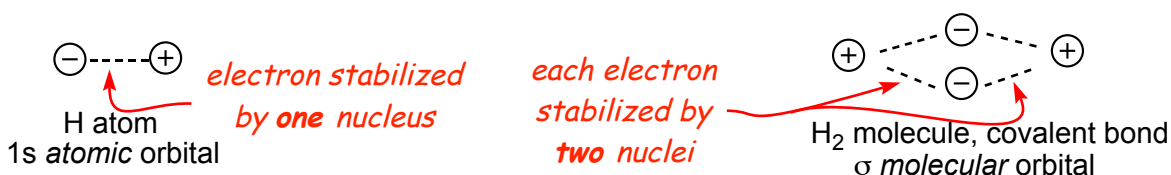


1.3 Energies of Electrons in Molecules, e.g. Hydrogen

- We can **also** measure energies of electrons in molecules as Ionization Potentials.
- The energies of electron in molecules are generally lower than the energies of electrons in atoms.



- The **ionization energy** of the **electron** in the **hydrogen atom is smaller** and the ionization potential of the electron in the **hydrogen molecule is larger**.
- Therefore, the **energy of the electron** in the **molecule must be lower** than the energy of the electron in the atom.
- Why is this? Because in the **electrons in the molecule are in a bond** - this is really **important!**



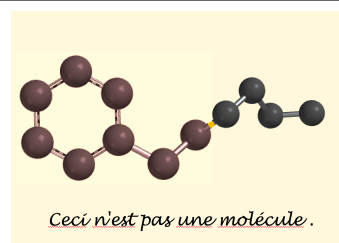
- In the atom the **negatively charge electron** is **stabilized by one** positively charge **nucleus**, in the **molecule** the negatively charged electrons are **stabilized by two positively charged nuclei**.
- In the molecule, the **nuclei are shielded** from each other by the **two** electrons.
- In the molecule there is an **electrostatically stable configuration** for the two negatively and two positively charged particles (the electrons and the protons).
- This is the **standard model** explanation for why the energies of electrons are lowered when in a bond, later we will learn about better model

We have already learned **two of the most critical concepts** for understanding organic chemistry:

1. **Forming bonds stabilizes** (lowers the energies of) **electrons**.
2. **Higher energy electrons** are more **chemically reactive** (because they want to form bonds).

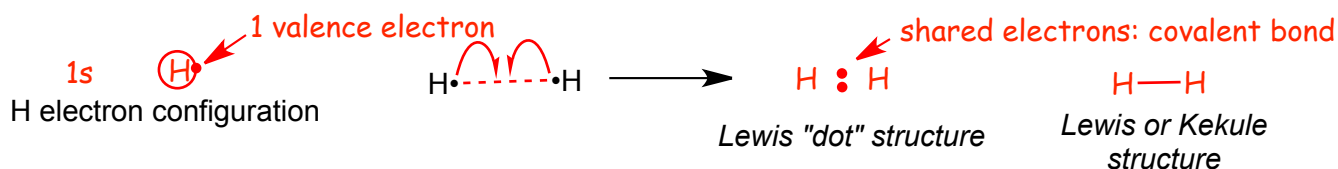
2 Introduction to Bonding in Molecules: The Lewis Structure Model

- Lewis structures represent a **model** for describing the bonding in organic molecules, Lewis structures are not always accurate, but are still very useful because they are simple, and we tend to **use the simplest model** to explain what we need to explain.
- The **Lewis structure model** is particularly useful to describe the bonding in the elements normally encountered in organic chemistry, i.e. C, H, N, O etc.
- In the Lewis **model**, electrons are localized in specific bonds or localized as non-bonding on specific atoms.



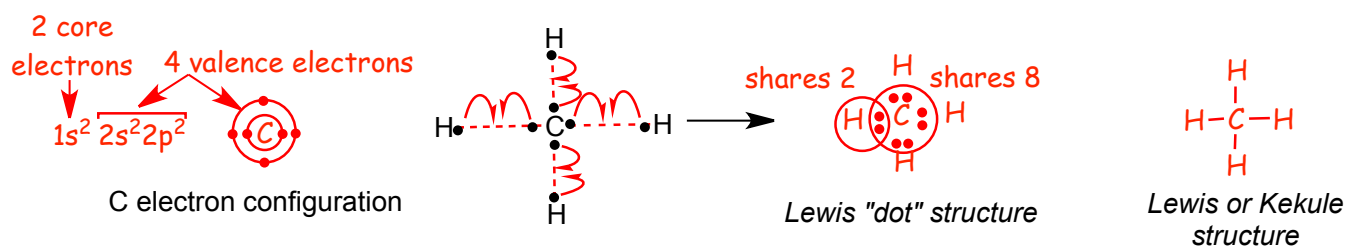
2.1 Atomic Valence and Lewis Structures

Making a Molecule of hydrogen (H₂) as a Simple Example:



- Each hydrogen atom makes one bond, because in doing so it lowers the energy of its one electron.
- Hydrogen can only make one bond because it only has one **valence** electron.
- Making one bond **fills the first shell** with 2 electrons.
- **Note** the use of **curved arrow** notation, "move or use an electron from each atom to make a new bond".

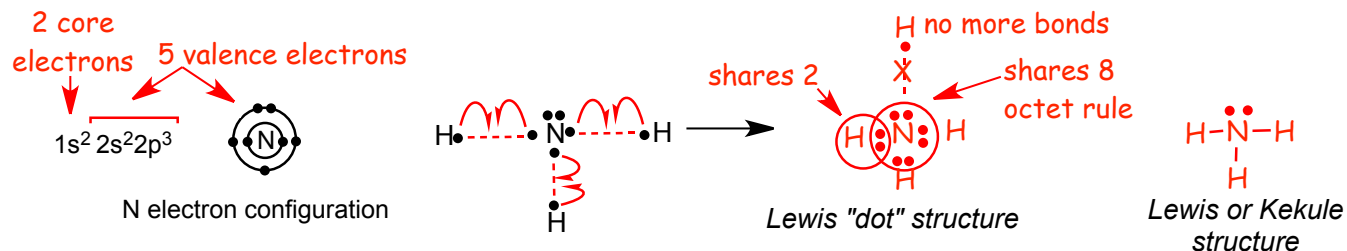
Making a Molecule of CH₄ as an Example:



- Carbon has four valence electrons, therefore it lowers the energy of four electrons by making four bonds.

- After making four bonds, according to the Lewis dot model its second outer shell is now "full" with 8 **shared** electrons, it obeys the "filled shell", sometimes called **the "octet rule"** for second row elements.
- But what it **really** did was not follow a rule, we lowered the energies of as many electrons as it could, the four valence electrons.
- The hydrogens also have a "full" first shell with two electrons.
- The filled shell rule and the pictures of the Lewis dot structures are **models** of organic structures.

Making a Molecule of NH₃ as a Simple Example:



- **Nitrogen** has **five valence electrons**, but can only lower the energy of three electrons to make bonds before "filling" the outer electron shell, attempting to make another bond "overfills" the shell and violates the "filled shell/octet rule" (later we will show that attempting to make another bond increases electron energy instead of decreasing it, which is the real origin of the filled-shell rule).
- Nitrogen in this case has two **non-bonding** electrons in the outer shell.
- The octet rule and the pictures of the atoms and molecules as Lewis dot and Lewis structures are **models** (we use the simplest useful model).
- **Lewis "dot" structures** are **tedious to draw**, we will use them **only rarely**.

Unfortunately, there is more than one use of the word Valence:

1. The outer shell is the **valence shell**, the electrons in the outer shell are the **valence electrons**.
 2. The number of bonds an atom normally makes without violating the "filled shell rule" is the **normal valence**.
- "Normal" Bonding Patterns (normal valence) for various atoms obtained from the atomic configuration and by using the filled shell rule (*again, a better model is coming soon!*).

Do not memorize this table, learn the **Normal Valences** by working with them by building organic structures.

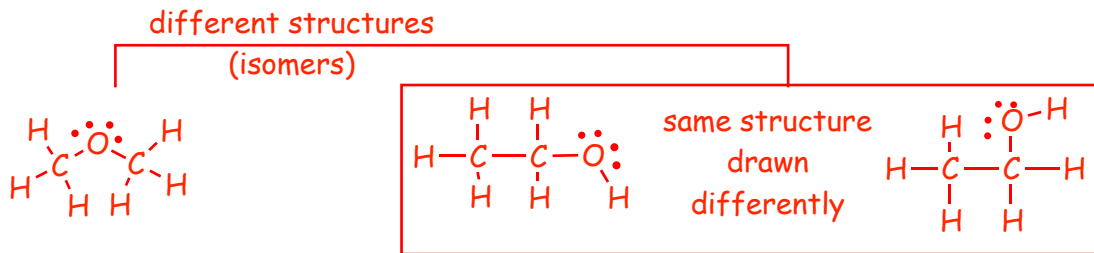
	atom	electron configuration	# valence electrons	maximum possible number of electrons in outer shell	normal valence (normal # of covalent bonds)
1st shell	H	1s	1	2	1
	B	1s ² 2s ² 2p ¹	3	8	3 only 3 valence e's
	C	1s ² 2s ² 2p ²	4	8	4
2nd shell	N	1s ² 2s ² 2p ³	5	8	3 octet "rule"
	O	1s ² 2s ² 2p ⁴	6	8	2 octet "rule"
	F	1s ² 2s ² 2p ⁵	7	8	1 octet "rule"
3rd shell	P	1s ² 2s ² 2p ⁶ 3s ² 3p ³	5	8	3 or 5! violate
	S	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴	6	8	2, 4, or 6! octet rule!

- The number of **valence electrons** is equal to the number of electrons in highest energy shell.
- **Normal valence** is the number of electrons required to fill the highest energy shell with shared electrons, it is equal to the number of bonds an atom "normally" makes.
- **Boron** has only 3 valence electrons and so it can only make 3 bonds, it has a normal valence of three, it does not have enough electrons to fill the shell, even if all are involved in bonding.
- **Nitrogen** has 5 valence electrons, but after making 3 bonds the valence shell is full and the remaining two electrons cannot make bonds, therefore, the normal valence of nitrogen is also 3.
- **Oxygen** has 6 valence electrons, but after making 2 bonds the valence shell is full and the remaining four electrons cannot make bonds, therefore, the normal valence of oxygen is 2.
- The filled shell or octet rule doesn't really work for 3rd row elements, e.g. phosphorus and sulfur.
- Obeying the filled shell "rule" is the same as obeying the normal **rules of valence** (normal number of bands), i.e. 4 bonds to each C, 3 bonds to each N, 2 bonds to each O etc.

Example Problem: Draw two **different** Lewis structures for C_2H_6O .

The filled shell "rule"/Normal Valence Requires.....

- Four bonds to each **tetravalent** carbon (each carbon wants to make **four** bonds).
- Two bonds to each **divalent** oxygen (each oxygen wants to make **two** bonds).
- One bond to each **monovalent** hydrogen (each hydrogen wants to make **one** bond).
- To **generate Lewis structures** we will **not use rules**, but we will learn to assemble molecules using common organic structural motifs, e.g. a carbon connected to 3 hydrogen atoms at the end of a chain.



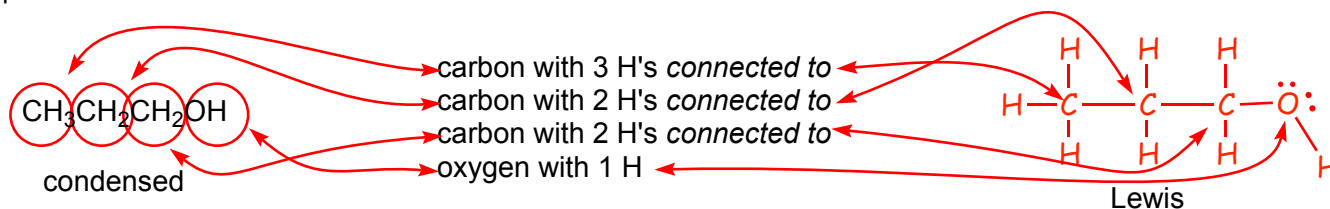
- The oxygen "shares" 4 electrons in the 2 bonds, it "has" 4 non-bonding electrons, thus "owns" 6 electrons.
- Lewis/Kekule structures indicate connectivity of atoms, the orientation or the direction the bonds point doesn't matter (at least for now).
- Different Lewis (Kekule) structures are **isomers**, more on isomers later.

2.2 Condensed Structures

- These are equivalent to abbreviated Lewis structures, the order of atom connectivity/bonding is implied by the "written" order of the atoms, but the bonds are **not explicitly shown**, they are implied.
- This means that the normal valencies for the atoms in the structure must be assumed otherwise the bonding order cannot be determined.

Example Problem 1: Convert the provided condensed formula into a Lewis/Kekule structure.

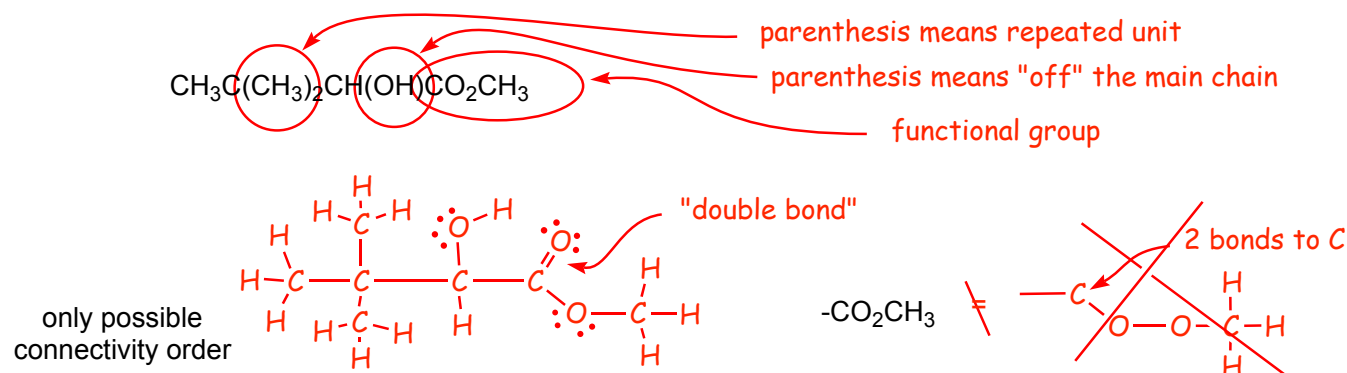
- Obeying the normal rules of valence for C (4 bonds), H (1 bond) and O (2 bonds) can generate only one possible Lewis structure.



- Note that the non-bonding electrons **are** shown in Lewis structures.
- H_3C- is a common structural motif in organic structures (end of a chain).
- The normal valence for the atoms (e.g. 4 for carbon etc.) **must** be assumed when interpreting condensed formulae.

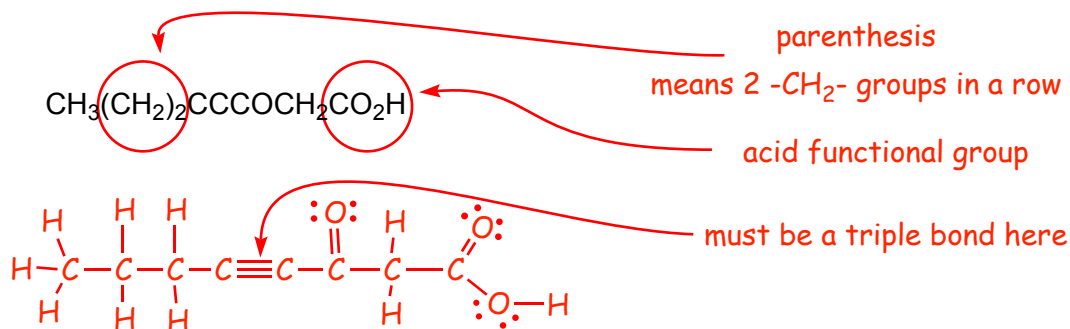
Example Problem 2: Convert the provided condensed formula into a Lewis/Kekule structure.

- Obeying the normal rules of valence for C (4 bonds), H (1 bond) and O (2 bonds) can generate only one possible Lewis structure.



- Note the carbon to oxygen **double bond**, which is required to satisfy the normal rules of valence for all atoms
- Note **two different uses of parentheses**:
 1. Parentheses can be used to indicate a part of the structure that comes "off" the main chain.
 2. Parentheses can **also** be used to indicate repeating units along the main chain.

Example Problem 3: Convert the provided condensed formula into a Lewis/Kekule structure.

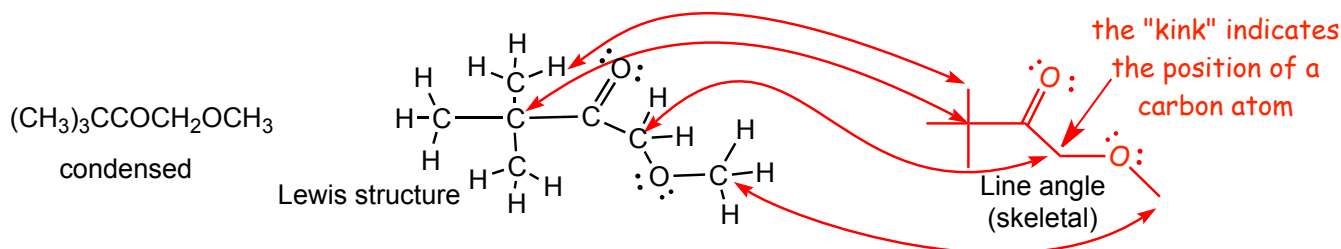


- Note the use of parentheses to indicate repeating units (the other use is to represent a group "off" the main chain). These two uses are easily distinguishable using the normal rules of valence, only one will "work" in a particular context.

2.3 Line-angle Structures

- **Line-angle structures** are **most commonly** used in organic chemistry, they are sometimes also called **skeletal** structures.
- The lines show bonds between carbon atoms, **hydrogen atoms are not included** unless they are **part of a functional group** (see later for definition).

Example 1:

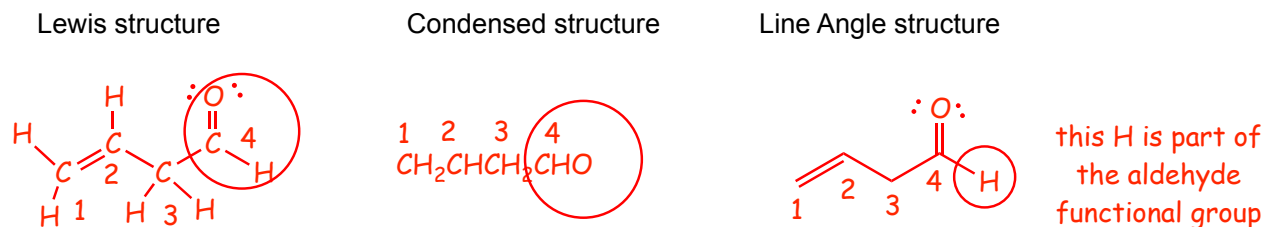


- There is an atom (carbon unless otherwise specified) at each "end" of each line, each line is a covalent bond.
- Full Lewis structures sometimes just take too long to draw, and we will usually use line-angle (skeletal) structures instead (especially for rings).

Example 2:

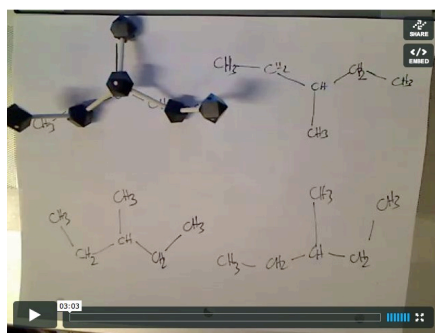
Draw an example of a Lewis (Kekule), condensed and line angle structures for $\text{C}_4\text{H}_6\text{O}$. Several different structures are possible that could be drawn here, these would be **isomers** (see the next section).

- **One possible, example, structure is shown here** (you could not predict which structure we would draw from the molecular formula $\text{C}_4\text{H}_6\text{O}$ alone).



- Where reasonable, draw the angles roughly correct for the molecular shape, see later.
- Which kind of structure to draw (condensed, Lewis, line-angle etc.) depends upon the context, we will use mainly line angle or a line angle/Lewis mix.

- These are all the same structure, none of them are isomers.
- The direction in which the bonds "point" is irrelevant, these structures are all the same because they have the same atoms bonded to each other in the same order.
- Rotation around single C-C bonds does **not** generate a new chemical structure, just the same structure drawn a different way (later we will see that these different ways of drawing the structures are called conformers).



Visualize Isomers, or Lack Of!

4 Formal Charges

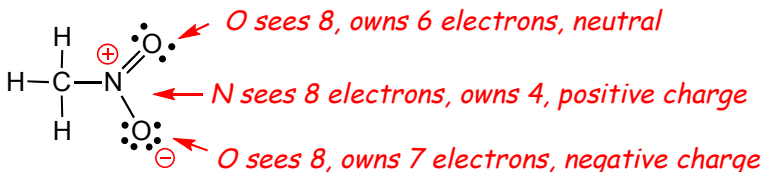
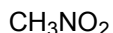
- The Lewis structure model attempts to obey the filled shell/octet rule for as many atoms as possible by getting as many electrons as possible into bonds (remember, forming bonds lowers electron energy).
- Sometimes this can result in structures that disobey the normal rules of valence, resulting in an atom "owning" either more or less electrons than its normal number of valence electrons. This results in an atom with a mismatch of protons and electron, which in turn results in the atom having a **formal charge**.

Example 1:

of valence electrons

$$O = 6$$

$$N = 5$$

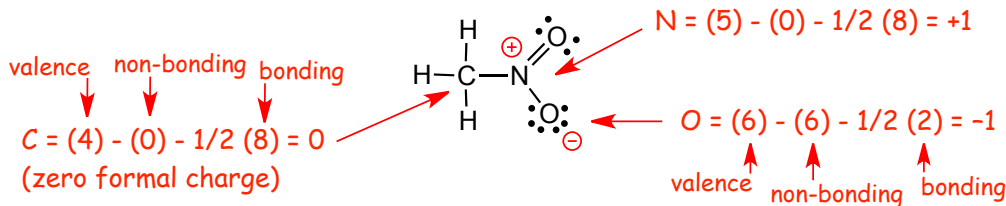


- This is the only reasonable way to draw a Lewis structure for CH_3NO_2 .
- The "filled shell/octet rule" is obeyed for all atoms, but the normal rules of valence are not (4 bonds to the nitrogen instead of 3, and 1 bond to the lower oxygen instead of two)
- The central nitrogen "sees" 8 electrons, i.e. the ones that are shared in the 4 bonds, and "owns" 4 electrons (half of the shared electrons), but requires 5 valence electrons to be neutral, there are thus one **fewer** electrons than required to balance the positive charge on the nucleus, the charge is thus +1
- The **lower** oxygen "sees" 8 electrons (6 non-bonding and the shared pair in the bond), it "owns" 7 electrons (the non-bonding ones and half the shared pair), but requires 6 valence electrons to be neutral, there is thus one **extra** electron than would be required to balance the positive charge on the nucleus, the charge is thus -1

The Calculation of formal charge using a formula:

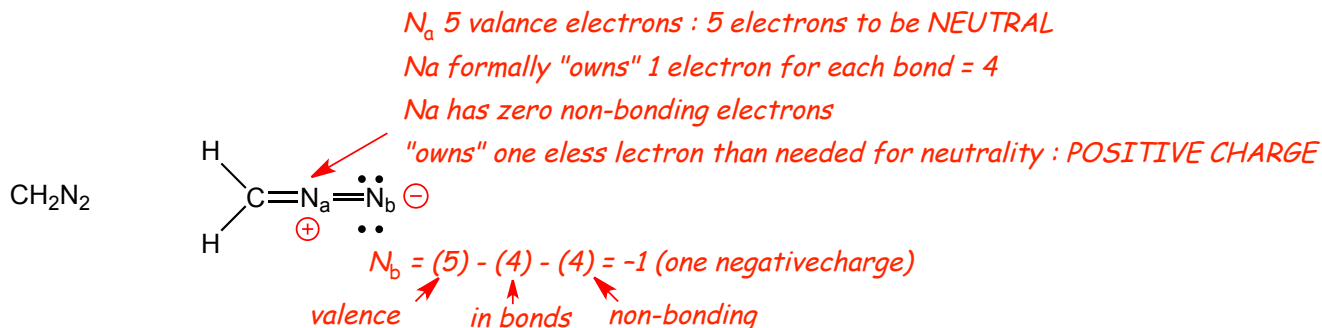
Formal charge = (# valence e's - (# non-bonding e's) - 1/2 (# e's in bonds) (for TWO electrons per bond)

Example 2:



- Later we will see that it is easier to determine formal charges **not** using this formula, but it may be useful to use the formula at this point as a way of making progress in understanding structures, but expect to stop using it fairly soon (this is in contrast to the degrees of unsaturation formula, which you will probably use regularly).

Example 3:



- The "filled shell/octet" rule is obeyed in all cases, but the normal rules of valence are not.
- Formal charges are associated with structures in which the normal rules of valence are not obeyed.

But.....



- This is methylene (you do not have to know this), it is very reactive (its lifetime is less than 0.000000001 second in solution), but we can still draw a valid Lewis structure for it.
- **The central carbon atom only has two bonds** but it also **has no formal charge**, not all atoms that disobey the normal valence rules have a formal charge!

5 Quantum Mechanical Description of Atomic Orbitals

- The Lewis structure model works well but doesn't give a proper and contemporary description of exactly where the electrons are in orbitals, we really need a much better understanding of.....
 - 1. **What do atomic and molecular orbitals really look like?** This tells us where the electrons are in atoms and molecules.
 - 2. **What are the (relative) energies of the electrons in atomic and molecular orbitals?** This tells us about the relative reactivities of electrons.
- We ALSO need to learn that electron properties are more complex than indicated by simple Lewis structure

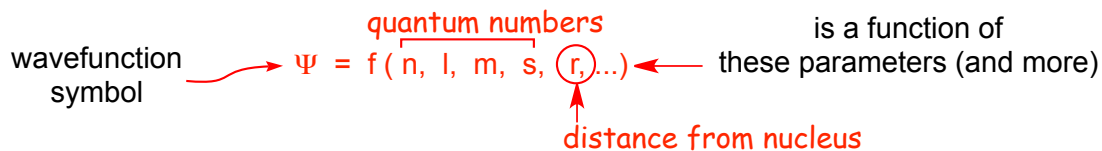
Quantum Mechanics provides a more realistic description of the location and energies of electrons in atomic and molecular orbitals:

An Apparent Problem: Quantum Mechanics shows that it is **impossible to say exactly where** an electron is in an orbital, only the **probability** of finding the electron at a particular point in space can be obtained.

- **However**, this is not really a problem, since this is a natural consequence of the **wave nature** of electrons. Without understanding this **wave nature of the electrons** we **cannot properly understand orbitals and bonding in molecules**.

Quantum Mechanics describes atomic and molecular orbitals in terms of a **wavefunction equation**, which incorporates and describes this **wave nature** of electrons in orbitals.

- The **wavefunction** is given the Greek letter capital Psi, and for atomic orbitals has the form:



Here, **n**, **l**, **m**, and **s** are the **quantum numbers** you encountered in General Chemistry:

- **n** = **principal** quantum number
- **l** = **angular momentum** quantum number
- **m** = **magnetic** quantum number
- **s** = **spin** quantum number

- Another parameter that is important for us is the **distance of the electron from the nucleus, r** .
- **Wavefunctions** exhibit **wave behavior**, i.e. just like any wave they can be positive, negative or zero
- Solving the **wave equation** for the **different quantum numbers** gives the **different atomic orbitals**.
- The **probability** of finding an electron at a particular distance from the nucleus, $P(r)$, is given by the value of the wavefunction squared, **this is our answer to where are the electrons in an orbital!**

$$P(r) = |\Psi(r)|^2$$

- Quantum Mechanics is highly mathematical, **however, we do it in pictures**, as a **plot or a pictorial representation** of the wavefunction (or wavefunction squared) versus distance from the nucleus, which is much easier!

Our Goals

1. Learn to draw **pictures** of the **wavefunctions** of an atomic orbital, they will **look like waves!**
2. Learn to **combine the pictures** of atomic orbital **wavefunctions**, so that we can **make bonding molecular orbitals**.
3. **Learn to draw pictures of bonding molecular wavefunctions**, so that we can understand where the electrons are in molecules, and thus get information about their relative energies, in molecules.

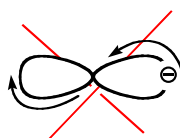
At this point you should be confused since all of this is difficult to understand without examples....

5.1 2p Atomic Orbital

- From general chemistry we know the values of the atomic quantum numbers n, l, m etc.....

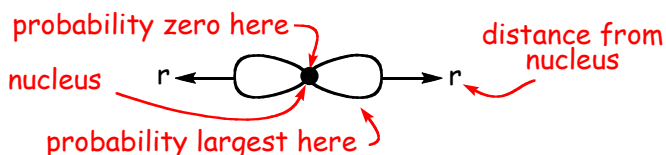
$$\Psi = f(n, l, m, s, r, \dots) \quad \text{in this case } n = 2, l = 1, m = 0, +1, -1$$

- $n = 2$ means the second shell.
- $l = 1$ in this case means a p A.O. and not an s A.O.
- $m = 0, +1, -1$ means that there are **three** p A.O.s, p_x, p_y and p_z .
- The **quantum numbers** define the **specific wave nature of the orbital**, including the number of nodes, which is given by the value of the principle quantum number, n , minus 1 (The nodal theorem).
- Thus, a **2p A.O. ($n = 2$) must have one node**, and it does, see below.
- Let's start with the familiar "hourglass" shape for the 2p atomic orbital:



WRONG!!

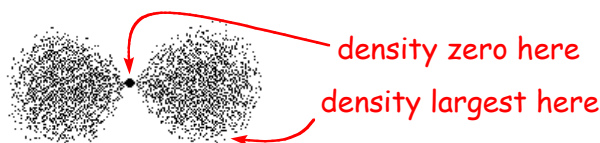
orbital shape should **NOT** be interpreted to illustrate a "figure of 8" movement of electrons



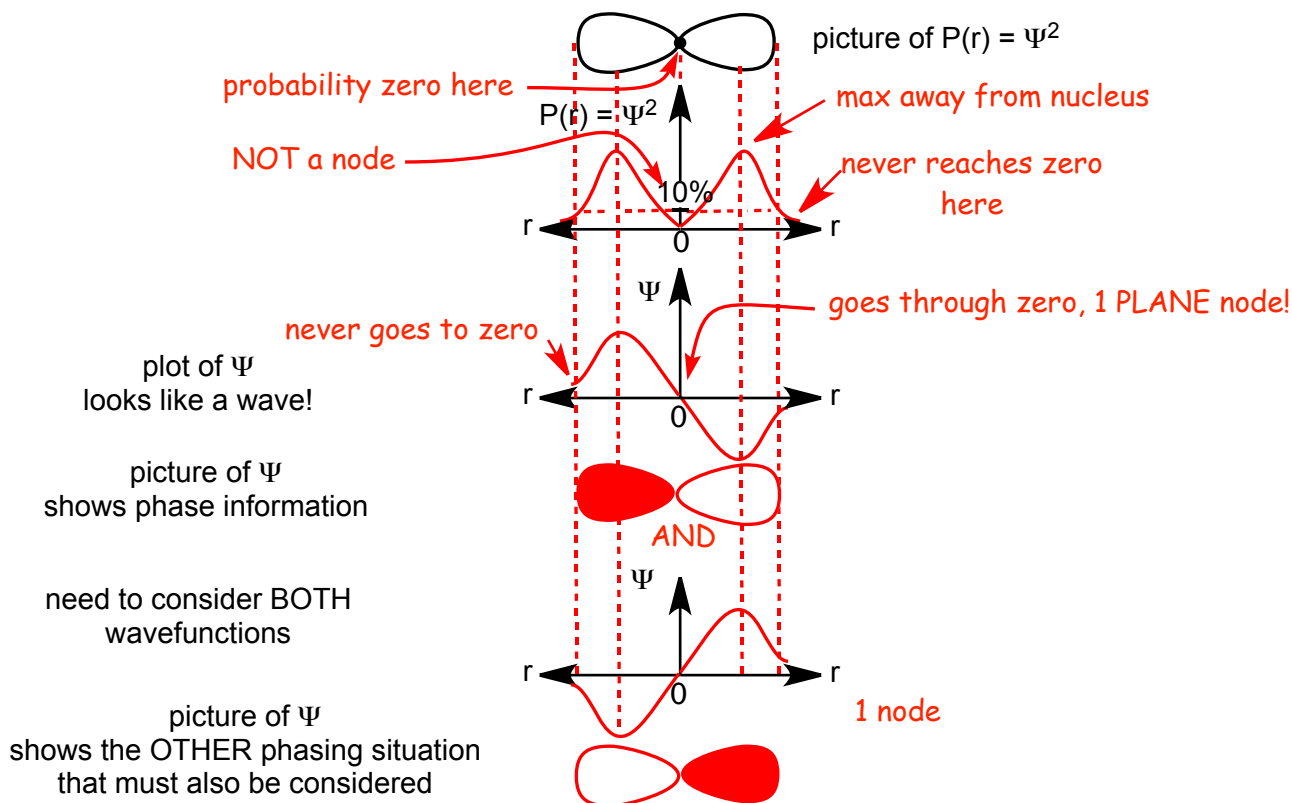
orbital shape **SHOULD** be interpreted to illustrate the **probability** of finding the electron

- The "Cloud" picture from general chemistry relates **the idea of electron density** to **probability of finding the electron**, the higher the probability of finding the electron, the "denser" the apparent electron cloud.

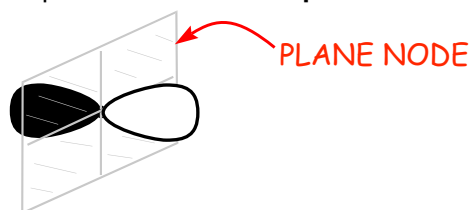
"cloud" picture of the electron density



- For now we will assume that electron density and electron probability are the same (not quite true, see later).
- We can **derive the shape** of the **wavefunction** for the 2p A.O. by making a plot of probability of finding the electron, $P(r) = \text{wavefunction squared}$, as a function of distance from the nucleus, r .
- **Then**, take the square root to get a plot of the **wavefunction**.



- The **wavefunction squared** gives the **probability** of finding the electron as a function of distance from the nucleus ($P(r)$). This probability plot contains **no phase information** since a probability (and also a number squared) can only be positive or zero, never negative.
- The plot of the **wavefunction** looks like a wave, it gives **phase information** associated with the wave, i.e. the positive AND negative regions due to the wave behavior.
- For the 2p A.O., the **wavefunction** has **one** node at the nucleus, i.e. the electron is **never** at the nucleus
- There are different kinds of nodes, the p atomic orbital has a **plane node**.

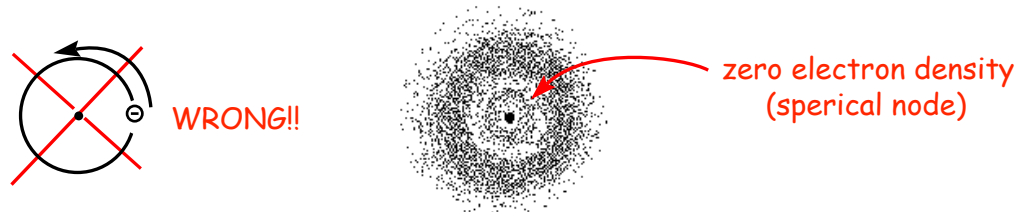


- The wavefunction is the square root of the probability plot, thus we don't know which phase is positive and which negative, which is why we need to consider possibilities, shown in **both** plots and **both** pictures. Positive and negative are **arbitrary** in **wavefunctions**, thus we distinguish the different phases by **shading (or coloring)** in the picture rather than assigning an absolute positive or negative sign.
- Understanding this **wave nature** is **essential** for **building molecular orbitals**, see later!
- The orbital shape defines an arbitrary "boundary" beyond which the probability of finding the electron is small.

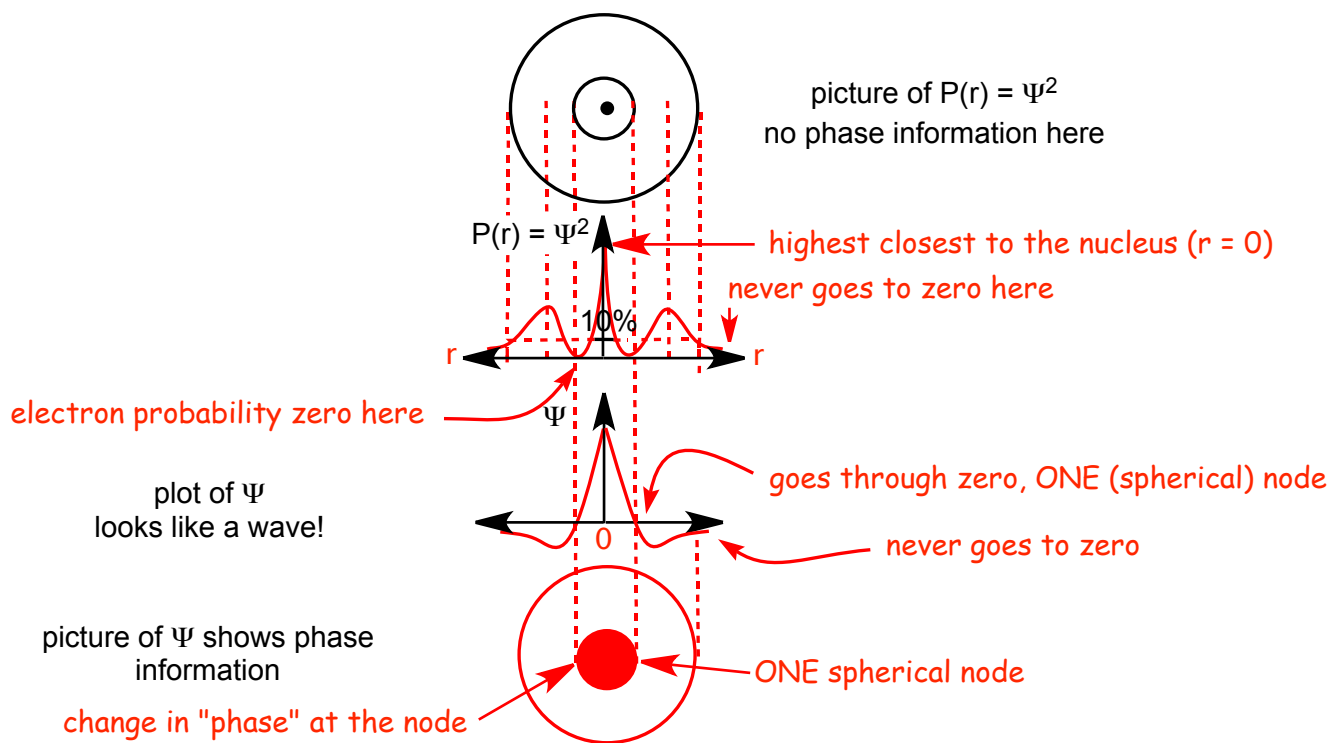
5.2 2s Atomic Orbital

$$\Psi = f(n, l, m, s, r, \dots) \quad \text{in this case } n = 2, l = 0, m = 0$$

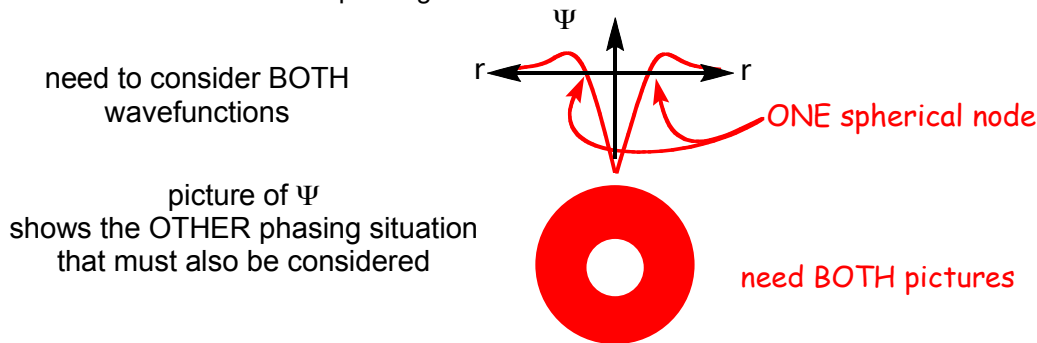
- **The Nodal Theorem:** The quantum numbers tell us about the wave nature of the orbitals, the number of nodes is the value of the principle quantum number $n - 1$, therefore, a 2s A.O. ($n = 2$) **must have one node**.



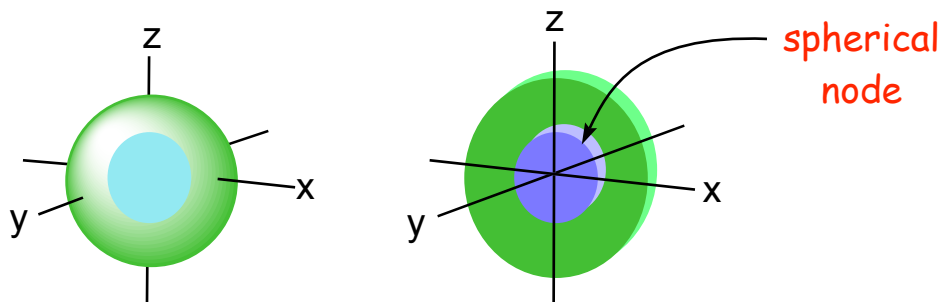
- The familiar spherical orbital should **not** be interpreted to illustrate a circular movement of electrons.
- The "cloud" picture of electron density reveals a spherical region where the electron density is zero, i.e. where the wavefunction must have a **node**.



- **Again**, we must also consider the other phasing of the wavefunction



- The **wavefunction squared** gives **probability** of finding the electron as a function of distance from the nucleus ($P(r)$). This probability plot contains **no phase information** since a probability (and also a number squared) can only be positive or zero, never negative.
- The plot of the **wavefunction** for the 2s A.O. looks like a **different** wave than that for the 2p A.O. Again, this wave gives **phase information**, i.e. the positive **and** negative regions due to the wave behavior.
- For the 2s A.O., the **wavefunction** has a node **away** from the nucleus, the probability of finding the electron this distance from the nucleus is zero.
- There are different kinds of nodes, the 2s atomic orbital has a single **spherical node**.



- The wavefunction is square root of the probability plot, thus we don't know which phase is positive and which negative, which is why we need to consider possibilities, shown in **both** plots and **both** pictures. Positive and negative are **arbitrary** in **wavefunctions**, thus we distinguish the different phases by **shading (or coloring)** in the picture rather than assigning an absolute positive or negative sign.
- Understanding this **wave nature** is **essential** for **building molecular orbitals/making Bonds**.
- The orbital shape defines an arbitrary "boundary" beyond which the probability of finding the electron is small.
- **Note** that the colors are arbitrary, the different colors are just like shading and non-shading, or red and white etc.

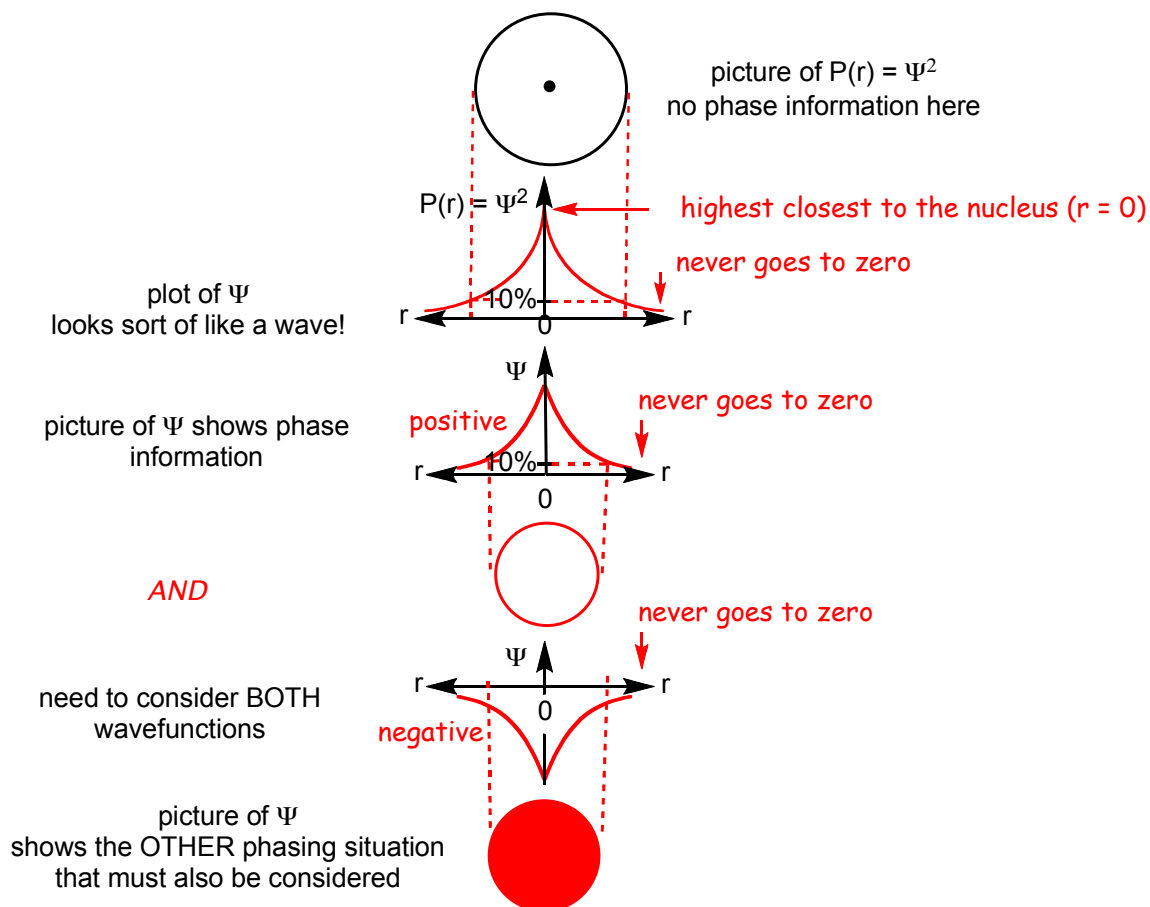
5.3 1s Atomic Orbital

$$\Psi = f(n, l, m, s, r, \dots) \quad \text{in this case } n = 1, l = 0, m = 0$$

- **The Nodal Theorem:** The quantum numbers tell us about the wave nature of the orbitals, the number of nodes is the value of the principle quantum number $n - 1$, therefore, a 1s A.O. ($n = 1$) **must have zero nodes**



- The familiar spherical orbital should NOT be interpreted to illustrate a circular movement of electrons.
- The "cloud" picture of electron density, **zero nodes** in this case.

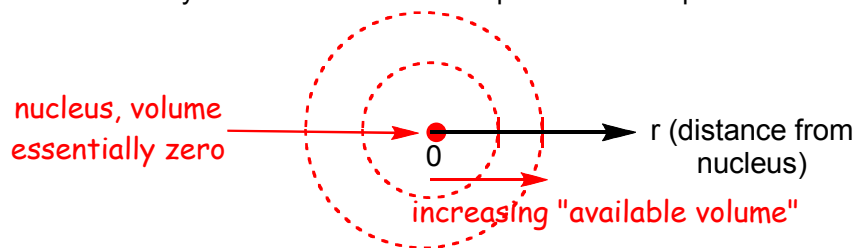


- We **need** this picture of the **phase information** to **make molecular orbitals, see later**.

5.4 Relative Energies of Electrons in Atomic Orbitals

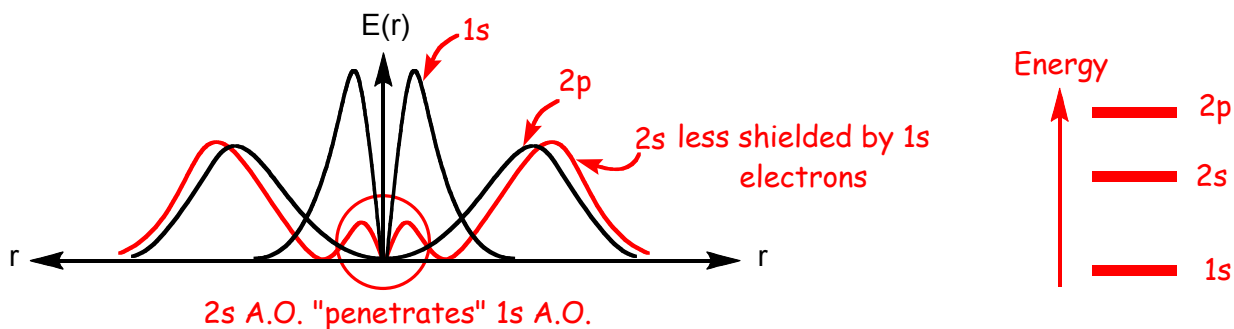
- **The probabilities** of finding the electrons as a function of distance from the nucleus, $P(r)$, are given by the **wavefunction squared**.

- However, electron locations in orbitals and their relative energies are better understood in terms of **electron densities** as a function of distance from the nucleus, $E(r)$
- To determine **ELECTRON DENSITIES, $E(r)$** , volume effects must be considered, i.e., there is only "one place" the electron can be that has zero distance from the nucleus, that is at the nucleus itself. With increasing distance from the nucleus, there are more places the electron can be (a larger volume of space that the electron can occupy), decreasing electron density towards the nucleus compared to that expected based on the $P(r)$ plot,



- with increasing distance from the nucleus, increasing r , there are more places that the electron be and still be at that same distance from the nucleus, the particle has a larger effective volume, and we need to take this into account to get the real electron density, $E(r)$, from the probability, $P(r)$.

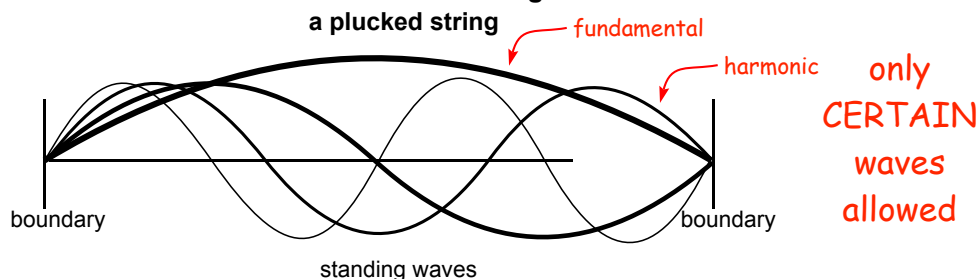
- For the example of a 1s A.O.: $E(r) = P(r) 4\pi r^2$
 $P(r) = \Psi^2$



- **Electron energy tends to increase with increasing number of orbital nodes**, 2s A.O. has one more node than 1s A.O., an electron in a 2s A.O. is higher in energy than an electron in a 1s A.O.
- maximum electron density in 2s and 2p A.O.s MUCH further from the nucleus than in the 1s A.O., electrons in 2s and 2p A.O.s are thus HIGHER in energy
- the maximum is actually further from the nucleus for the 2s compared to the 2p A.O., however, the extra "lobe" in the 2s A.O. "penetrates" the 1s A.O., resulting in some electron density closer to the nucleus and much LESS SHIELDED by the 1s A.O. electron density, energy of an electron in a 2s A.O. is thus LOWER than in a 2p A.O.
- This **ordering of electron energies** in orbitals is **very important**, it helps us to understand the energy ordering in molecules, where the electrons are in molecular orbitals
- This ordering, which you probably already knew from general chemistry, or before, as a fact, is now EXPLAINED in terms of the electron density functions ($E(r)$, which in turn depend upon the Probability functions $P(r)$, which in turn depend upon the wavefunctions, $\Psi(r)$. and so, EVERYTHING is determined and EXPLAINED by the WAVE NATURE of the electrons.

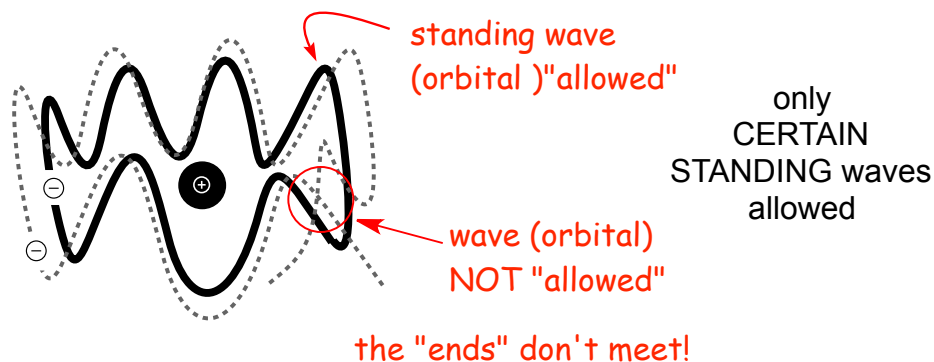
5.5 So, Why Are there Orbitals?

- The wave nature of electrons is an odd concept, it doesn't seem to make sense in our macroscopic world, however, **the wave nature of electrons is most important factor that determines their properties**
- Once we accept that electrons have wave nature, however, there **must** be orbitals, there is no other explanation **Consider the sound waves related to vibration of a string....**



- Only the fundamental wave and its harmonics are observed, because the boundary conditions imposed by the length of the string requires these to be STANDING WAVES, only CERTAIN STANDING WAVES are allowed

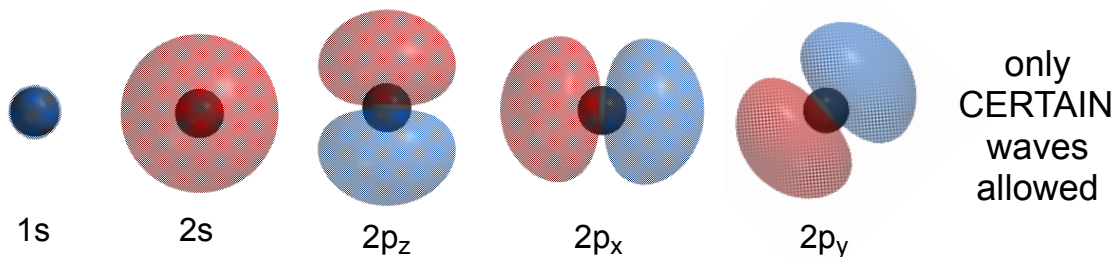
Consider the electron waves defined by the attraction of the negatively charged electron and a positively charged nucleus....



- Because of the boundary conditions of the charge on the nucleus and the requirement for proper overlap of the wave structure where it "meets", only CERTAIN STANDING WAVES are allowed
- These allowed standing waves define the distance of the electron from the nucleus and the electron energy
- These standing waves are the ORBITALS, the orbitals are a NECESSARY CONSEQUENCE of the wave nature of the electron
- **If the electron does not have wave nature then there are no standing waves there are no orbitals, there is no other way to explain the existence of orbitals without taking the wave nature of the electrons into account**

Atomic Orbitals versus Molecular Orbitals

- The familiar atomic orbitals are those available to electrons when they are associated with an atom, where the boundary condition that determines the allowed standing waves is the nucleus at the center of a single atom.....



- So what about the orbitals available to electrons not associated with a single atom, where the boundary conditions are changed because the electrons can now "see" more than one nucleus in the molecule? **The allowed wave structures should be different with different boundary conditions (i.e. when the electrons see more than one positive charge) the orbitals in molecules should be different and they are!**

6 The Molecular Orbital Theory Model of Bonding

6.1 Introduction to Localized Molecular Orbital Theory: The Simple Example of H₂

- Electrons in **atoms** are in **Atomic Orbitals (AOs)**, electrons in **molecules** are in **Molecular Orbitals (MOs)**
- Molecular orbitals can be constructed by starting with the familiar atomic orbitals and modifying them to consider the new boundary conditions, the new nuclei
- The method of combining the atomic orbitals is called a **Linear Combination of Atomic Orbitals (LCAO)**
- Completely accurate molecular orbital theory would take **all of the atomic orbitals** associated with all of the atoms in the molecule into account, which is impossible to do without complicated math, instead, we will use an approximate method to generate **localized molecular orbitals** which although not quite accurate, are still much more accurate than Lewis structures
- The **LCAO** model generates approximate molecular orbitals that are localized on individual bonds. In effect, localized molecular orbital theory pretends that molecular orbitals are localized between the two atoms that "make" the bond. This is the "next level" up from Lewis structures in models of bonding and structure. A complete and accurate M.O. theory is actually too detailed to be very useful to us.

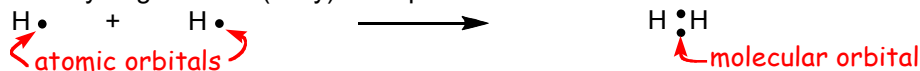
LCAO is very quantitative, but we will do it qualitatively, **using pictures!**

The LCAO "Rules" to make a pictorial **Localized MO** that describes a bond between two atoms are:

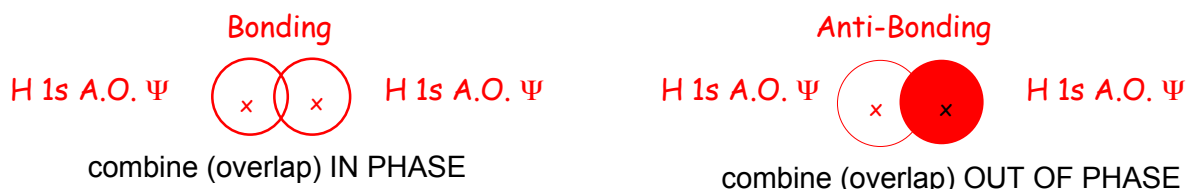
1. Choose the appropriate **two AOs** to make the bond (one from each atom)
 2. Draw **pictures of the two wavefunctions** that correspond to these A.O.s
 3. Make **two new MOs** by **combining (overlapping) the two AOs** both **in-phase AND out-of-phase**
- **THIS is why we need pictures of the phase information to make molecular orbitals**

Note that when the atomic orbitals are combined in a molecule, we must get both in-phase and out-of-phase overlap of the wavefunctions, which generates two new orbitals in the molecule (orbitals can't disappear, two atomic orbitals MUST make two molecular orbitals)

Let's look at Molecular Hydrogen as an (easy) example



- Overlap the **wavefunction** of one 1s A.O. from **each hydrogen atom** to make the new M.O.s



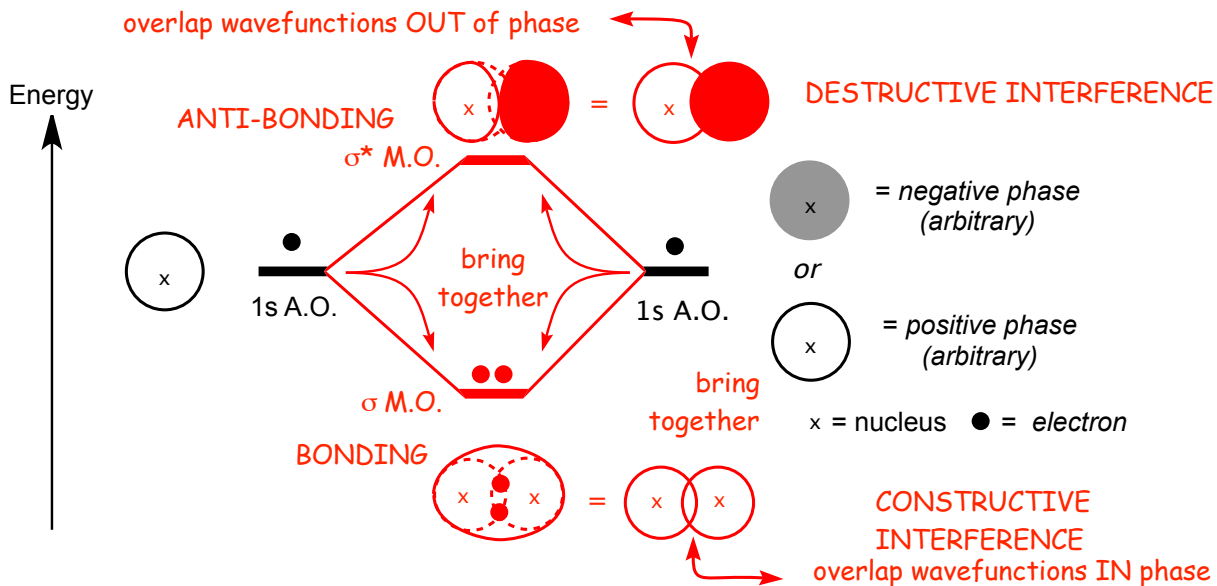
• If then overlapping (combining) IN PHASE happens, then combining (overlapping) OUT OF PHASE MUST also happen simultaneously, it is an unavoidable consequence of the wave nature of the orbitals. The two situations are called **BONDING (IN PHASE)** and **ANTI-BONDING (OUT OF PHASE)**.

• This is how the **TWO A.O.s** (one from each H atom) are combined to make the **two M.O.s in molecular hydrogen**

• Each hydrogen atom provides **one electron each to make the bond**

• One of these two **new M.O.s** will contain the 2 electrons in the new covalent bond in the hydrogen molecule

Energy Diagram for formation of Localized Molecular Orbitals:



- Bringing the atoms together to make a bond results in **overlap** of the atomic orbitals
- Because of the **wave nature** of the atomic orbitals, reflected in their wavefunctions, when they overlap they do so **both** "in-phase" and also "out-of-phase" at the **same time**
- Overlap of the atomic orbital wavefunctions **in-phase** results in **constructive interference of the wave structures** to generate a **new wave structure** that is a property of the **molecule**, this new structure is largest where constructive overlap is greatest, i.e. between the nuclei, the result is a localized **bonding molecular orbital**. This is where the two electrons "go", **lower in energy**,
- The corresponding overlap of the wavefunctions **out-of-phase** results in **destructive interference of the wave structures** to generate **another new wave structure**. This new structure **has a node** where the destructive

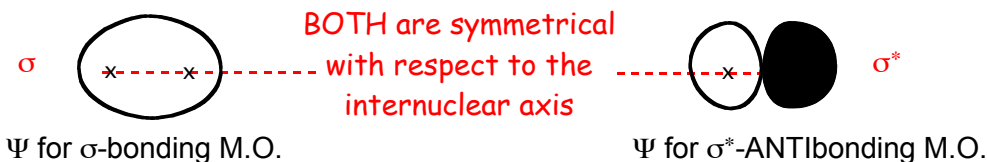
overlap occurs, i.e. between the nuclei, the result is a localized **anti-bonding molecular orbital**. The electrons do NOT "go" there, **since they would be higher in energy**

Anti-Bonding Orbitals: Anti-bonding orbitals **must be formed** if bonding orbitals are formed, the combination of 2 atomic orbitals **must** generate two molecular orbitals, orbitals can't disappear.

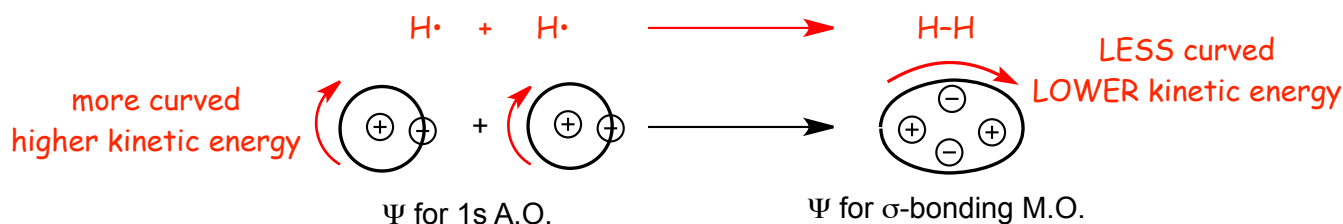
There is **no problem with having antibonding M.O.s with no electrons in them!** Think about a hydrogen atom, does it have a 2p A.O.? If an electron is added with appropriate energy, or if the electron in the 1s A.O. is provided with enough energy, then the H atom could have an electron in a 2p A.O., before that it was "empty", just like an anti-bonding M.O. in a molecule.

Anti-bonding orbitals become **important later when we come to chemical reactions**.

• The bonding sigma M.O. is lower in energy than both of the two atomic orbitals that were used to construct it, both electrons are thus lowered in energy, **this is the definition of bonding**.

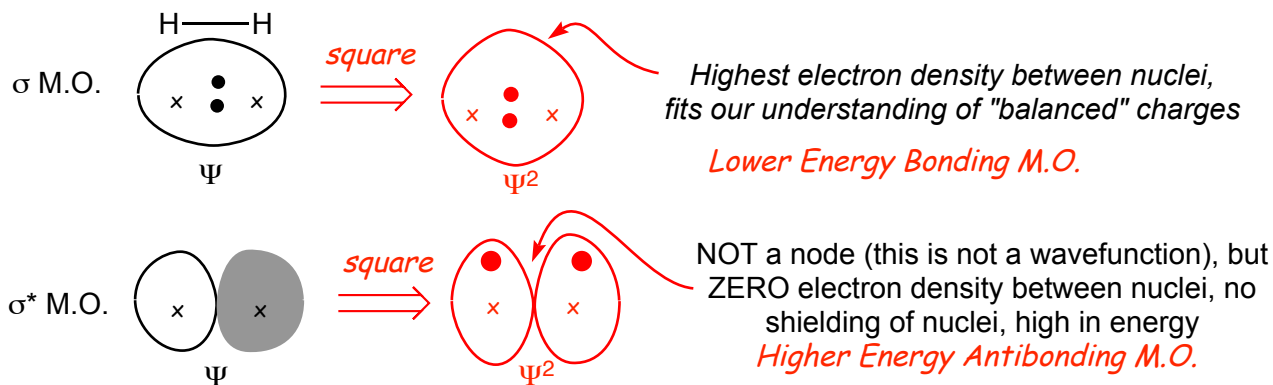


- **Both** of the orbitals are symmetrical with respect to the internuclear axis (they are both the same above and below the internuclear axis), which is why they are both sigma orbitals (antibonding is sigma*)
- This picture **also** gives us the **real explanation for why electrons form bonds**.
- The conventional explanation is that in the molecular orbitals the charges are "balanced", each electron "sees" two nuclei, in essence this an electrostatic argument, but it doesn't really make sense because in the M.O. the nuclei are very close to each other too, hmmm...



- The **best explanation** that is generally accepted today is that the new molecular orbital is less **curved** and is **larger** than the atomic orbitals that the electrons were in before making the bond, the electrons thus have **lower kinetic energy in the bond!**

Now, square the wavefunction to give the probability of finding the electrons in the MO:



- Both the bonding and the anti-bonding M.O.s are symmetrical with respect to the internuclear axis, therefore they are given the label sigma (means symmetrical with respect to the internuclear axis).

6.2 VSEPR Determines (almost) Everything

- Before we get to the more complex MOs, we need to learn how electrons are arranged in organic molecules.

HOW THE ELECTRONS ARE ARRANGED TELLS US HOW TO BUILD THE MOLECULAR ORBITALS FOR SITUATIONS MORE COMPLEX THAN H₂

Everything Starts With VSEPR

• In complex molecules, this is what really is happening.....

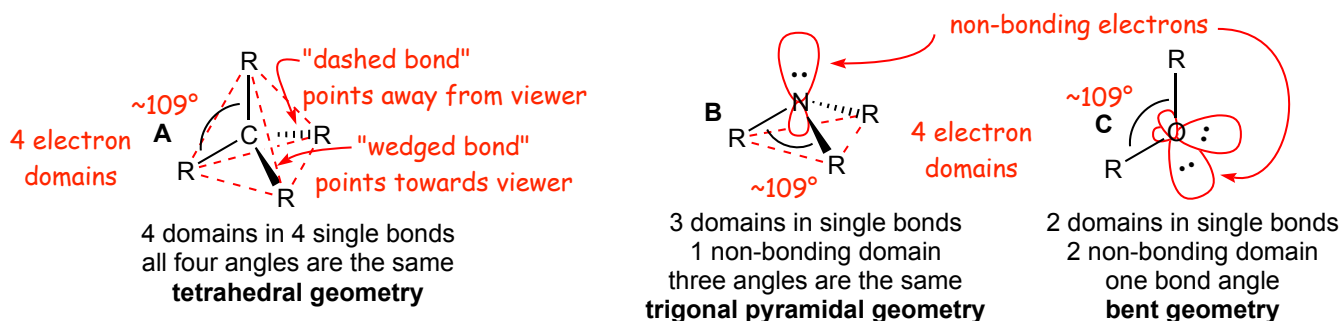
- the valence electrons make as many bonds as they can (lowering the energy of the maximum # of electrons), as we have learned, by sharing their electrons between two nuclei
- the bonding and the non-bonding valence electron pairs arrange themselves in space to lower their energy by **avoiding electron repulsion**
- the pure AOs are usually **not relevant** now, since the electrons now see more than one nucleus, the atoms are now in a **molecule** where they see multiple other charged nuclei and electrons
- this means that we can't, and should **not** use the normal AOs in LCAO to make the MOs, we need to use different (hybridized) AOs and it is the electron repulsion that allows us to work out how to do this
- **Valence Shell Electron Pair Repulsion (VSEPR)** takes all of this into account!

VSEPR:

1. Accounts for the locations of the other atoms around each atom, and in this way, the electron pairs that are either bonding or non-bonding.
2. Determines what each atom needs to "do", and where in space the electrons around each atom need to go. VSEPR thus determines hybridization, how the atomic orbitals must change, which determines how the localized MOs are built.

VSEPR with four Valence Electron Domains:

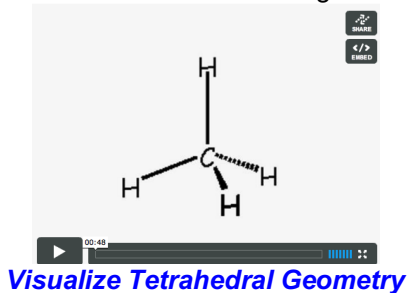
- The following structures have 4 sets or domains of valence electrons around a central atom, C, N and O
- The 4 sets or domains of electrons separate from each other as much as possible due to electron **repulsion**.



- **The locations of atoms (nuclei) can be well defined, but the locations of electrons can NOT**
- The geometry of structure **A** (above) can be exactly defined by the positions of the 5 atoms as **TETRAHEDRAL**
- For structure **B**, the geometry can only describe the positions of the 4 atoms: **TRIGONAL PYRAMIDAL**
- For structure **C** the geometry can only describe the positions of the H-O-H atoms, thus **BENT**

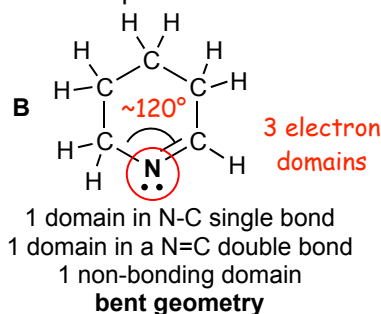
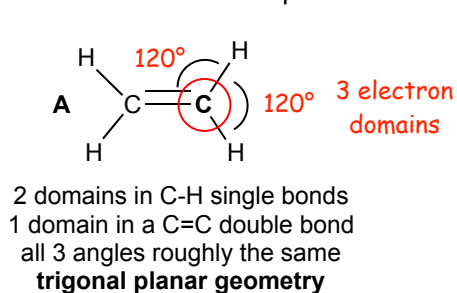
Knowing that we have four electrons domains around a particular atom will help us build the molecular orbitals involving that atom

NEW NOTATION: The wedged and dashed bonds are a method of describing a 3-dimensional structure on a 2-dimensional piece of paper that is very useful for TETRAHEDRAL geometries



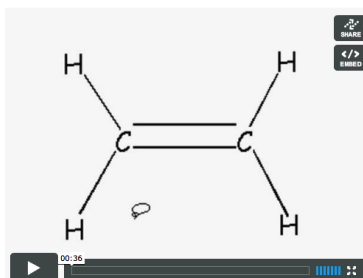
VSEPR with three Valence Electron Domains:

- The following structures have 3 sets or domains of valence electrons around the indicated C and N atom
- The 3 sets or domains of electrons separate from each other as much as possible due to electron REPULSION



- The geometry at CARBON in **A** (above) is defined by the positions of the 4 atoms as **TRIGONAL PLANAR**
- For structure **B**, the geometry at NITROGEN can only describe the positions of the C-N=C atoms: thus **BENT**

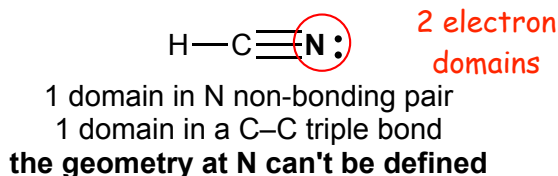
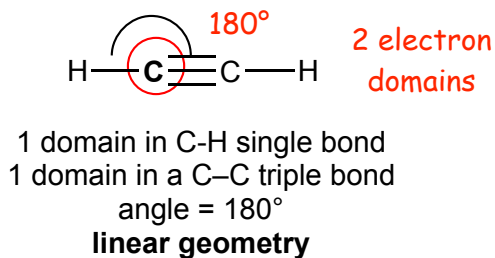
Knowing that we have three electrons domains around a particular atom will help us build the molecular orbitals involving that atom



Visualize Trigonal Planar Geometry

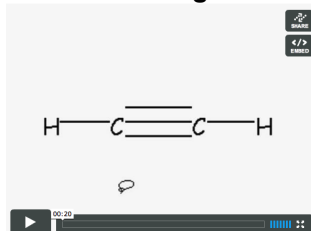
VSEPR with two Valence Electron Domains:

- The following structures have 2 sets or domains of valence electrons around the indicated C and N atom
- The 3 sets or domains of electrons separate from each other as much as possible due to electron REPULSION



- The geometry at **carbon** of structure **A** (above) is defined by the positions of the 2 atoms as **linear**.
- The geometry at **nitrogen** for structure **B** (above) can not be defined since the non-bonding electrons cannot be exactly located in space.

Knowing that we have two electrons domains around a particular atom will help us build the molecular orbitals involving that atom

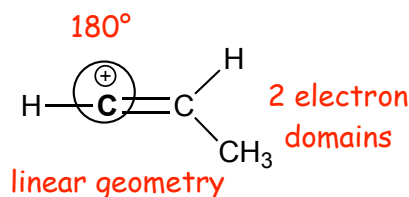
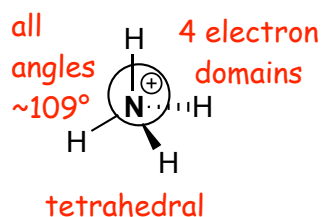
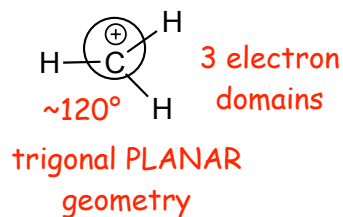
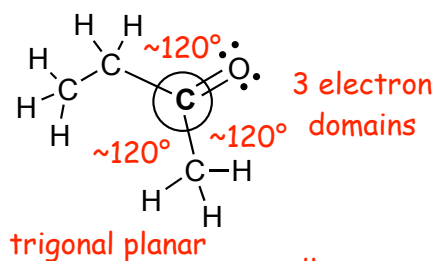


Visualize Linear Geometry

Practice Using VSEPR:

VSEPR analysis of geometries and angles considers **one atom** at a time in a molecule.

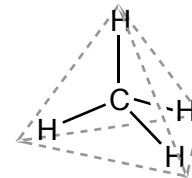
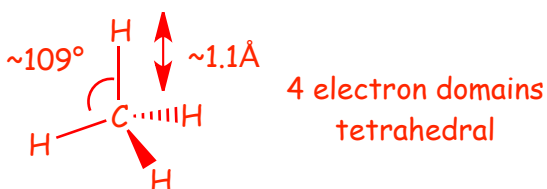
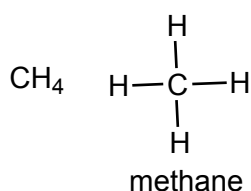
For the circled atoms below, count the number of electron domains around the atom and use **VSEPR** to determine the geometry and any relevant bond angles.



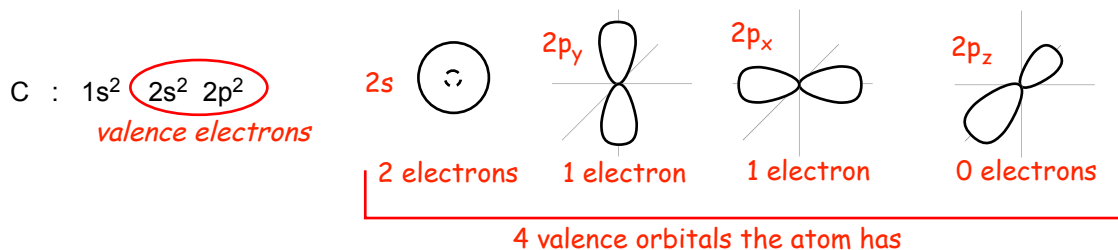
6.3 Methane as a (Simple!) More Complex Case Than H₂

Start with VSEPR:

- There are **four C-H bonds** around the central carbon atom, there are thus **four** domains of electrons that need to get as far apart from each other as possible to lower the total electron energy.

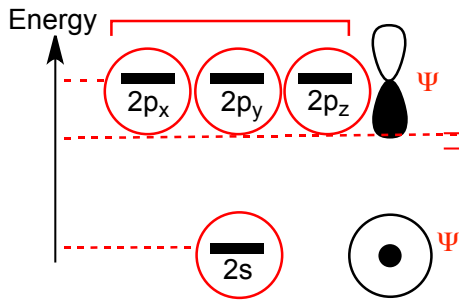


- The lowest energy geometry is **tetrahedral** at the central carbon atom, **all bond angles and bonds lengths must be identical by symmetry**.
- In methane, the central carbon thus needs **four identical** AOs to construct the **four identical** C-H bonds
- In methane these 4 AOs must be separated by $\sim 109^\circ$ in order to generate the correct structure and geometry **This can not happen with the normal AOs a carbon atom has when it is not in a molecule!**
- The Valence electrons in **atomic** carbon are associated with the 2s and the three 2p atomic orbitals.
- Methane **cannot** use these orbitals to make the 4 identical C-H bonds since these 4 orbitals are obviously not identical and they are not separated by angles of $\sim 109^\circ$.



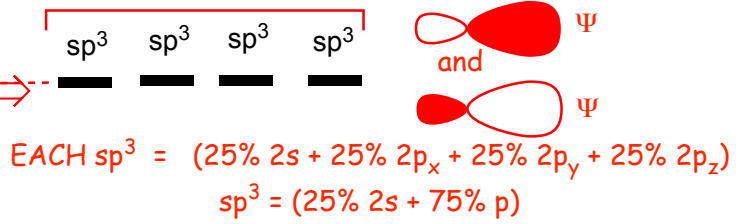
- The **hybridization model** describes how the AOs in carbon **change in response to the approach of the four hydrogen atoms (and their nuclei) as the bonds are formed**.
- Hybridize (mix together) the four **different** valence A.O.s that carbon has in an isolated atom to make four new **identical hybridized (mixed)** atomic orbitals that can make the required **four identical** bonds

4 valence orbitals the isolated atom has

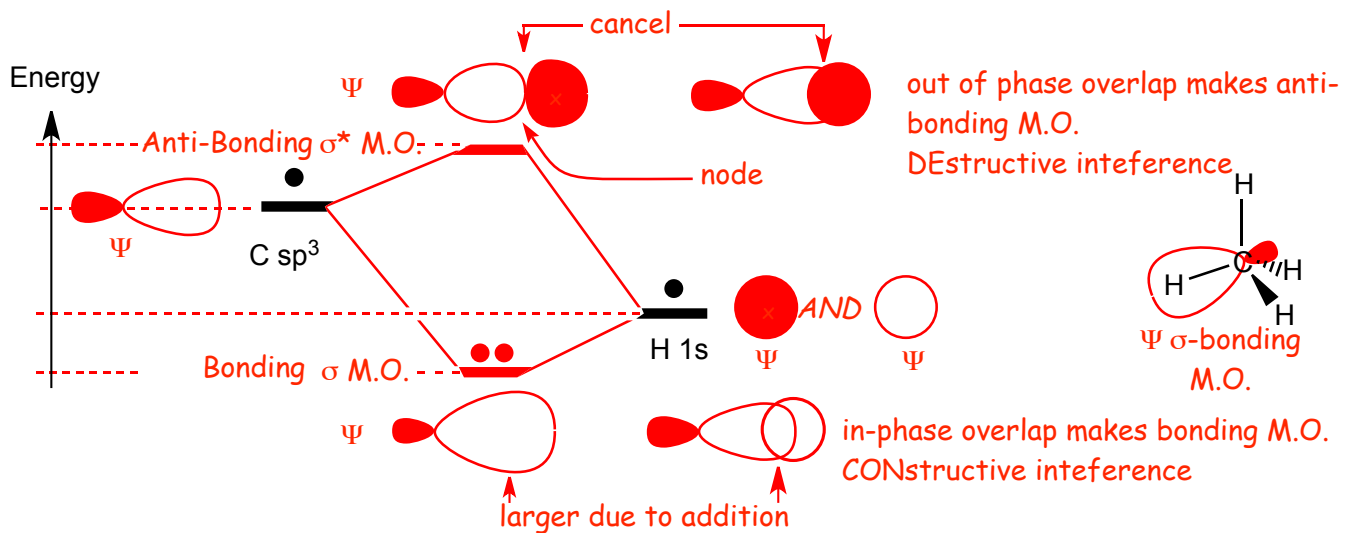


four identical sp^3 hybrid (mixed) orbitals

valence orbitals the carbon NEEDS in methane (molecule)



- Each new hybrid orbital consists of an equal mixture of a 2s, a 2p_x, a 2p_y and a 2p_z orbital, each one is **one** part s and **three** parts p: **i.e. we have four new hybridized sp^3 AOs** that are used to make 4 identical C-H bonds
- Mixing the four 2s, 2p, 2p and 2p AOs must make FOUR NEW hybridized sp^3 orbitals (orbitals can't disappear!)
- ALL of the valence orbitals are mixed, 2s, 2p_x, 2p_y and 2p_z, not just the orbitals that are occupied, we are mixing ORBITALS, not the electrons (the sp^3 notation comes not from the number of electrons, but from the number of orbitals that are mixed together, 3 p orbitals are mixed with one 2 orbital)
- An electron associated with an sp^3 (hybrid) AO would be lower in energy than one associated with a 2p AO (they have 25% 2s character), but significantly higher than one associated with a 2s AO (they have 75% 2p character)
- Carbon will use one of its 4 valence electrons in each of the sp^3 hybridized orbitals to make these 4 bonds
- Each C-H bond requires 1 sp^3 hybrid A.O. from C and 1 A.O. from H, combine a 1s A.O. from H with a sp^3 A.O. from C according to the pictorial LCAO "rules" to make a **LOCALIZED** molecular orbital for each bond

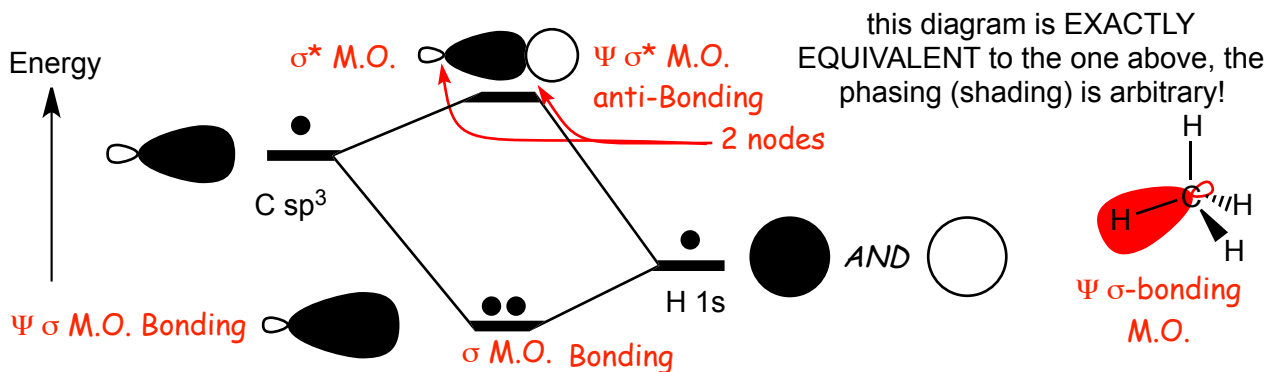


NOTE: the hydrogen 1s A.O. is lower in energy than the carbon sp^3 A.O

NOTE: the node in the M.O. is at the carbon nucleus, because there was one there in the sp^3 orbital

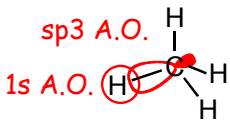
NOTE: both of the molecular orbitals are symmetrical with respect to the internuclear axis, therefore they are both sigma molecular orbitals, the bonding one is the sigma orbital, and the antibonding one has sigma*, the sigma* has one more node, exactly between the carbon and the hydrogen atoms.

NOTE: shading (phasing) of the orbitals is **ARBITRARY**, a diagram can ALSO be drawn with opposite shading

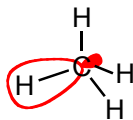


• Why doesn't the hydrogen atom also hybridize its AOs? The H atom only has to accommodate the presence of ONE NEW nucleus (it only makes one bond) this is a much smaller perturbation than the carbon experiences, hybridization is not necessary or beneficial to atoms that only make ONE BOND (we will see this again later...)

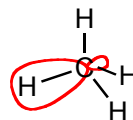
To Summarize:



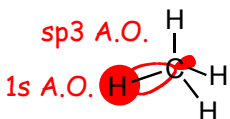
pictures of the Ψ for the A.O.s overlapping **IN PHASE** (these do NOT exist in the molecule)



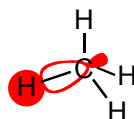
picture of the Ψ for the σ -bonding M.O. made by combining the A.O.s **IN PHASE**



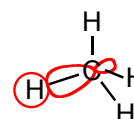
picture of Ψ^2 for the σ -bonding M.O., "where" the electrons are in the C-H bond



pictures of the Ψ for the A.O.s overlapping **OUT OF PHASE** (these do NOT exist in the molecule)

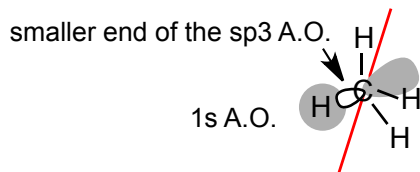


picture of the Ψ for the σ^* -**ANTIBONDING** M.O. made by combining the A.O.s **OUT OF PHASE**



picture of Ψ^2 for the σ^* -**ANTIBONDING** M.O., "where" the electrons WOULD BE if they were in the anti-bonding M.O.

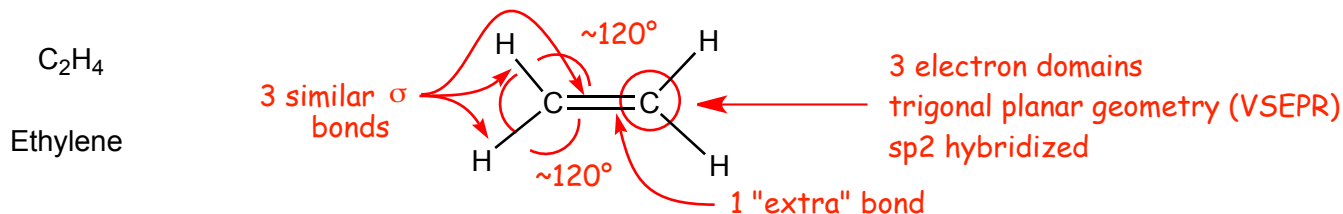
- The electrons in the C–H bond are never at the C nucleus (due to the node). The orbital encompasses the H atom because the 2s A.O. that we used did also.
- Always, the wavefunction squared of the M.O. to indicate the locations of the electrons
- The orbital is "largest" between the C and H, consistent with shared electrons **BETWEEN** the two atoms.
- When the atomic orbitals overlap they do so to make the strongest bond they can, which means the largest amount of atomic orbital overlap, and so it makes sense that the best overlap of the 1s A.O. is with the larger lobe of the sp3 A.O., i.e., the following does not occur



Alternatively, you can think of the nucleus of the hydrogen atom "pulling" the hybridized atomic orbital towards it, which is why the larger end of the sp3 A.O. points towards the hydrogen atom

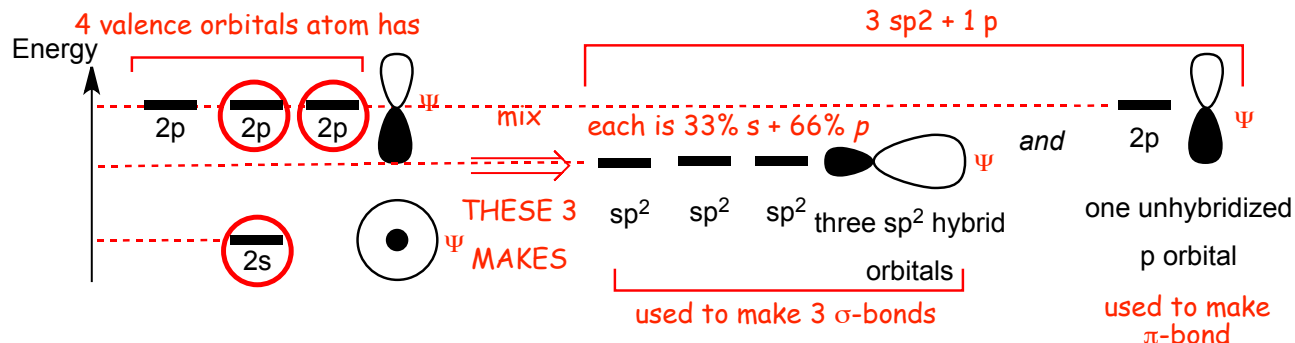
6.4 Structures with Double Bonds: Ethylene as a Simple Example

- **START WITH VSEPR:** There are THREE electron domains around each carbon atom that need to get as far apart from each other as possible to lower the total electron energy, the geometry is trigonal planar and the bond angles are all $\sim 120^\circ$
- An **ADDITIONAL** consideration is that the two bonds in the C=C double bond can NOT be the same, 2 pairs of electrons can NOT occupy the same area of space due to electron repulsion.

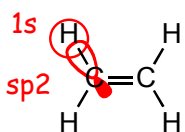


- To make three similar bonds that are separated by ca. 120° , each carbon needs three AOs on that are the same and that are separated by ca. 120°
- The carbon also needs to make one bond that is different, the second of the bonds in the C=C double bond
- the valence atomic orbitals that an isolated carbon atom (2s, 2p_x, 2p_y, 2p_z) will not be able to do this, certainly not with 120° bond angles, the carbon will need to hybridize (mix) its valence atomic orbitals to make new hybridized valence atomic orbitals

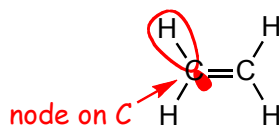
four valence orbitals the carbon NEEDS in ethylene (molecule)



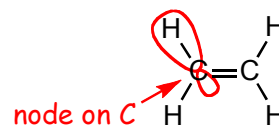
- Combine (hybridize or mix) **one 2s and two 2p to make three** new hybridized sp^2 orbitals
- Orbitals can't disappear, mixing 3 AOs must make 3 new AOs
- An electron associated with an sp^2 (hybrid) AO would be lower in energy than one associated with a 2p AO (they have 33% 2s character), but significantly higher than one associated with a 2s AO (they have 66% 2p character)
- Combine a 1s A.O. on H with an sp^2 AO on C to generate the Localized MOs associated with the C-H bonds
- Draw the wavefunction squared of the appropriate **LOCALIZED M.O.** to indicate the locations of the electrons



pictures of the Ψ for the A.O.s overlapping **IN PHASE** (these do NOT exist in the molecule)

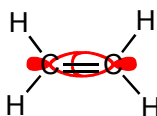


picture of the Ψ for the σ -bonding M.O. made by combining the A.O.s **IN PHASE**

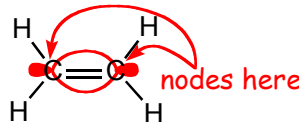


picture of Ψ^2 for the σ -bonding M.O., "where" the electrons are in the C-H bond

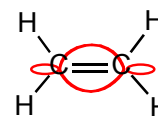
Where are the electrons in the C-C sigma bond? Combine an sp^2 A.O. on C with an sp^2 A.O. on C. Draw the wavefunction squared of the LOCALIZED M.O.



pictures of the Ψ for the A.O.s overlapping **IN PHASE** (these do NOT exist in the molecule)



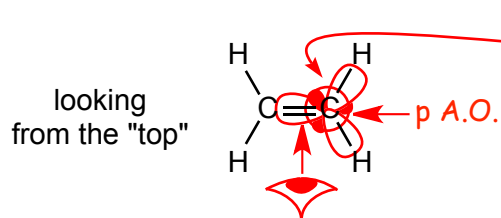
picture of the Ψ for the σ -bonding M.O. made by combining the A.O.s **IN PHASE**



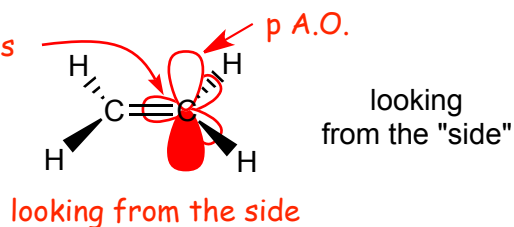
picture of Ψ^2 for the σ -bonding M.O., "where" the electrons are in the C-C sigma bond

What about the other ("extra") bond between the carbons? Use the one p A.O. on each carbon that is "left over" after the hybridization to make a "pi" bond

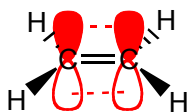
- The p atomic orbitals on each carbon are orthogonal to the plane that contains the sp^2 hybrid atomic orbitals, to see them properly we need to look at the molecules from the "side"



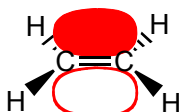
need to look from the **SIDE**



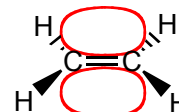
- Now we can see how the second bond in the double bond is built from the 2 p A.O.s



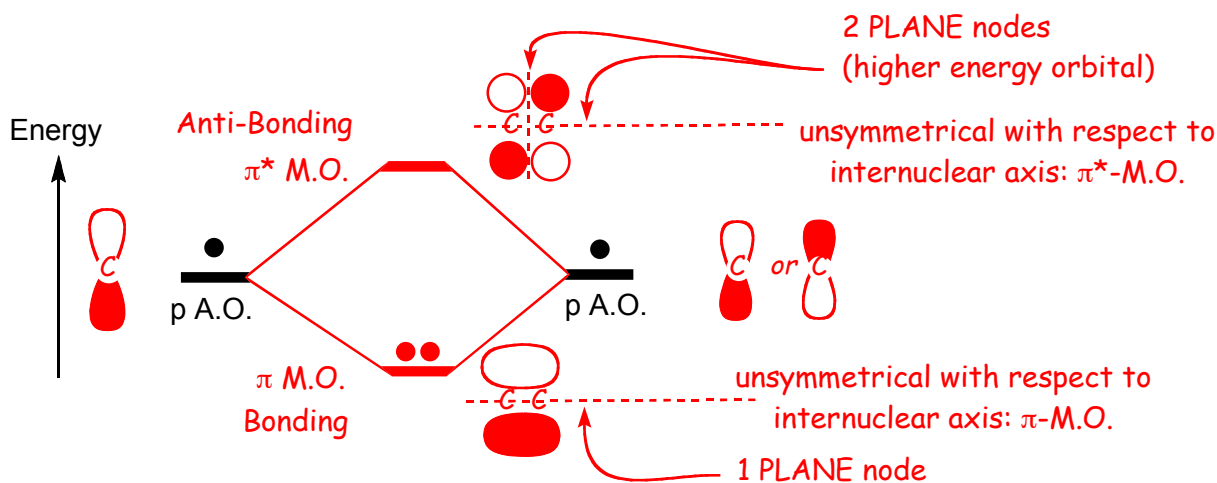
pictures of the Ψ for the A.O.s overlapping **IN PHASE**
(these do NOT exist in the molecule)



picture of the Ψ for the π -bonding M.O. made by combining the A.O.s **IN PHASE**

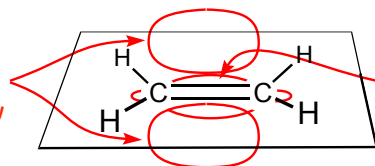


picture of Ψ^2 for the π -bonding M.O., "where" the electrons are in the C-C π -bond

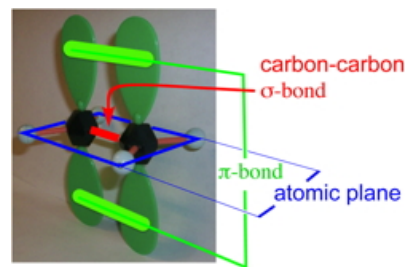


The diagram below shows the location of **all** of the electrons are in the **C=C double bond** (in drawings of wavefunctions squared), i.e. the **sigma- and the pi- bonds that together make up the double bond**

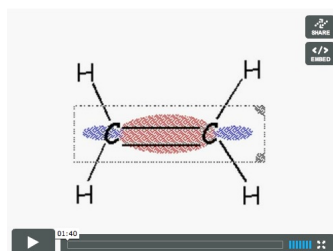
2 electrons in C-C π M.O. above and below plane



2 electrons in C-C σ M.O. in the plane



- All 6 atoms in (horizontal plane), **the pi-bond is above and below the plane.**
- **The electrons in the pi- and sigma- MOs occupy different regions of space!**
- The electrons in the pi-MO are further from nuclei, held less tightly, are higher in energy.
- **The pi-bond is weaker than the sigma bond** (electrons are higher in energy in the pi-bond).

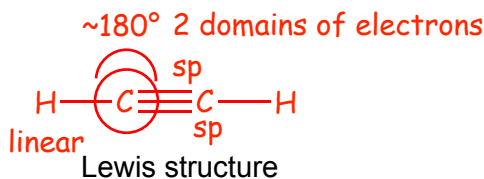


Visualize pi-Bonding and Anti-Bonding orbitals

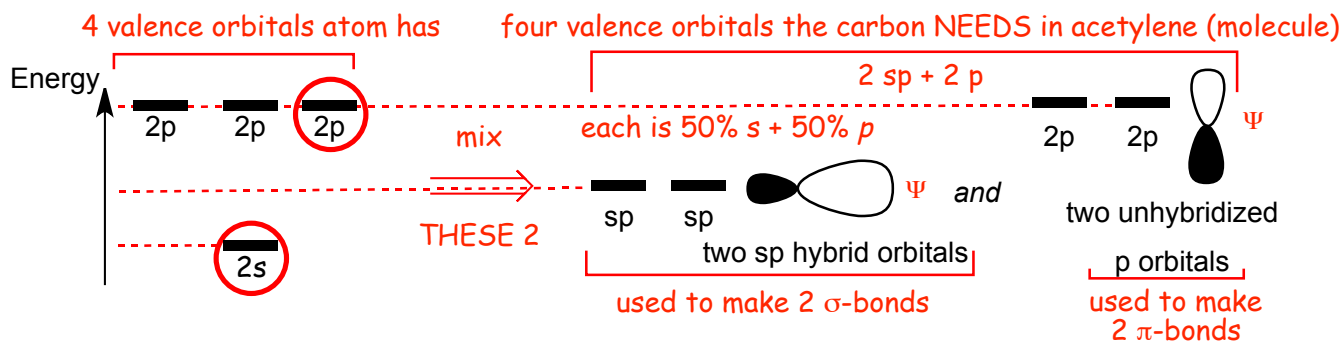
6.5 Structures with Triple Bonds: Acetylene as a Simple Example

- **Start with VSEPR:** There are **two** electron domains around each carbon atom that need to get as far apart from each other as possible, the geometry is this linear and the bond angles are all $\sim 180^\circ$.
- An **additional** consideration is that the three bonds in the C-C triple bond can **not** be the same, 3 pairs of electrons can **not** occupy the same area of space due to electron repulsion.

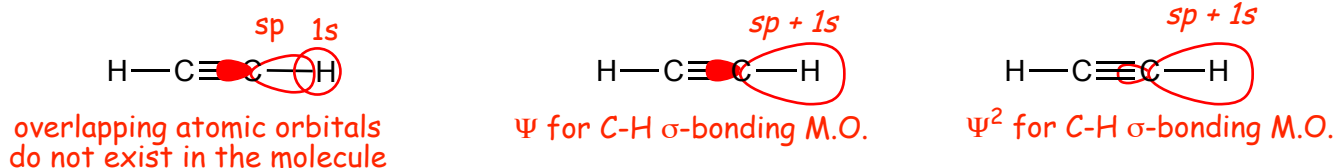
C_2H_2
Acetylene



- To make two similar bonds that are separated by 180°, each carbon needs two AOs on that are the same and that are separated by 180°.
- The carbon also needs to make two pi-bonds that are different.
- The valence atomic orbitals that an isolated carbon atom (2s, 2p_x, 2p_y, 2p_z) will not be able to do this, the carbon will need to hybridize (mix) its valence atomic orbitals to make new hybridized valence atomic orbitals.

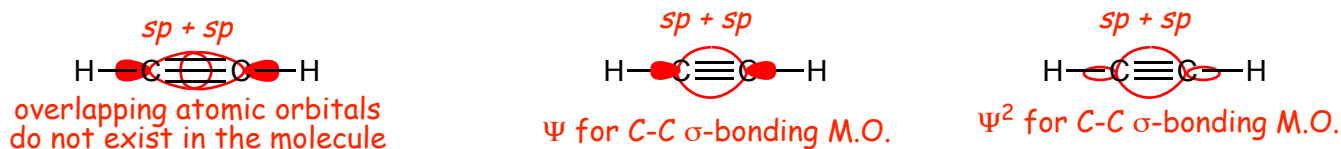


- Combine (hybridize or mix) **one 2s and one 2p to make two** new hybridized sp orbitals.
- Orbitals can't disappear, mixing 2 AOs must make 2 new AOs.
- An electron associated with an sp (hybrid) AO would be lower in energy than one associated with a 2p AO (they have 50% 2s character), but significantly higher than one associated with a 2s AO (they have 50% 2p character).
- Combine a 1s A.O. on H with an sp AO on C to generate the Localized MOs associated with the C-H sigma
- Draw the wavefunction squared of the appropriate **LOCALIZED** M.O. to indicate the locations of the electrons.

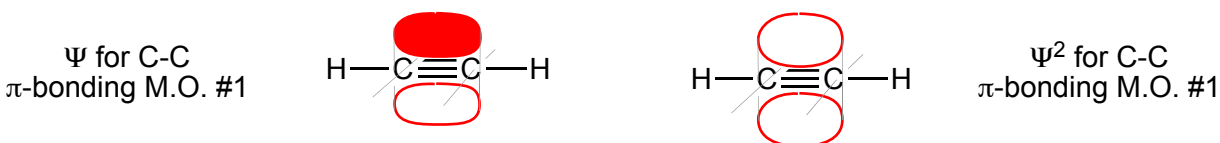


Where are the electrons in the C-C triple bond?

There are 2 electrons in a localized σ M.O. constructed by combining a 1s AO from H and an sp hybrid A.O. on each C

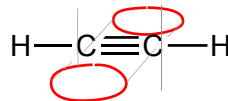
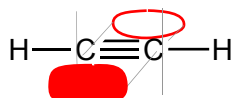


There are 2 electrons in π M.O. #1 that is constructed from 1 p A.O. on each C (top and bottom, wavefunction squared), it is easy to draw the first M.O. because it can be drawn in the plane of the paper

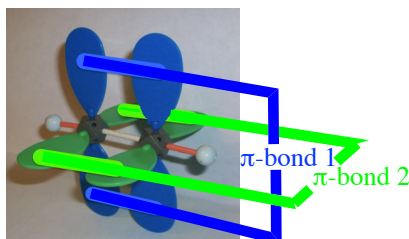
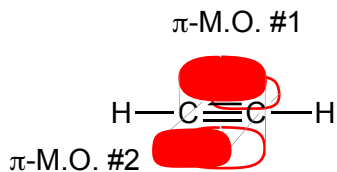


There are 2 electrons in a π M.O. #2 that is constructed from 1 p A.O. on each C (one lobe on each "side", wavefunction squared), the second pi-molecular orbital is at **right angles** to the first one, it's **difficult** to draw!

Ψ for C-C
 π -bonding M.O. #2

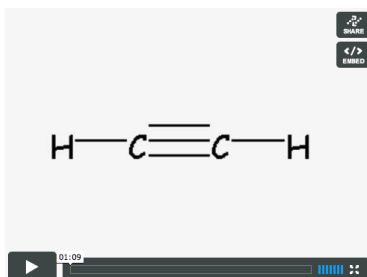


Ψ^2 for C-C
 π -bonding M.O. #2



molecular model showing the 2 π -bonds in acetylene

the bonds are orthogonal (90°) to minimize the overlap of the 2 sets of electrons in the 2 π -bonds

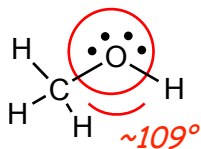


Visualize pi-Bonding in a Triple Bond

6.6 The Electrons in the molecule Methanol (for example)

- Start with VSEPR.

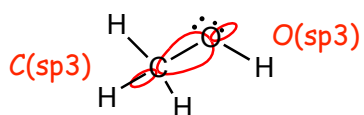
CH₃OH
methanol



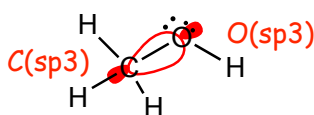
4 electron domains
*sp*³ hybridized - "tetrahedral-like"
BENT geometry

- **Four** "sets" or "domains" of electrons around the oxygen, 1 in the O–H bond, 1 in the O–C bond, 2 associated with the 2 non-bonding (lone) pairs, **bent** geometry.
- There are **four** "sets" or **domains** of electrons, and therefore the oxygen is *sp*³ hybridized.
(a detailed consideration of the local symmetries of the orbitals for the two non-bonding pairs of electrons tells us that they can't be exactly the same, they can't have the same energy, but that is an advanced concept and in this class we will assume that they are the same and that the oxygen atom is truly *sp*³ hybridized)

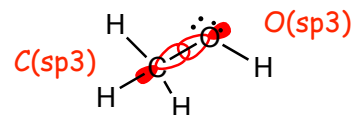
Combine an *sp*³ hybrid AO from C and an *sp*³ hybrid AO from O to make the MOs associated with the C–O bond



Ψ^2 for C–O σ -bonding M.O.



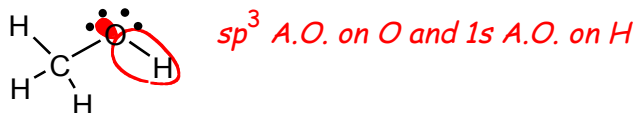
Ψ^2 for C–O σ -bonding M.O.



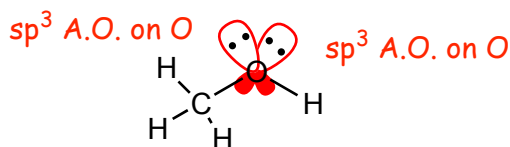
A.O.s USED to form the M.O.
(these do not exist in the molecule)

- The **bonding** M.O. is formed by in-phase overlap of the AOs.
- There is no phase information in the wavefunction squared picture because a probability can only be positive or zero, never negative, the wavefunction squared is not a wave, it does not have nodes.
- There is zero probability of finding the electrons in the bonds at the C and O nuclei because there was a node at these nuclei in the original hybrid *sp*³ A.O.s. The M.O. is larger towards the oxygen (see later).

- Draw the Wavefunction for the localized M.O. that describes the O-H bond: Need to include **phase** information in the wavefunction.



- Draw the wavefunction for the non-bonding electrons on the oxygen atom:



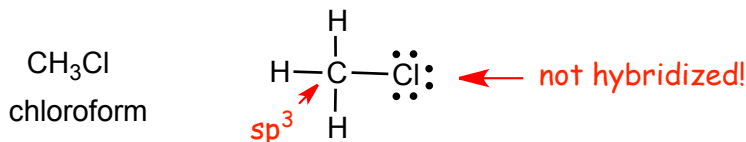
oxygen hybrid orbitals

sp^3	O-C σ -bond
sp^3	O-H σ -bond
sp^3	non-bonding pair #1
sp^3	non-bonding pair #2

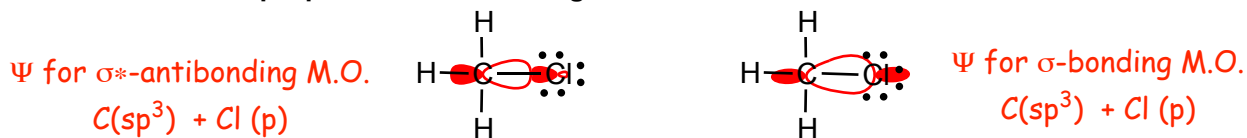
- The table explains exactly **how** the oxygen atom **uses** all of the hybrid orbitals.
- The orbitals that contain the non-bonding electrons are simply uncombined sp^3 hybrid AOs on the oxygen.

6.7 The Electrons in the molecule chloroform (for example)

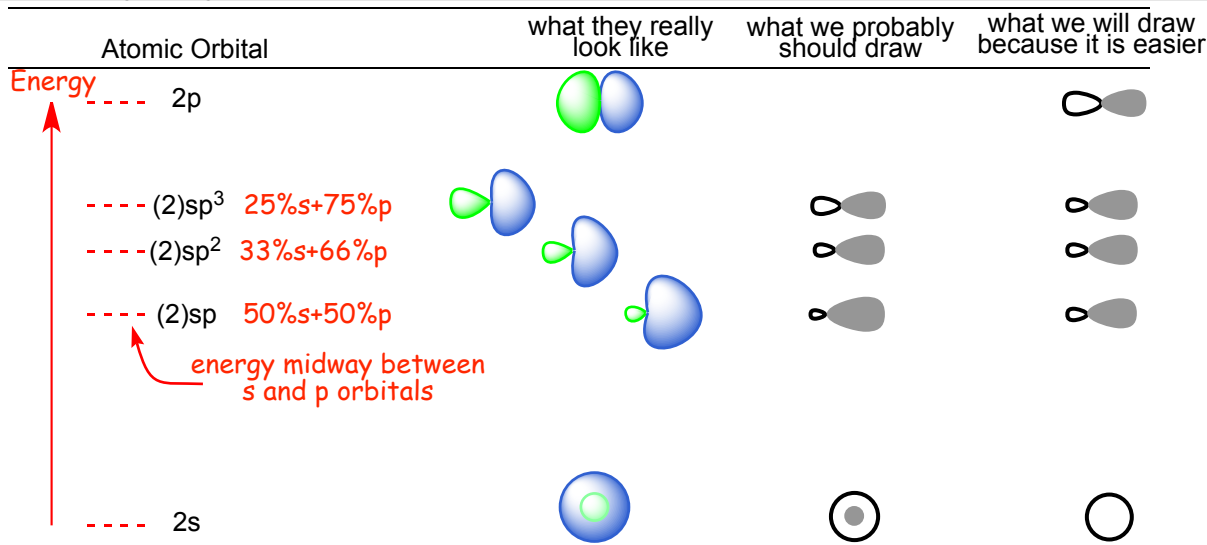
- **VSEPR is a bit different this time, because the Cl only makes one bond.**
- Hybridization does not occur when only one bond is made, the perturbation to the atomic orbitals that results by bringing only one new atom to make one new bond is not large enough to rehybridize the atomic orbitals, **the Cl atom does not hybridize.**



- The carbon makes 4 bonds and the hybridization is therefore sp^3 (as usual).
- The chlorine uses a **simple p A.O. to make the sigma-bond.**



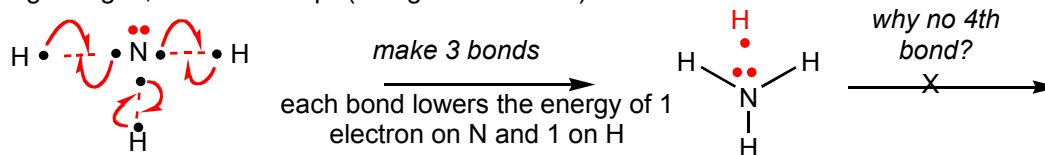
6.8 Summary of Hybrid Atomic Orbitals



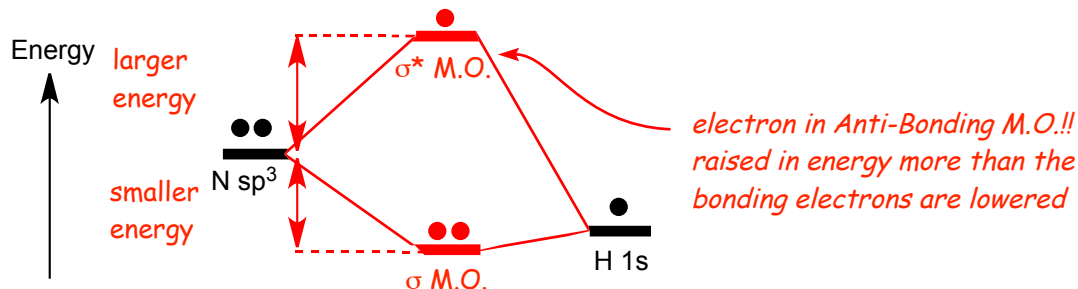
- The hybrid orbitals are really $2sp$, $2sp^2$ etc., but we usually drop the 2 (which is why it is in parenthesis above).
- The hybrid orbitals actually have quite complex shapes due to the overlapping wave nature and positions of the nodes in the $2s$ and the p atomic orbitals.
- Don't forget, energy doesn't mean the energy of the orbital, but the energy of an electron in that orbital.
- With increasing p -character the energy of hybrid orbitals increases and they also "look" more like p orbitals.
- Thinking about the energies in A.O.s, however, is a good guide to the energies of the electrons in M.O.s.
- The sp atomic orbital is 50% s + 50% p , its energy is midway between those of the pure s and p atomic orbitals.

6.9 Lewis Structures: Origin of the "Octet Rule"

Example using nitrogen, N : $1s^2 2s^2 2p^3$ (nitrogen is trivalent):



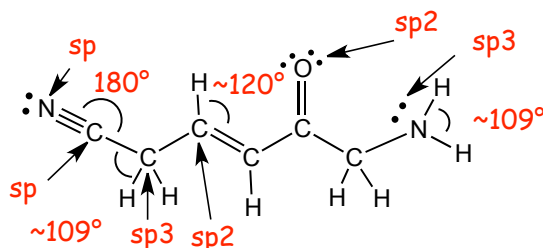
Energy Diagram for 4th bond, note that in this case there are **two electrons in the Nitrogen A.O.** we will use to make the molecular orbital



- Attempting to make a 4th bond puts an electron in an **anti-bonding M.O.** (because we have to accommodate three electrons now instead of the usual two), and the **energy of the electron in the anti-bonding orbital is raised in energy more than the energy of the other 2 electrons is lowered.**
- The electron in the anti-bonding M.O. is **raised in energy more** than electrons in bonding M.O. are lowered because the electrons in both orbitals are "pushed up" in energy due to the presence of other electrons in the molecule, which diminishes the beneficial effect of bonding and increases the nonbeneficial effect of anti-bonding
- **Also**, the bonding M.O. has **two** electrons in it, which also raises the energy of the bonding electrons compared to the anti-bonding electron.
- The fourth bond is therefore a very weak and does not form, and this is the **real origin** of the octet rule for atoms such as carbon, nitrogen and oxygen.

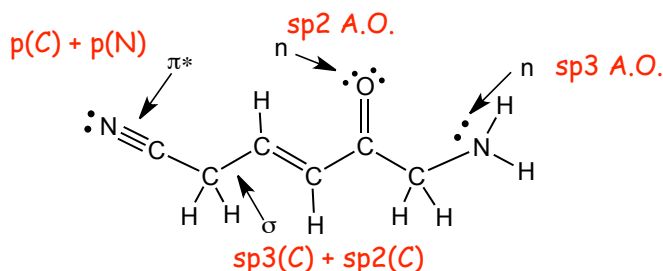
6.10 Putting It All Together: The Link Between VSEPR/Hybridization and Molecular Orbitals

First: fill in the missing angles using **VSEPR** to determine geometry from the number of "sets" or "domains" of electrons around each atom, in turn this determines the hybridization of each atom:

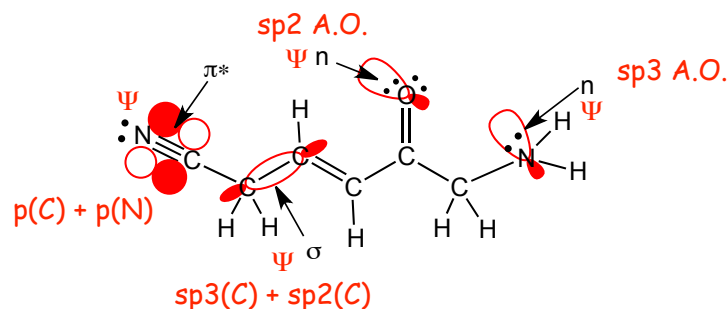


(the hybridization of oxygen in the $C=O$ double bond above left is a bit more complex than sp^2 due to orbital symmetry effects, but this is an advanced topic, and you should assume sp^2 hybridization for such atoms in this course)

Second: Give the A.O.s used to make the indicated bonds, or hold the non-bonding electrons. Consideration of the relevant hybridization that must occur when an atom is in the middle of a molecule gives the atomic orbitals that are used to construct the localized molecular orbitals:



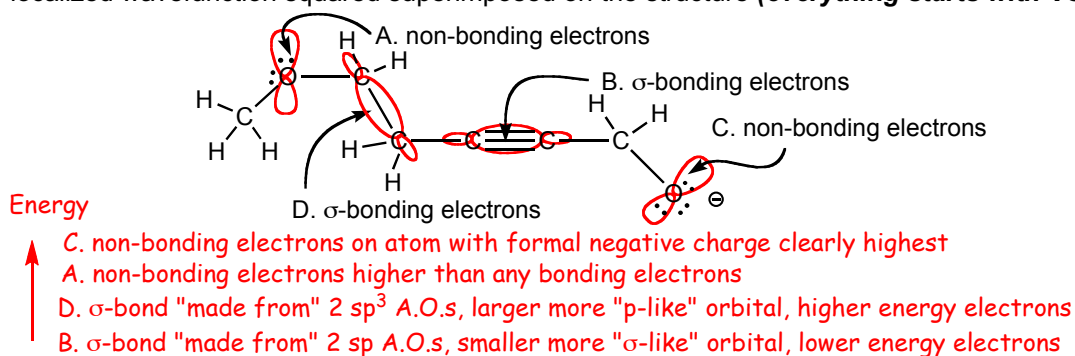
Third: Draw pictures of the localized wavefunctions for the indicated electrons and give the appropriate A.O.s
Construct localized M.O.s by in-phase (bonding) and out-of-phase (antibonding) combination of the A.O.s:



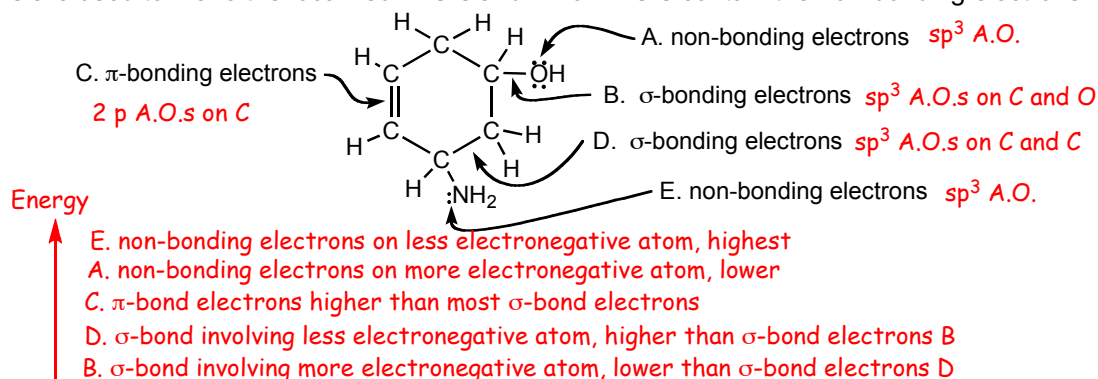
• We now have a very detailed understanding of exactly which orbitals the important electrons are in, and also, by extension, an idea of their relative energies, which in turn gives us information on their chemical reactivity - higher energy electrons tend to be more chemically reactive.

6.11 Connection to Electron Energies

Example Problem: Give the relative energies of the indicated electron pairs, and draw a picture of the appropriate localized wavefunction squared superimposed on the structure (**everything starts with VSEPR!**):



Example Problem: Give the relative energies of the indicated electron pairs and the orbital compositions, i.e., which A.O.s are used to make the localized M.O.s and which A.O.s contain the non-bonding electrons:



- Electron energies are related to strengths of bonds, bond dissociation energies (see later).
- **It is tempting to assign hybridization based on the number of pi-bonds, i.e. $sp^3 = \text{zero pi-bonds}$, $sp^2 = 1 \text{ pi-bond}$ and $sp = 2 \text{ pi-bonds}$, and this is usually the case, however, you should base hybridization only on the number of electron domains!**
- Note that the **number of non-bonding pairs is not important!** The non-bonding electrons are lower in energy on oxygen compared to those nitrogen because oxygen is more electronegative than nitrogen, even though oxygen has two non-bonding pairs. This is because the two non-bonding pairs "avoid" each other, they occupy different regions of space. This is different from the situation where two electrons occupy the same orbital. In that case the energy does go up because the electrons can't avoid each other in the same way when they are in the same orbital.

Let's talk about the anti-bonding orbitals. At this point many students are confused about these. What is the point of anti-bonding orbitals, what are they used for?

To be honest, right now anti-bonding orbitals aren't really much use at all, except that you need to understand that they do form, and you do need to know that the fact they form is a direct consequence of the peculiar quantum mechanics and wave nature of the electrons. No wave nature for the electrons then no anti-bonding orbitals, you can't have one without the other.

And so, by accepting that anti-bonding orbitals must form when 2 atoms approach each other, you are embracing the concept of quantum and wave mechanics for electrons, which is a pretty big deal. Electrons having wave nature is hard to understand since it is counter-intuitive, and yet without the wave nature of the electrons there are no orbital, of any kind, atomic, molecular, bonding or anti-bonding. And if there are no orbitals there is no you, no me, no organic chemistry course, no world, no planet, nothing!

Still, it would be better and more believable/understandable if they were a bit more concrete, if they were used for something.

Well, to some extent they are as understandable as, for example, a p atomic orbital on a hydrogen atom. Does a hydrogen atom have a p atomic orbital? Kind of! In a normal hydrogen atom, there are no electrons in any p atomic orbital, but you could promote an electron from the 1s orbital into a 2p orbital using light energy. And so, in this sense a hydrogen has p atomic orbitals, there just aren't normally any electrons in them.

Same with all of the orbitals a molecule has, molecules have lots of orbitals, they just don't all have electrons in them, anti-bonding orbitals are like this.

But how are they used? Well, a stable molecule not doing anything doesn't use them, they are empty. But, a molecule undergoing a chemical reaction is very different. Molecules that are reacting are making and breaking bonds by donating and accepting electrons, since bonds are made of electrons, it is electrons that determine just about everything about reactions. So, if a molecule needs to accept electrons in a reaction, where can the electrons go? They can't go into the bonding orbitals, since they are already full of electrons. If only the molecule had some orbitals that don't have any electrons in them that it could use. Wait! What about the anti-bonding orbitals, could they be used? Well yes, this is exactly what the anti-bonding orbitals are used for!

And more, if the electrons in the bonding orbitals serve to make bonds, when we put electrons into the anti-bonding orbitals they help to **break** bonds, and this is exactly what has to happen in a chemical reaction!

Later in the course we will look at reactions that can **only** be understood by considering the anti-bonding orbitals, and can only be understood by being able to draw the wavefunctions of the anti-bonding orbitals.

So, an application and use for anti-bonding orbitals is coming, promise!

Anti-bonding orbitals have other uses too, in color for example, but this is enough for now.

This is a difficult topic, quantum mechanics is so counter-intuitive, students really **should** be confused!

There is a famous quote by Niels Bohr, and an even more scary one by Richard Feynman:

* Those who are not shocked when they first come across quantum theory cannot possibly have understood it. Niels Bohr. ... * It is safe to say that nobody understands quantum mechanics. Richard Feynman.