

Chemistry 20A Notes, UCLA.

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This course will give you the necessary background to understand molecular-boding in chemistry. The tools and concepts developed here would be invaluable in the rest of your chemical education. Chemistry is an extremely important subject – global warming, energy, materials, medicines, to quote a few examples -- and with some work you'll soon be a part of this fascinating world!

These notes are to help you understand the lecture. They are not a substitute to the book. And remember: reading is an important but not the most important part of the course; real understating comes only with doing H.W., so do as many as you can, assigned and not-assigned!

So GOOD LUCK, and let's start.

Units

Note: it is important to be careful with units and significant figures.

For this class, the units are:

- g or kg;
- cm or m
- Coulombs (for charge). For reference, a Coulomb is the amount of charge that a 1 Ampere (i.e., 1 "Amp") DC current, like the one for your phone, yields in one second.
- T (temperature) measured in °C (later, in 20B, you'll switch to using Kelvin, but for now °C will do).

To see why you need to be careful about units, note that next page about how a satellite was lost when NASA and its contractor confused their velocity units, one using miles/s and the other km/s...

Mars Probe Lost Due to Simple Math Error

By ROBERT LEE HOTZ
TIMES SCIENCE WRITER

NASA lost its \$125-million Mars Climate Orbiter because spacecraft engineers failed to convert from English to metric measurements when exchanging vital data before the craft was launched, space agency officials said Thursday.

A navigation team at the Jet Propulsion Laboratory used the metric system of millimeters and meters in its calculations, while Lockheed Martin Astronautics in Denver, which designed and built the spacecraft, provided crucial acceleration data in the English system of inches, feet and pounds.

As a result, JPL engineers mistook acceleration readings measured in English units of pound-seconds for a metric measure of force called newton-seconds.

In a sense, the spacecraft was lost in translation.

"That is so dumb," said John
Please see MARS, A35

From LA TIMES, Oct. 1st, 1999, p. A1

Conserved Quantities

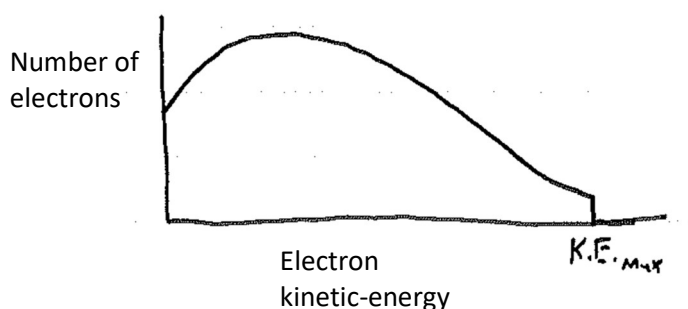
Charge, mass and energy are always conserved (if we ignore the $E = mc^2$ rule of relativity, which allows mass & energy to interconvert). Thus, in any chemical reaction we use, make sure mass & charge are always conserved.

Conservation laws have often resulted in new discoveries. For example, Fermi discovered the neutrinos (and got a Nobel prize for that!) in beta decay. This is a process where initially people thought that a neutron in a nucleus becomes just proton + electron, without anything else:



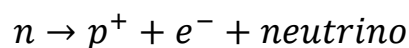
Since the neutrons are heavier than the combined mass of the p^+ and e^- , the extra energy upon the decay should be all in the kinetic energy of the electrons (and to a much smaller degree the protons), and this amount would always be the same, one fixed amount.

But instead of a fixed kinetic energy, the measured kinetic-energy shows a distribution:



**Note: the e's
don't all have
the same
speed....**

The only way to explain this was to invoke the presence of a 3rd emitted particle, labeled a "neutrino" (little neutral one), which carries the excess energy, so the true decay looks like:



Neutrinos interact very weakly with other stuff and are very difficult to detect!

Energy

Kinetic energy (labeled K.E.) is energy of motion, defined as

$$K.E. = \frac{1}{2}mv^2$$

K.E. has units of

$$\text{kg} \left(\frac{\text{m}}{\text{s}}\right)^2 = \frac{\text{kg m}^2}{\text{s}^2} \equiv 1 \text{ Joule}$$

Rarely you'll also see units of

$$\text{g} \left(\frac{\text{cm}}{\text{s}}\right)^2 = \frac{\text{g cm}^2}{\text{s}^2} \equiv 1 \text{ erg} = 10^{-7} \text{ Joule}$$

We also get energy from **force*distance ("F*d")**, and indeed the units match. Specifically, the units of force are

$$F = ma = \text{kg} \frac{\text{m}}{\text{s}^2}$$

So the units of force times distance are:

$$F * d = \text{kg} \frac{\text{m}}{\text{s}^2} * \text{m} = \text{kg} \frac{\text{m}^2}{\text{s}^2} = \text{Joule} !$$

When a force can act on an object over a certain distance, we say that the object has potential energy. (P.E.). I.e., there is a potential to convert that force into another form of energy, such as K.E.

For example: gravitational P.E. (labeled here "U")

The gravitational force is:

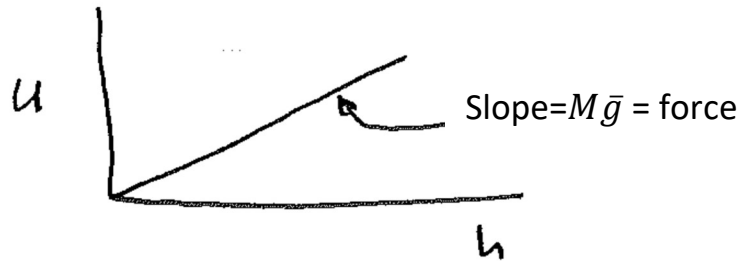
$$F_g = ma = m\bar{g}; \quad \bar{g} = 9.8 \frac{\text{m}}{\text{s}^2}$$

Usually the gravitational acceleration constant, which I label here as \bar{g} , is written as g ; but we use here "g" for grams, so to avoid confusion I write the grav. acceleration as \bar{g} .

The potential due to the gravitational force is:

$$U = F * h = m\bar{g}h$$

where $h \equiv \text{height}$. (Note that this is true only because the gravitational force F is presumed constant over the whole height h)



Example: If I hold a 100g eraser 2m off the floor and let go, what is the final speed before impact?

$$U \approx M \bar{g} h = 0.1 \text{ kg} * 10 \frac{\text{m}}{\text{s}^2} * 2\text{m} = 2 \text{ J}$$

If this (i.e., U) all becomes K.E. at the moment of impact, then

$$2\text{J} = \frac{1}{2} * 0.1 \text{ kg} * v^2$$

$$v^2 = 2 * \frac{2 \text{ J}}{0.1 \text{ kg}} = 40 \frac{\text{m}^2}{\text{s}^2} \rightarrow v = 6.3 \frac{\text{m}}{\text{s}}$$

In miles/hour this become

$$v = 6.3 \frac{\text{m}}{\text{s}} = 6.3 \frac{\text{m}}{\text{s}} * \frac{\text{mile}}{1609 \text{ m}} * \frac{3600 \text{ s}}{\text{hr}} = 14 \frac{\text{mile}}{\text{hr}}$$

What happens if I drop instead a 5kg bowling ball? We solved

$$\frac{1}{2} m v^2 = m \bar{g} h \rightarrow v = \sqrt{2 \bar{g} h},$$

i.e., the speed is independent of m !

Electrical Potential Energy (P.E.)

We also have other types of P.E., such as electrical P.E.

Since charges interact via the Coulomb force,

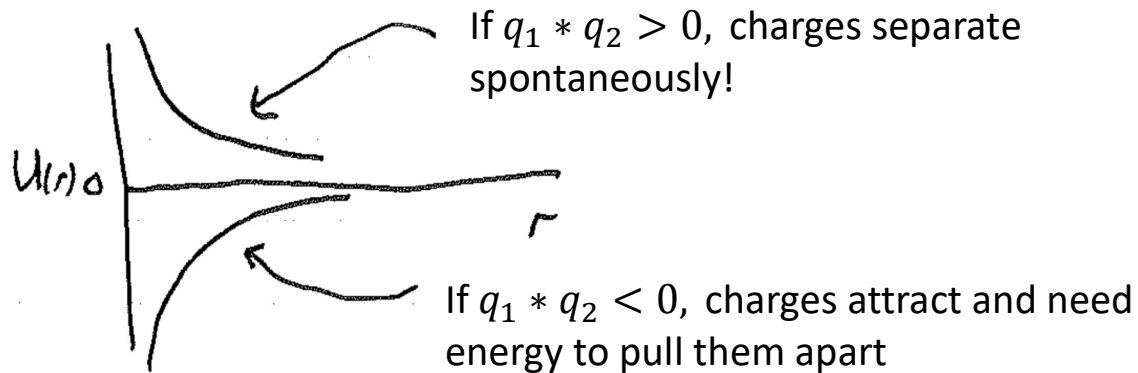
$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \quad \text{or} \quad U = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

where q_1 and q_2 are the charges, r is the distance between them, and

$$\epsilon_0 = 8.85 * 10^{-12} \frac{\text{C}^2}{\text{Jm}}$$

(Here, C is Coulomb, the unit we use for charge. Don't confuse with lower-case c, the velocity of light, introduced later.)

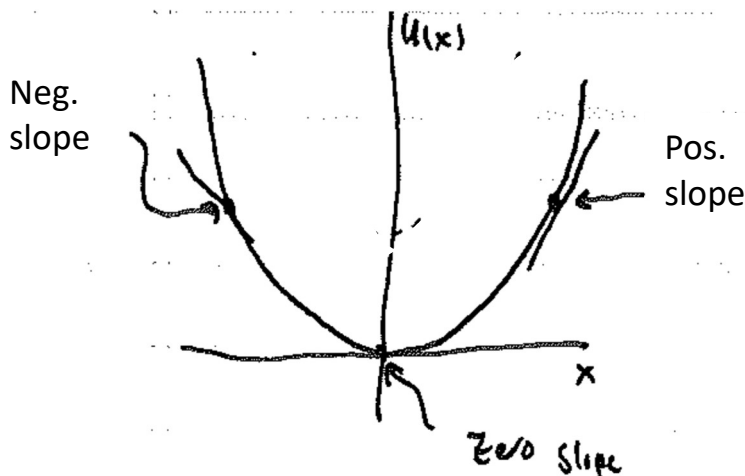
Pictorially



Challenge: If 2 like charges are held a distance r apart and are let go, what is the final relative speed when they are a distance R apart? What is the speed when $R \rightarrow \infty$?

Force and P.E.

Suppose our potential energy looks like this:



This could represent, for example:

- the track for a ball moving under gravity;
- or the potential of a mass on a spring;
- or the potential between 2 atoms in a diatomic molecule, when we look at distances which are not too far from the equilibrium distance (and x is the difference between the actual distance between the molecules and the equilibrium distance).

In all these cases:

$$U = \frac{1}{2} \kappa x^2$$

and from the potential we get the force:

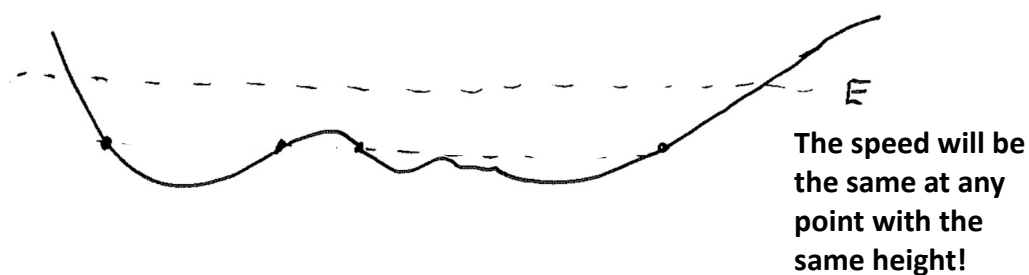
$$F = -(\text{slope of potential}) = -\frac{dU}{dx} = -\frac{d}{dx} \left(\frac{1}{2} \kappa x^2 \right) = -\kappa x$$

i.e., Hooke's law!

(Note: we won't use calculus much, but this is one of these times. If you don't recall what's a derivative, look in a simple calculus book).

Note that in the P.E. only differences are important, i.e., if we shift the entire potential up and down, i.e., $U(x) = \frac{1}{2}\kappa x^2 + A$ (where A is a constant), then the force doesn't change, remaining $F = -\kappa x$. This is like dropping the eraser, it doesn't matter whether it falls from 2m to 0m, or from 3m to 1m, we'll have the same change in P.E.

Using this idea, we could compute the force and the speed of a particle at any point along a complex P.E. surface:



P.E. is a critical concept for understanding how/why a chemical reaction occurs. In any system, including during a chemical reaction, we always have

$$E = \frac{1}{2}mv^2 + U(x) = \text{const.}$$

However, note that when there are many particles, only the total energy is conserved, not the energy of each one of them.

Atomic Structure

All atoms are constructed in the same basic way:

They have a nucleus, made of protons (with charge $+e = 1.6 \times 10^{-19}$ C) and neutrons (with no charge), both of which have a mass ≈ 1 amu.

The nucleus is tiny – 10^{-14} – 10^{-15} m; it is the e^- 's that occupy most of the space of the atom, even though their mass is $\sim \frac{1}{2000}$ amu.

Neutral atoms have equal #'s of protons and electrons. Atoms (or molecules) that have a fewer or greater # of electrons are called ions.

- Atoms with too few e^- 's (e.g., Li^+ , Mg^{2+}) are called cations.
- Atoms with a few extra e^- 's (e.g., I^- , O^{2-}) are called anions.

Atomic number

The chemical properties of an atom are determined by the # of electrons, which, if the atom is neutral, is the same as the # of protons or atomic number, Z.

The number of neutrons is denoted usually as N (don't confuse with N as the symbol for nitrogen!)

Isotopes

Atoms with the same Z, i.e., same # of protons and e^- 's, but with different number of neutrons N are called isotopes. These atoms are chemically identical but have different mass/atomic weight. These are called isotopes.

Examples:

H has $Z=1$, but can have 0, 1, or 2 neutrons.

- ^1H = hydrogen
- ^2H = deuterium
- ^3H = tritium (radioactive)

Or carbon:

- $^{12}\text{C} = 99\%$ most abundant
- $^{13}\text{C} = 1\%$
- $^{14}\text{C} = 0\%$

Avogadro's number and moles

We measure # of atoms by Avogadro's number,

$$N_{\text{Avog}} \approx 6.02 \times 10^{23}$$

So a "mol of atoms" means an N_{Avog} atoms. (Just like a "dozen of things" means 12 things)

The molecular weight of a specific isotope of an atom is how many gram a mol of this isotope is weighting.

For ^{12}C , the molecular mass is exactly $12 \frac{\text{g}}{\text{mol}}$ (that's actually could be viewed as a way to exactly define a mol – i.e., a way to define Avogadro's number).

Similarly, A mole of ^1H atoms will weigh about 1 gram (more precisely 1.007 g).

So we say that the molar mass of ^1H is $1.007 \frac{\text{g}}{\text{mol}}$

Often you'll see "amu", atomic-mass-unit, or even just "u" used instead of $\frac{\text{g}}{\text{mol}}$.

For an element with many isotopes, the atomic weight will be a weighted average of its isotope masses, e.g., for carbon it will be $0.99 \times 12 + 0.01 \times 13 = 12.01$, as reported in your periodic tables.

For any isotope, its molecular weight will be about the number of protons + neutrons, $N+Z$. This is almost but not exactly true, except for ^{12}C where it is a definition.

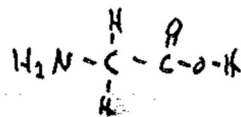
For example, the mass of ^4He , $4.002602 \frac{\text{g}}{\text{mol}}$, is about twice that of ^2H , 2.01401 but is not exactly twice same, even though ^4He contains exactly twice as many protons and neutrons (2 and 2) as ^2H does. The reason is relativistic effects. We'll often ignore these effects in our discussion for elements with one major isotope, such as hydrogen, carbon and oxygen, and treat their mass as if it 1, 12, 14, and $16 \frac{\text{g}}{\text{mol}}$ respectively (but not chlorine – it is about $\frac{1}{4}$ ^{37}Cl and about $\frac{3}{4}$ is ^{35}Cl , so its molecular mass is the weighed average, $35.5 \frac{\text{g}}{\text{mol}}$).

Molecular formula:

Lists the ratios of different atoms in a molecule.

Example: glycine, $C_2H_5O_2N$.

Not very useful, since this formula does not tell us the structure, which is:



A mass measurement gives the formula, but we need spectroscopy for finding the structure.

Empirical formula

The simplest possible formula for a substance (again, lacks any structural details).

For example, $NaCl$ instead of Na_2Cl_2

We can calculate % composition from the empirical formula. For example using $M_{Na}=23$, $M_{Cl}=35.5$, we can calculate that for $NaCl$:

$$\% \text{ Na (by weight)} = \frac{M_{Na}}{M_{Na} + M_{Cl}} = \frac{23}{23 + 35.5} * 100\% = 39\% \text{ by mass}$$

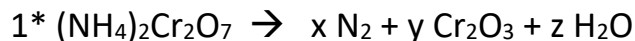
(obviously it's 50% by mole).

This is useful because if I do an experiment that determines that a compound is 39% by mass Na and that the only other element is Cl, then I know that the compound is $NaCl$ (or more precisely, I know that the empirical formula for the element is $NaCl$).

Balancing Chemical Reactions

Example: $\underline{\quad} (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \underline{\quad} \text{N}_2 + \underline{\quad} \text{Cr}_2\text{O}_3 + \underline{\quad} \text{H}_2\text{O}$

Step 1: put 1 in front of the compound with the most-different types of elements, and letters in front of the other compounds, signifying unknowns:



Step 2: balance mass, first putting elements that occur only once per side

$$\text{N:} \quad \text{LHS: } 2 \quad \text{RHS: } 2 * x \quad \rightarrow \quad x=1$$

$$\text{H:} \quad \text{LHS: } 8 \quad \text{RHS: } 2 * z \quad \rightarrow \quad z=4$$

$$\text{Cr:} \quad \text{LHS: } 2 \quad \text{RHS: } 2 * y \quad \rightarrow \quad y=1$$

If we did this correctly, the O's should balance

$$\text{O:} \quad \text{LHS: } 7 \quad \text{RHS: } 1 * 0 + 1 * 3 + 4 * 1 = 7 \quad \checkmark$$

Also note that sometimes solving this way gives fractional coefficients. If you get a fraction multiply the LHS and RHS by 2 or 3 etc. until all the coefficients are integer.

Limiting Reagents

First, balance the chemical rxns, then convert to moles (if you are given the masses) to find the number of moles of each reagent.

- 1) If the reactants combine in a 1:1 ratio, then the limiting reagent is the one with the least number of moles. Thus, the # of moles of this limiting reagent determine how many moles of the other reagent will be used, as well as the number of moles of products formed, depending on stoichiometry.

- 2) If the reactants don't combine in a 1:1 ratio, use the molar ratios from the balanced rxn to see how many moles of each reactant are needed. One reagent will be limiting, determining the number of moles of product formed.

Example: If we're given 20g of H₂ and 2g of O₂, how much H₂O do we make?

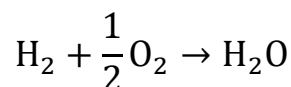
Recall, (M.W. means "molecular weight"):

$$\text{M. W.}_{\text{H}_2} = 2 \frac{\text{g}}{\text{mol}} \quad \text{M. W.}_{\text{O}_2} = 32 \frac{\text{g}}{\text{mol}}$$

So, since we have we have 20g of H₂ and 2g of O₂,

$$10 \text{mol of H}_2 \text{ and } \frac{1}{16} \text{mol of O}_2.$$

Now, balance the reaction:



Thus,

$$\frac{1}{16} \text{mol of O}_2 \text{ will react with } \frac{1}{8} \text{mol of H}_2 \text{ to make } \frac{1}{8} \text{mol of H}_2\text{O}$$

Since H₂O has a MW of 18, we can make

$$\frac{1}{8} \text{ moles} \times 18 \frac{\text{g}}{\text{mol}} = \frac{9}{4} \text{g H}_2\text{O}.$$

We also have the remaining left over:

$$\left(10 - \frac{1}{8}\right) = 9\frac{7}{8} \text{ moles of H}_2 = 19\frac{3}{4} \text{g H}_2$$

Note that mass is conserved of course, as it should be

$$20\text{g} + 2\text{g} = \frac{9}{4}\text{g} + 19\frac{3}{4}\text{g} \quad \checkmark$$

Now let's follow up on this example.

Say we had 4g of H₂ and 32g of O₂, the stoichiometric ratio. Now all reagents react to produce 2moles of H₂O, which is 36g. Again, mass is conserved.

What this implies for this reaction is that if we were to start with this stoichiometric ratio of gases and do the reaction, there will only be liquid water left, i.e., all gases will be gone!

But if we were to start with too much H₂ or too much O₂ some gas will be left

Another example:

Oxidation of 1g of MBr in excess MnO₂/H₂SO₄



where M= K, Rb, or Cs

Question: which of these M gives the largest amount of Br₂ after rxn?

Answer: K has the lowest MW among these, so 1g of KBr has the most total mass of Br (i.e., the most moles of MBr). Thus, this will produce the most moles of Br₂

eV (and kJ/mol, kcal/mol) energy units

So far we used J (Joules) for energy. That's fine officially, but is hard in practice to develop an intuition as atomic energies are tiny in Joule

There are several energy scales used for microscopic systems (kJ/mol, kcal/mole, Hartree, wavenumbers, and more), but we'll use mostly "eV", i.e., the energy that a single electron gains upon being accelerated by an electrical potential of one volt.

You may recall from high school physics that **charge*voltage = energy**; the macroscopic unit of charge is called Coulomb, so we have

$$1 \text{ Coulomb} \cdot 1\text{Volt} = 1 \text{ Joule}$$

Details: one Coulomb is the charge that passes in one second when the electron current is 1Amp; so when your advanced USB charger outputs 2A at a voltage of 5V, it means that in one second, it can output a charge of $2\text{A} \cdot 1\text{sec} = 2 \text{ A} \cdot \text{sec} = 2 \text{ Coulomb}$ and overall the energy from that will be

$$2 \text{ Coulomb (per second)} \cdot 5\text{Volt} = 10 \frac{\text{Coulomb} \cdot \text{Volt}}{\text{s}} = 10 \frac{\text{J}}{\text{s}}$$

There are about $6.8 \cdot 10^{18}$ charges of e (proton charge, or minus the electron charge) in a Coulomb, and we can write it conversely

$$e = 1.609 \cdot 10^{-19} \text{ Coulomb}$$

Therefore, an electron volt, which is a charge of one electron times a voltage of 1 Volt, will be

$$eV = 1e \cdot 1\text{Volt} = 1.609 \cdot 10^{-19} \text{ Coulomb} \cdot \text{Volt}$$

i.e.,

$$eV = 1.609 \cdot 10^{-19} \text{ J}$$

Two (among a few other) energy units you should be familiar with are:

- kJ/mol ; from its name we can calculate it:

$$1 \frac{\text{kJ}}{\text{mol}} = \frac{10^3 \text{J}}{6.022 \cdot 10^{23}} = 1.66 \cdot 10^{-21} \text{J}$$

i.e.,

$$\frac{1 \text{eV}}{1 \frac{\text{kJ}}{\text{mol}}} = \frac{1.609 \cdot 10^{-19} \text{J}}{1.66 \cdot 10^{-2} \text{J}} \simeq 96$$

i.e.,

$$1 \text{eV} = 96 \frac{\text{kJ}}{\text{mol}}$$

- $\frac{\text{kcal}}{\text{mol}}$: since $1 \text{cal} = 4.2 \text{J}$, and $\frac{96}{4.2} = 23$, : $1 \text{eV} = 23 \frac{\text{kcal}}{\text{mol}}$ (or $\frac{\text{kcal}}{\text{mol}} \sim 0.043 \text{ eV}$)

We may see more energy units later.

Wave-particle duality

So far we dealt with stuff which many of you saw in high-school chem.

Now we start from “the bottom”, to eventually understand from basics the periodic table, i.e., why electrons are in discrete (i.e., non-continuous) “shells”.

A spoiler: we’ll eventually see that the reason for discrete shells is that electrons in an atom are like sound-waves in a guitar, where there’s the fundamental sound and the harmonics.

So let’s start.

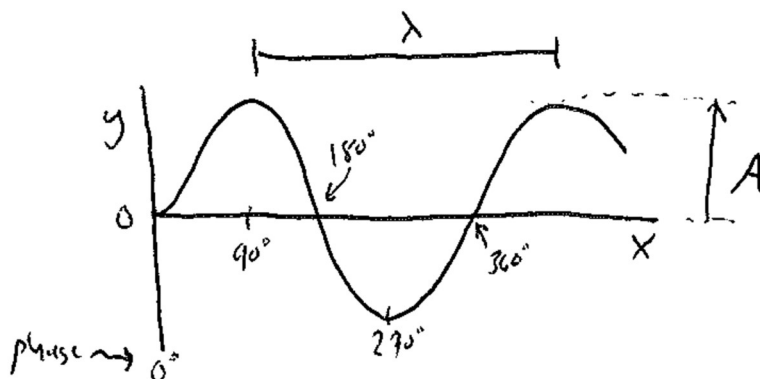
So far we referred to subatomic entities such as e’s, as particles. However, we’ll see that sometimes what we think of as a particle behaves more like a wave.

How do we describe waves?

They are “oscillatory” functions.

E.g.,

$$y = A \sin\left(\frac{2\pi x}{\lambda}\right)$$



Here:

- A is the wave’s amplitude
- λ is the wavelength (peak-to-peak or trough-to-trough or twice zero-to-zero)

Further, this wave can move in time. Then, we’ll define:

- ν is the frequency (i.e., # of peaks that pass a given point per time)
- v is the speed (how fast a peak moves through space)

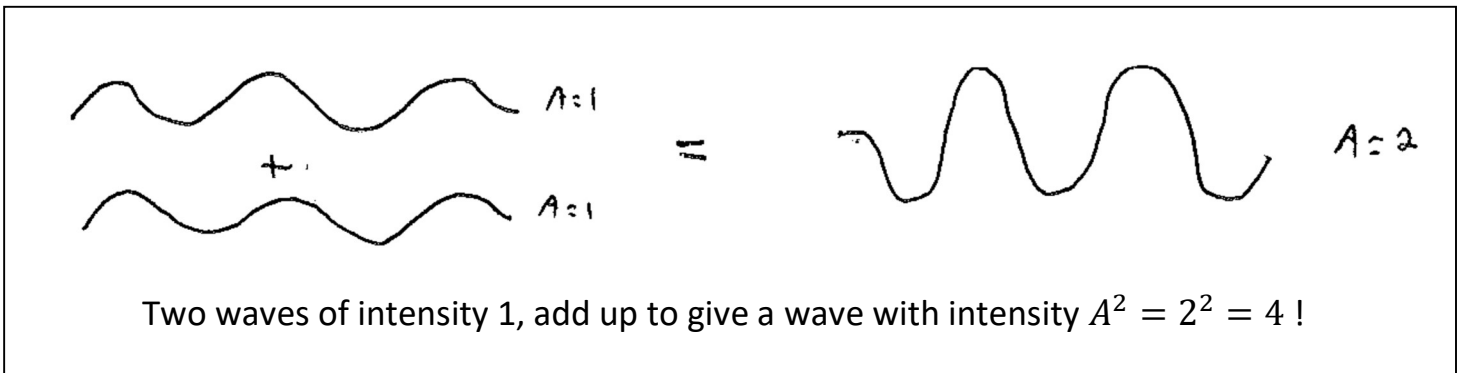
$$v = \frac{\text{distance}}{\text{time}} = \frac{\text{distance}}{\text{cycle}} * \frac{\text{cycles}}{\text{time}} = \lambda * \nu$$

For electromagnetic waves (light, x-ray, microwaves, radio, etc.) the velocity is constant, and labeled c ; $c \approx 300,000 \frac{\text{km}}{\text{s}} = 3 * 10^8 \frac{\text{m}}{\text{s}}$

The energy carried by the wave (labeled the intensity) is $\propto A^2$.

Interference

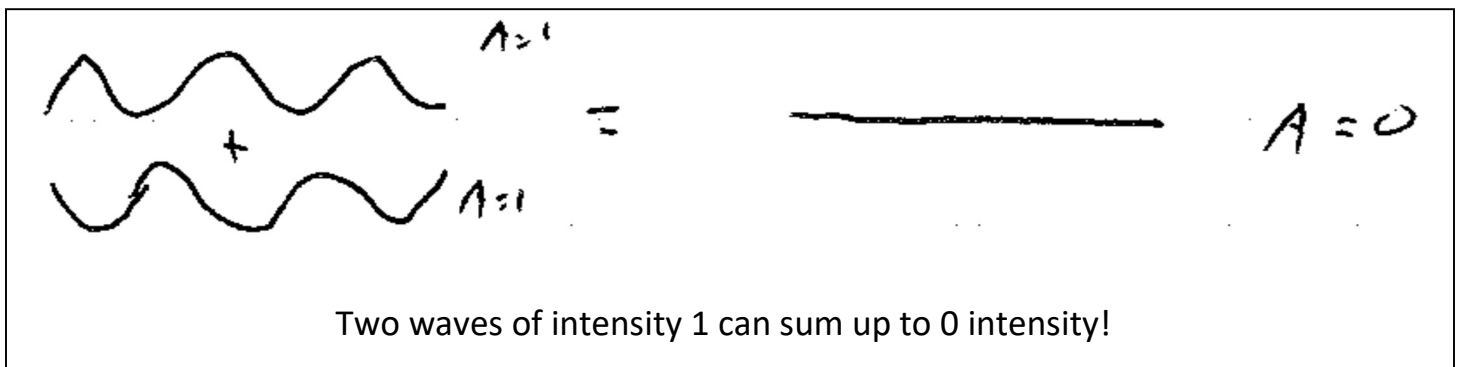
Waves, unlike particles, can interfere:



The diagram shows two sine waves, each with an amplitude of 1 (labeled $A=1$), being added together. A plus sign is placed between them. The resulting wave has a double amplitude of 2 (labeled $A=2$). Below the diagram, text states: "Two waves of intensity 1, add up to give a wave with intensity $A^2 = 2^2 = 4!$ "

This is called constructive interference, which occurs whenever the waves being added have a relative phase of 0° or 360° , etc. (or the distance between them is $n\lambda$, where $n = 0,1,2, \dots$)

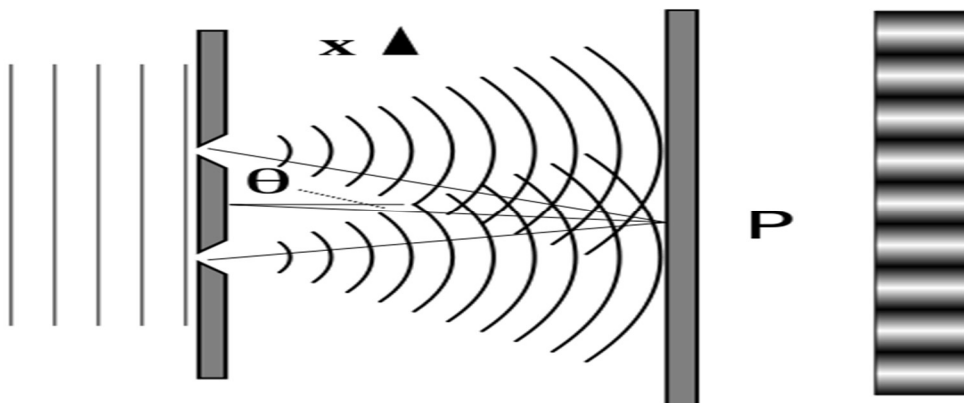
But waves can also interfere destructively:



The diagram shows two sine waves, each with an amplitude of 1 (labeled $A=1$), being added together. A plus sign is placed between them. The resulting wave is a flat line, indicating zero amplitude (labeled $A=0$). Below the diagram, text states: "Two waves of intensity 1 can sum up to 0 intensity!"

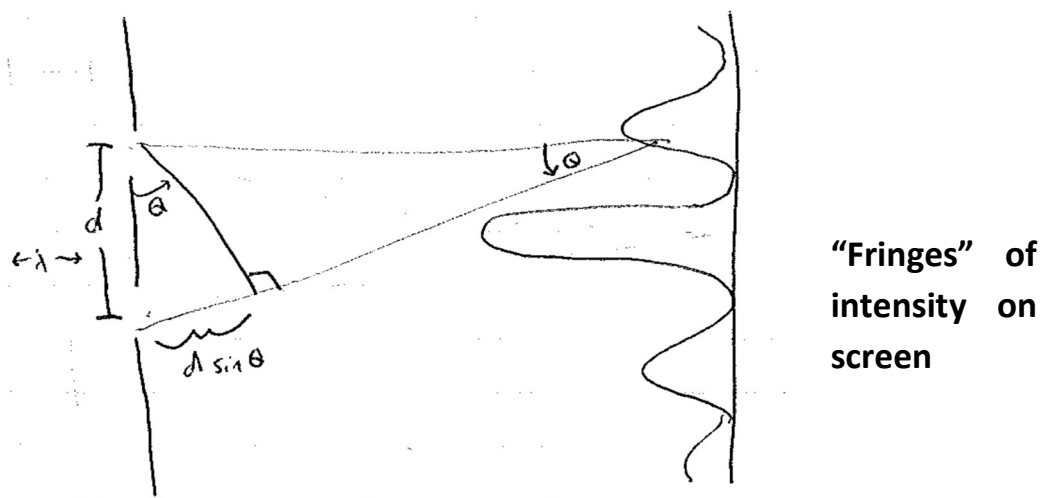
This is destructive interference, which occurs when waves that are added have a relative phase of 180° , or a distance of $(n + \frac{1}{2})\lambda$, $n = 0,1,2, \dots$

Interference can be readily seen in the double-slit experiment¹



Young's experiment. Light from a far-away candle on the left passes through two narrow slits and reaches the screen. On the far right you see the image on the screen, showing diffraction pattern due to destructive interference (dark strips), and constructive interference (bright strips).

Or in more mathematical detail:



(Note, by the way, that for light it is the electric field $F_{electric}$ that oscillates up and down.)

¹ Image taken from:
<https://chem.libretexts.org/@api/deki/files/54672/514px-Doubleslit.svg.png?revision=1&size=bestfit&width=400&height=366>

For constructive interference, the waves hit the 2 slits exactly in phase.

If we look at a point on the screen that is situated exactly between the 2 slits, then both waves travel the same distance and thus arrive in phase; so for $\theta = 0^\circ$ we get constructive interference. At this point, $A = 2$ and $I = |A|^2 = 4$

Question: Where does the next maximum occur?

Answer: When the wave from one slit has travelled exactly λ farther than the wave from the other slit. This happens when

$$d \sin \theta = \lambda$$

This generalizes to other peaks, resulting in the Bragg relations:

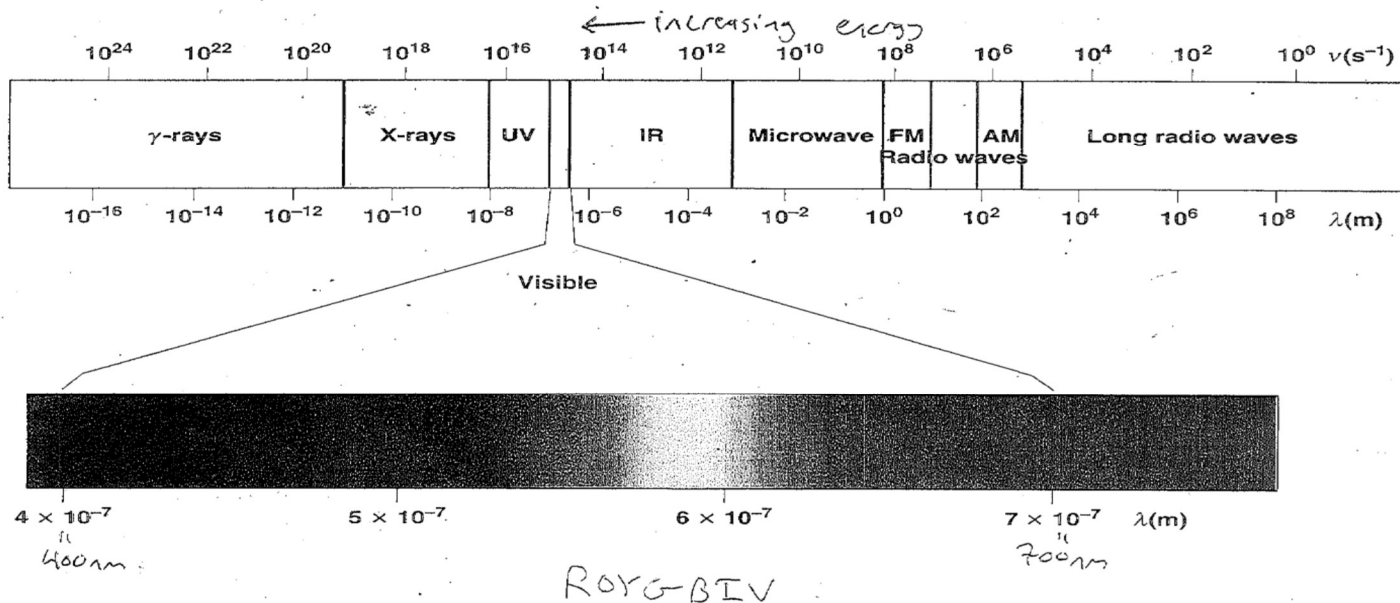
Intensity maxima occur at $d \sin \theta = n\lambda$, $n = 0,1,2, \dots$

Intensity minima occur at $d \sin \theta = \left(n + \frac{1}{2}\right)\lambda$, $n = 0,1,2, \dots$

Clearly, the spacing between the bright spots (“fringes”) depends on $\frac{\lambda}{d}$.

- If $\lambda \ll d$ the fringes run together, and this is why we don’t see them around everyday macroscopic objects
- But for radio waves, with $\lambda \sim$ meters, we do get “hot” and “cold” spots when driving between tall buildings (e.g., on Wilshire).

For E.M. waves we have the following spectrum (Taken from Oxtoby et al.):



Harcourt Brace & Company

Photons – waves can be particles

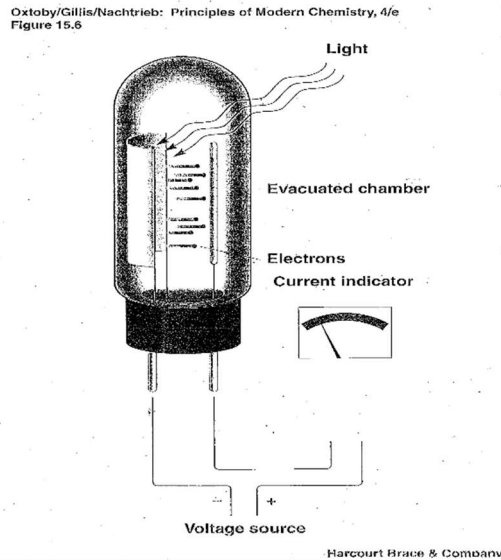
What's unusual is that light doesn't always behave like a wave – sometimes it behaves like a particle!

Experimentally, we find that when light hits an object, the object can only absorb a certain amount of energy, which depends only on the λ of the light. More intense light gives more of these energy-particles, or “quanta”, but does not change the “size” (i.e., the energy) of each of these quanta.

For a quick analogy – think of an red or infra-red light as of lots of tennis balls; and think of UV or X-ray light as bullets. If you throw large amounts of tennis balls (infrared light) you can impart lots of energy, but the damage due to a single bullet (UV or X-ray light) will always be large.

The first experiment showing the “quanta” aspect of light is the:

Photoelectric effect



Experimentally (see picture above), one takes an empty glass tube on which external light impinges.

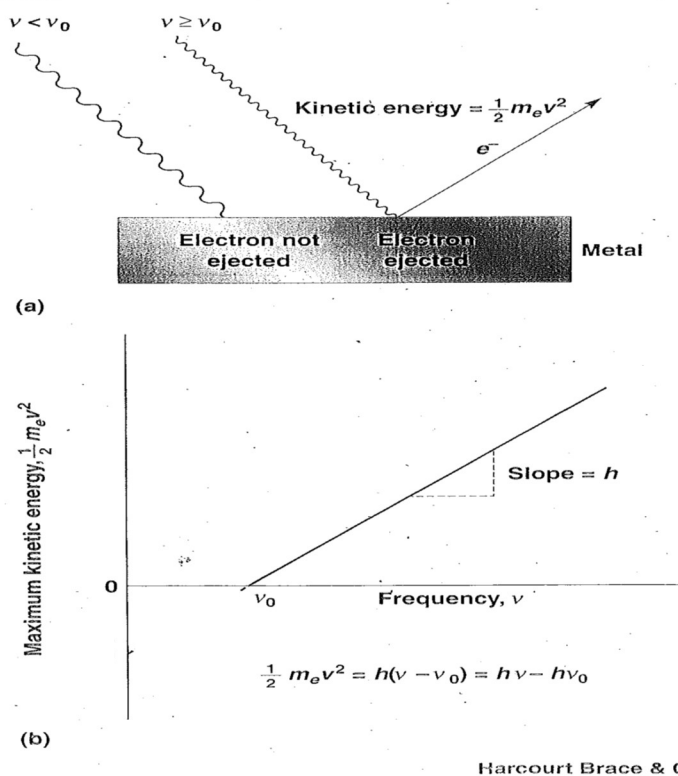
Electrons are ejected from one metal electrode in the glass tube.

The electrons travel to another, (the “accepting”) piece of metal and then can go back.

Experimental observations:

- e^- 's are ejected from the metal only when the frequency of the incident light is high enough, above a certain threshold frequency of the metal, i.e., $\nu > \nu_0$ or $\lambda < \lambda_0$. Here, ν_0 (and therefore $\lambda_0 = \frac{c}{\nu_0}$) is different for every metal.
- The K.E. of the emitted e^- 's depends on how far ν is above ν_0 . But the slope (labeled h) of the K.E. vs. the frequency ν is universal, and is the same as measured by Planck in a different experiment.
- The intensity of the light determines the # of ejected electrons, but not their K.E.

Oxtoby/Gillis/Nachtrieb: Principles of Modern Chemistry, 4/e
Figure 15.7



To explain all of this, Einstein came up with:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

where

$$h = 6.626 \times 10^{-34} \text{ J s} = \text{Planck's constant}$$

and

$$c \approx 3 \times 10^8 \frac{\text{m}}{\text{s}}$$

is the velocity of the light we saw earlier.

This is what Einstein got the Nobel Prize for, not the theory of relativity!

Note: Einstein was so unhappy that he got the Nobel prize for the photoelectric effect and not the theory of relativity, that he did the “Bob Dylan” thing, i.e., found an excuse why he cannot come to the prize reception.

h in eV*s units

Note that it is useful to write h also in terms of a more microscopic unit, eV; since

$$J = \frac{1}{1.609 * 10^{-19}} \text{ eV}$$

Then

$$h = 6.626 * 10^{-34} \text{ J s} = \frac{6.626 * 10^{-34}}{1.609 * 10^{-19}} \text{ eV s}$$

i.e.,

$$h = 4.12 * 10^{-15} \text{ eV s}$$

Example:

Purple light with $\lambda = 400\text{nm}$ hits the metal Cs and e's are ejected with K.E.=0.96 eV

What is the energy it takes to release e's from Cs ? This energy is called the work function of Cs (we denote the work function by the symbol W , though don't confuse with the element Tungsten, which has also the symbol W ...).

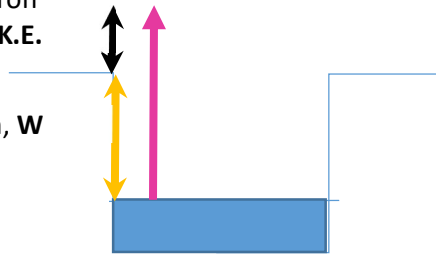
Put differently, what was the electron (negative) P.E. before ejection?

We can understand better what happens to the electron if we look at the graph below. Think of the material as a "bathtub", full of electrons (the electrons are like the "water in the bathtub"). Those electrons that are at the highest energy are like the "highest" water in the bathtub (the one near the air-water interface).

When a photon comes and is absorbed, the electron that absorbs it rises in energy (all the energy of the photon is given to the electron). If the electron has enough energy after absorption it will leave the material, just like if a water molecule in the bath is "kicked" and is given enough energy it can "splash out" of the bath.

Black arrow: ejected electron
remaining kinetic energy, **K.E.**

Gold arrow: work function, **W**



Purple: impinging photon energy, $h\nu$, which excites the “top most” electron in the sea (blue) of electrons.

Clearly:

$$h\nu = K.E. + W$$

In our case, the photon energy (corresponding to the length of the purple vector in the picture above) is:

$$E_{photo} = h \frac{c}{\lambda} = 4.12 * 10^{-15} \text{ eV s} \times \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}}}{400 \times 10^{-9} \text{ m}} = 3.09 \text{ eV}$$

But conservation of energy dictates that (see picture)

So

$$E_{photon} = h\nu = W + K.E.$$

(where “W” is, from the picture, the binding energy of the top-most electron, the one that’s easiest to eject). Pictorially, this is the same as saying that the length of the purple vector above is the same as the yellow one (i.e., the work function W) plus the black one (the K.E.)

So

$$W = E_{photon} - K.E. = 3.09 \text{ eV} - 0.96 \text{ eV} = \mathbf{2.13 \text{ eV}}$$

We can also turn this around and ask:

Question: what’s the λ and therefore the color of the lowest-energy light that can still eject an electron from Cs (with K.E.=0)?

Answer:

$$W(\text{Work function}) = h\nu_0 = \frac{hc}{\lambda_0} \rightarrow \lambda_0 = \frac{hc}{W}$$

So

$$\lambda_0 = \frac{4.12 \text{ eV} \cdot \text{s} \times 3 \times 10^8 \frac{\text{m}}{\text{s}}}{2.13}$$

i.e., you can solve this to get that:

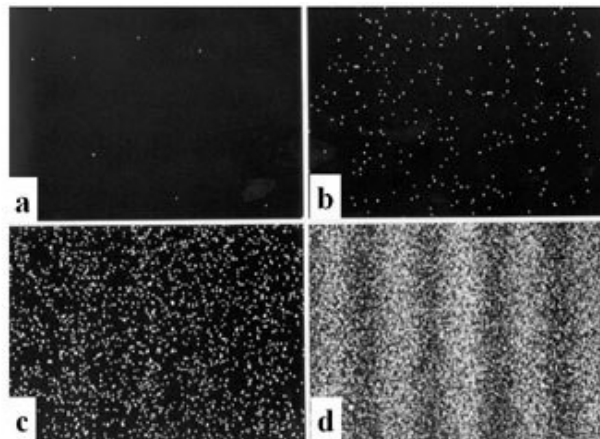
$$\lambda_0 = 580 * 10^{-7} \text{m} = 580 * 10^{-9} \text{m} = 580 \text{ nm} \quad (\text{orange light}).$$

Light (photons): particles and wave at the same time.

The photoelectric effect indicates that light is a packet of individual things, labeled “photons”. I.e., light behaves as a particle, i.e., the photon is a particle.

How can we then explain the double-slit experiment (which shows the light is also a wave?) We have to build up the interference pattern one photon at a time.

The picture below shows actual interference pattern as detected when we use very low intensity – you see the emergence of the interference “fringes” which will look more continuous once many more “photons” are detected:

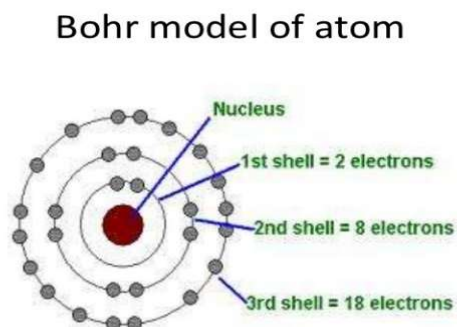


Single-particle build-up of interference pattern

Note – I am cheating here – the picture was not really taken with E.M. waves, so it is not of photons (it really is of electrons), but if we were to use light at light at very low intensities, counting photons, we would get a similar picture, as more recent experiments have verified.

Wave-particle duality

Let's recall the Bohr picture (see below²) you saw in high school: electrons zooming around the nucleus, as if they were satellites, and in specific orbitals.



You may or may not have seen in high school that the energies of the electron in these orbitals are also **quantized**, i.e., have discrete values. These values turn out (and we'll "motivate" these values below) to have energies that are in an interesting and simple relation;

A spoiler : an electron in the 2nd orbital will have, in hydrogen, an energy which is $\frac{1}{4}$ of the energy of an electron in the 1st orbital; an electron in the 3rd orbital will have, in hydrogen, an energy which is $\frac{1}{9}$ the energy of the electron in the 1st orbital; etc. We'll understand this somewhat better later.

Now this **Bohr picture is wrong**. Why?

If e's were orbiting the nucleus like little planets, they would have been **accelerating charges** (recall from physics that a rotating particle experiences acceleration towards the center – without the acceleration it would fly off).

But acceleration of charges causes them to **emit E-M radiation**. And such an emission would have caused the electrons (if they were classical particles accelerating) to lose energy, so the electrons would have **spiraled into the nucleus**.

The reason this does not happen is **that e's behave as waves!**

² Taken from <https://www.slideshare.net/chintanmehta007/dalton-and-bohr-chemistry-pro>

deBroglie's relation

deBroglie's big hypothesis (around 1923) was that we can get the wavelength or electrons (or any particle, since all particles are also waves!) from

$$\lambda = \frac{h}{p} = \frac{h}{Mv}$$

Here, M is the mass and p is the momentum of the particle, and recall high-school physics: $p = Mv$.

Note: deBroglie came to this formula by analogy with light and electromagnetic waves, as follows:

- Turns out that the photon has a momentum which happens to be $p = \frac{E}{c}$ (even though its "rest-mass" is zero). That's from relativity, and is true for any particle travelling at the speed of light, like the photons are.
- So when you account for Planck's relation, $E = h\nu = \frac{hc}{\lambda}$, you find that $p = \frac{h}{\lambda}$ or $\lambda = \frac{h}{p}$.
- deBroglie noticed that in his final formula ($\lambda = \frac{h}{p}$) there's no velocity of light, so he speculated that his formula this is true for all particles, even slow ones!

deBroglie's formula says that with small M and v (and therefore small p) we can get long λ 's (as $\lambda \propto \frac{1}{p}$) and thus get wave behavior.

Macroscopic objects

So why don't we see wave behavior for macroscopic objects?

Because with large M , you get short λ (unless v is exceedingly small), and with short λ there will be no interference effect!

Example: consider a 0.1kg eraser travelling at $10 \frac{\text{m}}{\text{s}}$; then

$$\lambda_{eraser} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{0.1 \text{ kg} \times 10 \frac{\text{m}}{\text{s}}} \simeq 6.6 \cdot 10^{-34} \frac{\text{J}}{\text{kg} \frac{\text{m}^2}{\text{s}^2}} \text{m} = 6.6 \cdot 10^{-34} \text{m} \quad \text{tiny!!!!}$$

(where we used: $\text{kg} \frac{\text{m}^2}{\text{s}^2} = \text{J}$) – so no wonder we don't see the wave fringes around an eraser.

But for an electron with $M = 9.11 \times 10^{-31} \text{kg}$ moving at typical speeds inside an atom, we'll get $\lambda \sim 10^{-10} \text{m}$ – the size of an atom!

So, if we pass a beam of e's through a double-slit that's the size of an atom, we get an interference pattern! This is how an electron-microscope works – the speed of the e's is adjusted to change λ , allowing us to look at objects that are too small to see with visible light.

Electron waves:

The question is then: “what's this electron wave”?

Answer: is relates to the probability to find an electron in a given point. In fact the **square of the electron wave** is the **probability** to find the electron in a given place., just like the intensity of light is the electrical field squared, $I = |F_{electric}|^2$.

Einstein hated this answer, saying “God does not play cubes”. He thought there is no such thing as “**probability**” to find an electron. Fundamentally, he thought that either there is a particle somewhere or there isn't. (This is an oversimplification of what he thought, but never mind).

Well... since the 60's we have experimental proofs that Einstein was wrong, and the electrons must be extended waves and not tiny particles. We won't have time to go over it, but take Quantum Mechanics classes if you are interested!

Atomic Spectra

Another example of how electrons behave as waves comes in the observation of discrete lines in atomic spectra; see example (from hot Hydrogen emitted from close to 7,000 degrees) – the example is just the optical spectrum from it, there are many more lines in the UV.



These line spectra cannot be explained correctly by any means other than assuming the e's behaves as waves.

Notes: for hydrogen, these spectra could be fitted by an interesting mathematical relation, which we'll see later; in fact, once the mathematical relation is guessed, we can even predict new spectral lines!

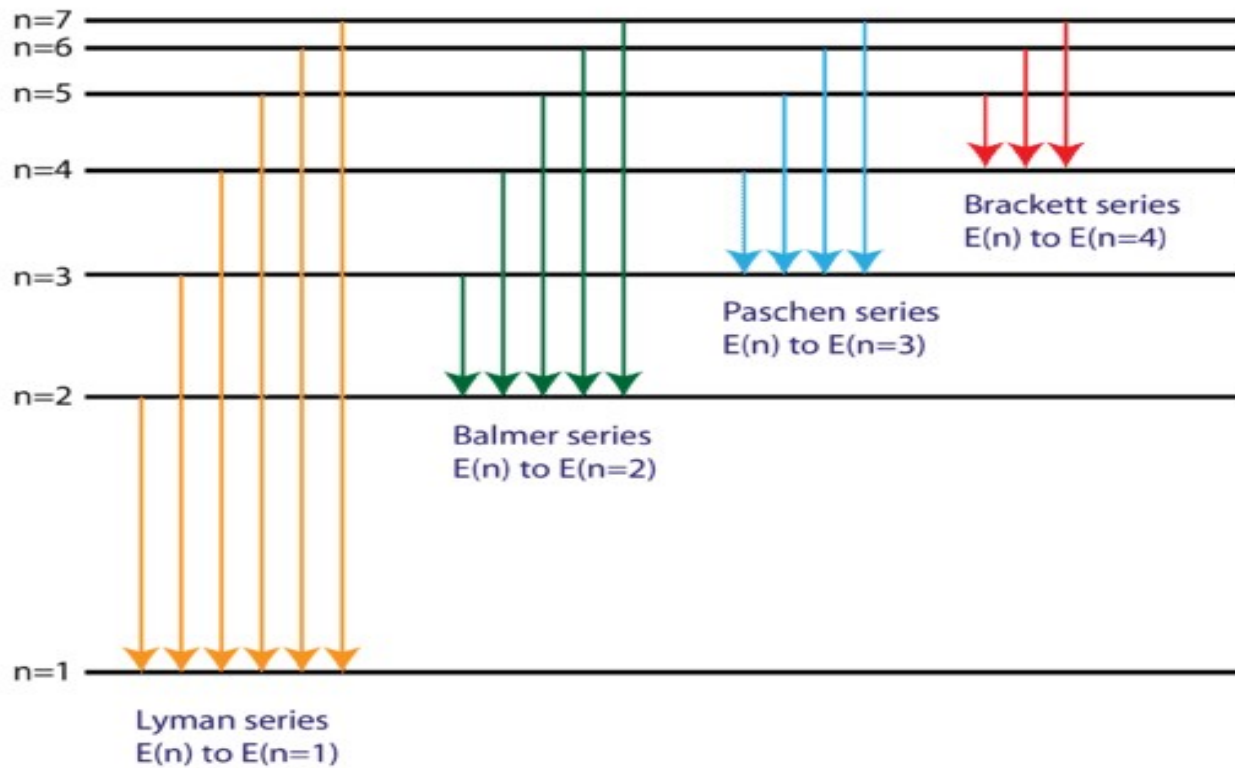
Bohr came up with his (incorrect) model directly for explaining these spectra.

The point is that if electrons are waves in discrete orbital energies, then the transition energies from one level to the next, will be discrete. See the attached picture:³

³

From [https://chem.libretexts.org/Textbook_Maps/Introductory_Chemistry_Textbook_Maps/Map%3A_Introductory_Chemistry_\(CK-12\)/05%3A_Electrons_in_Atoms/5.07%3A_Spectral_Lines_of_Hydrogen](https://chem.libretexts.org/Textbook_Maps/Introductory_Chemistry_Textbook_Maps/Map%3A_Introductory_Chemistry_(CK-12)/05%3A_Electrons_in_Atoms/5.07%3A_Spectral_Lines_of_Hydrogen)

Electron transitions for the Hydrogen atom

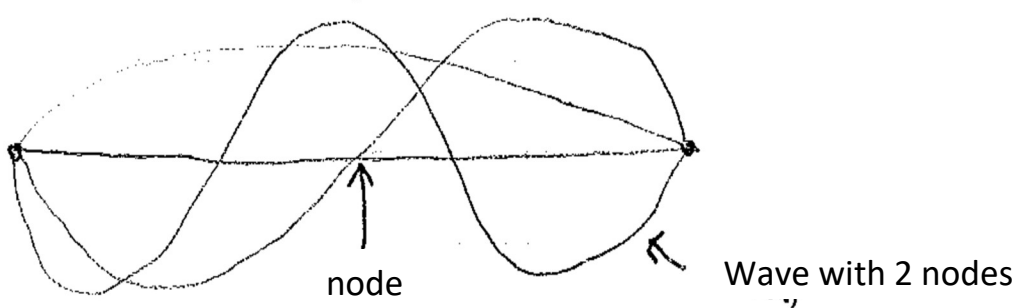


You see that if indeed the electron energies are “fixed”, discrete, and not continuous, then the emitted photon energies (and the associated photon frequencies and wavelengths) are specific discrete lines, not continuous.

So now we'll start explaining why the electron waves have discrete energies.

Specifically (next page):

We know that standing waves can have only certain wavelengths (and thus certain frequencies):



Example (picture above): waves in a guitar:

- **fundamental (no nodes)**
- **1st harmonic (1-node)**
- **2nd harmonic (2-nodes)**

“Nodes” refer to points where the wave is zero at all times. To the left and the right of a node a wave goes up and down, but at the node the wave is “clamped” to zero. Standing wave can have nodes, as plotted above.

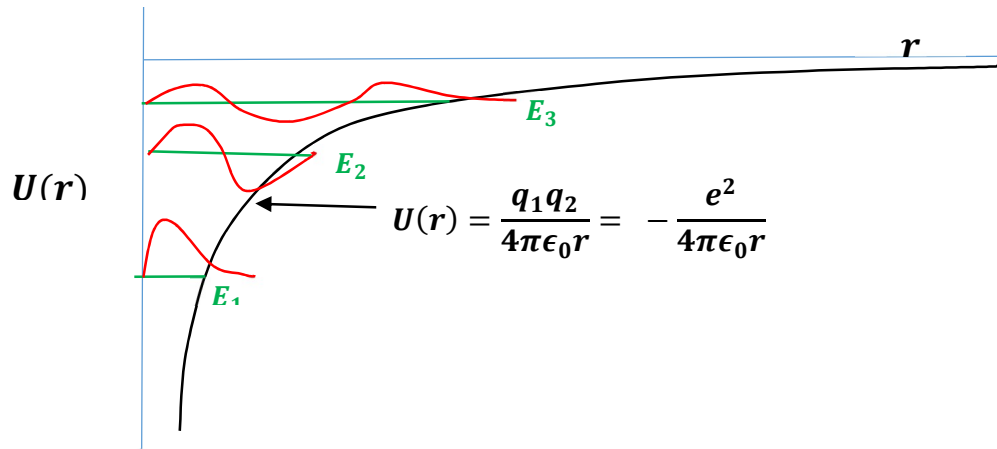
Waves in a hydrogen atom:

Since we expect that the energy of an electron in an atom is somehow related to the frequency of the wave, we have the possibility that the energy be quantized (i.e., have only discrete values, not be continuous).

In classical mechanics the electron falls to the nucleus at $r = 0$, where

$$U(r = 0) = -\infty.$$

But in Q.M. only certain values are allowed because the electron behaves as a standing wave. See the picture below:



Potential energy, **energy levels**, & **schematic electron wavefunctions** for the electron in a hydrogen atom. (Just a schematic with lots of mistakes, don't take too seriously)

Note that this picture is kind of complicated, since we draw several things.

- The Coulomb potential $-\frac{e^2}{4\pi\epsilon_0 r}$ that the electron feels (black)
- The energy levels that are allowed (**green**). In Q.M., only certain standing waves “fit” in this potential (there are more energy levels than I plotted, but we’re just qualitative here)
- And most confusingly, the **red** functions are the wavefunctions. We plot them traditionally with their axis on the green line, to indicate the regions they are allowed in; so if a red wavefunction line is above the associated green line it is positive, and otherwise negative.

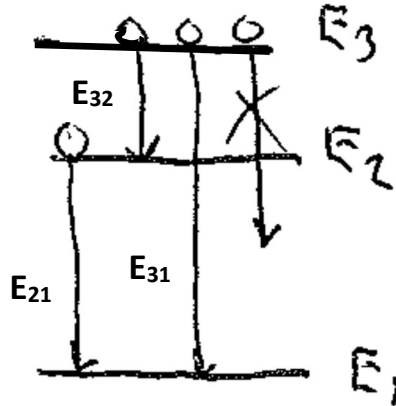
Note that the wavefunctions **penetrate** into a region which is **classically forbidden**, i.e., where the potential is higher than the energy. Q.M. allows the electrons to **tunnel** into these regions.

And of course there are more wavefunctions than we plotted...

The emission lines that we see correspond to differences in the allowed energies that the electron can have. The electron can only make transitions between these allowed energy levels.

For example, say all atoms were at the 3rd energy level, then we could get emission only to level 1 and 2 (emission is always to a lower energy state), and therefore the emission would have been to only two different frequencies:

$$E_{photo} = h\nu_{32} = E_3 - E_2, \quad \text{and} \quad E_{photo} = h\nu_{31} = E_3 - E_1$$



Other colors could not be emitted in this case (i.e., the rightmost line is forbidden) since the energy that the electron would remain with at the end, is simply not allowed.

Similarly, if the electron had an energy E_2 , only one emission line is allowed,

$$E_{photo} = h\nu_{21} = E_2 - E_1$$

If we have excited atoms in levels 2 and 3 we'll see lots of emission line, e.g.,

Intensity of emitted light if level 2 and level 3 could both be occupied (but not levels 4 nor 5, etc.)



(Of course, for a real hydrogen atom, at high enough temperatures we can excite also levels 4, 5, etc. ; but **emission is always downwards**, so if the hydrogen is at level 4 it can only go to levels 1,2 or 3, etc.)

Things we need to explain qualitatively:

- Why are the emission lines different for each element?
Fireworks take advantage of this; Sr for red, Ca for orange, Na for yellow, Cu for blue, etc.
- For H, and other ions with one electron (He^+ , Li^{2+} , etc.) why do the energy levels have specific and simple relation, i.e., they go as $\frac{1}{n^2}$, where $n = 1,2,3, \dots$ (i.e., the energy of the 2nd level is $\frac{1}{4}$ times the energy of the 1st, the energy of the 3rd level is $\frac{1}{9}$ the energy of the 1st, etc.)

The old Bohr model had a partial explanation for these questions. For one-electron atoms, and using as usual Z to denote the # of protons in the nucleus, we write the total energy as a sum of kinetic and potential:

$$E = \frac{1}{2} Mv^2 + \frac{(Ze)(-e)}{4\pi\epsilon_0 r} = \frac{1}{2} Mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Bohr hypothesized that the only orbitals that are allowed are those with **special values for the angular momentum**, i.e., those with

$$\text{Angular momentum} \equiv Mvr = n \hbar = n \frac{h}{2\pi}, \quad n = 1,2,3 \dots$$

i.e., Bohr assumed **that the angular momentum is quantized**. Of course, he had no real reason why this should be true, except to give the right answer! i.e., the right emission frequencies, which were known experimentally already then.

By using

$$|F| = \frac{Ze^2}{4\pi\epsilon_0 r^2} = \text{centrifugal force} = \frac{Mv^2}{r}$$

along with $Mvr = n\hbar$ along with $E = \frac{1}{2}Mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$ Bohr derived that the energy in of the n 'th orbital is

$$E_n = -\frac{R_\infty Z^2}{n^2}, \quad n = 1, 2, 3, \dots$$

where we defined

$$R_\infty \equiv \frac{e^2}{2a_0} = 2.18 \cdot 10^{-18} \text{J} = \frac{2.18 \cdot 10^{-18}}{1.609 \cdot 10^{-19}} \text{eV}$$

i.e.,

$$R_\infty = 13.6 \text{ eV}$$

Where

$$a_0 \equiv \hbar^2 \frac{4\pi\epsilon_0}{Me^2} = 0.529 \text{ \AA}.$$

and the radius in the n 'th orbital is shown to be

$$r_n = \frac{n^2}{Z} a_0,$$

where we defined the Bohr radius:

The lowest-energy state has $n = 1$, giving $E \propto -Z^2$; higher energy states have less negative energies.

Now we can qualitatively explain the line spacing of one-electron atoms.

- An initial state, from has energy E_{n_i} with no photons. Then a photon is emitted from this state, resulting in:
- A final state with energy E_{n_j} with a photon of energy

$$h\nu_{ij} = E_{n_i} - E_{n_j}$$

(note that we label the photon with a subscript, i, j , to denote that it moves from level i to level j)

i.e.,

$$h\nu_{i,j} = -R_{\infty}Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right) = R_{\infty}Z^2 \left(\frac{1}{n_j^2} - \frac{1}{n_i^2} \right)$$

where $n_i > n_j = 1, 2, 3, \dots$ for light to be emitted

So for example, the first few photon energies in hydrogen ($Z=1$) would be:

- $n_j = 2, n_i = 1 \rightarrow h\nu_{2,1} = R_{\infty} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R_{\infty}$

i.e.,

$$\nu_{2,1} = \frac{3 R_{\infty}}{4 h} = \frac{3}{4} * \frac{13.6 \text{ eV}}{4.12 * 10^{-15} \text{ eV} \cdot \text{s}} = 2.47 * 10^{15} \text{ s}^{-1}$$

The associated wavelength is

$$\lambda_{2,1} = \frac{c}{\nu_{2,1}} = \frac{\left(3.00 * 10^8 \frac{\text{m}}{\text{s}} \right)}{2.47 * 10^{15} \frac{1}{\text{s}}} = 1.21 * 10^{-7} \text{ m} = 121 \text{ nm}$$

This is a deep UV wavelength (note that the lowest visible wavelength is about 400nm).

- $n_j = 3, n_i = 1 \rightarrow h\nu_{3,1} = R_{\infty} \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = \frac{8}{9} R_{\infty}$
- $n_j = 3, n_i = 2 \rightarrow h\nu_{3,2} = R_{\infty} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_{\infty} = \frac{5}{36} * 13.6 \text{ eV} = 1.89 \text{ eV}.$

The associated wavelength is interesting, since it is in the visible range; we can calculate the transition wavelength easily from our previous result; note that

$$\nu_{3,2} = \frac{5}{36} \frac{R_{\infty}}{h} = \frac{5}{36} \frac{4}{3} \nu_{2,1} = \frac{5}{27} \nu_{2,1}$$

And therefore (since the wavelength is inversely proportional to the frequency)

$$\lambda_{3,2} = \frac{27}{5} \nu_{2,1} = \frac{27}{5} * 121 \text{ nm} = 655 \text{ nm (red photon)}$$

- $n_j = 4, n_i = 1 \rightarrow h\nu = R_{\infty} \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = \frac{15}{16} R_{\infty}$

- etc. ...

Quantum Mechanics and Uncertainty

In QM, we will use a new equation to describe particles, known as Schrödinger's Equation, which is a wave equation:

In 1D, Schrodinger's equation is (space is 3D, but 1D is easier to consider):

$$-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} \psi(x) + U(x)\psi(x) = E\psi(x)$$

We cannot derive it, this equation is like $F = ma$ in classical mechanics, i.e., it is stipulated. Here, $\psi(x)$ is the wave function, which tells us everything we can know about the particle.

Insert: we can't prove but we can at least "motivate" the Schrodinger's equation.

Take the deBroglie relation ($p = \frac{h}{\lambda}$); square it to get $p^2 = \frac{h^2}{\lambda^2}$: Multiply it by the wavefunction to get:

$$p^2\psi(x) = \frac{h^2}{\lambda^2}\psi(x)$$

This is meaningful for a wave where λ is well defined (an oscillating wave at a single frequency). But what about a general wave? It turns out that the as far as the electron wave, the action of the momentum squared is the "same" as acting by a scaled second derivative, i.e.,

$$p^2\psi(x) = -\hbar^2 \frac{\partial^2}{\partial x^2} \psi(x)$$

This relation looks strange but it really quite similar to the deBroglie's relation ($p = \frac{h}{\lambda}$); We won't prove it but will "motivate" it:

If a wavefunction is highly oscillatory, then its derivative, which measures its rate of change (after all, a derivative measures slope) should be quite large; but a wavefunction which is highly oscillatory will have a small λ and therefore a large $p = \frac{h}{\lambda}$.

So: higher $p \leftrightarrow$ more oscillations \leftrightarrow higher derivative

And therefore the relation $p^2\psi(x) = -\hbar^2 \frac{\partial^2}{\partial x^2} \psi(x)$ makes sense.

Now the total energy is the sum of the kinetic energy and potential energy, i.e.,

$$K.E. + U(x) = E$$

But the kinetic energy $K.E. = \frac{1}{2}Mv^2 = \frac{\frac{1}{2}(Mv)^2}{M} = \frac{p^2}{2M}$ so

$$\frac{1}{2M}p^2 + U(x) = E$$

Multiply by $\psi(x)$ from the right to get

$$\frac{1}{2M}p^2\psi + U(x)\psi(x) = E\psi(x)$$

And replacing the p^2 by the 2nd derivative, we get the Schrodinger's equation, as we promised,

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x) = E\psi(x)$$

End of Insert

As the name suggests, $\psi(x)$ will look like a wave.

We interpret $|\psi(x)|^2$ as the probability density to observe the particle at a position x – exactly like we interpreted the double-slit experiments with electrons!

In practice, we distinguish one chemical system from another by specifying its $U(x)$. We plug $U(x)$ into the Schrodinger Equation, and for the standing waves $\psi_n(x)$ and the E_n 's that satisfy the equation.

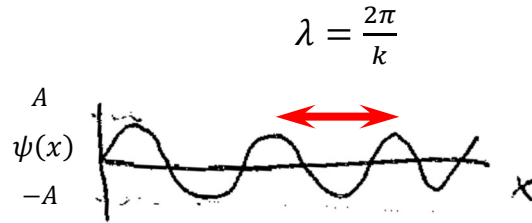
If we plug in $U(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$ we get $E_n = -\frac{R_\infty Z^2}{n^2}$, just like in Bohr's model! The associated $\psi_n(x)$ are then called the hydrogenic orbitals. More on these later.

The Uncertainty Principle:

One consequence of an electron being a wave is that waves naturally follow an uncertainty principle.

Consider a wavefunction that looks like a sin-wave:

$$\psi(x) = A \sin(kx)$$



This function goes on forever! Except at the nodes, we can find the electron everywhere.

Thus the uncertainty in the electron's position for this $\psi(x)$ is $\Delta x = \infty$, even though we know the momentum precisely from deBroglie's equation,

$$p = \frac{h}{\lambda} = \frac{h}{\frac{2\pi}{k}} = \frac{hk}{2\pi} = \hbar k$$

so $\Delta p = 0$.

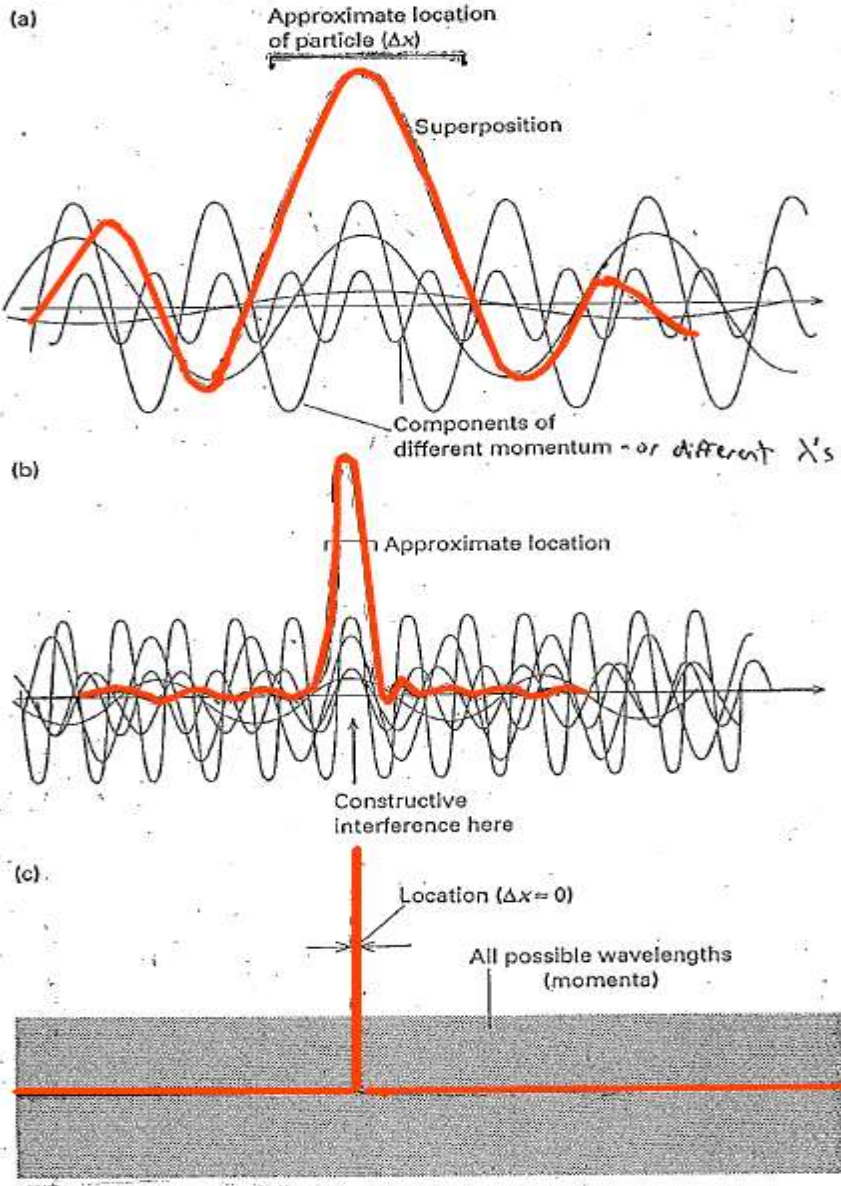
How to reduce the uncertainty in x ?

We could add a few sin-waves with different wavelengths:

$$\psi(x) = A_1 \sin k_1 x + A_2 \sin k_2 x + A_3 \sin k_3 x + \dots$$

Example: adding 4, 10, and infinitely many waves. The **RED** line in each panel is the sum of different sine-waves, and all the other lines are the individual sine-waves. The top panel is for combining **4 different waves**, next is a panel with combination of **10 waves**, which looks indeed more localized; finally, we can get a truly localized (needle-like wavefunction) if we **combine infinitely many waves**.

11 Quantum theory: introduction and principles



Note that as **we add more waves, the momentum becomes less precise, since $p = \hbar k$, and we have more and more k 's (of higher values, i.e., more oscillating)** as we try to localize the wavefunction. (E.g., **note how much more highly-oscillating waves** there are in the 2nd panel, where the wavefunction is more localized in x .)

So we start with $\Delta x = \infty$, $\Delta p = 0$, and as we make Δx smaller, Δp increases!

Mathematically, the relation is **the Heisenberg Uncertainty Relation:**

$$\Delta x \Delta p \geq \frac{\hbar}{2} = \frac{h}{4\pi}$$

QM Stability and the H atom

Now we can understand why being a standing wave allows the H atom to be stable. First, as we saw earlier:

$$K.E. = \frac{1}{2} M v^2 = \frac{1}{2} \frac{M^2 v^2}{M} = \frac{p^2}{2M}$$

But unless $\Delta x = \infty$, we'll have $\Delta p \neq 0$, so the smallest K.E. we can have is from the smallest momentum range, i.e., from Δp , i.e.,

$$\text{Min. K. E.} = \frac{(\Delta p)^2}{2M}$$

Where

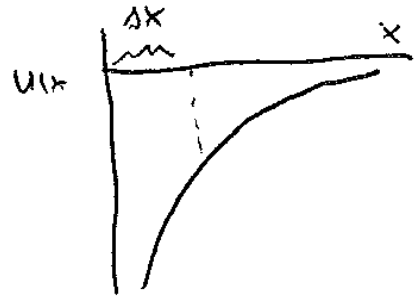
$$\Delta p \geq \frac{\hbar}{2\Delta x}$$

Or

$$\text{Min (K. E.)} = \frac{1}{2M} \frac{\hbar^2}{4\Delta x^2} \propto \frac{1}{(\Delta x)^2}.$$

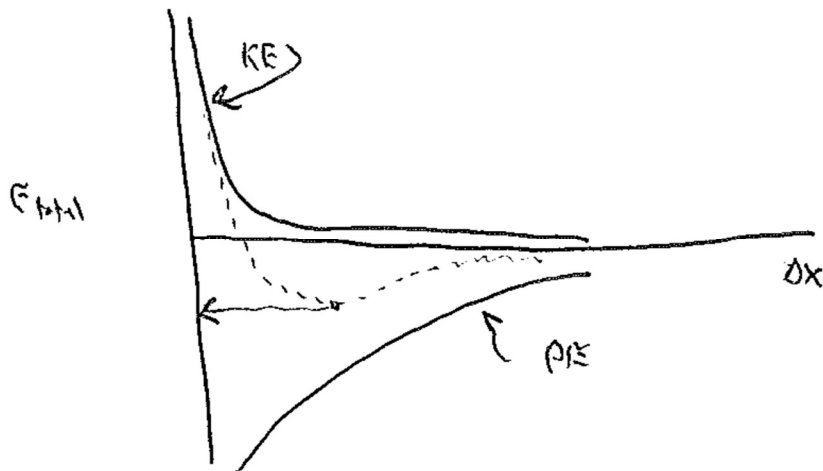
The P.E. at this point is

$$U = -\frac{Ze^2}{4\pi\epsilon_0\Delta x} \propto -\frac{1}{\Delta x}$$



Thus

$$E_{total} = K.E. + P.E. \propto \frac{1}{(\Delta x)^2} - \frac{1}{\Delta x}$$



Thus, the lowest energy is not at $\Delta x = 0$, but at a finite value of Δx where the K.E. is not too high and the potential energy sufficiently negative. The figure above shows that total energy as a dashed line, and the minimum of that energy is the optimal size of the wavefunction, which is not 0, but turns out (if we put all the constants into the equations above) to be ~ 1 Angstrom, as we argued before!

Note because of the uncertainty principle, if an electron spiraled into the nucleus, then $\Delta x \rightarrow 0$ and $\Delta p \rightarrow \infty$, meaning an infinite K.E.! The electron must have a finite-size w.f.!

Back to the Schrodinger's Equation

For our “particle waves”, we have (now in 3D):

$$|\psi(x, y, z)|^2 = \frac{\text{Prob. to find particle around position } x, y, z}{\text{Unit volume}}$$

Thus, the probability to find the electron in a small region from x to $x+dx$, y to $y+dy$, and z to $z+dz$, is $|\psi(x, y, z)|^2 dV$, where $dV = dx \cdot dy \cdot dz$

Like any wave equation with standing wave solutions, only certain functions $\psi(x, y, z)$ satisfy the Schrödinger Equation, and these solutions have certain energies.

Thus both the energy and the orbital where we can find the e's are quantized.

Note: $\psi(x, y, z)$ can be both ≥ 0 or ≤ 0 , like any standing wave. We have nodes separating regions where the w.f. is positive and negative, i.e., the nodes are the regions where $\psi = 0$. But the density of the electron measured at any point is always non-negative it is $|\psi(x, y, z)|^2$, regardless of whether the wavefunction is positive or not.

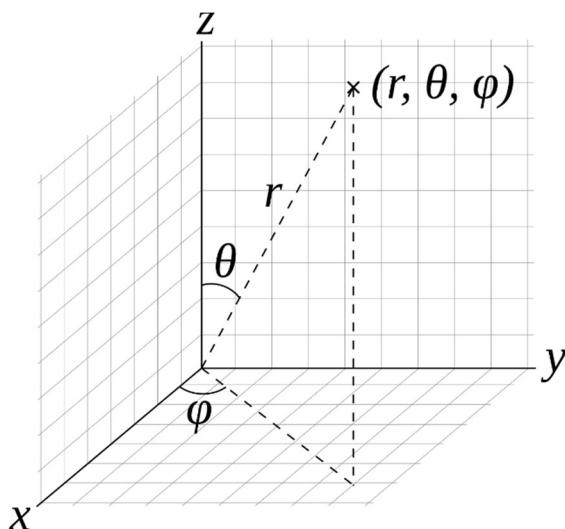
The H Atom: “Correct” Picture

The Schrödinger equation for an hydrogen is:

$$-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(x, y, z) = E\psi(x, y, z)$$

This equation is usually solved in detail in Chem. 113A, so we'll just gloss over it.

It is much easier to solve in spherical coordinates, see the Wikipedia image:



Orbitals and quantum numbers

Because we deal with 3 dimensions it turns out that there are 3 quantized integer or quantum numbers that characterize each orbital. The integers are labeled n, l, m (**don't confuse this m with mass**)

Overall, the solutions, called “orbitals”, can generally be written as a function of the distance from the nucleus times a function of the direction,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi).$$

(There is no relation between the “ R ” in R_{nl} and R_∞ , the energy constant; we just don't have enough letters in the alphabet).

The meaning and possible values of the quantum numbers are:

i)

$$n = \text{principal quantum \#} = 1, 2, 3, 4, \dots$$

The value of n is: 1 plus the number of “nodes”, i.e., regions of sign changes, are in the wavefunction (how “sliced” it looks);

(ii)

$$l = \text{ang. momentum quantum \#} = 0, 1, 2, \dots, n - 1$$

l denotes how many of these “nodes” do we see if we look at the molecule from different angles (don’t worry, you’ll soon see an example). l essentially tells us the “shape” of the orbital when we look at it from far away.

A bit of history – we often use letters for the l quantum number instead of numbers.

- $l = 0$: “s” (sharp)
- $l = 1$: “p” (principle)
- $l = 2$: “d” (diffuse)
- $l = 3$: “f” (fine)
- $l = 4$: “g”

And then the letters rise alphabetically (h,i,j, etc.)

Now recall that we just said that n is 1+the total number of nodes of the orbitals; so we can think of n as

$$n = 1 + \# \text{ of nodes in the } Y_{lm}(\theta, \phi) \text{ angular part} \\ + \# \text{ of nodes in the } R_{nl}(r) \text{ radial part}$$

so since l is the number of angular nodes, i.e., nodes in the $Y_{lm}(\theta, \phi)$ part of the orbital, we get that

$$n = 1 + l + \# \text{ of radial nodes}$$

(iii)

$$m = \text{magnetic quantum \#}: 2l + 1 \text{ values.}$$

m tells us the directionality (and in some cases also the shape).

Note that: for $l = 0$ there is only value of m ;

For $l = 1$, there are 3 values of m ;

For $l = 2$, there are 5 values of m , etc.

Energies of H or 1-electron ions

We'll deal with the orbitals in more detail very soon, but before we should mention that the energy of the orbitals turns out to be the correct value (as it should), i.e., $-R_\infty, -\frac{R_\infty}{4}, -\frac{R_\infty}{9}, \text{etc.}$ Specifically, it is for hydrogen or hydrogen-like ions (i.e., atoms with one electron, such as H, or He^+ , or Li^{2+} , etc.)

$$E_n = -\frac{R_\infty Z^2}{n^2}$$

where we introduced $R_\infty = -2.18 \cdot 10^{-18}$ J earlier, and Z is, as you recall, the nuclear charge.

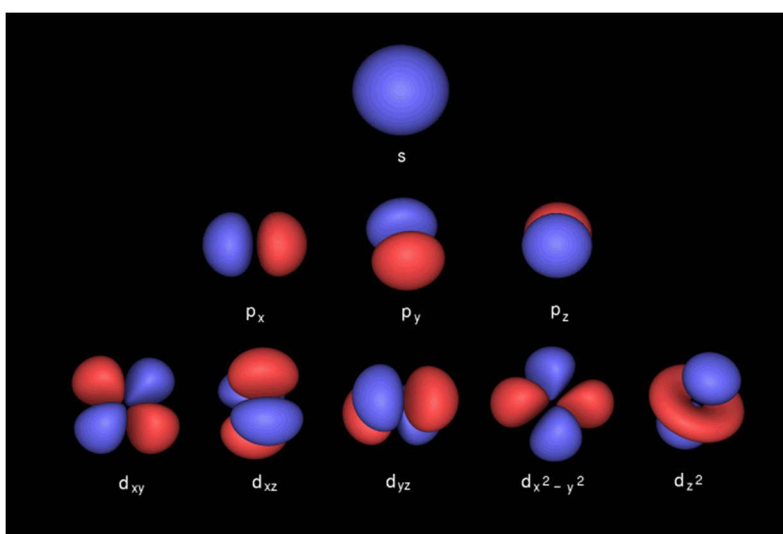
(Note that the energy depends only on n , the principal quantum #, and not on l neither on m . This is not a general feature of atomic orbitals and is true only for single-electron atoms or ions; **in fact, the energies of orbitals of electrons in a many-electron atoms will depend on l too**, as we'll discuss later)

Back to orbitals

The hydrogenic orbitals are standing waves in the r, θ, ϕ directions.

Generally (see picture⁴)

- s orbitals are spherically symmetric; they depend only on r , not on θ , nor ϕ , and have no angular nodes.
- p orbitals have one angular node and depend on r, θ, ϕ
- d orbitals: two angular nodes, etc.



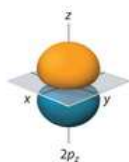
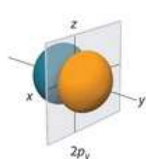
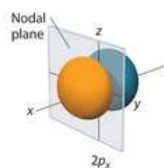
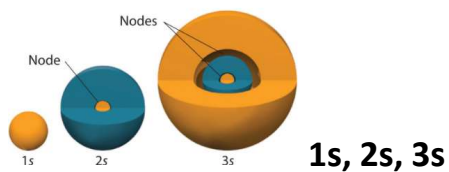
This picture is for orbitals without radial nodes, i.e., orbitals with $n = l + 1$:

- s orbitals with $n=1$ (the “1s” orbital)
- p orbital ($l = 1$) with $n=2$, i.e., 2p orbitals
- d orbital ($l = 2$) with $n=3$, i.e., 3d orbitals.

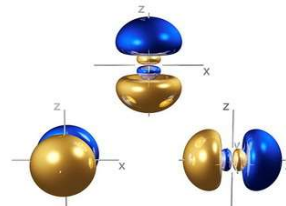
Note: See how the 2p orbitals have one nodal surface, and 3d have two nodal surfaces (for four of the 5 depicted d orbitals, the two surfaces are two perpendicular planes that “cut” through the molecule, like cutting pizza to four by two cuts, top-bottom and left-right; for the right-most one it is a little more complicated).

⁴ Taken from <http://chemistry.umeche.maine.edu/CHY251/Quantum.html>

A more “comprehensive” set of pictures is (from ⁵, ⁶ and ⁷):



2p



We won't draw d orbitals beyond the 3d ones we gave, but you can imagine how they look, with more “radial cuts”. Now let's get back from the pictures, to a:

⁵ Taken from <https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s10-05-atomic-orbitals-and-their-ener.html>

⁶ Taken from <https://socratic.org/questions/what-is-the-structural-difference-between-a-2p-and-a-3p-orbital>

⁷ From: chemwiki.ucdavis.edu

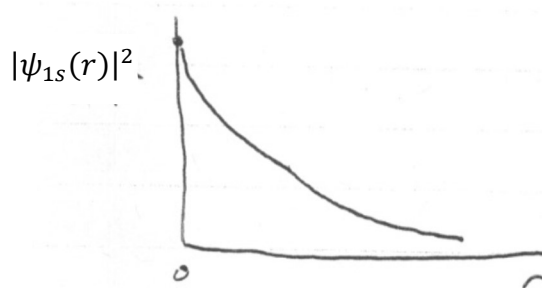
Detailed discussion of atomic orbitals

The lowest energy orbital has $n=1, l=0, m=0$. We call it the "1s" orbital, and it is:

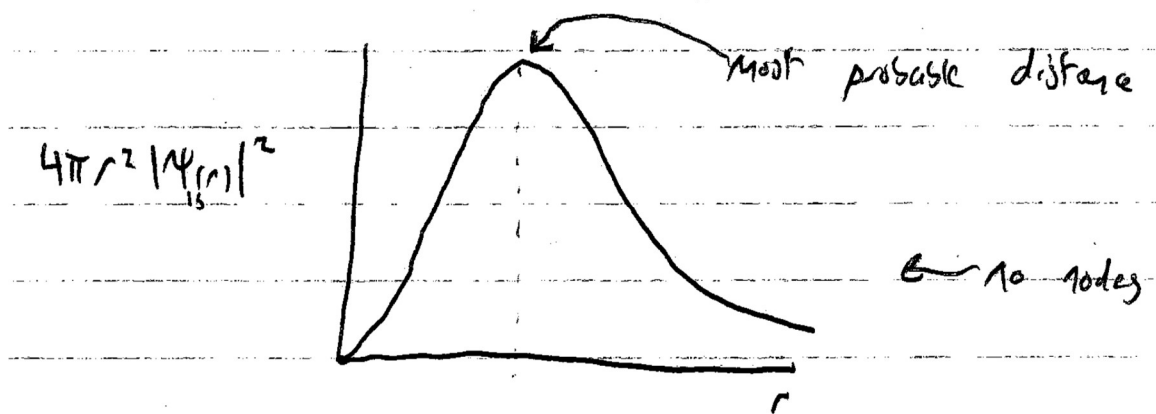
$$\psi_{1s}(r) = \frac{2}{\sqrt{4\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

and recall $a_0 = \frac{\hbar^2 4\pi\epsilon_0}{Me^2} = 0.529 \text{ \AA}$.

The radial distribution function (i.e., orbital **squared**) is below $r=0$ is the nucleus.



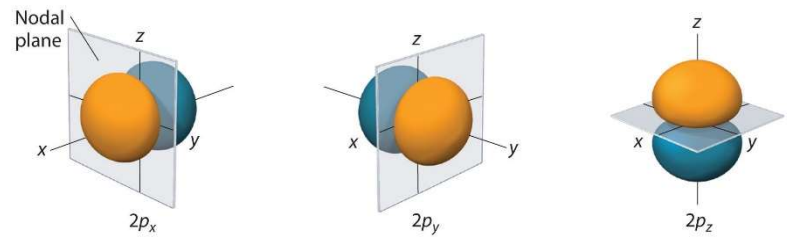
We could also ask what's the prob. to find the e^- at a **distance r in any direction** from the nucleus? For that **multiply $|\psi|^2$ by an area of a sphere of radius r :**



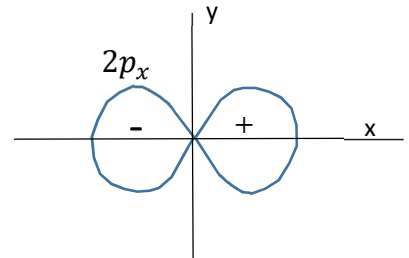
What about p orbitals?

For $n = 2$ and $l = 1$ (i.e., “2p” orbitals) we can have $m = -1, 0, 1$.

We can add these together to form ψ_{2p_x} , ψ_{2p_y} , ψ_{2p_z} orbitals that we saw earlier: here, for example, yellow is positive and blue negative.



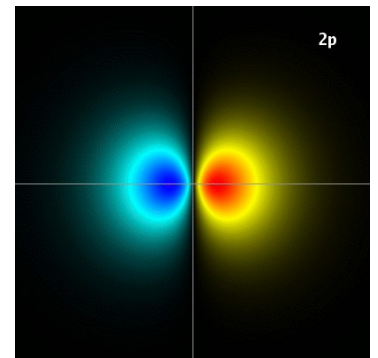
We usually draw them much simpler as, e.g., with the sign telling us the phase of the wavefunction:



Note: that is just a quick figure chemists make. **Don't think of the electron as running in orbitals.**

If you need to, think of an orbital (and an electron in it) more like a **jelly** which can have plus colors or minus colors (as long as you don't push the analogy too far, and account for interference – see the discussion of molecular orbitals later).

The diagram on the right is a truer picture;⁸ it is bright red where the orbital is, say, very positive, and deep blue when it is negative.



The electron does not hop from one point to another. It is a wave that's exist everywhere, and mostly in the indicated regions.

Mathematically, for the $2p_z$, for example:

$$\psi_{2p_z}(r, \theta, \phi) = \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^{1.5} e^{-\frac{Zr}{2a_0}} * \cos(\theta)$$

where:

⁸ Taken from <http://users.aber.ac.uk/ruw/teach/237/lcao.php>

- the stuff to the left of the " * " is a radial part, which is the same for all 2p orbitals,
- and the part to the right, $\cos(\theta) = \frac{z}{r}$, is associated with the "z" direction of $2p_z$, and will be of course $\frac{x}{r}$ and $\frac{y}{r}$ for the other 2p orbitals.

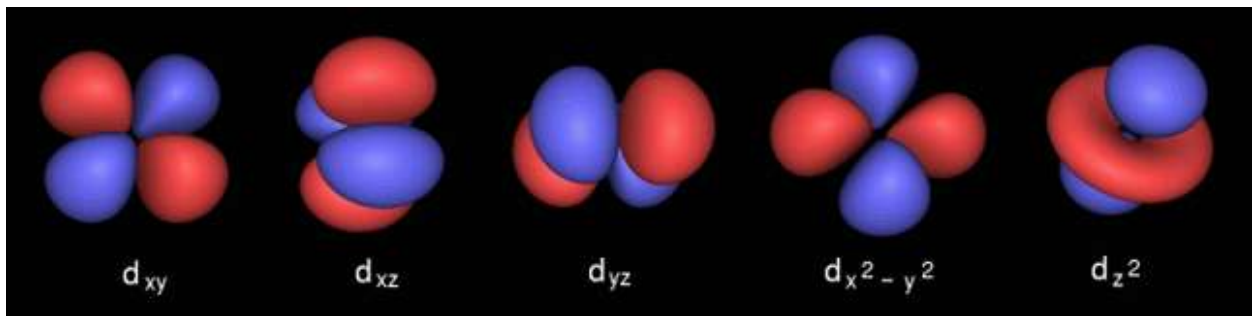
In general the hydrogenic orbitals can be separated always to:

- a radial part, $R_{nl}(r)$, that depends on n and l (but not on the direction quantum number, m), times
- an angular part, $Y_{lm}(\theta, \phi)$, which specifies the direction and depends on l, m only but not on the radial quantum number, n :

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

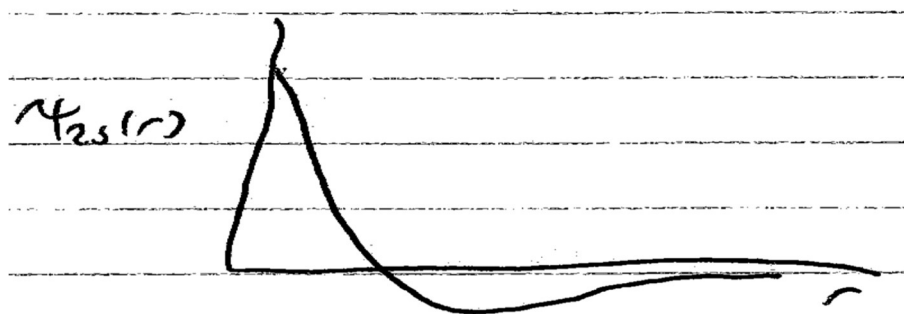
Question to you: what will be the angular part for $2p_x$, $2p_y$ and $2p_z$ orbitals? Actually, your answer will be correct up to an overall numerical factor which we don't care about.

What about **d orbitals**? The lowest energy ones are the 3d orbitals with 0 radial nodes (so $l=2, n=3$). Of course there are 5 of those, with $m=-2, -1, 0, 1, 2$ and all have 2 angular nodes. We can make linear combinations of them that are easier to visualize, as we plotted earlier, also with 2 angular nodes:

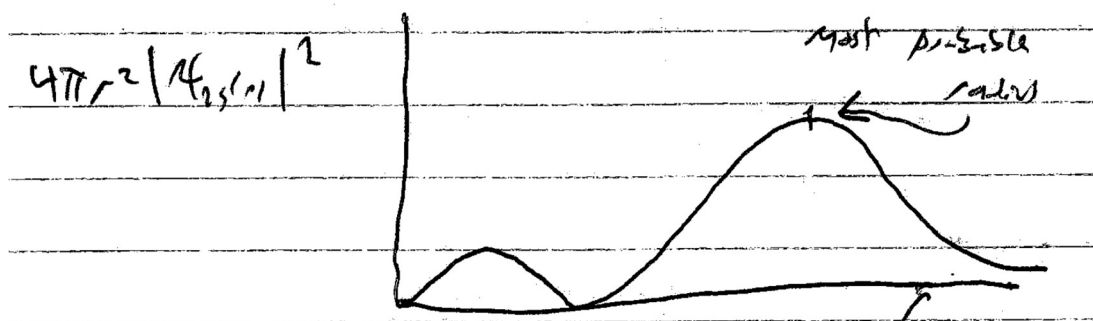


Orbitals with radial nodes

We can also have orbitals with radial nodes: standing waves with nodes in the "r" direction, e.g., the 2s orbital:



Or we can show the radial distribution function, i.e., the square of the wavefunction multiplied with the surface-area factor $4\pi r^2$:



The pictures for the other orbital with radial nodes (3s, 4s, ..., 3p, 4p, ..., 4d, etc.) are analogous, and you can guess what they look like.

Most probable radii and number of nodes

One can prove that for the H atom,

$$r_{nl}^{most\ prob.} \propto \frac{1}{Z} (n^2 - l(l+1))$$

so that

$$r_{ns} > r_{np} > r_{nd}$$

We also have $n-1$ nodes in each orbital, and as we saw they are distributed so l are angular and $n - l - 1$ are radial

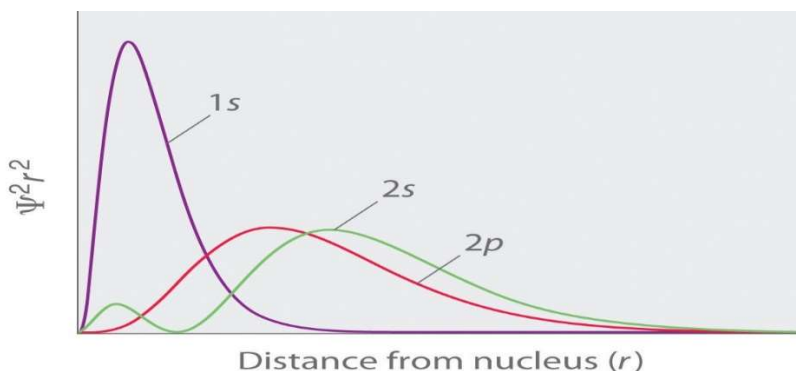
Example: $n = 1, l = 0$ has 0 nodes (“1s”)

$n = 2, l = 1$ has 1 angular nodes and 0 radial nodes (“2p”)

$n = 2, l = 0$ has 0 angular nodes and 1 radial nodes (“2s”)

The following picture⁹ shows the wavefunction squared (times $4\pi r^2$, the “surface factor”). You see that **1s is much closer to the nucleus in average than the $n=2$ orbitals**, and that for the latter, **2p is concentrated while 2s is extended**, from near the nucleus to far away.

Similarly, from the picture clearly the most probable value of “ r ” is farther out for 2s than 2p, i.e., $r_{2s} > r_{2p}$ indeed.



⁹ From

https://chem.libretexts.org/LibreTexts/Howard_University/General_Chemistry%3A_An_Atoms_First_Approach/Unit_1%3A_Atomic_Structure/Chapter_2%3A_Atomic_Structure/Chapter_2.5%3A_Atomic_Orbitals_and_Their_Energies

How to find the **nodes**? You look at the mathematical form of $\psi_{nlm}(r, \theta, \phi)$ from the Schrodinger equation and set $\psi_{nlm}(r, \theta, \phi) = 0$ and solve for r, θ, ϕ .

Usually, the more nodes the higher the energy (in our case, “higher energy” means less negative energy). (We’ll see exceptions in multi-electron atoms!)

For hydrogen and one-electron ions (H, He⁺, Li²⁺, etc.) the number of degenerate orbitals, i.e., orbitals with the same energy, is n^2

Example: n=1: 1s, $1^2 = 1$

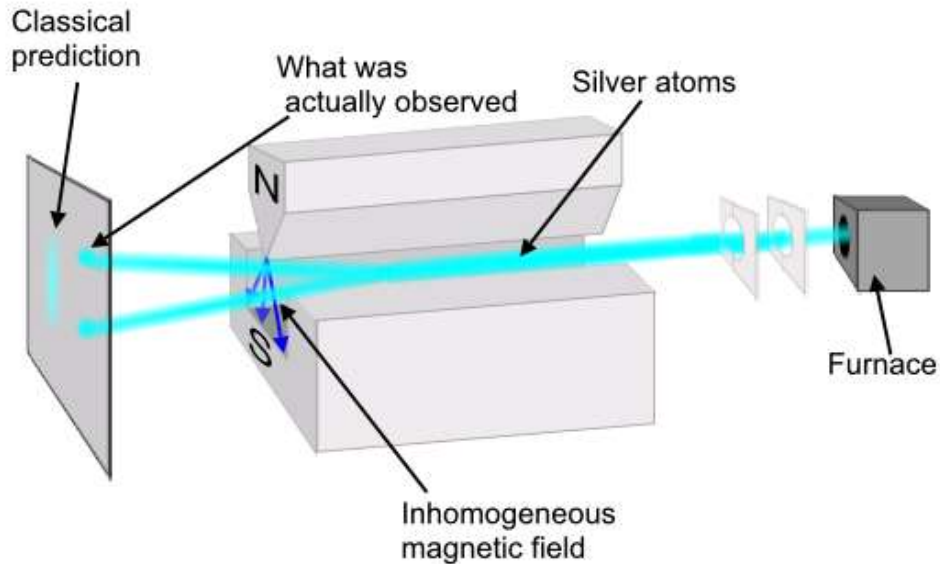
n=2: 2s, 2p_x, 2p_y, 2p_z gives $4=n^2$

n=3: test for yourself!

Electron spin: the 4th quantum number

For electrons in atoms, we would guess that specifying 3 quantum #'s, n, l, m , would tell us everything about the electron standing waves.

But, there's still one more experiment (the Stern Gerlach experiment) that needs to be explained:¹⁰



We have a beam of ions that have one electron in an s orbital so $l = m = 0$, and there should be only one type since all the ions are identical; instead two spots are seen, indicating two beams.

Note: Stern and Gerlach used Ag^+ ions; the Ag^+ ion has many electrons, but only one is in the outer shell, the $5s$ shell, and the others are in a “core” as well see in the many-electron discussion later, and don't affect the experiment

The 2 beams indicate that there are two types of electrons!

To distinguish them, we use a 4th quantum #, called “spin”, which can take on one of 2 values:

¹⁰ Image taken from Wikipedia

$$m_s = \begin{cases} \text{"up"} & \text{or } +\frac{1}{2} & \text{or } \alpha \\ \text{"down"} & \text{or } -\frac{1}{2} & \text{or } \beta \end{cases}$$

Thus, a full description of the electron in an H atom requires 4 quantum numbers, n, l, m, m_s and the wavefunction requires an extra term specifying the spin.

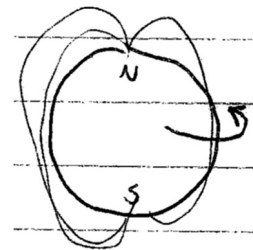
$$\psi_{nlm m_s}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \chi_{m_s}$$

where

$$\chi_{m_s} = \text{"up"} \text{ or "down"}.$$

The closest classical analogue would be to think of the electron as a small sphere of charge **spinning** on its own axis. The spinning charge would create a magnetic dipole that would interact with the external magnetic field:

Simplistic but wrong classical picture:



The weird thing is that all the electrons spin left or right, not at any other angle. Of course, the electron is really a probability wave, so the classical picture is not fully correct.

Note: spin is fascinating, but we'll leave its complications to more advanced QM classes.

Summary of the H atom:

The Schrödinger Equation gives a suite of standing waves for the electron in an H atom.

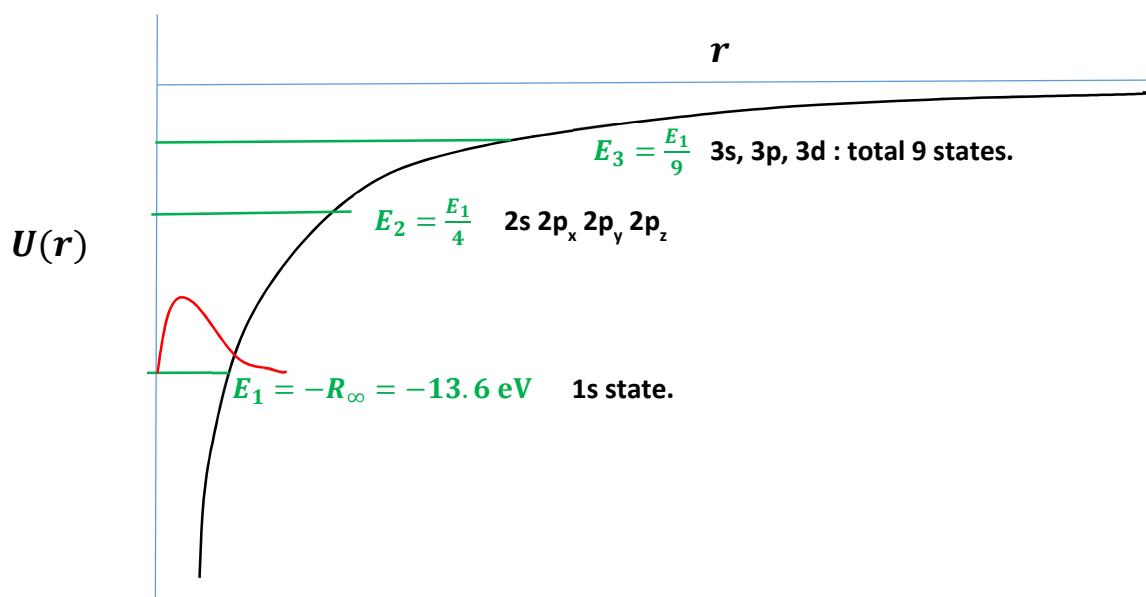
The waves are characterized by 3 quantum #'s , and by the spin: n, l, m, m_s

Only certain energies are allowed, giving:

$$E_n = -R_\infty \frac{Z^2}{n^2}$$

For each orbital, there are l angular nodes and $n-1$ total nodes.

The orbital energy depends only on n . The degeneracy of each allowed energy is n^2

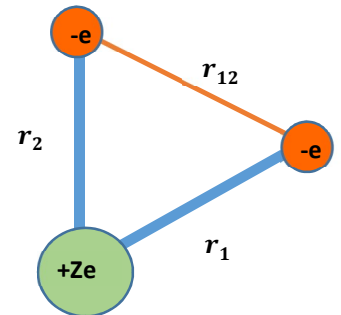


Many-e atoms.

Let's now consider a 2-e' atom, such as He. The Schrödinger equation looks now much more complicated, since the wavefunction is now a function of 6 variables – the x, y, z of the first particle (labeled x_1, y_1, z_1) and the coordinates for the 2nd particle, i.e., x_2, y_2, z_2 .

Similarly, the kinetic energy part becomes the sum of the two kinetic energies;

While the potential is now the sum of the attraction of the first electron to the nucleus, the 2nd electron to the nucleus, and the electron-electron repulsion.



So since the Schrödinger equation is

$$(K.E. + P.E.)\psi = E\psi$$

in the present case it becomes:

$$\begin{aligned} & -\frac{\hbar^2}{2M} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dy_1^2} + \frac{d^2}{dz_1^2} + \frac{d^2}{dx_2^2} + \frac{d^2}{dy_2^2} + \frac{d^2}{dz_2^2} \right) \psi(x_1, y_1, z_1, x_2, y_2, z_2) \\ & + \frac{1}{4\pi\epsilon_0} \left(-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right) \psi(x_1, y_1, z_1, x_2, y_2, z_2) \\ & = E \psi(x_1, y_1, z_1, x_2, y_2, z_2) \end{aligned}$$

where we highlighted the electron-electron repulsion.

This equation is already a monster for two electrons...gets progressively worse as there are more electrons.

The e-e repulsion makes this equation unsolvable numerically, but we can solve it numerically on a computer. The solutions are NOT the H-atom standing waves, but are pretty close to it.

As an **approximation**, for the rest of the class we will assume that the orbital shapes are H-like, and that the effect of the e-e repulsion is only to change the energy levels (and to somewhat “compress” or “decompress” the orbitals, but without changing their overall shape).

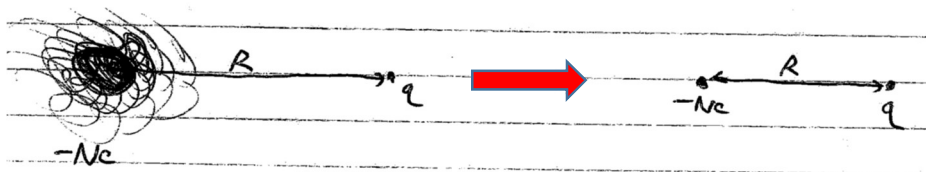
This makes sense even if we don't use QM.

First, think of the planets orbiting the earth. To a very good approximation we approximate that they move in simple orbits as if each one of them only sees the sun, (even though of course the planets attract each other so the motion is not really in simple orbits).

Screening/Shielding

From electromagnetism you may have studied in physics, Gauss Law that that for interaction of any charge q with a spherical charge distribution:

- if q is far away it sees the entire other charge as if it was in the center.
Pictorially:



- If q is inside the spherical charge distribution it does not feel any repulsion, it is as if it is free.

Now consider a He atom: If the 2nd electron was completely **outside** the 1st electron (i.e., if it was at distances which are so far that the 1st electron never visits) it would “see” an “effective” Coulomb potential as if

$$Z \text{ (seemingly)} = \text{nuclear charge} - \text{other electron} = 2 - 1 = 1.$$

I.e., the first electron “cancels” part of the $Z = 2$ attraction to the nucleus.

This gives us the idea of an effective nuclear charge: Z_{eff}

Z_{eff} = the net reduced nuclear charge felt overall by an electrons because of the repulsion from the other e's compensates for some of the full nuclear charge.

Consider an N-electrons atom, with $Z \cdot (+e)$ still being the charge of the nucleus; (recall that if $Z \neq N$, then of course the system is an ion).

As far as shielding, the screening must be somewhere between the two extremes;

- A maximal screening of the nucleus by the other electrons;
- or no screening.

Mathematically,

$$Z - (N - 1) \leq Z_{eff} \leq Z$$

where $Z - (N - 1)$ would be maximal screening of the nucleus by all the remaining N-1 electrons; and the other extreme, $Z_{eff} = Z$, is the case of no-shielding at all by the other e's!

This indicates that electrons in a multiple-electron atom see less attraction to the nucleus but otherwise behave as if they were in a one-e atom.

Specifically:

- Consider the potential on one of the electrons, call it electron "1". If that electron was alone orbiting the nucleus, i.e., if N=1, then the potential would be

$$U^{1-e \text{ atom}}(r) = \frac{1}{4\pi\epsilon_0} \left(-\frac{Ze^2}{r} \right)$$

But in a multi electron environment, our electron will also feel the repulsion due to the other electrons:

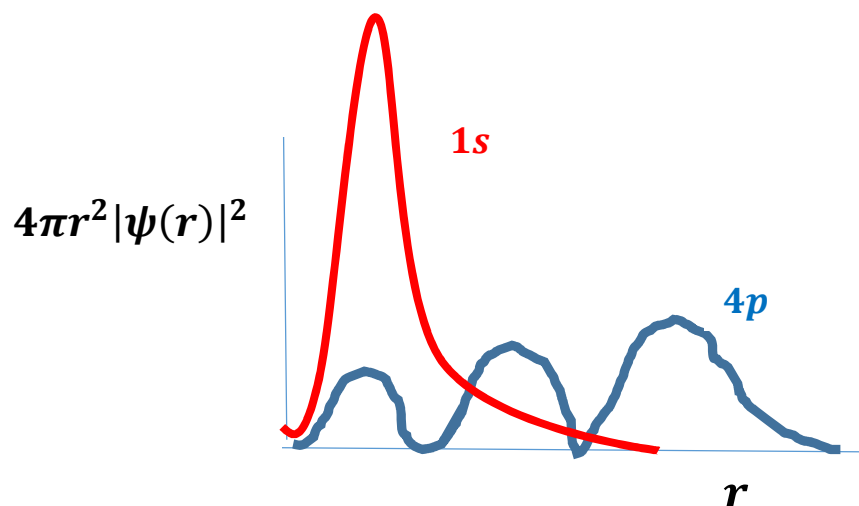
$$U^{multi \text{ atom}}(r) = \frac{1}{4\pi\epsilon_0} \left(-\frac{Ze^2}{r} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \dots \right) \approx \frac{1}{4\pi\epsilon_0} \left(-\frac{Z_{eff}e^2}{r} \right)$$

(where r_{12} is the distance between the electron we consider and the 2nd electron, r_{13} is the distance to the 3rd electron, etc.)

Clearly adding other electrons raises the interaction, i.e., makes it less negative, or putting it differently: Z_{eff} is smaller than Z .

Since the P.E. of an electron in a multi-e atom is higher (less negative) than an electron in a one-e atom, a multiple-e atom will have a lower ionization energy.

Example: consider a multi-electron atom with both a 1s and a 4p electron:



Essentially all the 4p electron is “outside” the 1s electron, so the 1s electron essentially completely shields the 4p.

Conversely, very little shielding of 1s is done by the 4p electron.

Thus e’s with low n’s see much higher Z_{eff} than e’s with high n’s.

Since $I. E. \approx R_{\infty} \frac{Z_{eff}^2}{n^2}$, **the outermost electrons, with a higher n, are much easier to remove** (for two reasons: **both lower Z_{eff} and a smaller $1/n^2$**) than inner electrons.

Shielding: Broken degeneracy

In one-e atoms, all e’s with the same n have the same energy (are degenerate). In a multi-e atom, this is no longer true, so, for example **in multi-electron atoms, 2s and 2p do not have the same energy, and 3s,3p,3d don’t have all the same energy, etc.**

Example: s wavefunctions go right up to the nucleus but p wavefunctions do not – they have a node at the nucleus. Thus:

$$Z_{\text{eff}}^{ns} > Z_{\text{eff}}^{np}$$

and in general,

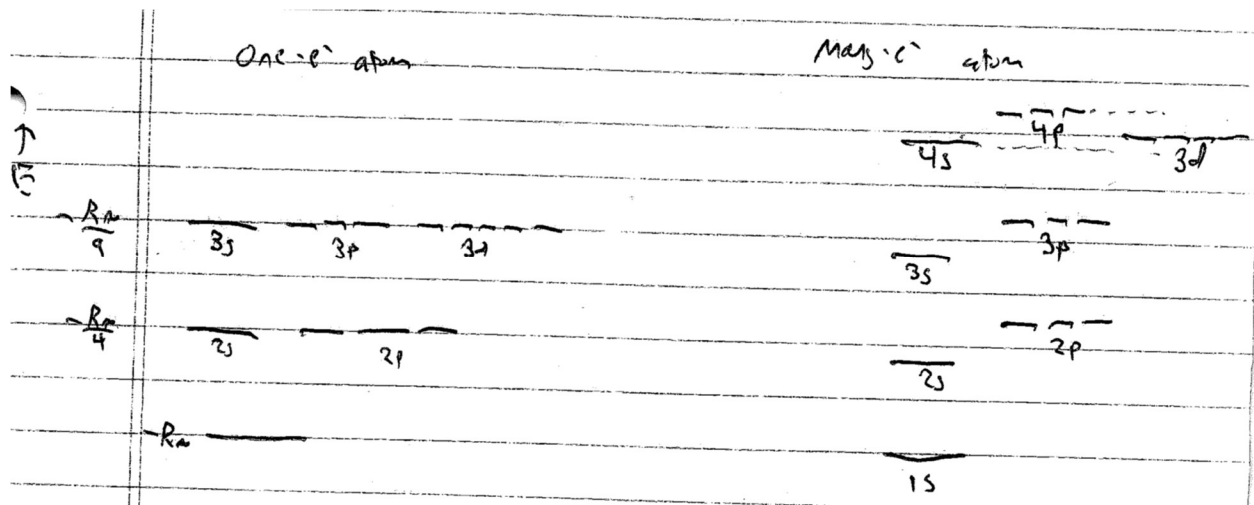
$$Z_{\text{eff}}^{ns} > Z_{\text{eff}}^{np} > Z_{\text{eff}}^{nd} > Z_{\text{eff}}^{nf}$$

and since

$$E_{nl} \simeq -R_{\infty} \frac{(Z_{\text{eff}}^{nl})^2}{n^2}, \quad E_{ns} < E_{np} < E_{nd} < E_{nf}$$

For example, E_{2s} is more negative, i.e., lower than, E_{2p} .

And in general the levels therefore change, and are non-degenerate. :



Note how the 3p rises above 3s, and especially note how 3d rises to be close to the 4s,4p shell. That affects transition metals.

Note: for a many-e atom,

$$r_{nl} \propto \frac{1}{Z_{\text{eff}}(n, l)} (n^2 - l(l+1))$$

But because Z_{eff} depends on l strongly, we have

$$r_{ns} < r_{np} < r_{nd} < r_{nf}$$

just the opposite of the 1e atom! Note again the physical reason – due to the shielding by s electrons the p electrons feel less attraction so they are further away, and analogously for the d, and then f electrons.

Estimating Z_{eff}

The simplest model to estimate Z_{eff} says:

- e's with lower n completely shield e's with higher n
- e's with the same n shield each other by around $\frac{1}{2}$
- e's with higher n don't shield e's with lower n

$$Z_{\text{eff}} \simeq Z - \# \text{ of } e^- \text{ in lower shells} - \frac{1}{2} (\# \text{ of } e^- \text{ in same } n)$$

Example:

Be has $Z = 4$ with two $n = 1$ and two $n = 2$ e's;

The $n = 2$ e's are completely screened by $n = 1$ ones, and $\frac{1}{2}$ screen each other.

And the $n = 1$ e's half-screen each other but don't see the $n = 2$ ones.

Thus:

$$Z_{\text{eff}}^{n=2, \text{Be}} = 4 - 2 - \frac{1}{2} \cdot 1 = 1.5$$

For the $n=1$ e's, that half-screen each other but don't see the $n=2$ e's,

$$Z_{\text{eff}}^{n=1, \text{Be}} = 4 - 0 - \frac{1}{2} \cdot 1 = 3.5$$

Thus, the 2 core e's "feel" the nucleus much more than the two valence (outer) e's.

In the following, we **abbreviate** Z_{eff} as Z_{eff}^n for the outermost shell, i.e., the valence shell; this is because the chemical properties such as the energies to add or remove electrons depend on the outermost electrons, as we'll discuss later too.

So for Be, we'll abbreviate $Z_{\text{eff}}^{\text{Be}}$ for $Z_{\text{eff}}^{n=2, \text{Be}}$

We can estimate the I.E. of Be as if there is only the valence electron, which feels an effective charge of $Z_{\text{eff}}^{\text{Be}} \equiv Z_{\text{eff}}^{n=2, \text{Be}}$. We know that the I.E. is proportional to the charge squared – and in this case it is the effective charge squared – over n^2 , i.e.,

$$\text{I.E. (Be)} \simeq R_{\infty} \frac{(Z_{\text{eff}}^{\text{Be}})^2}{n^2} = R_{\infty} \frac{(1.5)^2}{2^2} = 13.6\text{eV} \cdot \frac{2.25}{4} = \mathbf{7.6 \text{ eV}}$$

Experimentally, **I.E.(Be)=9.4 eV**; the agreement is not perfect but we'll see later that Be is more stable indeed (to electron removal) because it has a complete sub-shell.

What about the ion Be^+ ? Since it has only one $n = 2$ electron, the screening is changed:

$$Z_{\text{eff}}^{\text{Be}^+} \simeq 4 - 2 - \frac{1}{2} \cdot 0 = 2$$

Thus $Z_{\text{eff}}^{\text{Be}^+} > Z_{\text{eff}}^{\text{Be}}$, so it takes more energy to remove the 2nd electron than the 1st.

Negative ions and subshells: The argument we give can also be used to try to qualitatively understand electron affinity, i.e., the extra stabilization of an electron in a negative ion (i.e., in this what's the difference in energy for example, Be^- than in Be). However, we'll need to change the formula to make any sense for this specific case of Beryllium. Turns out (as we'll soon discuss) that in Be the 2s electrons compose a sub-shell, which is lower in energy as we'll soon see, and which shields completely the extra electron in the 2p orbital in Be^- , so the correct formula for $Z_{\text{eff}}^{\text{Be}^-}$ is

$$Z_{\text{eff}}^{\text{Be}^-} = \text{nuclear charge} - \#\text{elec. (n = 1)} - \mathbf{1} * \#\text{elec(2s shell)} = 4 - 2 - 2 = 0$$

i.e., Be^- is not expected to be bound, and indeed experimentally it isn't. Here the **1 is in red** in the formula to emphasize that in this case we **don't divide the # of other electrons in the n=2 shell by two, since the other electrons are in a lower subshell (2s) than the outermost electron in the 2p subshell.**

Aufbau Principle and Hund's Rule

Aufbau means “building up”, i.e., how we distribute the e’s in a multi-e atom. We alluded to that above, but let’s present systematically.

Generally, all electrons will like to have the lowest possible energy, but we also know that electrons don’t like to be in the same place at the same time. This is codified by the Pauli Exclusion Principle, which states that no two electron can have the same 4 quantum #'s.

This means that for a given spatial orbital, ψ_{nlm} , we can put two electrons: one with spin up ($m_s = +\frac{1}{2}$), and the other with spin down ($m_s = -\frac{1}{2}$). The 2 e’s have the exact same spatial ψ and are in the same place. Thus, just based on the Pauli principle there’s some probability to have them in the same place.

If we go into the theory further we’ll find that this (two e’s in the same place) is an artifact of our approximate description that electrons are in independent hydrogen-like orbitals; actually, because they repel, two electrons will never truly be in the same place; but the approximate description we have is so powerful that we won’t go beyond that. To do a better description you’ll need to learn graduate quantum mechanics

We use a shorthand notation to describe the spatial orbital of e’s in multi-e atoms:



What about C? $[\text{He}](2s)^2(2p)^2$?

How do we distribute the two 2p e’s? In the same orbitals or different orbitals?

All the p-orbitals are identical in shape, they just point 90° apart. However:

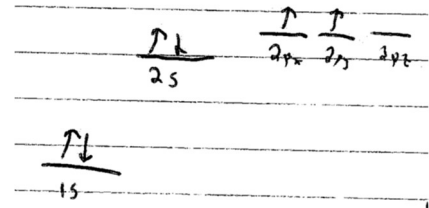
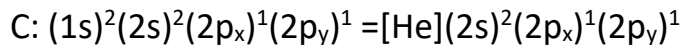
- Two e’s in the same orbital repel each other more than two e’s in different orbitals.
- It is also lower in energy for 2 e’s in different orbitals to have the same spin.

The physical reason that electrons like to have the same spin is that this “naturally” keeps them apart. This is a mathematical consequence of the Pauli principle, that you’ll understand in 113A or in graduate QM.

These two facts lead to:

Hund's Rule: The lowest energy state of a multi-e atom has the e's in separate orbitals with the same energy and spin aligned parallel.

Thus,



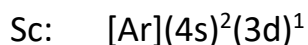
Note: there are actually $6=2*3$ such combination with two electrons with the same spin in the 2p orbitals in C:

- Both electrons can have either be both spin up or both down (factor of 2)
- and further a factor of 3 since the two e's in the p orbitals can also be e.g., one in p_y and one in p_z , i.e., $[\text{He}](2s)^2(2p_y)^1(2p_z)^1$; or one e in in p_x and one in p_z .

So which is the “lowest” energy configuration ? Answer: for a single C atom these six possibilities will all have the same energy, and it could be in any one of those. For a molecule, however, often, but definitely not always, only one configuration of all the electron will be possible (this will be then what we call “singlet closed-shell”, just like what happens for He or Ne) as we'll see later.

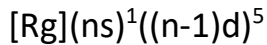
The Aufbau Principle for transition metals and others.

We already saw that $Z_{\text{eff}}^{4s} > Z_{\text{eff}}^{3d}$ so we can again see that there will be changes to the usual ordering by n , especially for (and just before) the transition metals, since there $E_{4s} < E_{3d}$ and 4s fills first. Specifically:



Some exceptions are (& there are more):

Cr, Mo



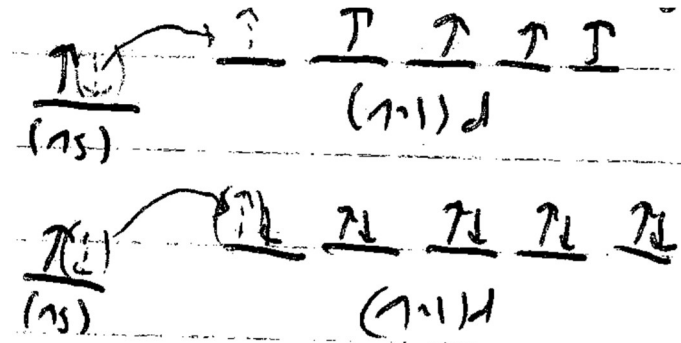
where Rg means Rare gas

Cu, Ag, Au: $[\text{Rg}](ns)^1((n-1)d)^{10}$

This are both because the d's do screen the s somewhat and when they fill (or 1/2 fill) the d-shell is lowered the d relative to s.

Finally, after the end of the transition metals, the (n-1)d shell is lowered so much, so that once we put even more electrons, e.g., for Ga (when n=4), we can treat the lower d shell (here 3d) as so deep that we can ignore it, i.e., **the valence shell for Ga is $(4s)^2(4p)^1$** , so it is completely analogous to Li and Al which have $(2s)^2(2p)^1$ and $(3s)^2(3p)^1$ valence shells.

We'll talk about that later.



Periodic Properties

First, a few concepts, some of which we saw earlier

1) Magnetic properties tell us about the electronic configuration:

Paramagnetic : atoms with one or more unpaired electron

Diamagnetic: atoms in which all e's are paired

2) Atomic/Ionic radii: for outermost electron:

$$r \simeq a_0 \frac{n^2}{Z_{\text{eff}}}$$

(we discussed this earlier).

3) Energies of outer electrons: for outermost electrons the energy will be

$$\epsilon_n = R_{\infty} \frac{Z_{\text{eff}}^2}{n^2}$$

where this is the same expression as for hydrogen and hydrogen-like atoms, (where there's a single electron, i.e., H, He⁺, etc.) except that here Z_{eff} replaces Z .

Of course, Z_{eff} depends on the orbital, as we discussed, and is smaller for the outer orbitals.

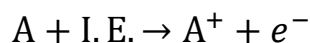
So now we can deal with:

Electron Ionization

I.E. = energy needed to remove most weakly bound electron from an atom

2nd I.E. = energy needed to remove most weakly electron from the above ion.

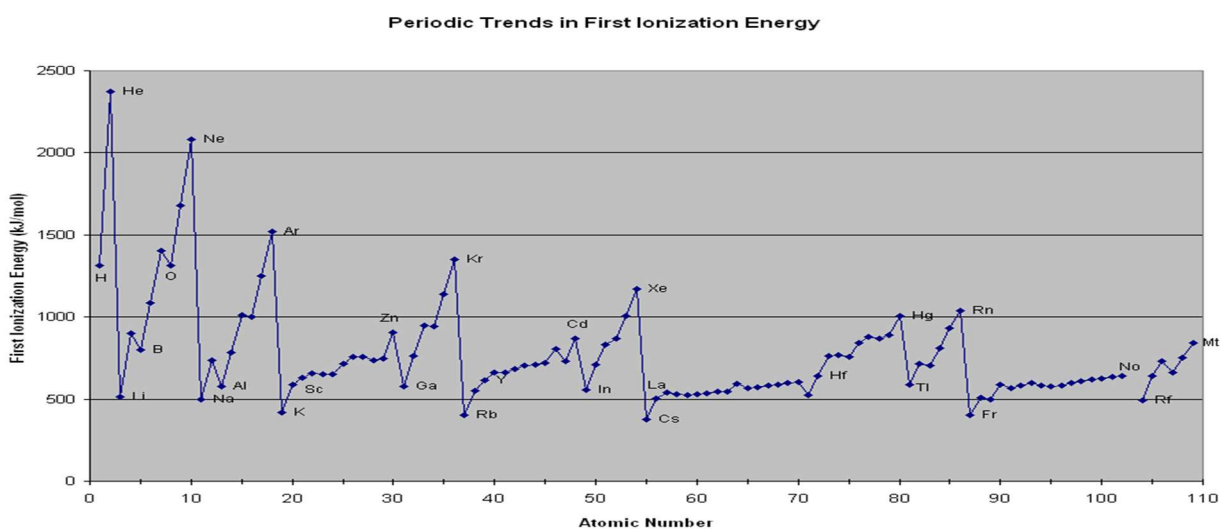
The definition of the ionization energy is that when we give it to an atom A then the atom will break to A⁺ and e⁻



Now we know that $\text{I.E.} \approx R_\infty \frac{Z_{\text{eff}}^2}{n^2}$ using Z_{eff} , n for outermost electrons. And because Z_{eff} is always larger for the +1 ions (less shielding) than for the neutral of the same atom, then always (for all atoms) then:

$$2^{\text{nd}} \text{ I.E.} > 1^{\text{st}} \text{ I.E.}$$

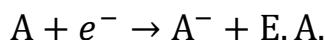
A picture of the 1st ionization energy is:¹¹ (the units are kJ/mol, divide by approximately 100 to get the I.E. in eV)



¹¹ From: https://www.angelo.edu/faculty/kboudrea/periodic/trends_ionization_energy.htm

Electron Affinity (EA)

Formally defined as the I.E. of the negative ion, or put differently as the energy released when an electron is attached



It is again calculated as

$$E. A. \simeq R_{\infty} \frac{Z_{\text{eff}}^2}{n^2} \quad \text{where } Z_{\text{eff}} \text{ is now calculated for } A^{-}, \text{ the negative ion}$$

IE and EA for different groups

IE and EA for Alkali metals: Li, Na, K, Rb, Cs, Fr . All have $[Rg](ns)^1$ (recall Rg=rare gas).

Thus we expect $Z_{\text{eff}} \sim 1$ (or similar) for the valence electron (the “ns” electron).

So we expect $IE \simeq R_{\infty} \frac{1^2}{n^2}$ so as n rises the IE decreases:

$$IE_{\text{Cs}} < IE_{\text{Rb}} < IE_{\text{K}} < IE_{\text{Na}} < IE_{\text{Li}}$$

This trend is fulfilled experimentally.

We can also compare the actual value of each IE to the experimental prediction. Let's do it for **Li**.

$$IE(\text{experimental}) = 5.4 \text{ eV}$$

$$IE(\text{theoretical, } n=2, Z_{\text{eff}}=1) \simeq R_{\infty} \frac{Z_{\text{eff}}^2}{n^2} = R_{\infty} \frac{1^2}{2^2} = \frac{R_{\infty}}{4} = \frac{13.6 \text{ eV}}{4} = 3.4$$

The experimental value is higher by 60% than the theoretical prediction when using $Z_{\text{eff}}=1$; this indicates that Z_{eff} for Li is higher than 1.

In general Z_{eff} increases down a column, partially compensating for increasing n. **Thus, the IE does decrease down a column, but not as fast as $\frac{1}{n^2}$** (note the figure

a few pages ago of the I.E., and how it slowly decreases each time we jump by a row, e.g., from Li to Na, etc.)

Electron Affinity of Alkalis: What about the EA of alkalis? From our crude model, Z_{eff} of the extra electron in a negative alkali ion will be 0.5. Specifically, for such a negative ion, take of one electrons in the outer “s” shell (for example, one of the electrons in the 3s shell for Na^-). For this electron, almost all the other electrons mask the nucleus, except for the last electron (the other one in the 3s shell) which only half masks it; so

$$Z_{\text{eff}}(\text{Na}^-) = 3(\text{from nucleus}) - 2(\text{the two } 1s \text{ e}^-) - 0.5(\text{the } 2s \text{ electron}) = 0.5$$

So

$$\text{EA}(\text{alkali}) = R_{\infty} \frac{Z_{\text{eff}}^2}{n^2} = R_{\infty} \frac{(0.5)^2}{n^2} = 13.6 \text{ eV} * \frac{1}{4} = \frac{3.4\text{eV}}{n^2}$$

So we would expect, e.g., for Li and Na and K (i.e., $n=2,3,4$, respectively)

$$\text{EA}(\text{alkali, predicted}) = \text{Li: } 0.85 \text{ , Na: } 0.38, \text{ K: } 0.2\text{eV}$$

Experimentally, the values are in the same ballpark but showing a different overall trend:

$$\text{EA}(\text{alkali, experiment}) = \text{Li: } 0.63 \text{ , Na: } 0.55, \text{ K: } 0.5\text{eV}$$

Since the electron affinity tells us about the effective charge of the negative ion, we learn that:

- For Li, for the EA experiment is lower than theory, so the effective charge in Li^- is less than $\frac{1}{2}$, i.e., the two valence electrons in Li^- shield each other excellently.
- This is not true anymore for Na^- and K^- where the shielding is less effective and therefore the theoretical prediction of the electron affinity of Na and K underestimates the experiment, i.e., the effective charge in Na^- and K^- is higher than 1.

Doubly ionized Alkali atoms

Now let's move back to ionization, but this time double ionization. As you can figure once we remove an electron from an Alkali atom, the remaining configuration is very stable, and therefore if we try to remove another electron we will need to invest a lot of energy.

Put differently, the energy to make Na^{2+} etc. is very high.

We can understand it in terms of effective charge: in Na^+ the valence electron is in the $n=2$ shell, so Z_{eff} for Na^+ now includes partial shielding from the "other" five electrons in 2p and the two electrons in 2s, i.e.,

$$Z_{\text{eff}}(\text{Na}^+) = 11 \text{ (nucleus)} - 2(1s \text{ core}) - \frac{1}{2} * 7 \text{ (five 2p and two 2s } e^-) = 5.5$$

This is much larger than $Z_{\text{eff}} \sim 1$ for neutral sodium, so moving down a shell makes

$$2^{\text{nd}} \text{ IE(alkali)} \gg 1^{\text{st}} \text{ IE (alkali)}$$

Magnetic properties of Alkali Metals: Since alkali metals have an unpaired ns electron, we expect that they will have a net spin so they should be paramagnetic, as experiment verifies.

Further, experiment also verifies that when we remove an electron from an alkali metal, the remaining configuration is fully paired, i.e., alkali ions are diamagnetic.

IE and EA for Halogens:

Now we can similarly understand why halogens (F, Cl, Br, I) have

- large IE
- large EA (i.e., even with an extra electron they have a high Z_{eff}).

Note that there are no double anions for halogens (e.g., no F^{2-}). The 2nd extra electron would have gone into an “(n+1)s” orbitals, with all the others in the nth shell or lower. Therefore, Z_{eff} would have been negative.

Example: Let's see if we can have F^{2-} . The 2nd extra electron would have been in n=3. So

$$Z_{\text{eff}} = +9(\text{nucleus}) - 10(\text{all other electrons in } F^{2-}, \text{ all in } n=1 \text{ and } n=2)$$

$$Z_{\text{eff}} = +9 - 10 = -1$$

A negative effective charge means no attraction for the (negative) electron, so there would be no F^{2-} .

IE and EA for Noble gases:

Are stable because they

- Have high IE with their filled shell
- Have EA=0 since $Z_{\text{eff}}=0$ for an electron in the next shell.

IE and EA across a row:

As we move to the right, Z_{eff} increases by $\sim \frac{1}{2}$ for each electron all the way to the noble gas

Thus, we expect (and it is true) that the IE increases across a row except for a small dip when the “ns” shell is filled. In the n=2 row, the dip is at B.

Let’s see the #'s for the I.E. (as well as the e configuration) for the first few atoms in the n=2 row:¹²

Lithium (Li)	[He]2s ¹	5.5 eV
Beryllium (Be)	[He]2s ²	9.4 eV
Boron (B)	[He]2s ² 2p ¹	8.3eV
Carbon (C)	[He]2s ² 2p ²	11eV

Specifically, for n=2, we expect $Z_{\text{eff}}^{2s} = 1.0$ for Li, $Z_{\text{eff}}^{2s} = 1.5$ for Be.

But for B, the 2s electrons screens the valence 2p electron relatively well, better than $\frac{1}{2}$. So $1 \leq Z_{\text{eff}}^{\text{B}} \leq 1.5$

EA across a row: similar trend expected, but, for example for the n=2 row, there’s a dip now at Be because of filled 2s, and of course there’s a large dip at Ne when the 2p shell is filled.

¹² Taken from https://en.wikibooks.org/wiki/High_School_Chemistry/Ionization_Energy

Final Exception: Transition Metal Ions

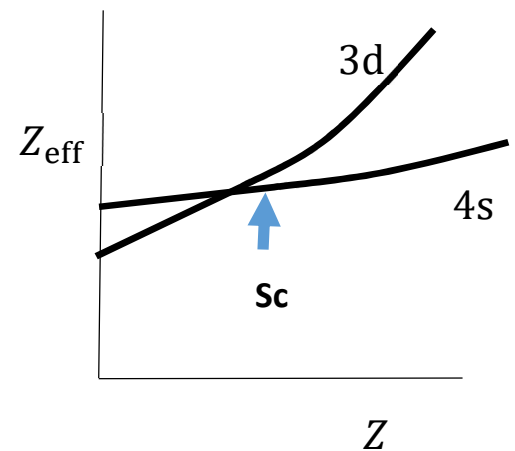
Take for example the 3rd row (K and rightwards). We know that for K, an alkali metal (first column) the single valence electron feels $Z_{\text{eff}}^{4s} > Z_{\text{eff}}^{3d}$ since 4s is closer to the nucleus.

However as we move **rightward** things change:

- Z_{eff}^{4s} rises only gently since the 3d electrons shield the 4s fairly well.
- In contrast, the 3d electrons shield each other less well than they do the 4s, so Z_{eff}^{3d} rises fairly fast.

As a result, the curves for Z_{eff}^{4s} and Z_{eff}^{3d} cross before Sc (the 1st TM)!

Thus, when ionizing TM, the electron comes out of 4s first! This is for Sc and most TM, where the ions are +2 (as both 4s electrons are easily ionized).



Chemical bonds

We've already seen that QM tells us how atoms assemble with a well-defined structure. Only certain energies are allowed, and e's are found only in certain places with some probability.

What happens when we have 2 nuclei plus a bunch of e's? Each electron is attracted to both nuclei and repelled by all the other e's. In essence the 2 nuclei have a "tug-of-war" over the e's !

Usually the most stable state, as determined by solving the Schrödinger equations, involves bringing the nuclei close together so that e's can be simultaneously attracted to both nuclei. This is called a chemical bond.

We distinguish 3 types of chemical bonds.

- Ionic: $A^+ - B^-$ electron transfer.
- Covalent $A - A$ or $A - B$ electrons shared equally or near equally.
- Dative (donor acceptor) $A: \rightarrow B$. A covalent bond with an electron pair that's delocalized, but both electrons come from the same nucleus. Important for TM complexes.

The properties that define what types of bonds form are the IE and EA of the atoms. These tell us who wins the tug-of-war.

Electronegative atoms "want" e's – so they have high IE and high EA (e.g., F, O, Cl)

Electropositive atoms: "don't like" e's, so they have low IE and low EA (e.g., Na, K)

We define (Mulliken's) Electronegativity (the desire for an atom to "steal" an electron from another atom) as

$$EN = \frac{IE+EA}{2}$$

When we write down the formula of a compound, we always write the most electropositive (least electronegative) atom first (examples: H₂O, NaCl, ClF)

So to summarize:

Ionic bonds: bond A-B, where A has low IE, B has high EA, and there's a large electronegativity difference; Example: Na^+Cl^-

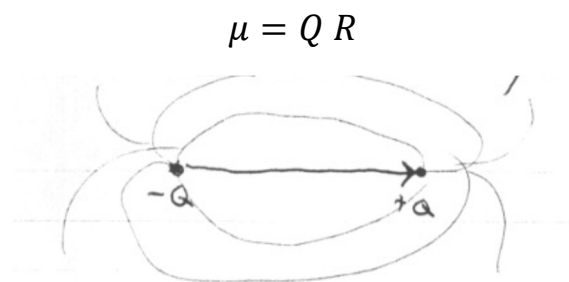
Covalent: A & B have similar EN. Examples: N_2 , F_2 , CO , etc.

Dative: A has a lone pair of e's and B an empty orbital. Example: $\text{H}_3\text{N}:\rightarrow\text{BH}_3$ (the lone pair of e's on N shares an orbital on N and an orbital on B)

Most bonds are polar-covalent: a mixture of lone and covalent character. Only homonuclear bonds are truly covalent. Heteronuclear bonds are usually somewhat ionic.

Dipole moments and a bond's ionic character

We can determine the % ionic character of a bond from its dipole moment,



Dipole is a vector which points from negative to positive charge. Q is the extra charge (positive on one side, negative on the other) and R the distance between the nuclei.

The units for dipole are charge-distance; the usual unit used is Debye, defined as

$$1 \cdot \text{D} = 0.2082 e \cdot \text{\AA}$$

i.e., one Debye is almost 5 times smaller than $e \cdot \text{\AA}$, so a dipole moment measured in Debye will be 5 times larger than the same dipole moment measured in $e \cdot \text{\AA}$ (just like 330 feet is about 100 meter, i.e., feet is smaller so the number of feet is larger.)

So if we measure R (from spectroscopy of electron diffraction) and we know μ we can calculate the size of $Q = \delta \cdot e$ (where I remind you is that δ is the amount of extra charge in units of e) from

$$\mu(\text{Debye}) = \frac{R(\text{\AA})}{0.2082} \delta$$

Examples:

$$\text{H} - \text{Cl}: R = 1.284 \text{ \AA}, \mu = 1.10 \text{ D} \rightarrow \delta = 0.18 \quad (Q = 0.18 e)$$

$$\text{Na} - \text{Cl}: R = 2.365 \text{ \AA}, \mu = 9.00 \text{ D} \rightarrow \delta = 0.79 \quad (Q = 0.79 e)$$

Note: A higher EN difference leads to a more ionic bond, i.e., higher δ , i.e., large μ .

Lewis Dot Structures

We can explain and predict the bonding in all 3 types of molecules using Lewis dot structures. Works only for main group elements (and even then there are exceptions as we'll see for O₂ later); does not work for bonding with d valence electrons.

Rules for Lewis Structures

- 1) Arrange atoms so that monovalent atoms (e.g., H, Alkali, Halogens) surround a central atom, which is usually (not always) the least EN atom.

Specifically:

valency = # of covalent bonds that can form per atom
= # of unpaired e's in highest shell:

Monovalent:	H, alkali, halogens
Divalent:	Be, alkaline earth, chalcogens (O, S, etc.)
Trivalent:	B, N, etc.
Tetravalent:	C, Si, etc.

- 2) Use pairs of valence e's to form single bonds between neighboring atoms, and try to satisfy the octet rule by sharing e pairs.

Octet rule: p-block elements want 8 e's like a noble gas, H wants two e's (to be like He). Alkali and Alkali-earth metals prefer to shed their electrons.

So:

of shared e's = $\frac{1}{2}$ (2* # H atoms + 8* # p block atoms - # e's available)

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Noble-gas fantasy	reality

e's which are not shared and stay on their original atoms are called **lone pairs** (more precisely, a lone pair can accommodate 2 electrons).

- 3) Share the # of pairs from the above equation (so that each atom has at least one pair connecting it to the molecule) and then place lone pairs on atoms that need them to satisfy the octet rule. To do that count the # of electrons around each atom.

And of course double check that the total # of electrons is the # of valence electrons available.

Molecules are stable if they

- a) Satisfy the octet rule for all (or at least most) atoms, and
- b) They have the least possible charge separation.

We check the charge separation by calculating formal charges

Formal charge = # of e's gained of lost in the Lewis structure compared with a neutral atom.

For purposes of counting formal charge, only one electron in each covalent bond pair counts.

1st Example:

CO₂ Total # of valence e's = 4+6-6=16

1) C is least electronegative, and therefore is the central atom

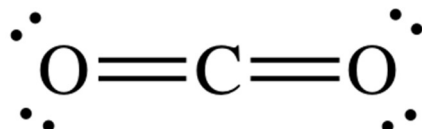
2) # of shared e's = 8 * 3 - 16 = 24-16=8

Octet rule * 3 atoms - # valence e's

So: # of shared pairs = 8/2 = 4



i.e.,



Double check: total # of dots = 16 = # of valence e's, and everybody satisfies the octet rule

Check formal charge: C: has 4, originally 4 → formal charge 0. Good.

O: has 6, originally 6 → formal charge 0. Good.

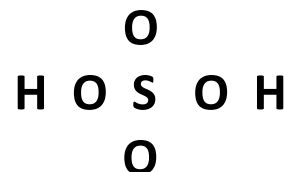
So this is the only possible structure. I.e., there's no resonance.

Resonance structures

Sometimes there's more than one way to satisfy the rules. Usually by distributing formal charges differently. These structures are called resonance structures, and we'll now exemplify them:

2nd example: H₂SO₄.

Should have S in the middle, O outside. H's usually outside of the most EN atom, in this case O, i.e., the structure should be something like:

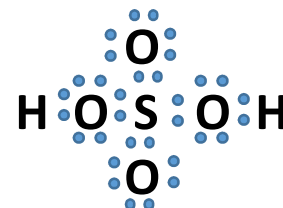


Now put in the electrons.

Total # of valence e's = $2 \cdot 1 + 6 + 4 \cdot 6 = 32$

shared e-pairs = $\frac{1}{2} \cdot (2 \cdot 2 + 5 \cdot 8 - 32) = \frac{1}{2} \cdot 12 = 6$.

So 1st possibility: 6 single bonds & for O's add 4 e's to each O, for the octet rule.



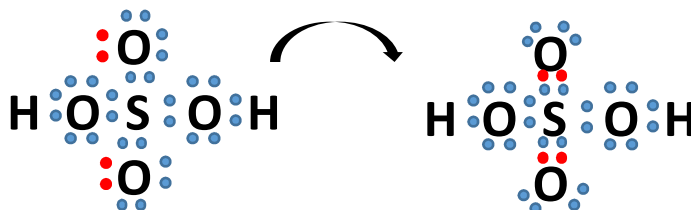
Now we should in principle now count all the e's, to ensure we have 32 e's; that's painstaking, so as a shortcut we can just **calculate that the sum of formal charges is the overall charge of the molecule, i.e., zero.** Clearly:

- Formal charge(H) = $1 - \frac{1}{2} \cdot 2 = 0$;
- Formal charge(S) = $6 - \frac{1}{2} \cdot 8 = +2$;
- Formal charge(O bonded to H) = $6 - (\frac{1}{2} \cdot 4 + 4) = 0$
- Formal charge (lone O) = $6 - (\frac{1}{2} \cdot 2 + 6) = -1$

So overall the total formal charge is $+2 - 1 - 1 = 0$. Works.

While the total # of electrons is correct, there's a problem – the formal charge of three atoms isn't zero. And molecules like minimum formal charge on each atom.

We can remedy by violating the octet rule. I.e., move from each of the lone-O a pair of electrons (**red below**), to change the single-bond with S to a double bond.

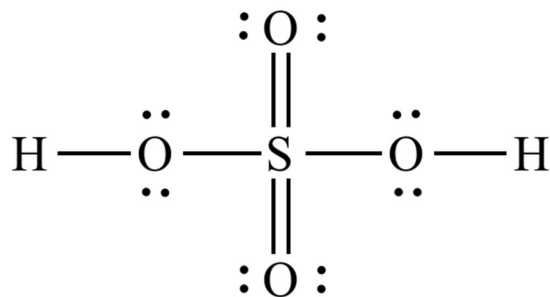


The right structure has 0 formal charges on all atoms, but the octet rule is violated for S!

I.e., both structures violate something – either the octet rule is violated or the formal charges are non-zero.

So officially we'll have here a resonance structure between the right and left structure (and actually two more intermediate structures). **But in practice having zero formal charges is in this case much more important, so the structure on the right in the figure above is the dominant one**, and we usually don't worry about the one on the left.

Finally, we can write the final structure (on the right above) with bonds as¹³



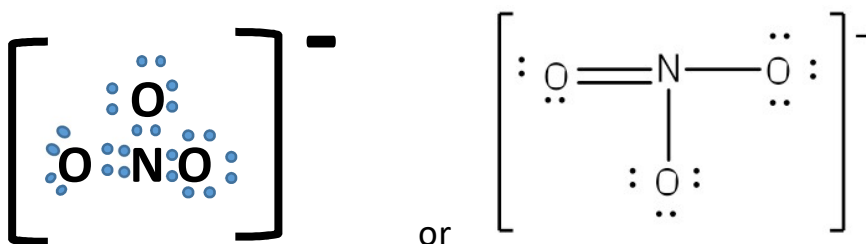
¹³ From the website of a UCLA colleague, http://www.chem.ucla.edu/~harding/IGOC/S/sulfuric_acid.html

3. Another example: NO_3^-

$$\# \text{ valence e's : } 5 \cdot 1(\text{N}) + 3 \cdot 6(\text{O}) + 1 (\text{neg. ion}) = 24$$

$$\# \text{ shared pairs: } \frac{1}{2} * (4 \times 8 - 24) = 4$$

N is the most electropositive atom here, so the structure, dots and bonds are:

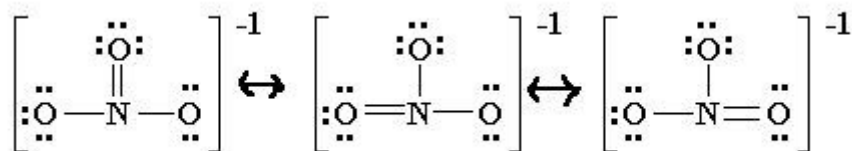


Again, to verify we have put the right number of orbitals, calculate the formal charge on each:

- Formal charge(O with double bond) = $6 - (4 + 4/2) = 0$;
- Formal charge(each O with single bond) = $6 - (6 + \frac{1}{2} * 2) = -1$,
- Formal charge(N) = $5 - \frac{1}{2} * (2 + 2 + 4) = +1$

So the sum of the formal charge = $-1 -1 +1 = -1$, the same as the true total charge.
So our counting of Lewis dot is correct.

There are actually not one but three resonance structures:¹⁴



All 3 contribute equally, so all N-O bonds are of the same length!

¹⁴ Picture taken from: <https://apchemrev.wikispaces.com/Valence+Bond+Theory+-orbitals%3B+resonance%3B+sigma+and+pi+bonds>

VESPR—Valence Shell Electron Pair Repulsion Theory

Basic idea is that electron pairs repel each other. We worry about lone and binding pairs because the Pauli principle says that 2 e's with the same spin cannot occupy the same region of space (orbital).

Thus, e-pairs around a central atom will stay as far apart as possible. The geometry of the molecule is determined by the positions of the bonding pairs.

So the VESPR algorithm is:

- I. Draw Lewis structure
- II. Count the # of electron pairs around the central (least EN) atom. This is called the steric number. The e-pairs will arrange themselves to be as far apart as possible. See list and graph¹⁵

Steric #: Arrangement Angle

2 linear 180°

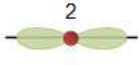


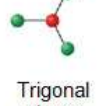
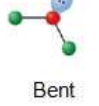
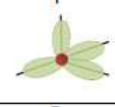
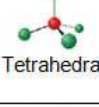
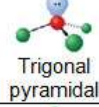
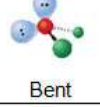

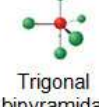
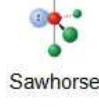
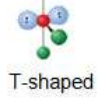
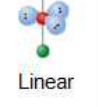
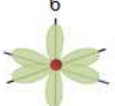

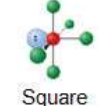
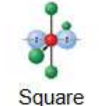
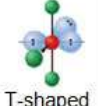
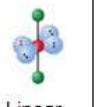
3 trigonal planar 120°

4 tetrahedral 109.5°

5 trigonal-bipyramid
3@120°, 2@90°

Steric #'s 5 & 6 violate octet rule

6 octahedral 90°

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2 	Linear	 Linear				
3 	Trigonal planar	 Trigonal planar	 Bent			
4 	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5 	Trigonal bipyramidal	 Trigonal bipyramidal	 Sawhorse	 T-shaped	 Linear	
6 	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear

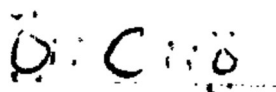
¹⁵ From <https://www.texasgateway.org/resource/valence-shell-electron-pair-repulsion>

III. Distinguish between bonding pairs and line pairs to determine the structures.

Examples:

2 e-pairs:

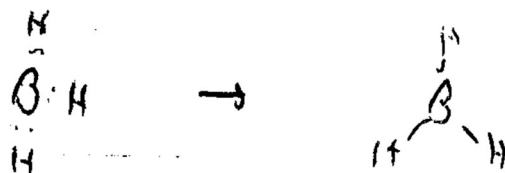
molecule is linear.



3 e-pairs ($3 \cdot 1 + 3 = 6$ e's

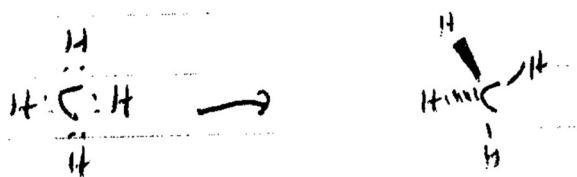
(e's mean here valence e's):

Trigonal bipyramid

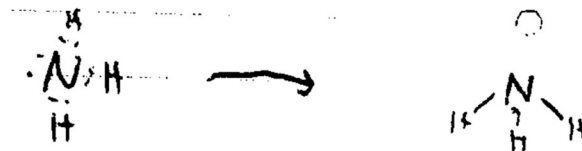


4 e-pairs:

($4 \cdot 1 + 4 = 8$ valence e's): tetrahedral



($3 \cdot 1 + 5 = 8$ valence e's): pyramidal



($2 \cdot 1 + 6 = 8$ valence e's): bent



Reinforcement to model: lone pairs take up more space than bonding pairs.

LP-LP repulsion > LP-BP repulsion > BP-BP repulsion

The larger LP-LP repulsion can cause bond angles decrease.

Example: H-C-H angle in methane = 109.5°

H-N-H angle in ammonia (NH_3) = 107°

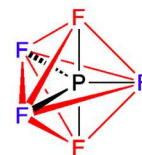
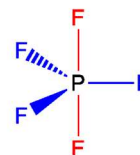
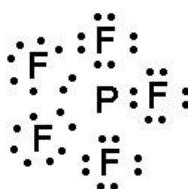
H-O-H angle in H_2O = 104°

Back to the examples:

5 e-pairs:

PF_5 : $7 \cdot 5 + 5 = 40$ e's,¹⁶

Trigonal bipyramid.



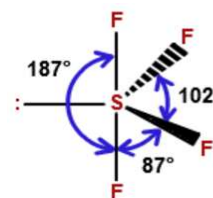
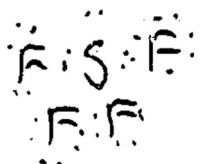
Axial F atoms are in a different environment to the equatorial F atoms

The red lines outline a trigonal bipyramid. Black lines show the covalent bonds

(note that the octet rule is violated for P, and for the central atoms in the molecules below)

SF_4 : $7 \cdot 4 + 6 = 34$ e's¹⁷ . 1LP

See-saw (i.e., a trigonal-bipyramid where we don't see one of the arms, a lone pair).

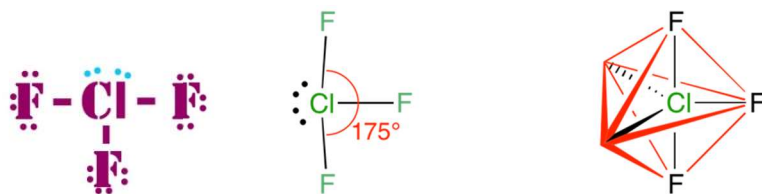


¹⁶ Images from <http://myweb.astate.edu/mdraganj/LewisDotanswers.html> and <http://www.chemtube3d.com/VSEPRShapePF5.html>

¹⁷ Image from: <http://chemistry.tutorvista.com/inorganic-chemistry/molecular-geometry.html>

ClF₃: $7 \times 4 = 28$ e's¹⁸. T-shaped. 2 LP.

Note that the lone pairs repel the bonding pairs, as in SF₄; here therefore the FClF axis is bent.

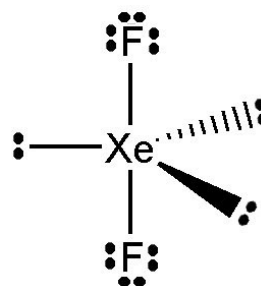


The F-Cl-F angle involving the axial F atoms is 175°

The red lines outline a trigonal bipyramid. Black lines show the electron pairs

XeF₂: $8 + 7 \times 2 = 22$ e's.¹⁹ 3 LP. Linear.

(Count here: 2+2+2+6+6 lone e's, 3 pairs*2 per single bond, total 22)



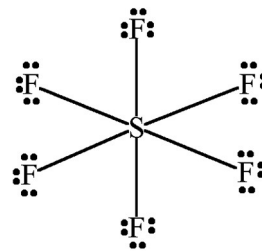
¹⁸ Images from <http://www.biochemhelp.com/lewis-structure-of-clf3.html> and <http://www.chemtube3d.com/VSEPRShapeClF3.html>

¹⁹ Image from <https://socratic.org/questions/does-the-vsepr-theory-predict-that-xef2-is-linear>

6 e-pairs:

SF₆ : octahedral.

7*6+6=48 e's; 6*6 lone e's +6*2(in bonds)=48, count is correct.

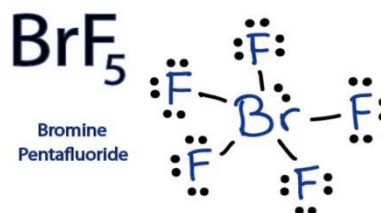


BrF₅: square pyramidal

6*7=42 e's;

5*6 lone + 5*2 (from pairs) =42, count is correct.

(structure is "squished" by lone pair, seesaw.)



XeF₄: square planar. Exercise – prove that it has the right number of e's, and outline the structure and lone pairs.

To summarize VESPR:

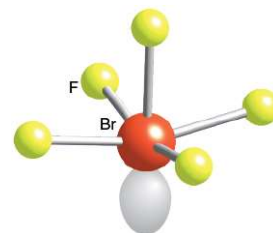
VESPR shows that molecular structure is very rich, even for the same number of atoms, depending on the number of LP (lone pairs), BP (bonding pairs) and their sum SN(Steric Number) = LP + BP.

- Triatomics can be:
 - Linear (BP=2,LP=0→SN=2) or (BP=2,LP=3→SN=5) or (BP=2,LP=4→SN=6)
 - Bent@120° (BP=2,LP=1→SN=3)
 - Bent@109.5° (BP=2,LP=2→SN=4)
- Tetratomics can be:
 - Trigonal planar (BP=3,LP=0→SN=3)
 - Trigonal pyramid (BP=3,LP=1→SN=4)
 - T-shaped (BP=3,LP=2→SN=5) or (BP=3,LP=3→SN=6)
- Penta-atomics can be:
 - Tetrahedral (BP=4,LP=0→SN=4)
 - Seesaw (BP=4,LP=1→SN=5)
 - Square planar (BP=4,LP=2→SN=6)
- Hexa-atomics (hexa means 6) can be:
 - Trigonal-bipyramid (BP=5,LP=0→SN=5)
 - Square-bipyramid (BP=5,LP=1→SN=6)
- Hepta-atomics (hepta means 7) will be
 - Octahedral (BP=6,LP=0→SN=6)

Molecular dipole moments

Figure out the overall molecular dipole moment

as if each bond has a charge, and then add each of them vectorially.
(TA's may discuss this in more detail in the sections).



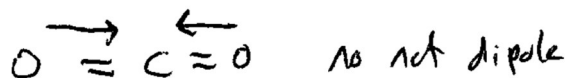
Recall from our discussion a few lessons ago that a dipole can be thought of as the extra charge ($Q = e \delta$, and δ is a dimensionless number) on one atom and the opposite on another, separated by the bond distance. The value of the dipole is

$$\mu = \frac{R \delta}{0.2082}$$

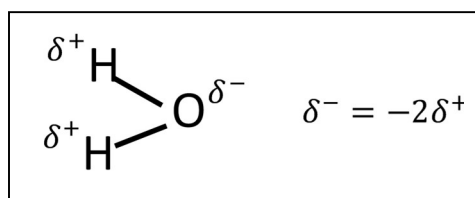
And its direction is along the bond. When there is more than one bond, we need to **vectorially add the bond dipoles to create the molecular dipole**

Practice makes perfect, so let's exemplify (without #'s for now).

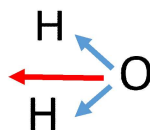
- CO_2 :



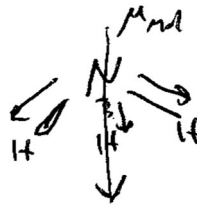
- Water: Recall the picture we had,



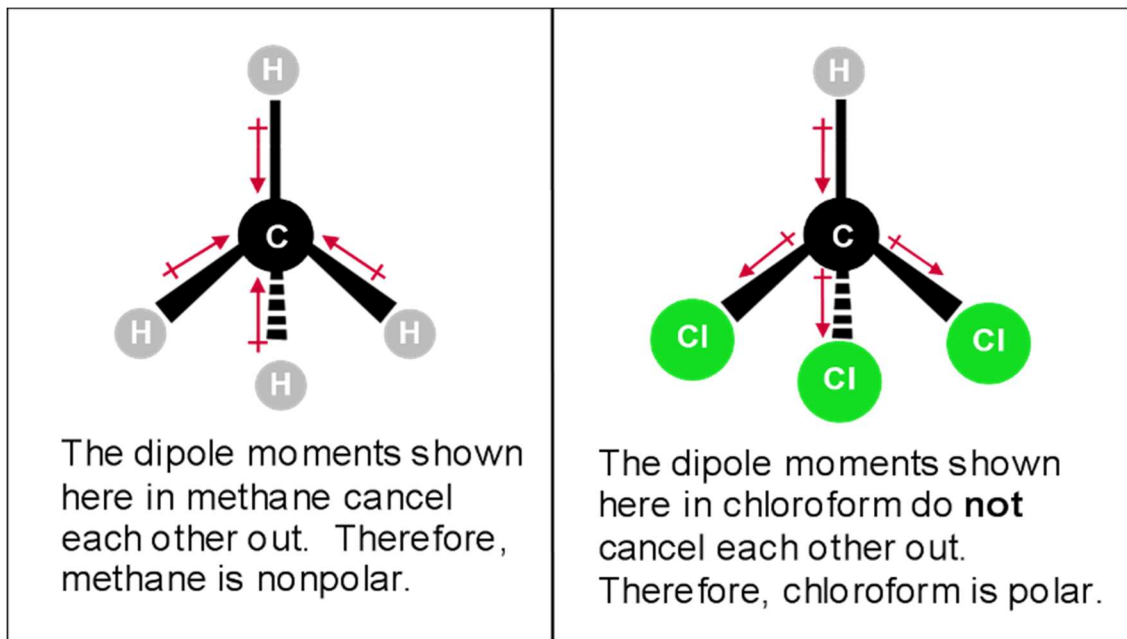
That meant that there were two **bond dipole**, reproduced in blue below. The vector sum of these bond dipole gives the total **molecular dipole**, in red below,



- Similarly, the dipole in ammonia will be



- Similarly, methane will have no dipole moment, the bond dipoles will cancel each other; but similar substituted compounds will have if they are not totally symmetric, such as chloroform (CHCl_3)²⁰

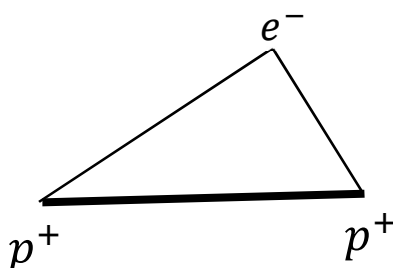


²⁰ Image taken from http://lorpub.gadoe.org/State%20of%20Georgia/GAVS%20Shared/Science/APChem_Bonding_Shared/APChem_Bonding_Shared_print.html

Molecular Orbitals

Heart and core of course!

Now that we have our empirical “rules” to determine molecular shapes, let’s see how they work quantum mechanically. Start with H_2^+



The electron (e^-) is attracted to both protons, and the two protons repel.

If the electron stays between the 2 protons, the attraction of it to each of the two protons will be much stronger than the repulsion of the two protons. Thus the electron, **if it is between the protons, then the electron acts as a “glue” to hold the two protons together.**²¹



But if the electron spends most of its time outside the two protons, it will not force them to be together.

But of course the electron is not a localized particle, but is rather a standing wave. So we will talk about **molecular orbitals** – just like **AO’s (atomic orbitals)**, but **no longer have spherical symmetry**.

We’ll distinguish three types of MO’s:

- **Bonding MO’s:** MO’s in which the electron has a large probability to be found between the MO’s. Each molecule needs to have a sufficient number of bonding MO’s to keep itself together.

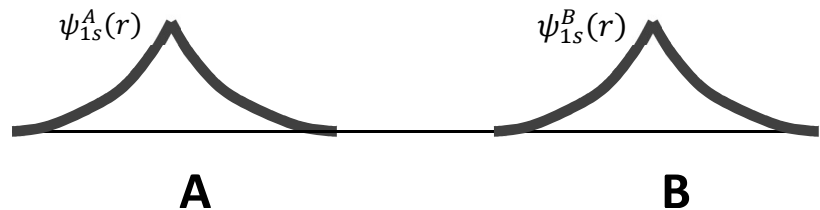
²¹ Image from https://www.123rf.com/stock-photo/weight_lifting_cartoon.html

- **Antibonding MO's** : MO's with a node between the nuclei. Those MOs will not tend to make the electrons come together, and if anything will tend to keep them apart. We'll denote such MO's with an asterisk, * .
- **Nonbonding MO's** : There are actually also non-bonding MO's that don't care one way or another, and don't tend to strengthen or weaken to molecule in those orbital the MO. In these MO the density of the MO looks almost the same as that of the individual atom.

The LCAO approximation

Mathematically we will assume that MOs can be written as a sum of AOs from each atom: this is the LCAO (Linear Combination of Atomic Orbitals) approximation.

When the A-B distance (R) $\rightarrow \infty$, i.e., two separate atoms, each proton holds its own electron:



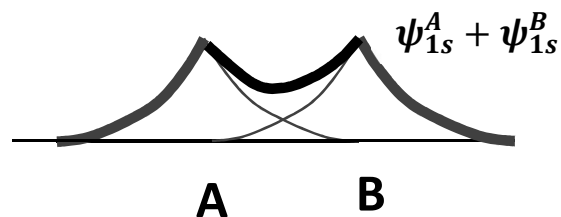
And pictorially,



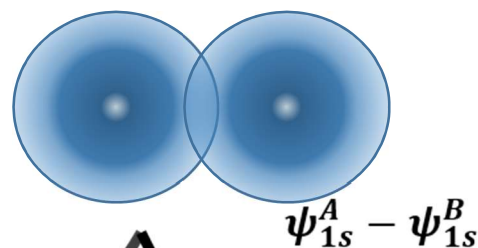
But when the two nuclei get **closer together**, we'll get **overlap (constructive interference)** between the 1s orbitals:

We'll call this a σ_{1s} orbital

$$\sigma_{1s}^{(H_2^+)} = A[\psi_{1s}^A + \psi_{1s}^B]$$

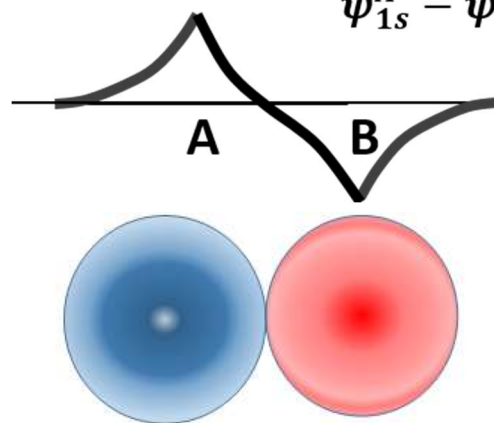


Where A is a normalization constant A is chosen to ensure a unit probability to find the electron, if it is in the MO, when we look over all space.



Of course we could have added the wave **destructively**, i.e., out of phase, leading here to an **antibonding orbital**:

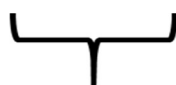
$$\sigma_{1s}^{*(H_2^+)} = A' [\psi_{1s}^A - \psi_{1s}^B]$$



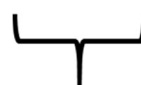
The probability to find the electron is given by $|\psi|^2$

$$|\sigma_{1s}|^2 = |N|^2 [|\psi_{1s}^A|^2 + |\psi_{1s}^B|^2 + 2\psi_{1s}^A\psi_{1s}^B]$$

$$|\sigma_{1s}^*|^2 = |N'|^2 [|\psi_{1s}^A|^2 + |\psi_{1s}^B|^2 - 2\psi_{1s}^A\psi_{1s}^B]$$



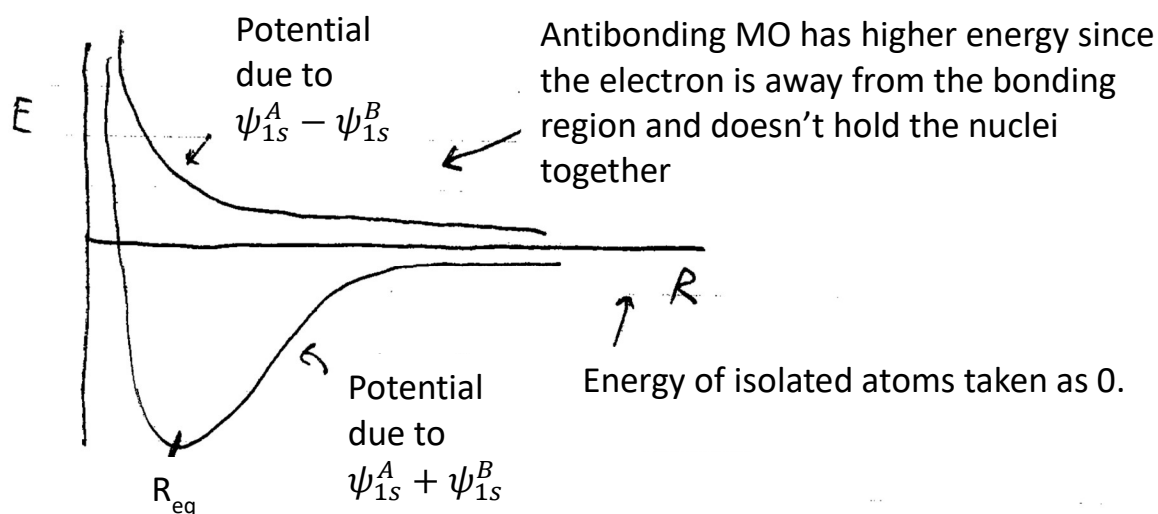
Prob. as if e^- was on different atoms



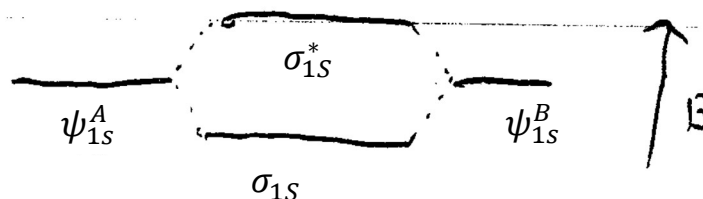
Interference resulting from AO overlap

If the interference term is ~ 0 (or if it sums up to close to 0, i.e., in some regions of space it is positive, and in some negative, and the positive and negative cancel each other) then the orbital is non-bonding

Potential energy surface due to bonding and antibonding orbitals:



Assuming we're at R_{eq} , a shorthand notation for this idea is:



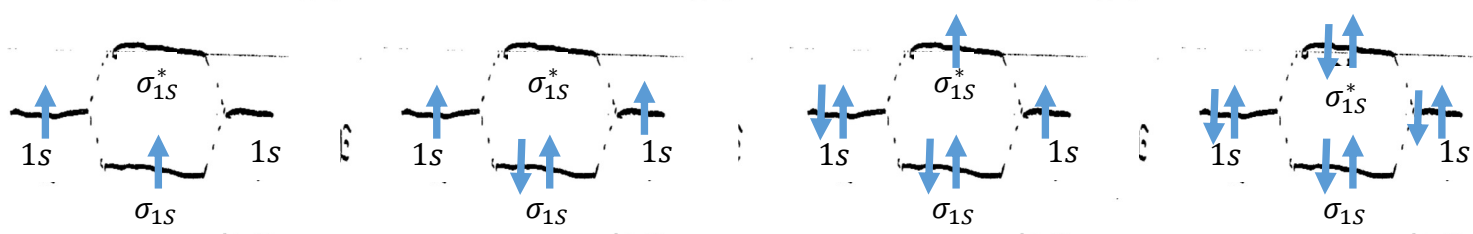
We can prove rigorously that the number of distinct MO's we can make by LCAO is the same as the number of AO's being added.

Now we can construct a theory for diatomic molecules

- 1) Construct LCAO-MO's for all occupied AOs. For N total AOs, we expect to get N total MOs
- 2) Construct the energy level diagram (assuming the molecule is at R_{eq}).
- 3) Using the ideas of the Aufbau principle and Pauli exclusion, predict the
 - molecular electron configuration,
 - bond order
 - paramagnetism
 - relative bond lengths,
 - etc.

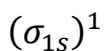
$$\text{Bond-Order} = \frac{1}{2} (\# \text{ of e's in bonding MO's} - \# \text{ of e's in antibonding MO's}).$$

The first 4 homonuclear diatomics are simple:



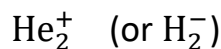
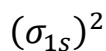
Paramagnetic

$$\text{B.O.} = \frac{1}{2}$$



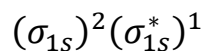
Diamagnetic

$$\text{B.O.} = 1$$



Paramagnetic

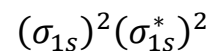
$$\text{B.O.} = \frac{1}{2}$$



Diamagnetic

$$\text{B.O.} = 0$$

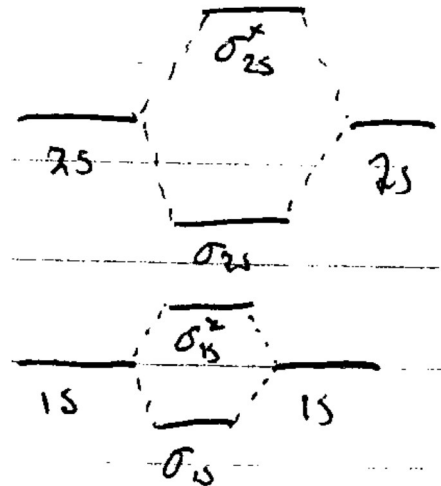
(extremely weakly bonded)



2S orbitals

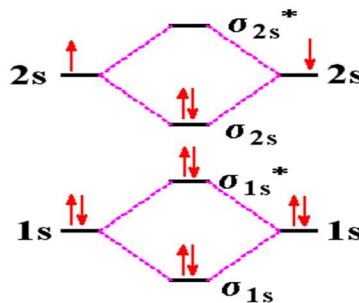
What about atoms with 2s orbitals, like Li or Be?

The overlap of two 2s orbitals looks qualitatively like those of 1s orbitals, but we get more interference (since in a given atom the 2s orbitals are bigger and more spread out than the 1s orbitals in these orbitals, which are more compact), see picture below



Example:²² Li₂ (dilithium)

Lithium, Li₂



$$\text{Bond Order} = \frac{4 - 2}{2} = 1$$

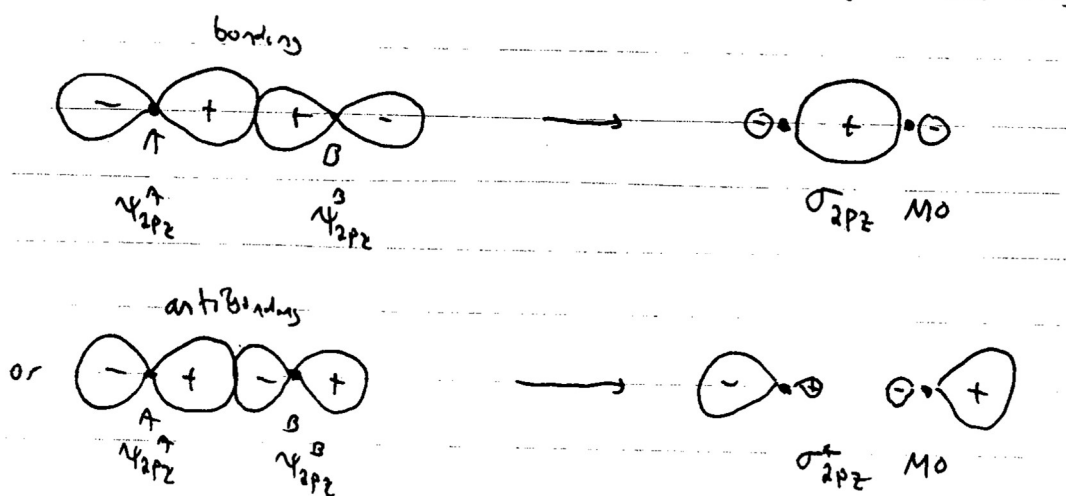
Diamagnetic. Molecule exists (same name used in Star Trek for a fictional substance...)

²² Image taken from: http://people.uwplatt.edu/~sundin/114/l114_32.htm

Diatomic molecules with 2p electrons.

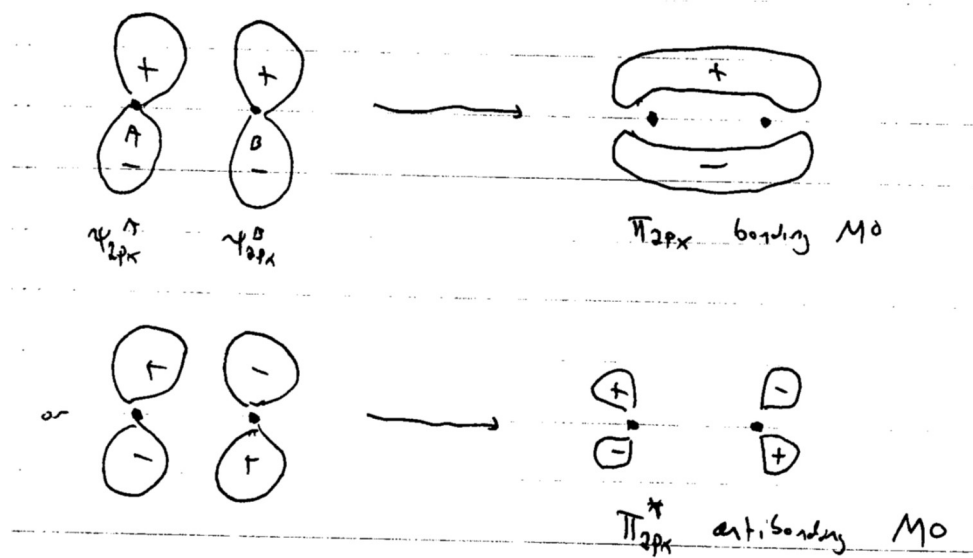
What happens when we get to a molecule with 2p e's? Now we have **choices of how to add the orbitals** since they are not spherically symmetric.

First, add or subtract the orbitals **along the axis connecting the atoms** (recall that we call it the "z" axis):



Note that just like the $\sigma_{2s}, \sigma_{2s}^*$ these $\sigma_{2p_z}, \sigma_{2p_z}^*$ orbitals do not have any angular nodes, i.e., if we rotate them around the axis they look the same.

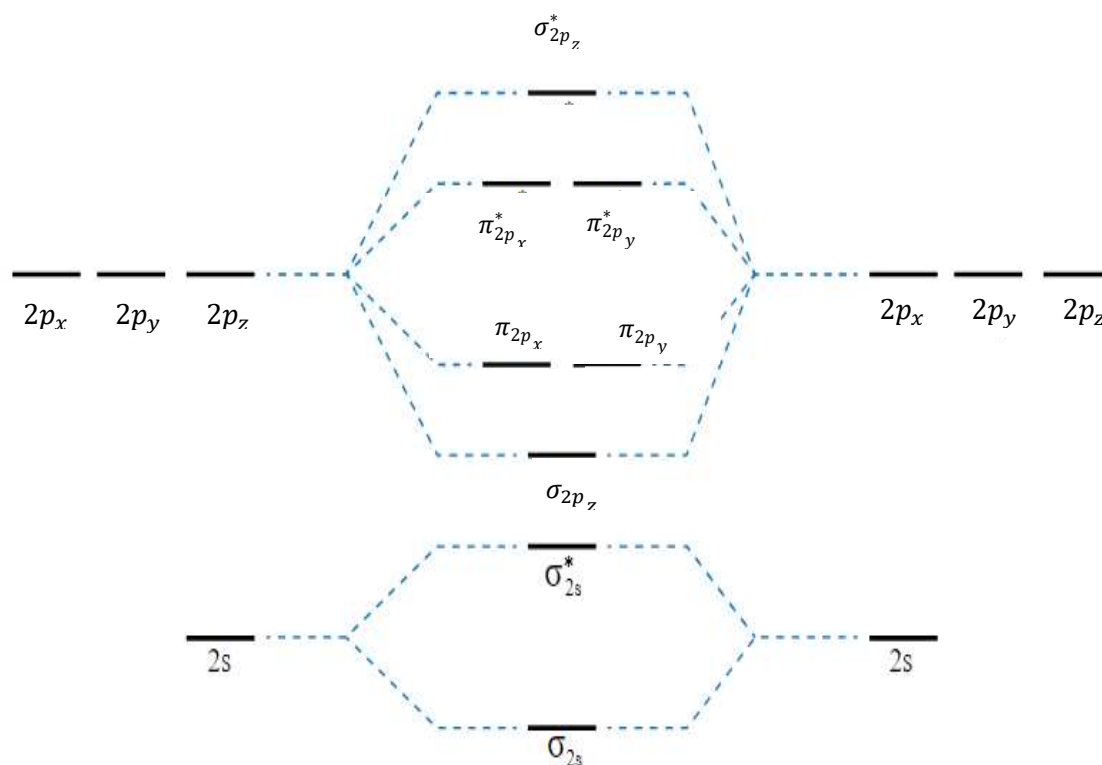
However, there's another way to add the 2p orbitals. For example, add the $2p_x$ orbitals:



Here, π denotes a nodal plane containing the internuclear axis, i.e., the z-axis here. (BTW, a Δ orbital would be an orbital with 2 nodal planes that contain the internuclear axis). The * in this case (i.e., in $\pi_{2p_x}^*$) denotes a nodal plane between the nuclei, i.e., perpendicular to the nuclear axis.

Note that we clearly get the exact same picture, rotated by 90 degrees, if we use p_y orbitals – i.e., the π_{2p_x} and the π_{2p_y} orbitals are **degenerate** (i.e., have the same energy). Similarly of course for $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ which are also degenerate.

Clearly, the σ molecular orbitals (MOs) have better overlap than π MOs. Thus, they are more bonding & antibonding. This gives a **homonuclear diatomic energy level diagram** like²³



Molecular orbital diagram for O_2 , F_2 Ne_2

Exercise: work out on your own: What is the electron configuration of F_2 ; Show that the bond order of F_2 is 1; and that F_2 is diamagnetic.

²³ Taken from <https://ch301.cm.utexas.edu/section2.php?target=imfs/mo/secondrow-diatomic-mos.html>

Unfortunately, this picture does not work for B_2 , C_2 or N_2 .

Why not?

- From our picture of σ_{2p_z} and σ_{2s} orbitals, we know that both have high electron density between the nucleus.
- Usually being between the nuclei is good, since an electron feels more attraction when it is between the nuclei.
- But for these molecules we have a problem. **There are already a lot of electron between the nuclei** (especially electrons in the σ_{2s} , σ_{2s}^* orbitals).
- The Pauli principle tells us that **being in a region of space where there are many other electrons** is energetically unfavorable; therefore σ_{2p_z} rises above π_{2p_x} and π_{2p_y} , as the latter are in different region of space (**orange arrow below**)

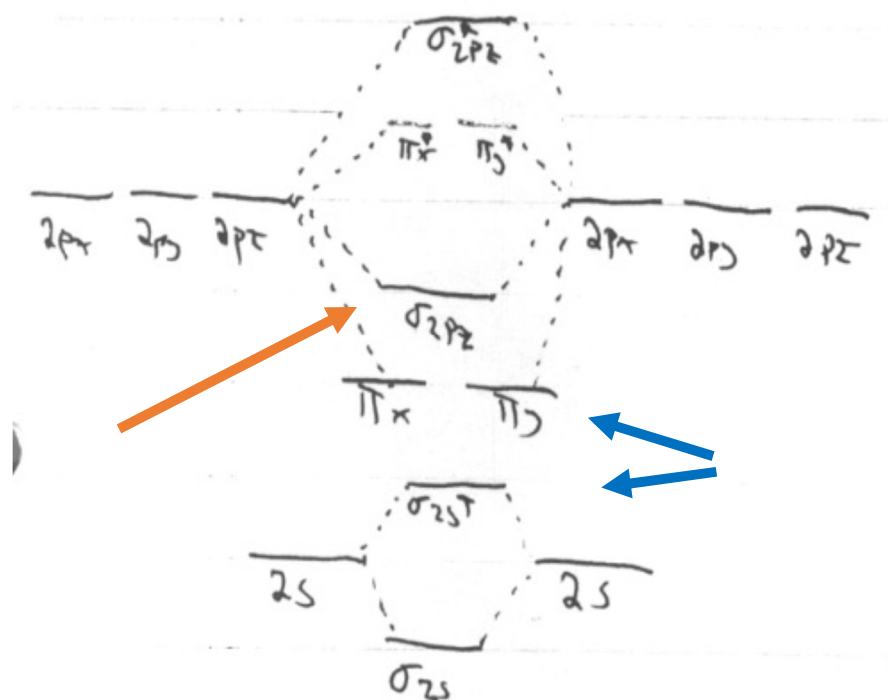


Diagram for Li_2 through N_2

Note: The situation is **even more complicated than the diagram above shows**. As we move across the row, Z_{eff} rises faster for s orbitals than for p orbitals (the latter are better shielded and they do not penetrate the region near the nucleus). Thus,

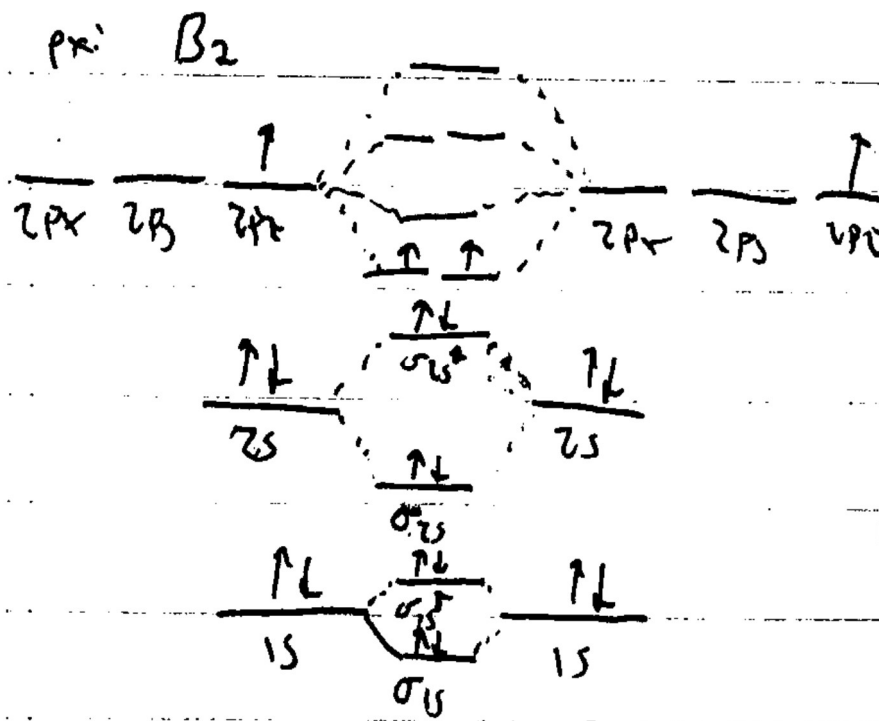
the s orbitals are more compact (each is more compact near its nucleus and extends less into the internuclear region). Therefore, the p orbitals, with their high overlap, lead to a strongly bonding π orbitals, that extend to the region of the σ_{2s}^* orbitals. Thus, **the order of the orbitals denoted by blue in the diagram above can be inverted**. To understand bonding up to N_2 we really have to mix the s and p orbitals, and we'll touch on that soon in a different context.

- **Luckily, all these complications almost disappear by the time we get to O_2 and F_2 .** In these molecules the 2s orbitals are so deep that they do not influence the diagram (i.e., we don't have to worry about the blue arrows getting close in the diagram above). As these 2s orbitals are so deep they don't influence the σ_{2p_z} orbital too much and they don't push it up. Together, we stay with the diagram we saw 2 pages ago, i.e., in O_2 and beyond the bonding σ_{2p_z} orbital is lower than the bonding π_x and π_y ones.

Examples:

B₂ is paramagnetic, has B.O.=1 and electron configuration (we denote π_x instead of π_{2p_x}):

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_x)^1(\pi_y)^1$$

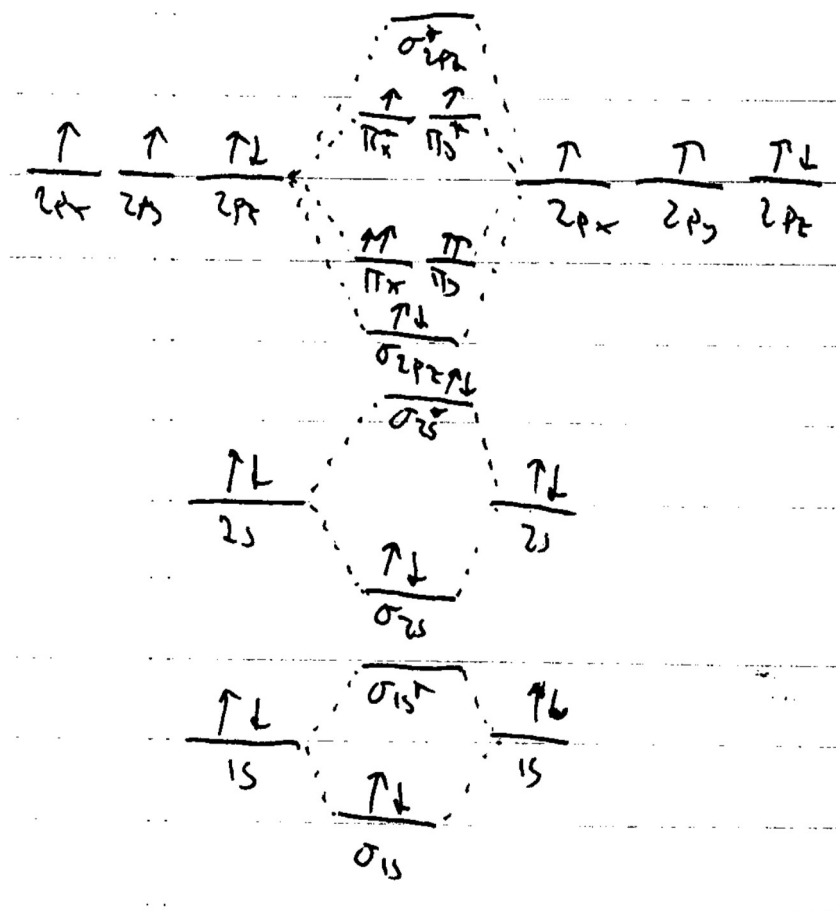


We can do the same thing for **N₂**:

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_x)^2(\pi_y)^2(\sigma_{2p_z})^2$$

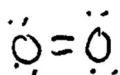
With a B.O.=3, and no unpaired e's, just like the Lewis dot structure :N ≡ N:

What about O_2 ? Here we need the previous diagram



The M.O. diagram shows B.O.=2, just like the Lewis dot diagram. **But O_2 is paramagnetic as it has two unpaired electrons!**

And that's something that a Lewis diagram does not show us:



So the prediction of paramagnetism for O_2 is a victory for the M.O. picture!

Polyatomic MO's and Hybridization

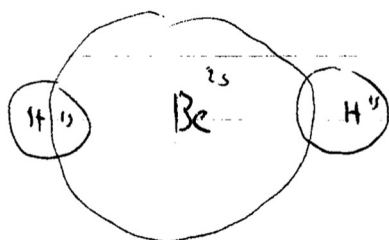
In our study of polyatomics we found that there are two basic types of MO's: σ MOs formed by the LCAO of either s and p_z orbitals, and π MOs, formed by the LCAO of p_x or p_y orbitals.

What happens when we have 3 or more atoms?

To a first approximation, we assume that each bond behaves as if it were in a diatomic, though the approximation will fail for molecules like benzene, where e's are delocalized over more than 2 atoms.

We'll start with one of the simplest triatomics: BeH_2

We know from VSEPR that this is a linear molecule. Thus, we might expect that the MOs look like:

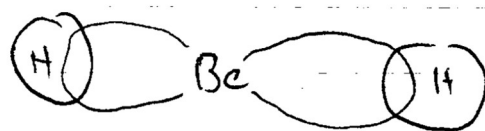


Note that in this picture only valence e's participate in the bonding.

1 electron from 1s on each H, and each of the two Be 2s e's

The problem is that we don't get much overlap between the orbitals (Be 2s and H 1s). Further, we have **4 electrons, they can't fit in this single orbital** (one spatial orbital can accommodate 2 electrons).

What if we use the $2p_z$ on the Be instead?

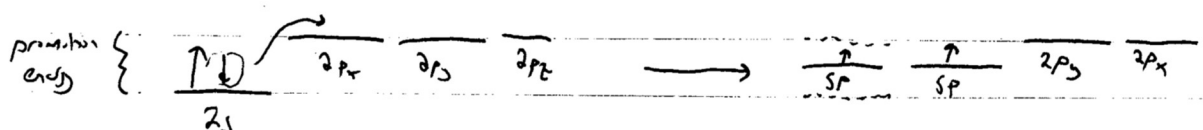


We can make much better overlap since the electron density in $2p_z$ is farther from the nucleus than the in 2s.

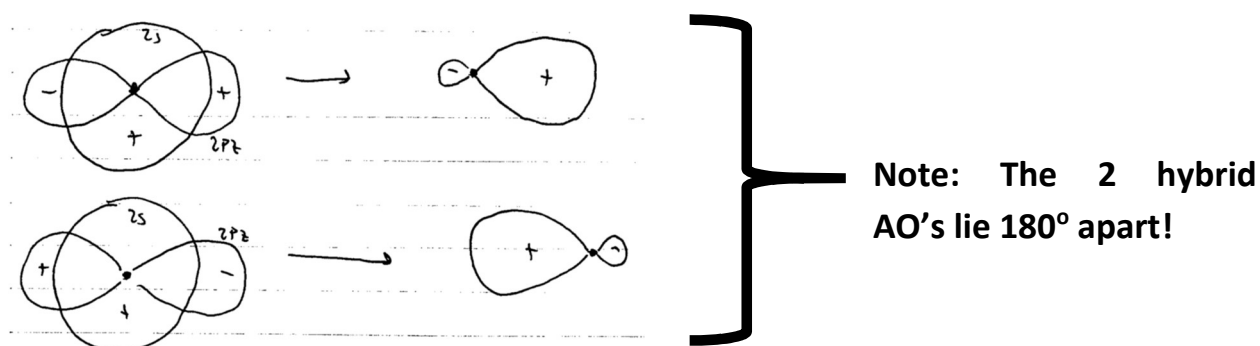
But problem: there are no e's in $2p_z$ in Be! I.e., there's an energy price to pay to put the electron in the $2p_z$ in Be!

This energy price is called the promotion energy

What actually happens is that **the $2s$ and $2p_z$ orbitals mix, or "hybridize", to minimize the promotion energy while maximizing the bond overlap.**

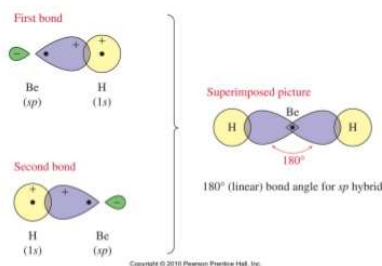


What do these hybrid AO's look like?



Now we can form MOs from Linear Combinations (LCs) of hybridized orbitals.²⁴

The Bonding of BeH_2



- The bond angle in BeH_2 is 180° and the geometry is linear.

Chapter 2

15

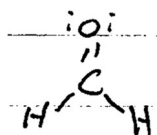
²⁴ From: <https://image.slidesharecdn.com/02-structureandpropertiesoforganicmolecules-wade7th-140409015631-phpapp01/95/02-structure-and-properties-of-organic-molecules-wade-7th-15-638.jpg?cb=1397008615>

This mixing of one s and one p orbital on an atom to form two opposing orbitals is called **sp hybridization**.

We could also consider

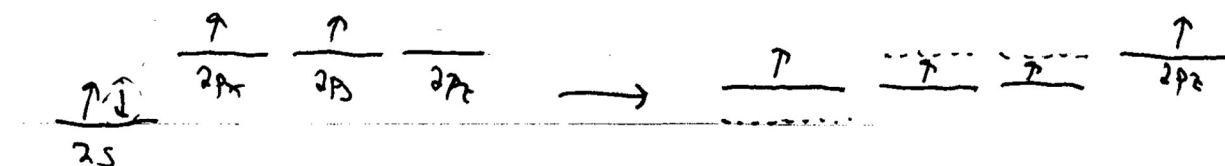
sp² hybridization:

Happens when we mix the one 2s orbital with **two** 2p orbitals to get three equivalent sp₂ orbitals that are trigonal planar:



Example: formaldehyde, H₂CO

From VSEPR, we know the molecule is trigonal planar. So we expect C to be sp² hybridized.

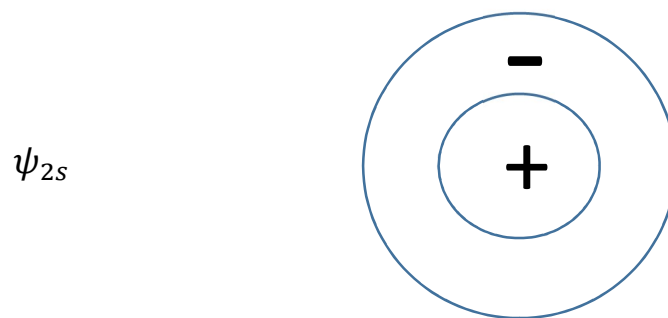


How do we mix three orbitals? Well the results depend on the **signs and magnitude we give to each orbital**.

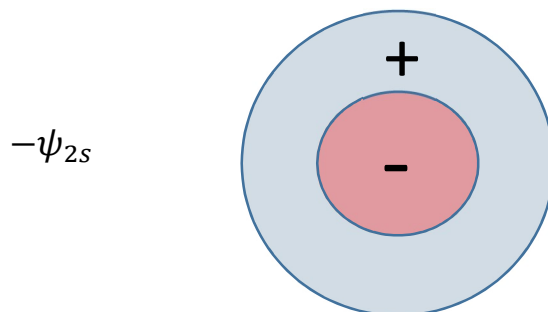
Let's, for simplicity, add the orbital graphically **giving the same weight to each orbital, i.e., to 2s and 2p_x and to 2p_y**

What do I mean add?

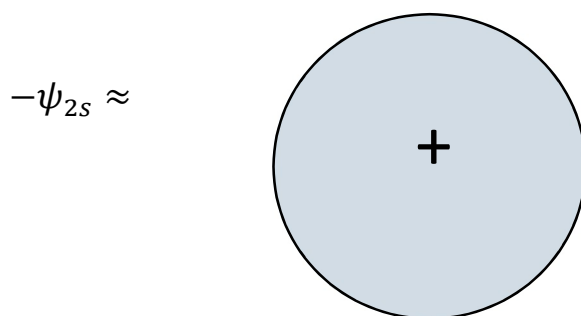
Let's start with 2s. It really looks like



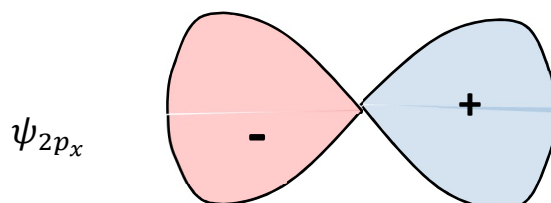
Let's reverse its sign (that will not change the orbital) and give color, so when the orbital is positive it is blue and when negative red.



Now let's forget about the inner core, i.e., look at $-\psi_{2s}$ as if it was a ψ_{1s} orbital. That's OK since we're interested in the outer part of the orbital mostly.

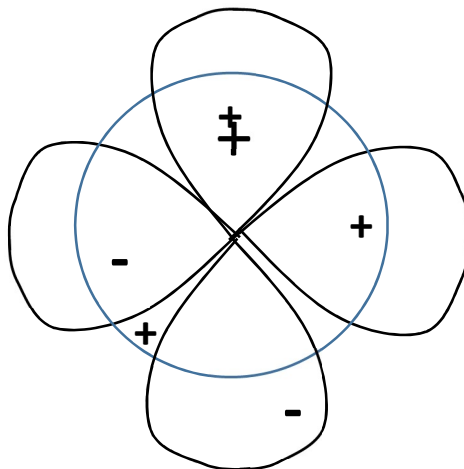


Now let's consider the $2p_x$ orbital



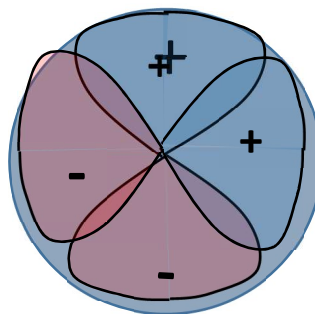
And similarly there's the $2p_x$ orbital. Let's then add the three orbitals

$$\frac{-\psi_{2s} + \psi_{2p_x} + \psi_{2p_z}}{\sqrt{3}} \approx$$

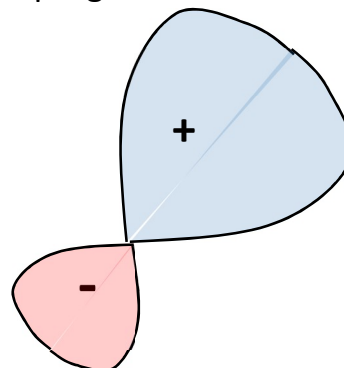


This diagram may be confusing, so remember – we are adding three orbitals that are **all on the same atom**.. Clearly there will be completely constructive interference (i.e., where all orbitals have the same sign, i.e., all positive or all negative) only in the top right corner. This can also be visualized, perhaps more easily, in color

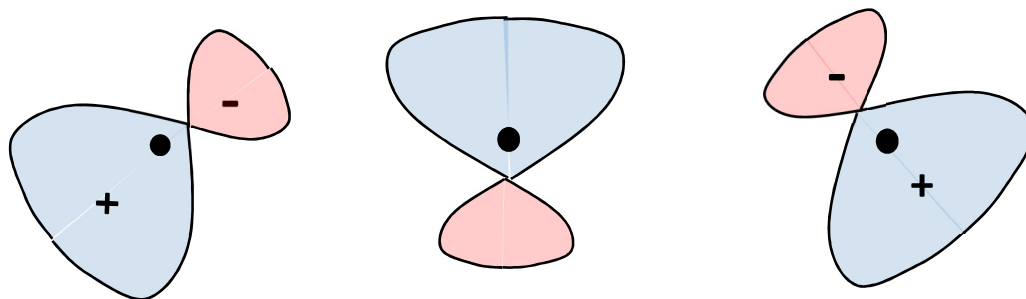
$$\frac{-\psi_{2s} + \psi_{2p_x} + \psi_{2p_z}}{\sqrt{3}} \approx$$



You see again completely constructive interference (all colors the same) only in the top right. The emerging hybrid orbital points indeed top-right



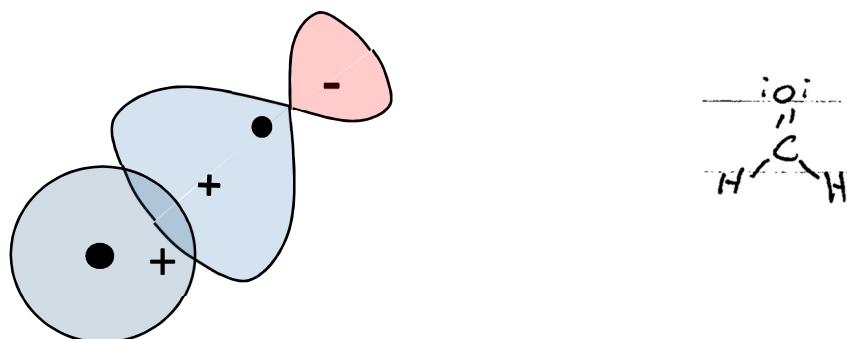
And when we do the calculations, it turns out we can make three such independent orbitals (mathematically it means that they are “orthogonal”, i.e., are totally separate orbitals, so if two electrons are in one of these orbitals, for example, the Pauli principle will still allow us to put electrons in the other ones)



(The black dot indicates the C nucleus in all cases).

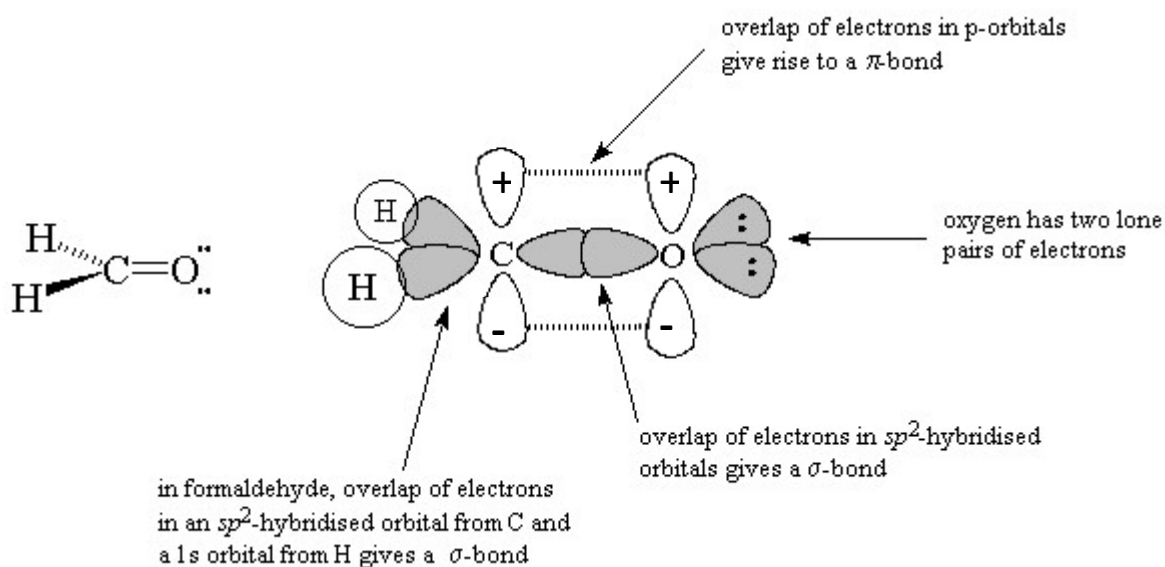
By symmetry, the sp^2 hybrid orbitals need to be 120° to each other.

And obviously, once we have the sp^2 hybrid AO we can use them to make hybrid MOs, so one of the orbitals in formaldehyde will be, for example,



Where the black dots indicate of course the C and the left-H nuclei.

Note that for our formaldehyde, we can expect the O to also be sp^2 hybridized to get better overlap with C and to minimize LP-LP repulsion:²⁵



Note that generally, except for $n=2$ (i.e., 1st row atoms up to Ne), pi bonds are quite weak.

Also note that:

- double bonds are $1\sigma - 1\pi$
- triple bonds are $1\sigma - 2\pi$'s

sp^3 hybridization

Next, we consider sp^3 hybridization, that occurs e.g., in CH_4 , or in O in H_2O , etc.

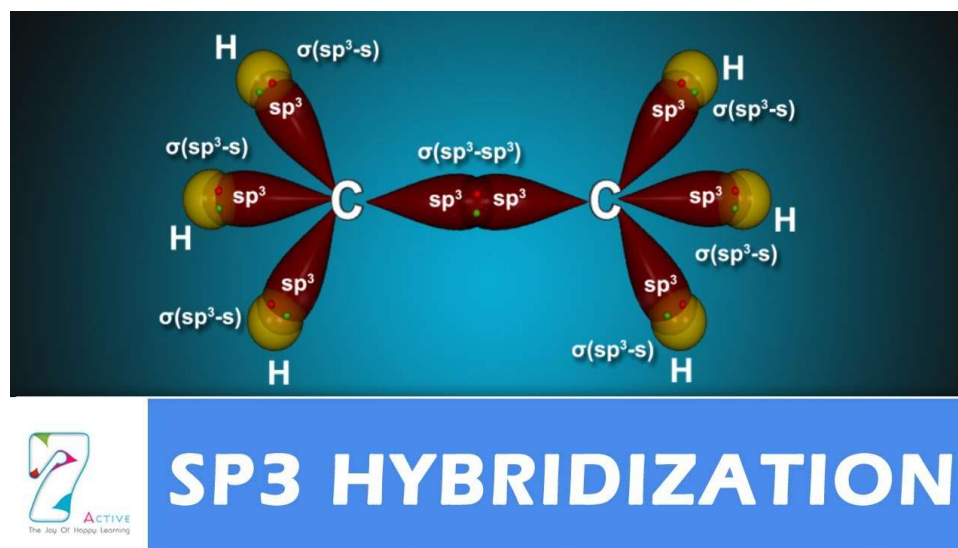
Note a pattern:

- In sp hybridization, one s and one p orbital hybridized, to create two sp hybrid AO (that are as far as possible from each other, i.e., 180°)

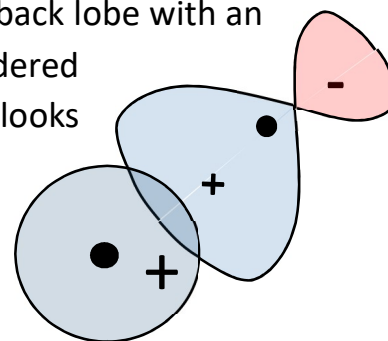
²⁵ Image taken from: <https://derekcarrsavvy-chemist.blogspot.com.cy/2016/04/carbonyl-compounds-1-structure-of.html>

- In sp^2 hybridization, one s and two p orbital hybridized, to create three sp^2 orbitals (that are as far as possible from each other, i.e., 120° from each other)
- In sp^3 hybridization, therefore, one s and all three p orbitals combine to create four sp^3 orbitals that are tetrahedral, arranged to be as far away from each other as possible, i.e., are at 109° to each other.
- An atom where the AO are sp^3 hybridized will not have π -bonds, obviously. All the bond are directed, σ bonds. The AO that are used for π –bonding are already used in the sp^3 hybridized AO.

See picture ²⁶ for C_2H_4



Note that the picture above does not show the “tail” end of each sp^3 orbital, i.e., in reality the orbitals have each a big front lobe, and a small back lobe with an opposite sign, i.e., something like the sp^2 orbitals we considered earlier; i.e., the sp^2 hybridized MO we saw earlier, looks qualitatively similar to sp^3 orbitals (and to sp orbitals).



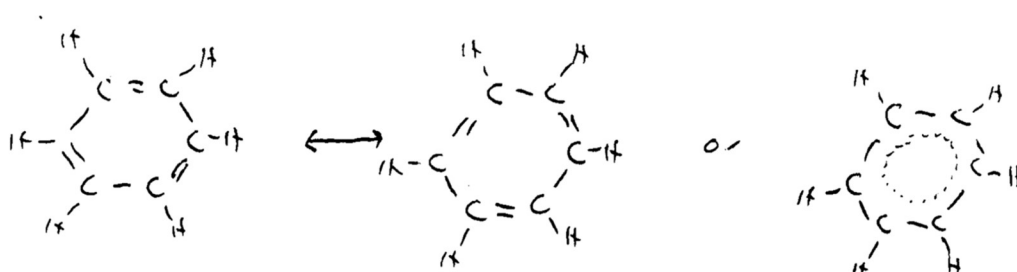
²⁶ Taken from <https://www.youtube.com/watch?v=hHHJhVRzhP8>

Note: If you take Organic Chemistry you'll understand there that sp orbitals are the most pointed (i.e., have the least "back lobe"), and sp^3 the least pointed.

Delocalized MOs:

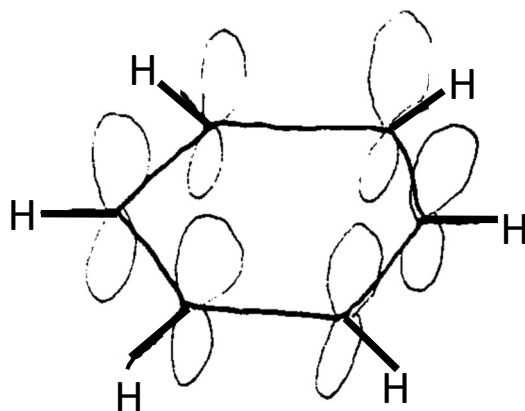
Sometimes an MO can be present over 3 or more atoms, not just 2. The classic example of this is benzene.

Note that the sp^2 hybridization for each C tells that the molecule should be **planar** (the plane is labeled x-y).



The sp^2 hybridized AO lead to σ bonds with the hydrogen and between each C.

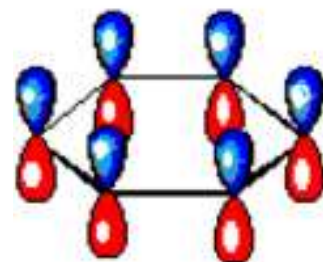
If we just draw lines for all the σ bonds, and use circles to denote the remaining p_z orbitals, we get this picture, where, of course, in addition, on each C we have the p_z orbital:



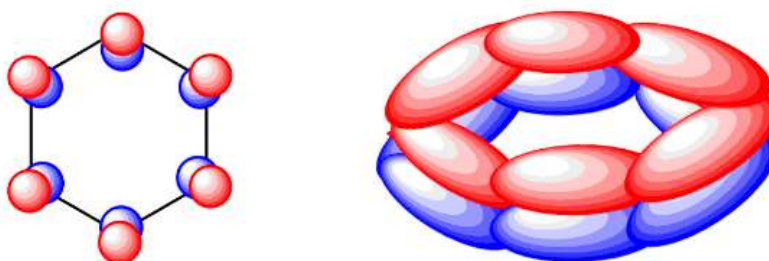
So now let's concentrate on the $2p_z$ orbitals

There are six $2p_z$ AOs which we can combine to make three bonding and three antibonding MOs, all of which are π -bonds!

The lowest energy of the three MO's has all $2p_z$ added in phase, i.e., looking like the picture on the right²⁷ (where the different color indicate different signs).



Note that this orbital is really more smeared (see the right picture below; the left one is a top view)²⁸



the lowest energy MO for benzene has all the p orbitals combining in-phase

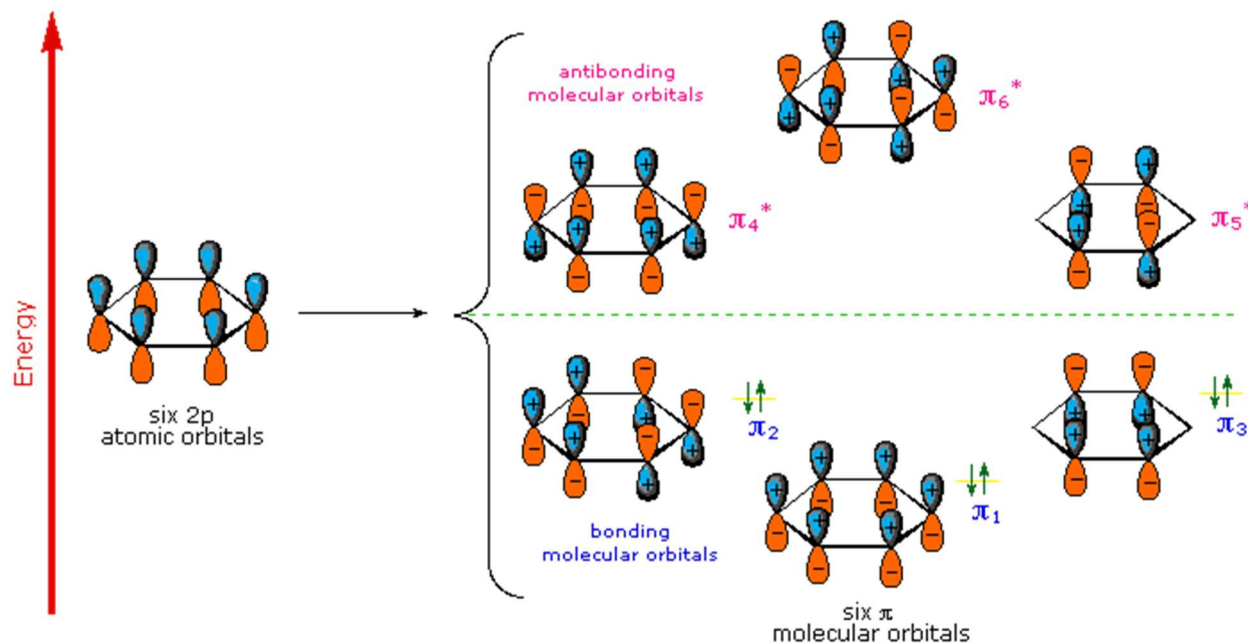
Also, only two electrons of course could be in this completely bonding π -orbital. There are six MO altogether (you can make 6 “orthogonal” MOs from 6 AOs). So this was the LOWEST energy one.

It is also easy to guess the HIGHEST energy MO: one where there is the maximum number of sign changes, i.e., maximum number of nodes – just alternate the sign between each neighbor, i.e., the picture in the next page

²⁷ From <https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/special0.htm>

²⁸ From <http://www.chemtube3d.com/orbitalsbenzene.htm>

The actual energy level diagram for the π orbitals, and the orbital for each, looks like this: (coincidentally, the energy level diagram looks a little like the molecule itself...)²⁹



Note that there are 3 bonding orbitals (the totally symmetric one we plotted earlier, and two more that have degenerate – i.e., the same – energies).

Since there are 6 electrons they fill the 3 bonding MOs. This “filling of the MO shell” makes benzene a very stable molecule.

²⁹ Taken from

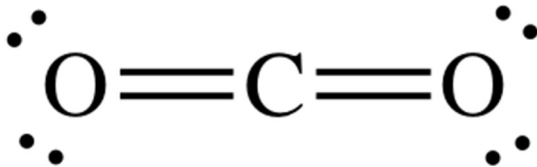
[https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/Map%3A_Organic_Chemistry_\(McMurry\)/Chapter_15%3A_Benzene_and_Aromaticity/15.02_Structure_and_Stability_of_Benzene](https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/Map%3A_Organic_Chemistry_(McMurry)/Chapter_15%3A_Benzene_and_Aromaticity/15.02_Structure_and_Stability_of_Benzene)

Molecular orbitals for CO₂

One final example: CO₂. A linear molecule (let's label the CO₂ axis as "x"). It has 4+2*6=16 valence e's.

In the discussion below the intermolecular axis is labeled as "x", not "z".

The Lewis dot diagram is: ³⁰



This diagram actually **does injustice to the MO** since the two O atoms seem to be sp² bonded. In reality they are not.

One thing is clear: The C atom is sp hybridized, since here SN=2. That leaves the question on what happens for O.

We'll understand in the next page **why the AO in O are not sp² hybridized here**. So since each O is not sp² hybridized, two electrons will fit in the 2s level for each O

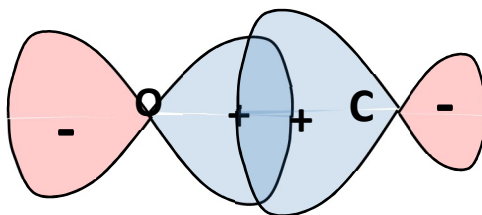
Also, each of the two linear sp AO on the C atom combines with p_x to produce a bonding σ molecular orbital:

Example: Here are the AOs involved in one of the σ bonds, i.e., the p_x of the left O and the left-leaning sp AO of the C:



And together they give a σ MO:

³⁰ Taken from: <https://socratic.org/questions/how-many-pi-bonds-are-there-in-co2>



The two σ bonds (one on each side of the C) accommodate 4 electrons.

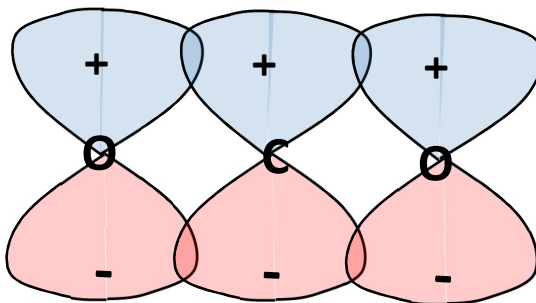
So totally we accounted for $4+4=8$ electrons. Where are the other $16-8=8$ electrons? We still have at our disposal 6 AOs: the p_y and p_z orbitals of the C and of each O.

From these 6 p_y and p_z AOs we can make, it turns out:

- 2 completely delocalized bonding π –MOs (with 2 electrons in each); these orbitals involve something like (not exactly, but close)

$$\frac{1}{\sqrt{3}}(\psi_{p_y}^{\text{left O}} + \psi_{p_y}^{\text{C}} + \psi_{p_y}^{\text{right O}})$$

Pictorially:



And of course a similar one involving p_z orbitals.

- two non-bonding π –MOs (with two electrons in each);
- and two empty antibonding π –MOs.

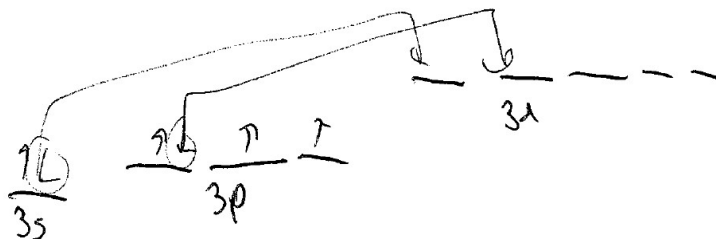
The extra bonding due to localization makes CO_2 quite stable.

Note that if each O was sp^2 hybridized then it would only have a single π bond so it would not have the energy lowering due to delocalization, and it would need to still pay the energy penalty associated with promotion from s to sp^2 , so for those reasons each O does not sp^2 hybridize here.

Expanded Octets

We learned about mechanisms responsible for hybrid sp , sp^2 and sp^3 atomic orbitals and the resulting MO due to the hybridization of these hybrid AO with AO (hybrid or not) of other atoms. The same mechanisms are of course relevant for other cases.

An example is expanded octets, where atoms at the $n=3$ row make hybrid AO where the electrons are promoted from the $3s$ and $3p$ shells to hybrids which combine $3s$, $3p$ and $3d$:



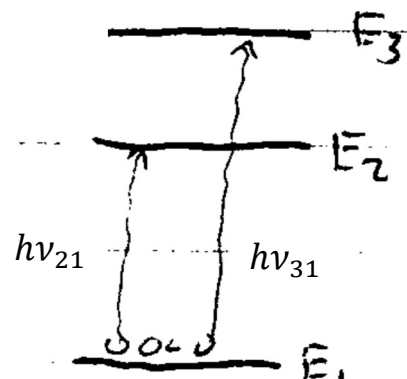
These leads to hybrid AO, the most important of which are sp^3d and sp^3d^2 orbitals.

We'll talk more about d orbitals at the end of the course, when we discuss transition metals.

Spectroscopy

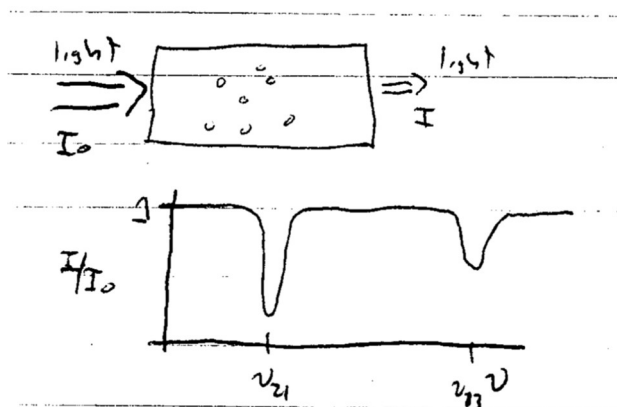
Spectroscopy is the study of the interaction between light and matter.

Light has an electric field, and this causes charges to move resulting in absorption. But moving charges create light, and that causes emission.³¹



Take a sample molecule with three levels. Let's assume that the levels are well separated so that, without field, all molecules will be at the lowest ("ground") state, E_1

We pass light through a chamber full of such molecules, and we notice, around two frequencies, a dip in the intensity of the light that comes out:



Since $E_{photo} = h\nu$, clearly absorption will occur when the photon can promote the molecule from the ground state to one of the two higher states, i.e., at ν_{21} which satisfies $h\nu_{21} = E_2 - E_1$, and also at ν_{31} which satisfies $h\nu_{31} = E_3 - E_1$.

Note: due to collisions and other disturbances the absorption does not occur only at exactly these frequencies, but also at a range of frequencies around them. That's why the dips in the picture above are not infinitely thin.

³¹ A purist would have us give more accurate descriptions, but let's not be purists.

So generally light is absorbed when $h\nu$ matches the energy level difference in a molecule. If the energy does not match – there’s no absorption. This is sometime called the **resonance condition**.

We can look at many different types of transitions.

$$\Delta E_{NMR} \ll \Delta E_{rotations} \approx \Delta E_{EPR} \ll \Delta E_{vib.} \ll \Delta E_{elec}$$

Flips of <u>nuclear spins</u> in a magnetic field. Radio waves, $\lambda > 0.1\text{m}$	Change how fast molecules rotate in space. microwaves $\lambda \sim 1\text{mm}$	Flips of <u>spins of electrons</u> in a magnetic field. microwaves $\lambda \sim 1\text{mm}$	Change vibrations between atoms within a molecule. Infrared. $\lambda \sim 3 - 10 \mu\text{m}$	Change energy levels in an atom or a molecule. Visible, UV or X-ray. $\lambda < 1\mu\text{m}$
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Let’s cover these one by one:

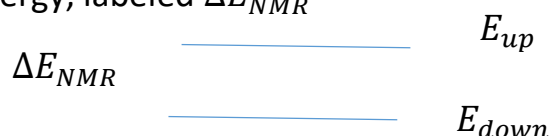
NMR

The nuclei of some molecules have spin and behave as tiny magnets.

If we put the sample in a magnetic field, we get 2 possible states:

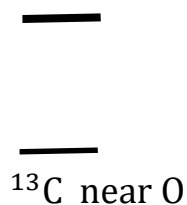
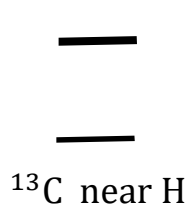


There will be a difference in energy, labeled ΔE_{NMR}



Because the atoms neighboring the nucleus will subtly affect the local strength of the magnetic field, we can learn about the local environment.

For example



The difference between the energies may be only a few parts per million, but we can measure it in the lab.

This is how MRI works to find tumors, look at damaged cartilage, etc. You will do NMR in the 20L lab.

ROTATIONS

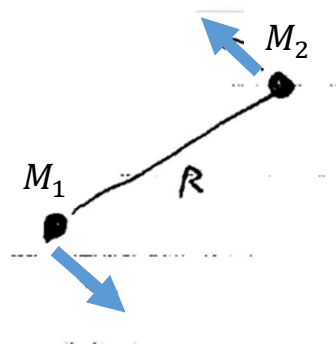
We can show from the Schrödinger Equation that only certain rotational energies are allowed.

Formally,

$$E_{rot,J} = \frac{\hbar^2}{2I} J(J + 1), \quad J = 0, 1, 2, \dots$$

And I is the moment of inertia; for example, for a diatom rotating (see picture on the right):

$$I = \frac{M_1 M_2}{M_1 + M_2} R^2 = \mu R^2$$

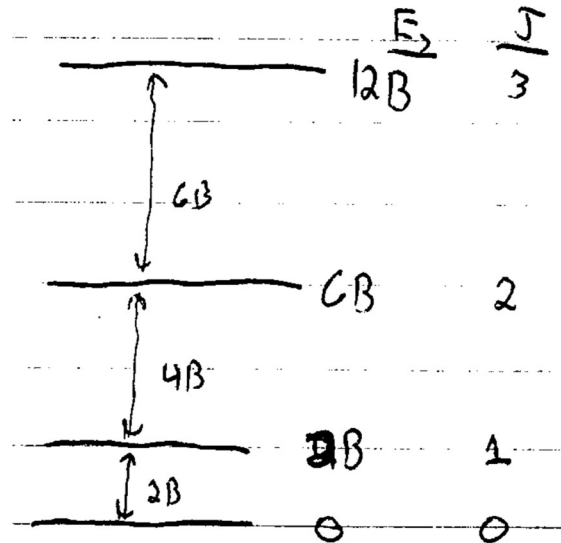


We can also write

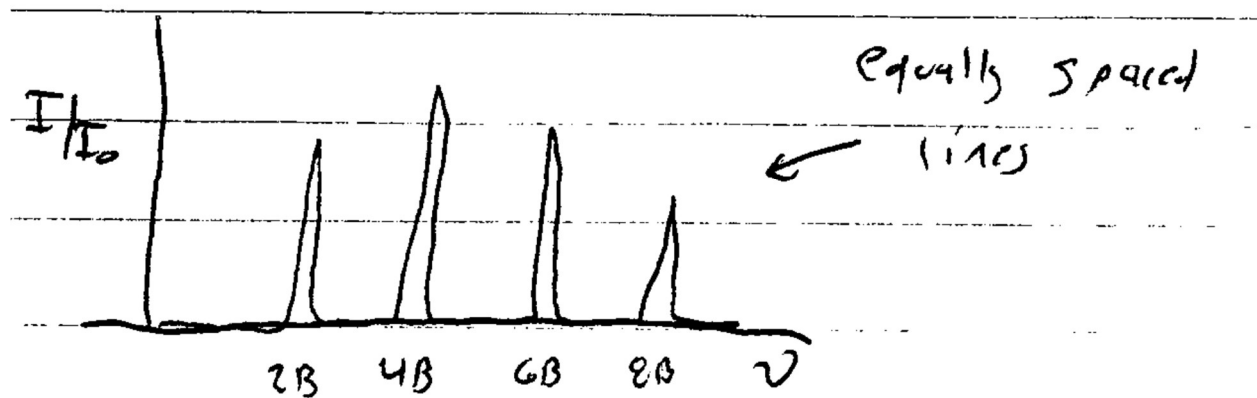
$$E = BJ(J + 1)$$

There's a **selection rule**. We can **only change from J to $J \pm 1$** , so clearly we can only absorb photons with

$$E = h\nu = 2B, 4B, 6B, \text{etc.}$$



The absorption spectrum will look like:

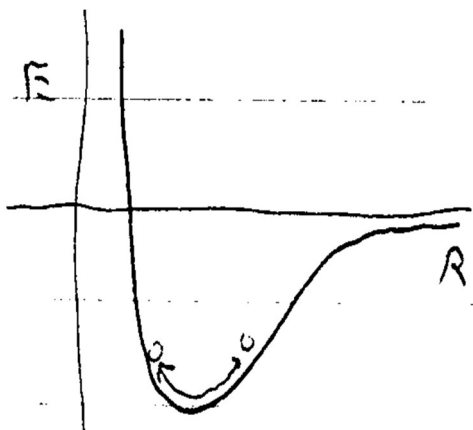


Note that we can:

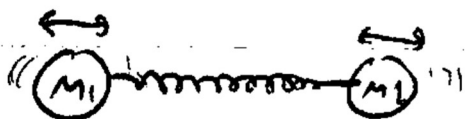
- measure spacings, thereby determine B .
- From $B = \frac{M_1 M_2}{M_1 + M_2} R^2$ and from knowing the masses, we can find R !

This is how we find experimental bond lengths and angles!

Vibrational Spectroscopy



Molecules can expand or contract like two balls on a spring:



We can show from the Schrödinger equation that only certain amounts of vibrations are allowed.

$$E_{vib,k} = h\nu_{osc} \left(k + \frac{1}{2} \right), \quad k = 0, 1, 2, \dots,$$

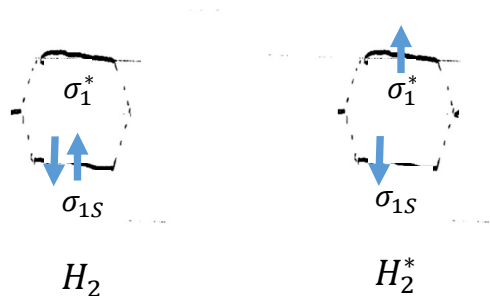
whereas we saw:

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}$$

and κ = force constant of spring ($F = -\kappa x$), and $\mu = \frac{M_1 M_2}{M_1 + M_2}$

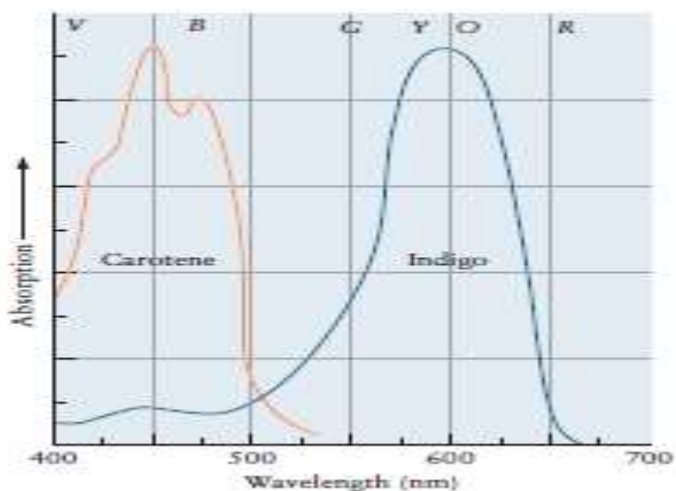
Electronic Spectroscopy

Electrons can be promoted from low molecular orbitals to higher orbitals. This makes the overall electronic configuration of the molecule “excited”. For example, we saw in H_2 that we can excite one electron from a bonding orbital to a non-bonding orbital:



Usually these electronic excitations are very broad.

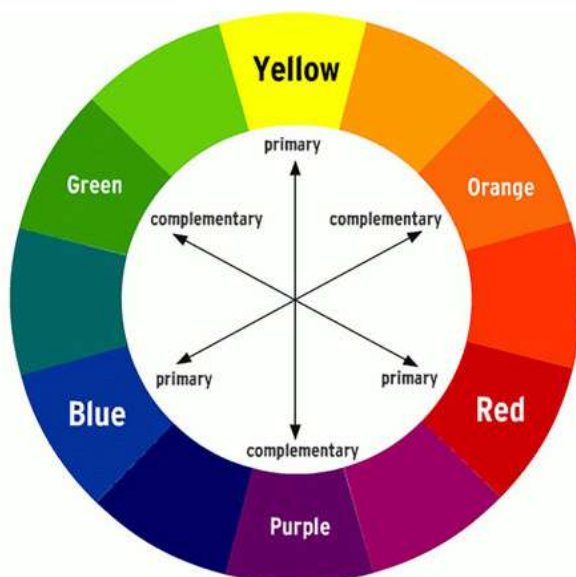
Let's look at the absorption of dyes, usually long organic molecules. Compare indigo (in Jeans) with carotene (in carrots): (image from your book by Oxtoby, Gillis and Campion)



How do the colors emerge?

When a sample absorbs a certain color, we observe the complementary color:³²

³² Taken from <http://www.myhomeandstudio.com/blog/the-color-circle/>



So to see orange, a substance will need to absorb blue, i.e., absorb light at frequencies 400-500nm, which is exactly what carotene does.

Real-molecules spectroscopy:

Real molecules can use photons to change electrons, rotational and vibrational states at the same time:

$$\Delta E = h\nu_{pho} = E_{vib,f} + E_{rot,f} + E_{elec,f} - (E_{vib,i} + E_{rot,i} + E_{elec,i})$$

Here, “f” means final and “i” is initial.

X-ray spectroscopy and photoelectrons

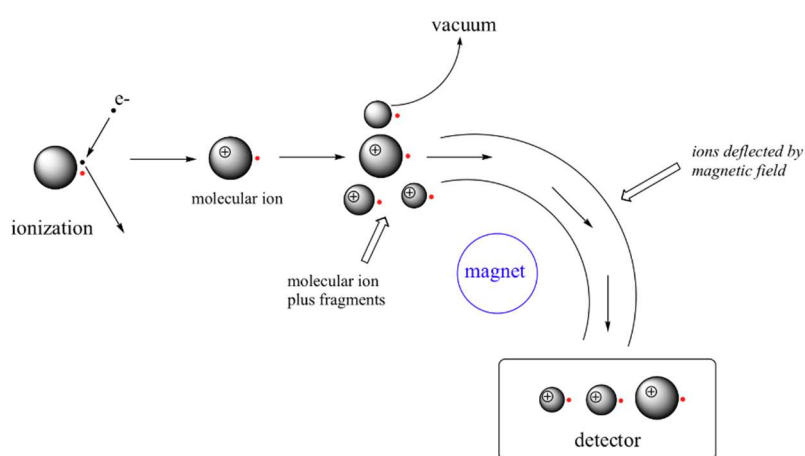
X-rays can be used to remove core level e’s from atoms. We can either measure the energy of the emitted electron to learn about the energy of the core levels (XPS: x-ray photoelectron spectroscopy), or we can do Auger Spectroscopy.

In Auger spectroscopy, the “hole” left by the removed core level is filled in an electron falling in to fill that level. That electron, when it falls in, sometimes kicks out secondary electron’s, which have characteristic energies for each element.

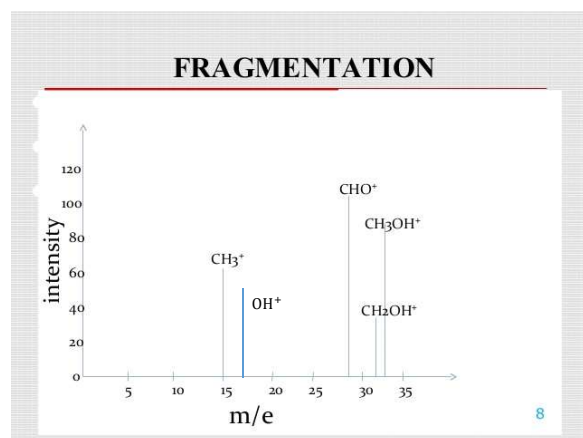
Other “spectroscopies”

Mass spectroscopy: ionizes molecules and then uses a magnetic field to separate the fragments by mass. After the ionization the non-ionized molecules leave, but the ionized molecules, since they have charge, will be bent by a magnetic field. The heavier molecules will be bent less (since the bending is related to the Force/mass, and their mass is bigger).

At the end of the bending-tube there's a screen. Heavier molecules will be found at a different spot on the screen (on the right on the picture below). Therefore, from the spot on the screen we can find the mass of the molecules! See picture:³³



Example: CH_3OH



³³ Taken (and modified) from: <https://orgspectroscopyint.blogspot.co.il/2014/12/mass-spectrometry.html>

EPR Spectroscopy

Like NMR, except looking at **unpaired electron spins**. Each molecule with unpaired electrons has a unique EPR signature depending on the unpaired electrons environment. Can also tell how many unpaired electrons there are.

But: EPR only works on molecules or atoms with unpaired electrons!

Organic Chemistry: an introduction

This is the chemistry of C and its compounds. Includes: proteins, sugars, fats, DNA, fuels, drugs, plastics, etc.

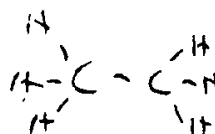
Simplest class of organic molecules is: **hydrocarbons** (abbreviated as **HC's**), consisting only of H or C.

Linear alkanes:

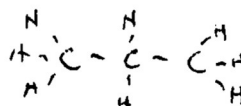
Have formulae C_nH_{n+2} – all C's in the molecule are sp_3 hybridized, each with 4 bonds. (Also called: solvated HC's, since all carbons have 4 bonds.)

CH₄ methane.

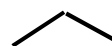
CH₃CH₃ ethane



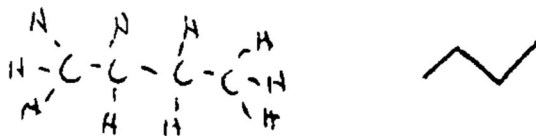
CH₃CH₂CH₃ propane³⁴



Or use short-hand notation, just draw bonds between the C's; each corner represents a CH₂ and the end points represent CH₃



³⁴ Taken from: <https://fineartamerica.com/featured/propane-molecule-.html>



$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ butane

Pentane: $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$



Hexane: $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$



Heptane: $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$



And the list goes on: octane (gasoline fuel); nonane, decane (diesel fuel), undecane, dodecane, etc.

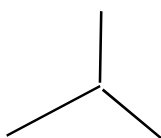
Branched Alkenes

Combust more easily and are added to gasoline to improve the “octane rating”.

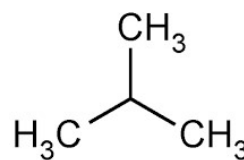
So: n-butane (i.e., normal-butane, not branched) is




While iso-butane is



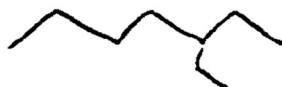
i.e.,³⁵



³⁵ From: http://www.pharmacopeia.cn/v29240/usp29nf24s0_m42630.html

Similarly,  isopentane or 2-methylpentane (i.e., a methyl group, CH₃, replaces one of the H's at the 2nd carbon.)

The bigger we go then there will be exponentially many isomers. See for example 3-ethyl-heptane:

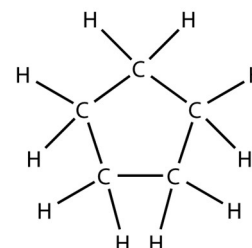
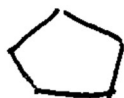


Obviously there could be many other isomers of heptane.

Cyclic Alkanes: C_nH_{2n}

Have 2 H's less than linear alkanes (which have the formula C_nH_{2n+2}) since there are no extra H's at the ends. For example, cyclopentane³⁶

or simply:



There are of course many other cyclo compounds, e.g., cyclohexane, cycloheptane, etc.

Unsaturated Hydrocarbons

Also have the formula C_nH_{2n} and are labeled **alkenes**.

Have a C=C double bonds, one σ and one π bonds, and thus have "lost H₂" relative to the saturated HC's

³⁶ Taken from

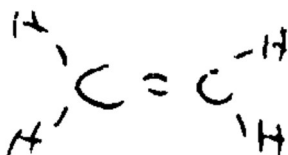
<http://www.chemeddl.org/alfresco/service/chemeddl/molecules/search.html?guest=true&pubchem=9253>

(The saturated HC's are called "saturated" since they have as many H's a possible for a given number of C's)

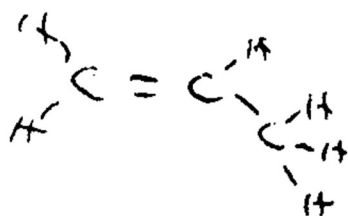
Also, obviously, if there is more than one C=C bond, the formula will be different, e.g., with two double bonds the formula will be C_nH_{2n-2} ; with three double bonds it will be C_nH_{2n-4} ; etc.

Examples for alkenes:

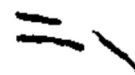
E.g., ethylene:



Or propylene:



or simply



For butelene there are two isomers:



1-butelene

or



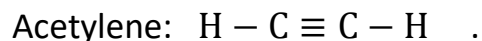
2-butelene

Alkynes:

Compounds that have at one $C \equiv C$ triple bonds with one σ and two π bonds are called alkynes.

For a single triple bond, the formula will be C_nH_{2n-2} , i.e., two H_2 less than saturated HC's; this is because two H_2 were left out of the compounds due to the two pi bonds.

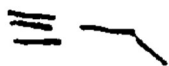
The simplest alkyne is



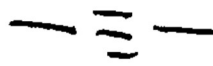
Next is:



Next are two isomers:



1-butyne

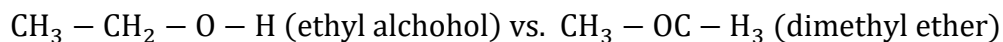


2-butyne

Isomers

Other examples of isomers are:

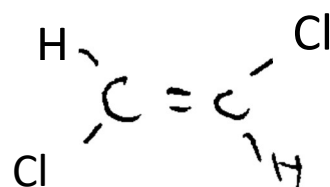
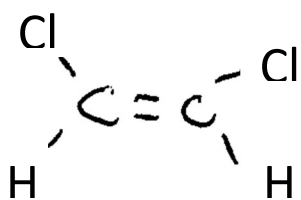
Structural isomers, e.



Geometrical isomers :

cis and trans configuration

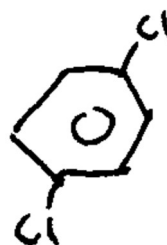
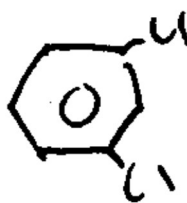
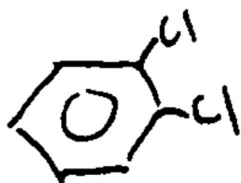
Cis: both H's on the same side. **Trans:** H's on opposite ends.



Ortho, meta, and para substitutions on benzene; e.g.,

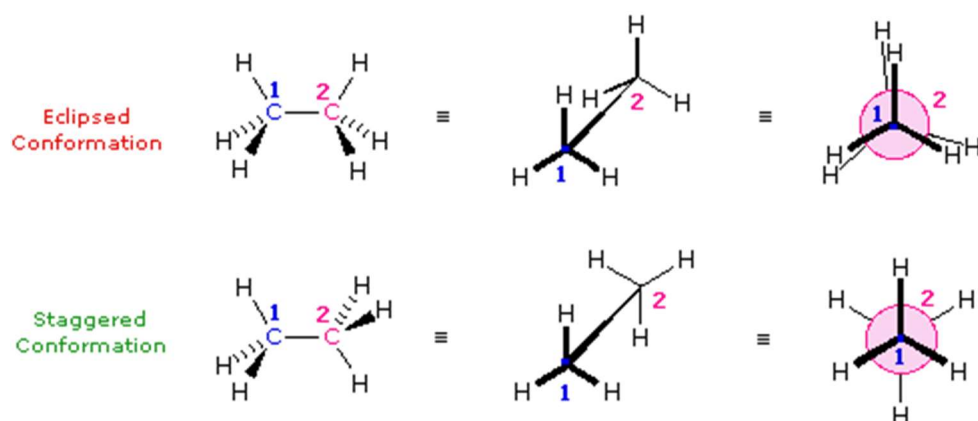
ortho dichlorobenzene;

meta dichlorobenzene; **para** dichlorobenzene.



Conformational isomers

Example:³⁷



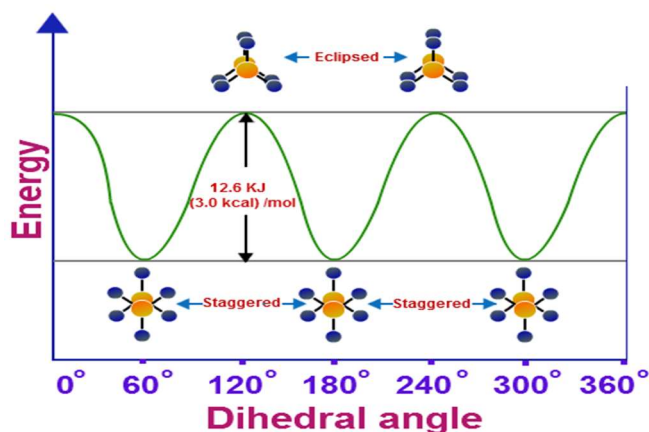
³⁷ From: <https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/sterisom.htm> s

The RHS (with the pink circle) is a Newman projection, where we view the molecule along its axis.

The eclipsed conformation has a higher energy, since the 1s orbitals of the hydrogens are closer (e.g., in this picture the “top” hydrogens on carbon 1 and carbon 2, etc.).

The staggered configuration has more distant hydrogens so there's less repulsion, i.e., lower energy.

Plotting as a function of rotation angle (of carbon 2 and its hydrogen relative to carbon 1 and its h's) gives³⁸ barriers of more than 0.1eV



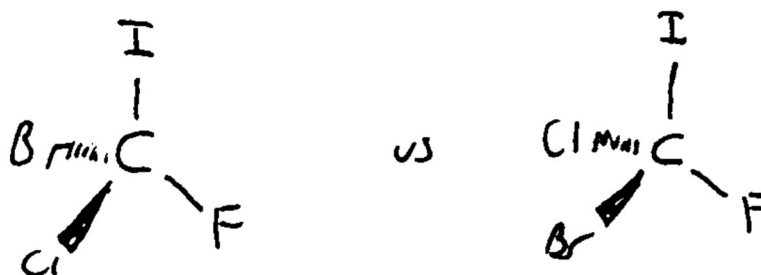
This barrier is small enough that molecules can freely spin at room temperature.

Stereoisomers

3D molecules can be handed (left or right handed). Another word for “handed” is chiral. Any C with 4 different attached groups can be chiral.

Example:

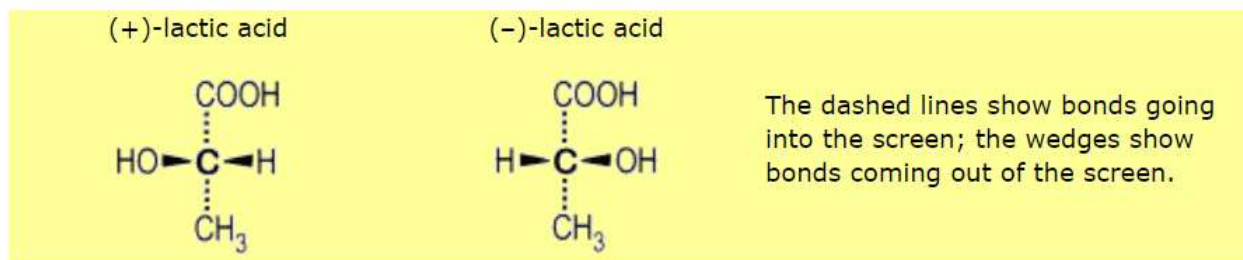
³⁸ From: <http://chemistry.tutorvista.com/organic-chemistry/isomers.html> s



Such pairs of molecules are called stereoisomers or enantiomers.

A mixture with both enantiomers is sometimes called a racemic mixture. Most biological molecules are chiral, and nearly everything in nature comes only in one handedness.

For example³⁹: two forms of lactic acid. The “+” enantiomer is in muscles, and the “-” form is spoiled milk (more precisely, spoiled milk has both the “+” and “-” enantiomers.)



One property of chiral molecules is that they rotate the plane of polarized light – molecules that rotate clockwise (right) are called D-enantiomers, and counterclockwise are L-enantiomers.

Racemic mixtures ($\frac{1}{2}$ and $\frac{1}{2}$ of both enantiomers) don't rotate polarized light at all!

³⁹ From: <https://www.creative-chemistry.org.uk/molecules/optical.htm>

Aromaticity

Molecules that have a delocalized π -electron system with $4n+2$ e's in the π -system have an extra, special, stability. They are called aromatic molecules:



Benzene: 6 delocalized e's.



Naphthalene: 10 delocalized e's.
(Moth balls)

Functional groups and compounds

Alkyl – saturated hydrocarbon chain;

For example, replacing H in CH_4 by a methyl group $-\text{CH}_3$ (one of the alkyl groups) gives CH_3-CH_3 . Other groups could be, e.g., $-\text{CH}_2\text{CH}_3$ (ethyl), etc.

An alkyl group is usually denoted as $-\text{R}$

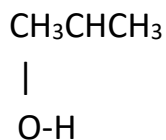
Alkene: $\text{C}=\text{C}$ in chain. E.g.,  or  1- or 2- butane.

Alcohols: are $\text{R}-\text{O}-\text{H}$.

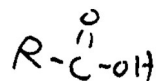
E.g., CH_3OH (methanol),

$\text{CH}_3\text{CH}_2\text{OH}$ is ethanol,

Isopropanol (rubbing alcohol):

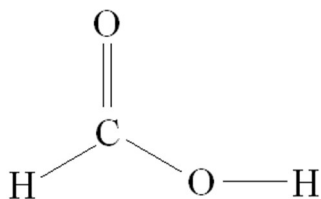


Carboxylic acid:



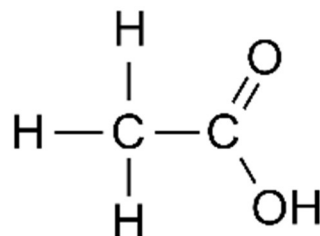
For example:

Formic acid (from ants)



Formic Acid

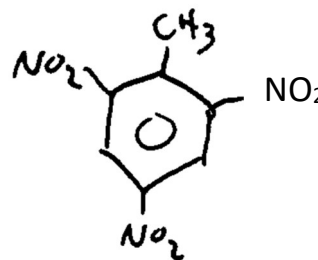
Acetic acid (vinegar)



Alkenes: compounds with $C \equiv C$, so alkene groups will have $C \equiv C$.

Nitrile: $R - C \equiv N$ (i.e., groups with $-C \equiv N$)

Nitro: $R-NO_2$ e.g., trinitrotoluene (TNT)

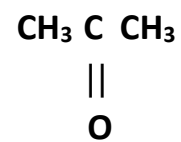


Ester: $R-\overset{\overset{O}{\parallel}}{C}-O-R'$

Amine: $R''-\overset{\overset{R'}{\mid}}{N}-R$

Ketone: $R-\overset{\text{O}}{\underset{||}{\text{C}}}-R'$

Example: acetone:



Ether: $R-O-R$

Example: $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, diethyl ether.

Thiol: $R\text{-SH}$

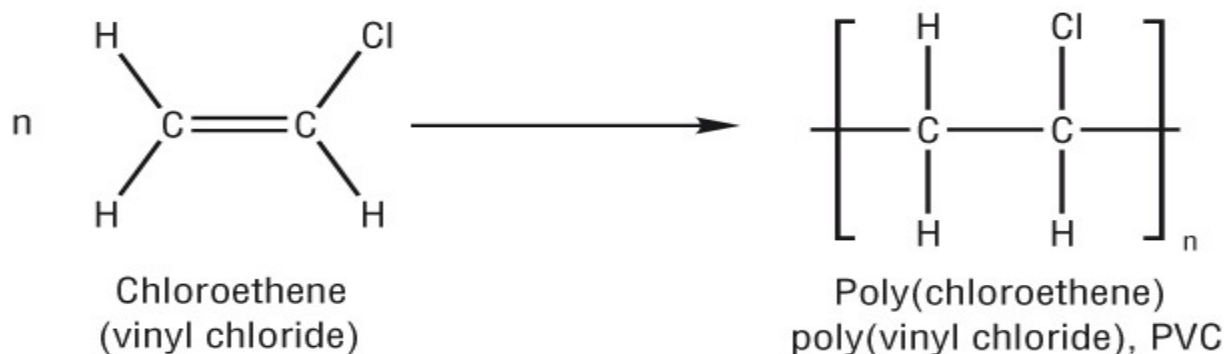
(smell bad! Skunk odor...)

Each functional group gives the molecule different properties and different activities.

Polymers:

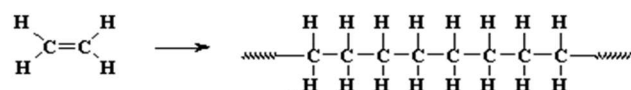
Link small organic groups (monomers) into an extended chain.

Example: using initiators with radicals we can turn “n” molecules of vinyl chloride (chloroethene) to a poly-vinyl-chloride (PVC) polymer ⁴⁰

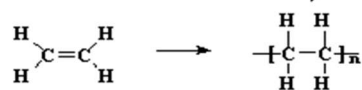


Examples of polymers include: latex for paint, adhesives, rubbers, plastics, fibers, mylars (audio/video tape in the old days), polyester, etc.

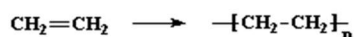
Other examples. Poly(ethylene):⁴¹



here's a shorter way to draw polyethylene



and here's an even shorter way!



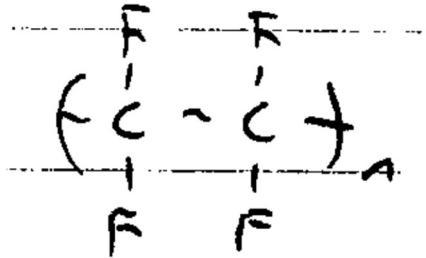
42

⁴⁰ http://www.physicsandmathstutor.com/chemistry-revision/gcse-edexcel_trashed/topic-9_trashed/polymers/

⁴¹ <http://www.pslc.ws/macrog/kidsmac/polyeth.htm>

See Nylon DEMO in class.

Poly(tetraflouroethylene): i.e., **Teflon**. Looks just like polyethylene but all the H's replaced by F:



Natural polymers:

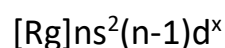
- proteins are polymers of amino acids;
- starches / cellulose / etc. are polymers of sugar molecules (e.g., cotton).
- DNA : polymers of organic bases, sugars, and phosphoric acids.

Transition Metal Complexes

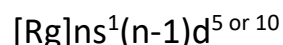
So far we discussed mostly the chemistry of the p-block elements, and how we can use s, p orbitals to bond. We occasionally used d orbitals for atoms like S or P, but not often.

Transition metals, on the other hand, have “d” electrons as their valence electrons. This gives them an especially rich colorful chemistry.

Recall that most TM’s have configuration (where “Rg”=Rare gas):



or occasionally:



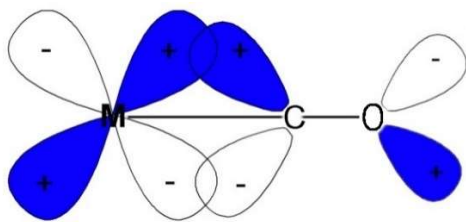
When we ionize TM’s, we remove the s electrons first! For example:

- Fe^0 is $[\text{Ar}]4s^23d^6$
- Fe^{2+} is $[\text{Ar}]3d^6$ (also called Fe(II))
- Fe^{3+} is $[\text{Ar}]3d^5$ (also called Fe(III))

The versatility in oxidation states means that TM’s can make a wide variety of chemical bonds.

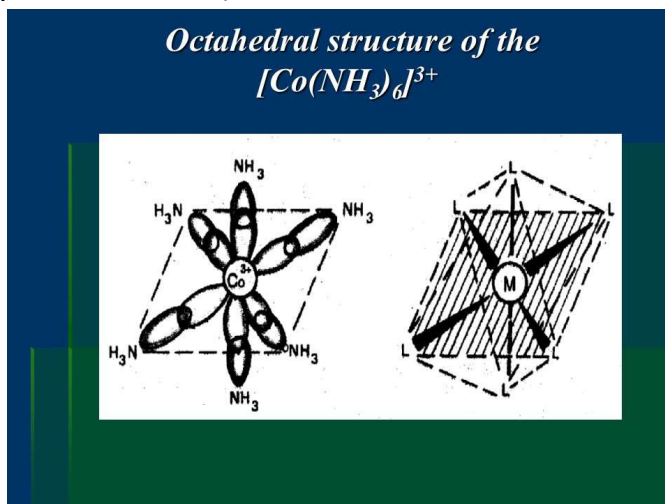
- I) **Ionic bonds:** such as ZrO_2 . These ionic compounds form nice, regular crystals. ZrO_2 has a cubic arrangement of atoms, and is used in costume jewelry
- II) **Covalent polar bonds** – TM’s with unpaired d or s e’s can form either σ or π bonds; also called σ –backbonding or π -backbonding; an example for the latter is⁴³

⁴³ <https://www.quora.com/What-is-backbonding>



Specifically, an empty unoccupied Π^* antibonding orbital on the C-O helps in the bonding of the C to the metal. I.e., the d-orbital on the metal is “enlarged” since it hybridizes with the Π^* unoccupied orbital.

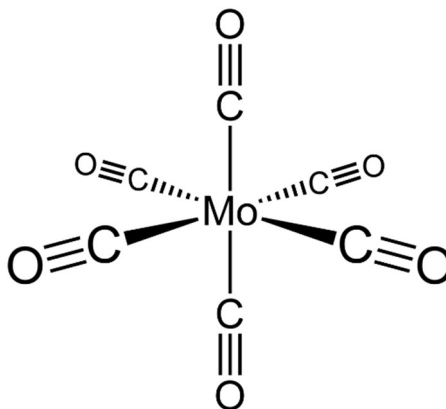
- III) **Dative or Donor/Acceptor bonds:** requires a lone pair of e^- on the donor, or ligand, and an empty orbital on the acceptor TM. For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$ (picture from ⁴⁴).



⁴⁴ From : <http://slideplayer.com/slide/7015731/>

Organometallic complexes: involve bonds between TM's and C or O ligands. Bonding is usually polar-covalent or dative. Usually these complexes make use of all valence orbitals, s, p, & d on the TM. Follow the 18 e^- rule (like the octet rule but including the 10 d-electrons).

Example: $\text{Mo}(\text{CO})_6$ (Molybdenum hexacarbonyl) (picture from ⁴⁵)



The 18 electron rule is sometimes not satisfied by the early TM's, just like the early p-block elements (e.g., B) don't always satisfy the octet rule.

Coordination complexes: involve one TM atom or ion surrounded by ligands, usually involving dative bonding between stable closed shell ligands and TM ions.

The coordination # is the # of bonds between the central TM and the ligands.

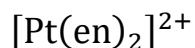
Most ligands form only 1 bond, "monodentate", for example: F^- , Br^- , Cl^- , I^- , NH_3 , H_2O , CO , CN^- , OH^-

But some ligands can form 2 (or more!) bonds, "**bidentate**". For example:

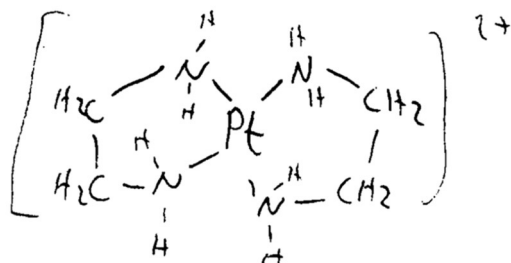


For example:

⁴⁵ From https://enThe.wikipedia.org/wiki/Molybdenum_hexacarbonyl

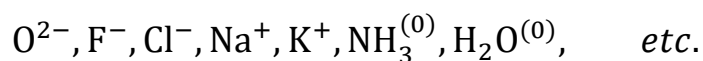


And pictorially:

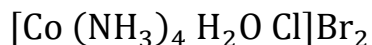


So the coordination # (of the middle TM, platinum) is **4** ; therefore, there will be a square planar geometry of the bonds around the metal.

Determining the TM electronic structure: For that use standard rules for the ligands, which are almost always closed shell, e.g.,



Example:



First, we have 2 Br^- counterions, not bonded to the metal, so the entire complex is 2+

Also, both NH_3 and H_2O are neutral so we expect Cl to be Cl^- , so the Co must be 3+ , labeled as Co(III)

You should know the charges of the common closed shell molecular ions:
 CN^- , OH^- , NO^+ , CO_3^{2-}

Example: $\text{K}[\text{Mn}(\text{CN})_5]$. Since the potassium will be K^+ , the complex has a -1 charge, while each CN is really CN^- so the total charge on the TM is **+4**, i.e., Mn(IV).

Structure:

Most TM complexes are octahedral (CN, i.e., Coordination Number, = 6 – don't confuse CN for coordination number with the ion CN^-);

Some are tetrahedral or square planar (CN=4)



“Early” (LHS) TM's tend to form tetrahedral (CN=4) complexes.

“Late” (RHS) TM's tend to form square planar (CN=4) complexes.

Of course, we can make all sorts of isomers



or optically active chiral molecules with 4 different ligands.

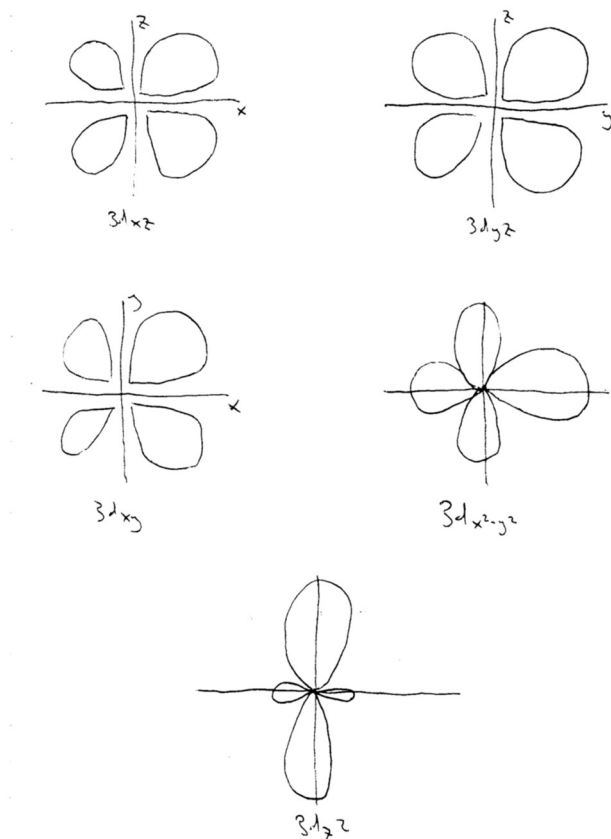
Crystal Field Theory

Explains the colors and magnetism of coordination complexes.

Complexes are highly colored because of the $d \rightarrow d$ transition on the metals.

- We can work out a full M.O. (molecular orbital) theory using all of the AOs (atomic orbitals), and this is called Ligand Field Theory;
- but most of what we need to know can be rationalized just from thinking about how the TM in the complex is different from the base TM, and this is called crystal field theory.

Specifically: consider the 5 d orbitals in a TM (and there's no need here to put the "+" and "-" in the d orbitals). Let's plot them, but note that many of the plots use different coordinate axis (x and y, or x and z, or y and z):



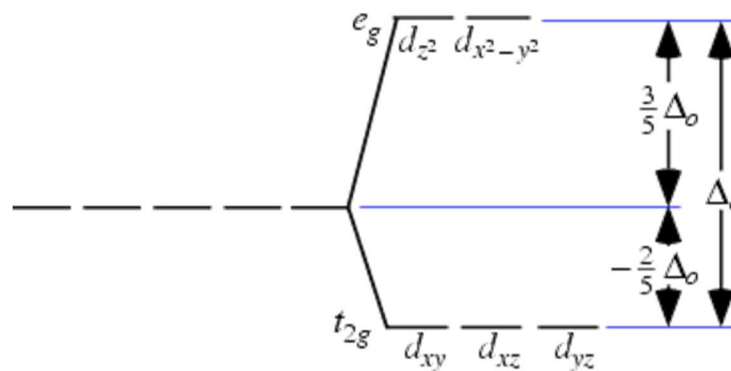
Octahedral complexes

If we have an octahedral arrangement of ligands, each bringing in a lone pair of e^- 's along the \pm directions of all three axis, we're going to have extra repulsion for those orbitals along these axis (x, y and z), so the orbitals $d_{x^2-y^2}$ and d_{z^2} , which point along these axis, are destabilised by the repulsion.

The other three d-orbitals fit nicely in between and are relatively stabilized.

This is depicted in the following diagram⁴⁶

octahedral (O_h) crystal field splitting



- On the left we show the degenerate (i.e., the “same”) orbital energies for the d orbitals without ligands.
- On the right we show the orbital energies when the ligands are on; they are split, as mentioned, and the $d_{x^2-y^2}$ and d_{z^2} rise in energy, while the others have lower energy. We label the splitting as Δ_0

Note that we draw the lines so that the average splitting is 0. (Here, for example, the average is constructed from 3 orbitals with negative $-\frac{2}{5}\Delta$, and two orbitals have $\frac{3}{5}\Delta$, so in average the splitting is $3 * \left(-\frac{2}{5}\Delta\right) + 2 * \left(\frac{3}{5}\Delta\right) = 0$.)

Of course, the average energy changes when we have ligands compared with not having ligands, but that is of less concern; only the relative energies due to the splitting.

The three lower orbitals are labeled as t_{2g} (this relates to their symmetry and direction) and the top two as e_g .

⁴⁶ From <http://scienceworld.wolfram.com/chemistry/CrystalFieldTheory.html>

Orbital filling

If the splitting is large, the lower orbitals (the t_{2g} ones here, for the octahedral complex in the previous page) are populated first.

So:

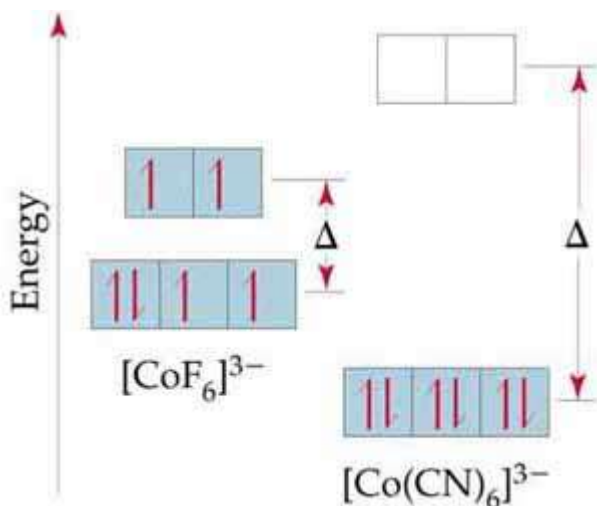
If the splitting is small, then the splitting it is not that important and the orbitals fill by the usual Hund's rules (i.e., the first 5 d-electrons will distribute to the 5 different orbitals, etc.) But if the splitting is large, electrons will be promoted to the higher levels only once the lower level fills up.

Large-splitting complexes will have, in contrast, low spin -- the maximum spin will be 3 unpaired spins in the complex, when 3 electrons are in the d-level. The 4th electron will already be of opposite spin. See picture

Small-splitting (small Δ_0) complex can have high spin, up to 5 times that of a single electron.

Examples: next page.

Example for orbital filling (from ⁴⁷) : $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{F})_6]^{3-}$



Here, in both cases, Co has a charge state of Co^{3+} , i.e., Co(III), i.e., it has the electronic configuration of $[\text{Ar}]3d^6$, i.e., 6 electrons in the valence d-shell.

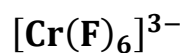
Let's analyze first:



CN^- is a "strong-field" ligand, i.e., it leads to a large Δ_0 , so all 6 d electrons from the Co(III) fill the t_{2g} levels;

So no unpaired electrons → **diamagnetic**.

Next:

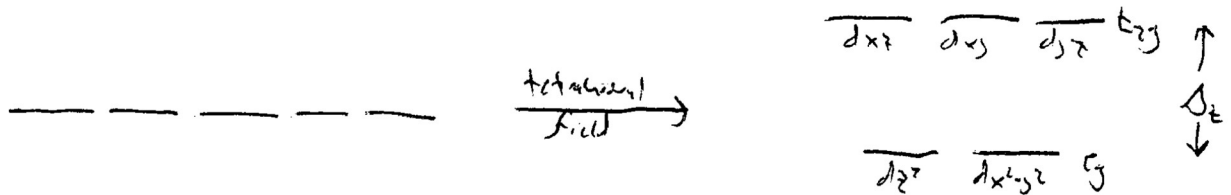


F^- is a weak field ligand, that produces a small Δ_0 . We fill all 5 levels first via Hund's rule → 4 unpaired electrons → **strongly paramagnetic**

⁴⁷ <https://socratic.org/questions/the-cof6-3-ion-is-paramagnetic-while-the-co-cn-6-3-ion-is-diamagnetic-explain-th>

Tetrahedral field

Now the d_{xy} , d_{yz} , d_{xz} are closest to the ligands; this gives the opposite splitting to an octahedral field:



This is the less common case; usually Δ_t is small and we get high spin complexes.

Square planar field:

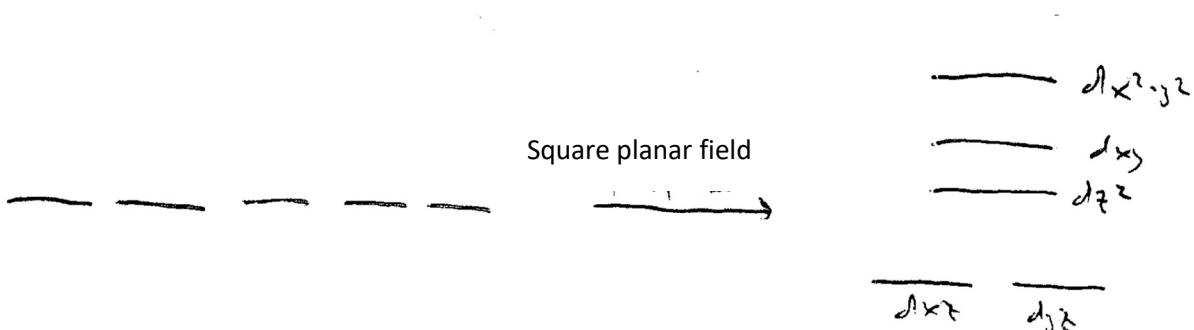
Often found for d^8 ions (example: Pt^{2+} .)

The 4 ligands lie along the x and y axis. As d_{xz} and d_{yz} have nodes in the xy plane, they will have the least repulsion, i.e., a very low-lying (very negative) energy.

The d_{z^2} orbital only has a tiny piece in the xy plane, so it will not have a lot of repulsion so it is the next d-valence orbital (counting from the bottom up).

Then, somewhat higher, will be the d_{xy} which is at least between the ligands, and finally $d_{x^2-y^2}$

Pictorially:

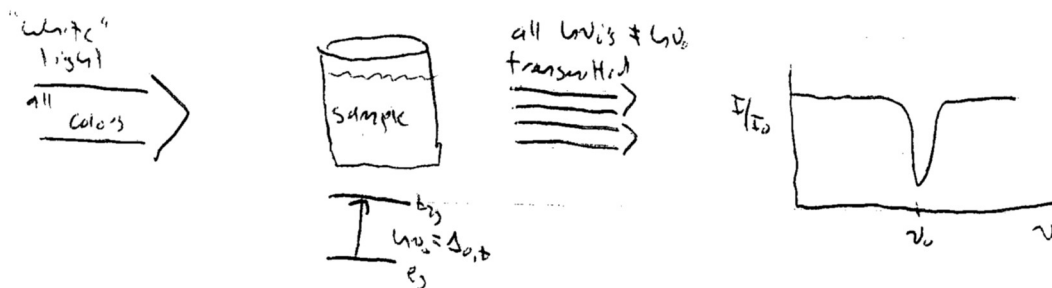


Magnetism, color and structure:

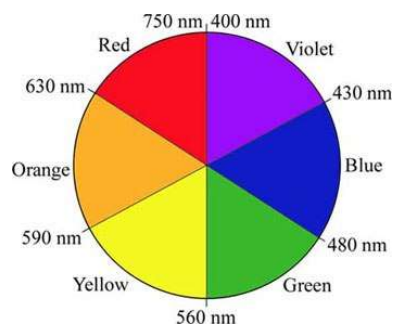
We can determine the electronic structure of the complex using magnetism and color:

Low spin \leftrightarrow large Δ , and vice-versa.

Note that for the octahedral or tetrahedral cases, where there are two energy levels, large Δ means that the photon frequency ν (associated with the distance from the lowest to highest level, i.e., $h\nu = \Delta_o$ or $h\nu = \Delta_t$) is in the blue/violet or UV.



Our eyes see what's transmitted, not what's absorbed. We see the complementary color⁴⁸



i.e.: blue dyes absorb orange light
orange dyes absorb blue light

⁴⁸ From <https://darwinsfinch.wordpress.com/2015/07/10/targaryens-gamora-and-nibiru-why-is-color-only-a-fantasy/>

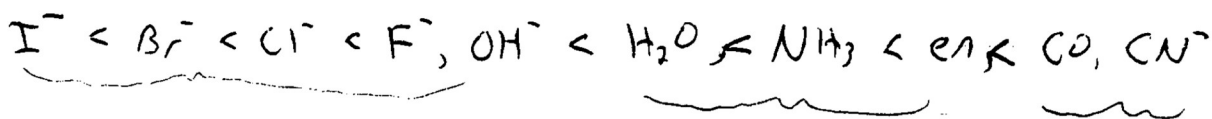
If Δ_o or Δ_t is large, we observe red, yellow, and orange color (since then higher frequency light, violet and blue, will be absorbed).

If Δ_o or Δ_t is large, we observe a blue, green, or violet color.

If all levels are occupied (e.g., d^{10} , like Zn^{2+}), the **light will not be absorbed specifically** at a frequency $\nu = \frac{\Delta}{h}$, since the upper level is fully occupied, so the compound is colorless or white (like ZnO, zinc oxide, a white powder which is a common sunscreen as it absorbs over a wide range of UV frequencies, not just one)

(Note that a compound which absorbs everywhere across the optical spectrum looks black.)

By measuring magnetism and absorption for many many ligands, we have the **spectrochemical series** of weak to strong fields.



Field:	weak	intermediate	strong
Spin:	high (as many unpolarized e's as possible)	intermediate	low (as few unpolarized e's as possible)
Absorb color:	red, orange, yellow	yellow, green	blue, violet
Appears:	green, blue, violet	violet, red	orange, yellow

Details:

- Different transition metals have different Δ 's depending on the size of the d-orbitals: Larger d orbitals \rightarrow more repulsion \rightarrow larger Δ 's.

2^{nd} and 3^{rd} row TM's have large d's, so essentially all ligands are "strong field" – all complexes are low spin and red, yellow or orange colored

For example: $[\text{PtCl}_6]^{2-}$. Even though Cl^- is weak for a first-row TM, since Pt is a 3rd row TM this complex is “strong” and therefore yellow.

- First row TM's have d's that decrease in size as we go across due to the increasing Z_{eff} : “late” TM's (RHS) have more weak-field ligands than “early” TM's

For example, Ni : has smallest d's, so only CN^- and CO are strong-field ligands and lead to absorption in violet; all other ligands are weak-field.

For example:

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green (absorbs red),
 $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is blue (absorbs orange).

Another example:

Fe^{3+} : H_2O and OH^- are strong field ligands (complexes of Fe^{3+} with water and/or OH^- look yellow, absorb violet).

Next:

Lanthanide Elements

Because the f orbitals are far from the nucleus, 4f electrons don't start filling until after the 6s orbitals and the first 5d one. Thus:

La: $[\text{Xe}]6s^25d^1$

Ce: $[\text{Xe}]6s^25d^14f^1$

Pr: $[\text{Xe}]6s^25d^14f^2$

etc.

Because of this, essentially all lanthanides form stable +3 ions with configuration $[\text{Xe}]4f^n$

As with TM's, we get exceptions when we can ½-fill the f-subshell, so Ea, Gd, Am, Cm all have f^7 configurations, and Yb has an f^{14} configurations (as does No, but it doesn't exist long enough to check).

As a result, Eu^{2+} and Yb^{2+} are also reasonably stable.

Because they have no outer-shell (ns) or $(n-1)d$ e's, lanthanides all behave similarly, as the f orbitals are buried. Therefore, they behave more like a +3 alkaline earth (Ca, Mg, Sr) than like Co^{3+} or Cr^{3+} .

Lanthanides thus tend to form ionic compounds.

Since f electrons provide poor screening, so Z_{eff} rises across the series, the atomic radius decreases dramatically (this is called "Lanthanide Contraction").

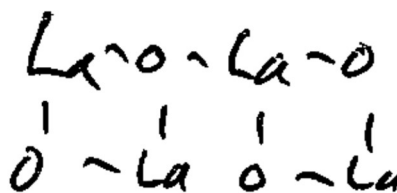
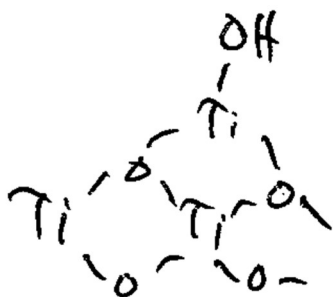
For example, Ho^{3+} is a smudge smaller than Y^{3+} and has almost the same chemistry. In fact, all lanthanides have similar chemistry, and are found together in the Earth (and are difficult to separate from each other).

Lanthanides have strong $f \rightarrow f$ absorption transitions, usually quite sharp, with only minor splitting from any ligands, so they are used as phosphors (emitting light at optical frequencies).

Most La's prefer to bond with F or O; can make complexes with highly electronegative ligands and coordinate up to 12 ligands.

Metal oxides of La's are ceramics, most of which are hydrophilic, but Lanthanum oxide (La_2O_3 type ceramics) is hydrophobic.

Specifically, compare titanium oxide (which is hydrophilic) with Lanthanum oxide:



vs.

In the right hand picture, the La has nothing for water to grab on to.

Epilogue

This is almost the end of the course; one thing we did not cover and may cover if we have time is Ligand Field Theory (the molecular orbital extension of crystal field theory).

You learned a huge amount of chemistry...and hopefully you'll continue your studies, both in 20B (which talks about states of matter, temperature and change) and later in more specialized courses, about organic, inorganic and physical chemistry.

Good Luck in the exam!