GENERAL CHEMISTRY SECTION I: ATOMIC THEORY

LECTURE 1: WAVE-PARTICLE DUALITY OF LIGHT

Time out for a first lesson on active learning. Most people make a cursory glance at an outline or summary and head immediately for the meat of the material. This is a really dumb and lazy idea. Instead, think how much better a context for the material you'd create if you started by **memorizing the summary**. For example, see if you can describe out loud to yourself the material in the outline below. After all, you will see me do it to start each class, and it's the main reason I don't really need to look at my notes during lecture – I have already proven to myself that I know what I will be talking about.

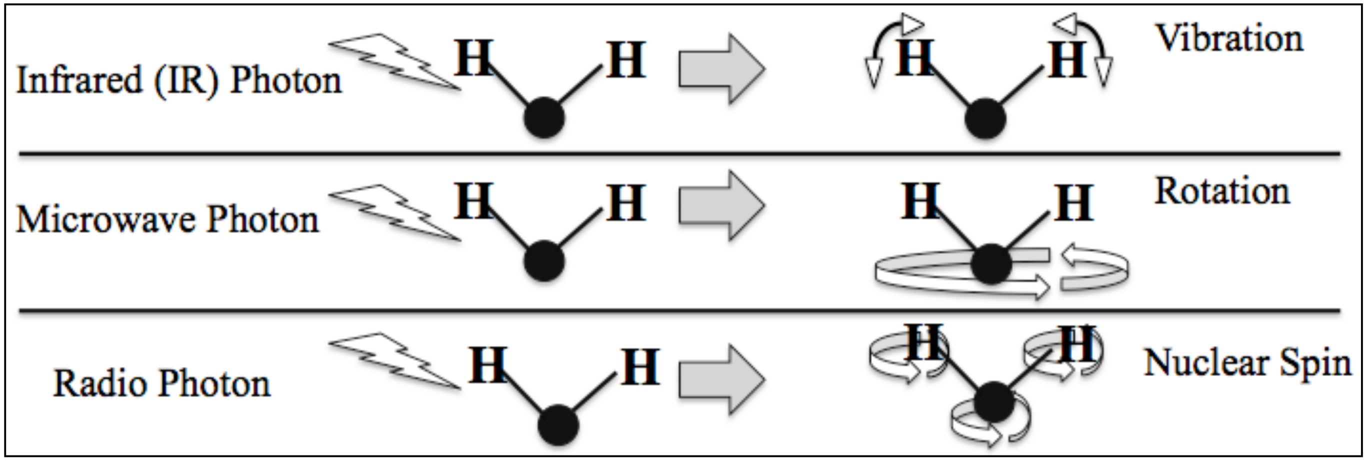
Chapter Summary

For any general chemistry course taught with an "atoms up" approach, an overview of the first chapter requires an argument for how light interacting with matter paved the way for a quantum mechanical revolution, which ultimately revealed the electronic configuration of atoms. Here is a summary of the argument:

- The best way to interrogate atomic and subatomic particles is with **electromagnetic radiation** (i.e., light; abbreviated "**EMR**"). So it's important to understand its properties, like wavelength and frequency.
- The classical interpretation of light is as a **wave** – but that idea breaks down in explanations of **blackbodies** and the **photoelectric effect**. So Planck and Einstein redefined light as a **particle** with **discrete energies**.
- DeBroglie says that there is a **duality (wave and particle)** to both **light** and **matter**.
- The **uncertainty principle** provides a lower bound for measurements of uncertainty when answering the question, where are electrons located in an atom at a given point in time?
- Schrödinger develops **quantum mechanics** so that he can identify the **wave functions** that describe physical systems, like the **particle in a box**.
- Balmer and Rydberg see discrete lines in **atomic spectra**. Schrödinger explains those with quantum mechanics.
- Using an appropriate **potential energy function**, the **quantum number** describing size of atoms, n, generates correct **energy levels**.
- Two more quantum numbers, ℓ and m_ℓ, explain **orientation** and **shape** of the orbits formed by electrons.
- A final quantum number, m_s, explains the discrete nature of an electron's **spin**.

ELECTROMAGNETIC RADIATION: CHARACTERISTICS

We are interested in electromagnetic radiation because it's used to probe the molecular, atomic, and subatomic nature of matter. Note how different light energies promote different kinds of motion in atoms and molecules:



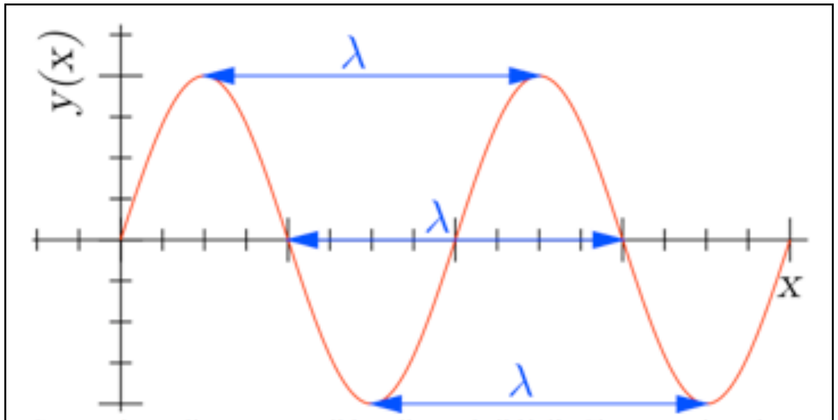
EMR characteristics: EMR radiation is classified by either **wavelength** (**λ**; "lambda") or **frequency** (**ν**; "nu"), and these are **inversely** related to each other through the constant, ***c***, which is the **speed of light**.

$$c = \lambda \nu$$

λ = wavelength (length, from meters to picometers)

ν = frequency in Hz (sec^{-1})

c = speed of light = 3.0×10^{8} m/s



Source: https://commons.wikimedia.org/wiki/File:Sine_wavelength.svg

Example: Calculate the wavelength of light from traffic signals (in nm).

Pertinent Data		Equations	Constants & Conversions
Green	5.75×10^{14} Hz	$\upsilon = c/\lambda$	$c = 3.0 \times 10^{8}$ m/s
Yellow	5.15×10^{14} Hz	$\lambda = c/\upsilon$	1 m = 10^{9} nm
Red	4.27×10^{14} Hz		

Solution:

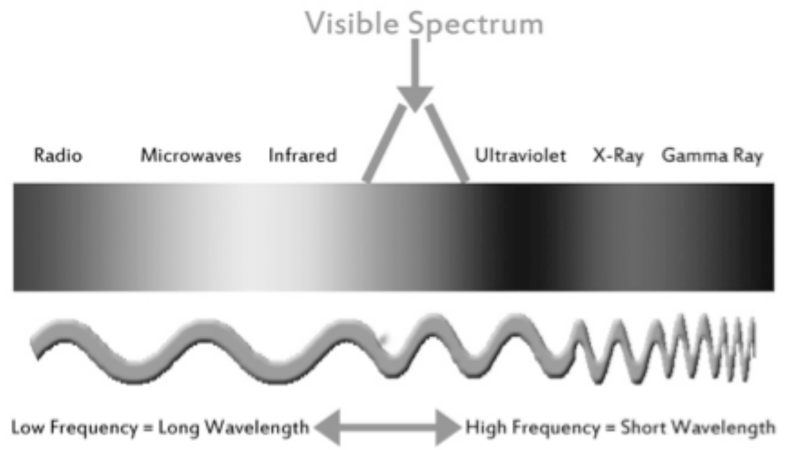
$$\lambda = \frac{3\times10^{8}\,{}^{m}/_{s}}{5.75\times10^{14}\,Hz} = 5.22\times10^{-7}\,m \quad \text{and} \quad (5.22\times10^{-7}\,m)\frac{(1\times10^{9}\,nm)}{1\,m} = 522\,nm$$

Similarly:

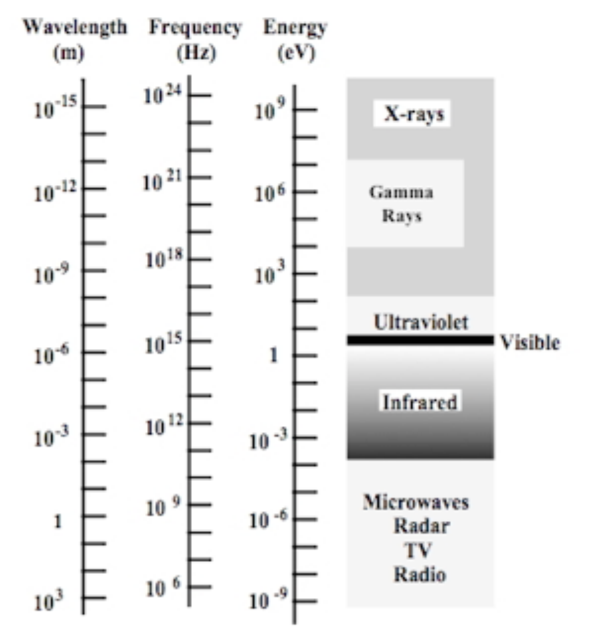
$$5.22\text{x}10^{14}\text{ Hz} \xrightarrow{\text{converts to}} 582\text{ nm} \quad \text{and} \quad 4.27\text{x}10^{14}\text{ Hz} \xrightarrow{\text{converts to}} 702\text{ nm}$$

Sensible? – Yes, since $c = \lambda\nu$, it makes sense that **as υ decreases, λ increases**.

Note the wide range of wavelengths in the EMR spectrum that are important to chemists, due to their interactions with matter. **Spectroscopy** – the measurement of **energy changes** resulting from **light's interaction with matter** – is a very useful investigative tool. For example, state troopers use it to find out your friend's blood alcohol content, and the doctor uses it to perform an MRI.



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



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

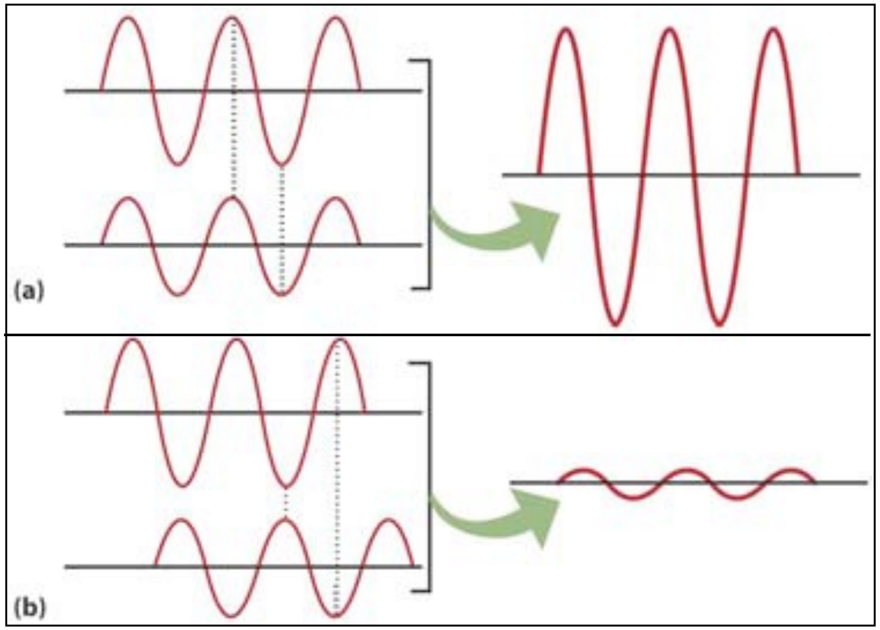
So why does EMR interact with matter? Think of it as two oscillators interacting **constructively** or **destructively**, much like the way you push a child on a swing constructively to go higher, or destructively to stop.

An example of this is a water molecule in your microwave. Here are the oscillators in our analogy:

- Oscillator 1 – the particle's motion, such as the spin of the water molecule.
- Oscillator 2 – the EMR, such as the frequency of the microwaves.

Then, when the microwave is tuned to the precise frequency at which it makes water spin, it causes an increase in the amplitude of the waves.

Spectroscopists typically monitor these changes in amplitude to know that something is going on.



Waves interacting constructively.

Waves interacting destructively.

DISCOVERING THE DUAL NATURE OF EMR

Everyone knows that we can think of EMR as a wave. Many wave-like properties of light are demonstrated by phenomena such as diffraction, dispersion, and the polarization of light. Just pick up a CD or DVD and watch the rainbow of colors flashing off the gratings (grooves), and think: waves.

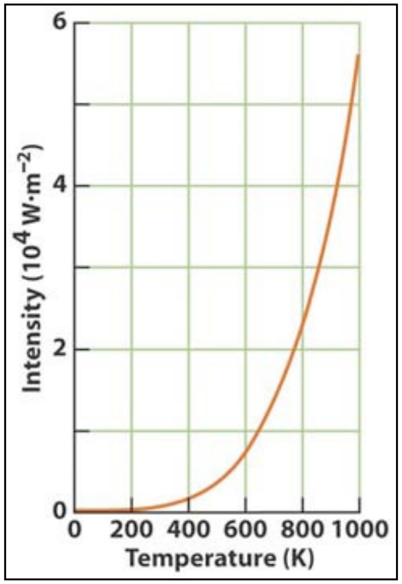
Sadly, at the turn of the 19th century, several observations of light's behavior **failed to be explained by classical physics**, indicating that other explanations about EMR's properties were needed. Consider the following:

- **Blackbody radiation** — wave theory suggests that blackbodies (**heat sources**) **transmit** radiation at **all** *υ*. **They don't.**
- **Photoelectric effect** — wave theory says **no energy minima** for **ejecting electrons** from **metal** surfaces. **There is.**

In an attempt to resolve this conflict, Planck and Einstein formed new theories about the nature of EMR. These theories suggested that **light** could be said to have a **particle nature**, with **discrete energy levels**.

BLACKBODY RADIATORS

By definition, **blackbody radiators** don't favor one wavelength of EMR over another. Was that confirmed experimentally?



1. In 1879, Stefan showed that the EMR's **intensity** (***I***) is **directly** related to the fourth power of **temperature**.

   $$\boxed{I = \text{(Power / Area)} = (W / m^2) = cT^4\text{, where } c = 5.7 \text{ x } 10^{-8}\ (W / (m^2K^4)}$$

2. In 1893, Wien demonstrated the **inverse** relationship of **temperature** (***T***) and **maximum wavelength** (λ_{max}) (as ***T*** **increases**, the blackbody shifts to **higher** *υ*). This is expressed in **Wien's Law**:

   $$\boxed{T\lambda_{max} = c_2 / 5\text{, where } c_2 = 1.44 \text{ x } 10^{-2} \text{ km}}$$

   This is why you see the color change on a heating element as its temperature increases.

Example: Calculate the temperature in deep space if the maximum λ for EMR is 1.05 mm.

Pertinent Data	Equations	Constants & Conversions
$\lambda max = 1.05$ mm	Wien's Law → $T\lambda max = c_2/5$	$c_2 = 1.44 \text{ x } 10^2$ km

Solution:

$$T = \frac{c_2}{5\lambda_{\max}} = \frac{1.44\times10^{-2}km}{(5)(1.05mm)(1m/1000mm)} = 2.7K$$

Sensible? – Yes, deep space is cold, as there are few particles to collide and transfer energy.

While classical mechanics was still accepted, experiments on blackbodies were conducted, and their results posed a problem: from the classical perspective, blackbodies should have no minimum or maximum EMR frequencies able to be absorbed and emitted. In other words, **classical mechanics** predicted that blackbodies could **absorb and emit** EMR of **infinite frequencies**.

But experiments showed that there *is* a **maximum frequency** of EMR that blackbodies can absorb and emit – in the **ultraviolet** region. How could this be explained? The answer came along with Planck's development of a **particle model** for EMR, which was a decidedly non-classical model for radiation. The idea of a discrete packet of energy allowed Planck to argue that, in blackbody radiators at **low temperatures**, there is **insufficient energy** to emit light at **ultraviolet and higher** frequencies (the frequencies with the highest energies).
Planck described the concept of a **photon** as a discrete packet of energy, with its energy dependent upon frequency.

$$\boldsymbol{E = hv}$$

v = EMR frequency

h = Planck's constant = $6.6 \text{ x } 10^{-34}$ Js

Example: What is E for a yellow photon with $v = 5.2 \text{ x } 10^{14}$ Hz?

Pertinent Data	Equations	Constants & Conversions
$5.2 \text{ x } 10^{14}$ Hz	$E = hv$	$h = 6.626 \text{ x } 10^{-34}$ Js

Solution:

$E = hv = (6.626 \text{ x } 10^{-34} \text{ Js})(5.2 \text{ x } 10^{14} \text{ sec}^{-1}) = 3.4 \text{ x } 10^{-19}$ J

Sensible? – Yes, one photon shouldn't produce much energy, so the answer must be a very small number.

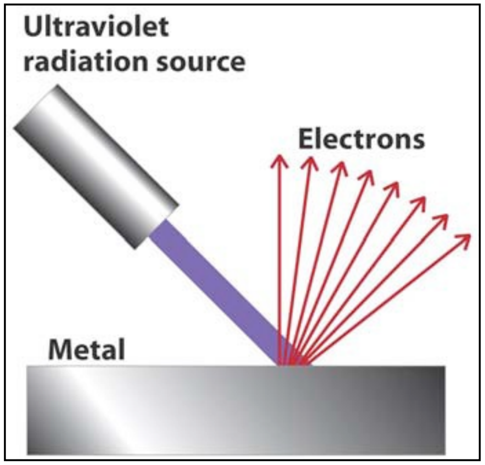
THE PHOTOELECTRIC EFFECT

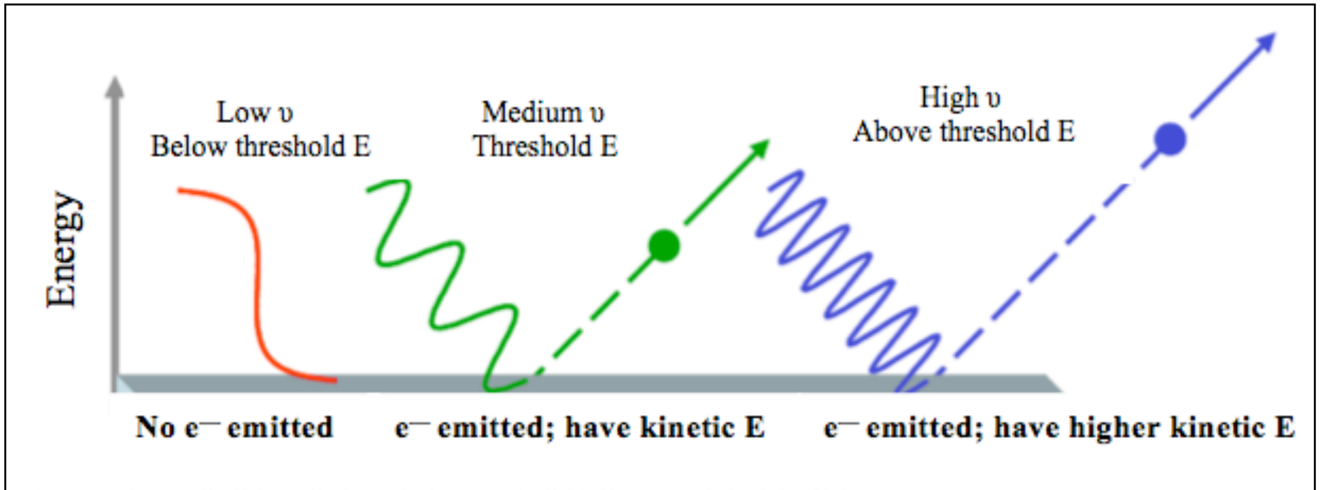
The photoelectric effect states that if you shine light on a **metal**, at a **certain** υ, electrons are **emitted**.

A **classical** model for the photoelectric effect could not be verified experimentally – it predicts that there is **no relationship** between the **intensity** of the incident light and the **energy** of the **expelled electrons**.

In his Nobel Prize winning work, Einstein explained the inconsistencies of classical theory, using the **particle model** for EMR: quantized photons must have a **minimum ejection energy**, Φ ("phi"), in order for electrons to be ejected with a **kinetic energy proportional to** υ.

$$\boxed{Ekin = \frac{1}{2} mv^2 = h\upsilon - \Phi}$$





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

The figure on the right shows how a **minimum threshold frequency** (or energy) is needed to get an electron to eject. Just as with blackbody radiators, the **particle model** was used to explain an experimental observation that had contradicted classical mechanics' prediction about the photoelectric effect.

It was clear that a new theory about EMR needed to be developed – one that could account for **light's wave-like *and* particle-like behavior**. This property of EMR came to be known as the **wave-particle duality of light.**

ALL EQUATIONS

$$\nu = \frac{c}{\lambda}$$

$$\Delta E = h\nu$$

$$\Delta E = h\frac{c}{\lambda}$$

The Speed of Light

$c = 3.0 \times 10^{8}$ m/s

Planck's Constant

$h = 6.626 \times 10^{-34}$ J·s

Lecture 2: The Development of Quantum Mechanics

Chapter Summary

Many important theoretical and experimental results would follow from the discovery of the particle nature of light.

- **Matter** also has a **wave-particle duality.** Turn about is fair play as deBroglie showed that matter, even people, have a wave-like nature. The **deBroglie wave equation for matter** is: "$\lambda = h / p$", where "$p = mv$", and m = momentum. (Recall: λ = wavelength, m = mass, v = velocity, and h = Planck's constant (6.6×10^{-34} Js)). From the wave equation, note the **inverse** relationship of ***m*** **and λ**. Which means that a 1g mass (heavy) moving at 1 m/s has $\lambda = 7 \times 10^{-33}$ m, whereas a proton (very, very lightweight) moving at the speed of light has $\lambda = 1 \times 10^{-11}$ m.
- The **uncertainty principle** says that if photons are waves, then – in the same way we can't pinpoint the location of a wave after we pluck a guitar string – we can't say where a photon is (or an e^-, for that matter).
- The **discrete lines** in **atomic spectra** suggest a particle-nature to EMR: the lines correspond to the transition of an emitted photon between an atom's energy levels; in other words, they show an electron moving between upper and lower stability regions of an atom.
- Schrödinger and Heisenberg develop **quantum mechanics**, in order to explain the behavior of the **fundamental particles** that make up the atom. By describing **electronic distributions** around the nucleus, it becomes possible to develop the modern theory of chemical bonding.

The Wave-Particle Duality of Matter

The last chapter talked about how light behaves as both a particle *and* a wave, but interestingly, light is not alone in that: matter has the same duality. So if **matter** has a **wave-particle duality**, shouldn't there be examples of matter exhibiting wave-like nature? **DeBroglie** helped solve this question when he generated an equation to predict the sign of matter's waves:

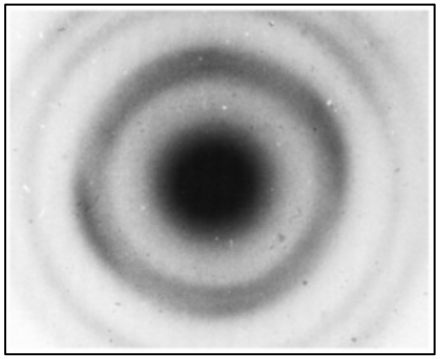
$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

λ = wavelength
m = mass
v = velocity
$mv = p$ = momentum

As expected, there is an **inverse** relationship between **mass** and **wavelength**. What are some examples of magnitudes in the relationship between λ and *m*?

- An e^- with mass of 10^{-31} kg can generate nm (nanometer; 10^{-9} m) waves
- A proton with mass of 10^{-27} kg can generate pm (picometer; 10^{-12} m) waves
- A 1 g marble can generate 10^{-31} m waves

So only atomic particles generate appreciable, detectable waves.



DeBroglie's theory of the wave-particle duality of matter was put to the test in 1925 by Davisson and Germer. The figure to the right shows what they found – a **diffraction pattern from electrons**. Diffraction is solely a wave phenomenon, but this experiment showed that electrons can do it, too.

In other words, an experimental success proved that **deBroglie was right!**
After this discovery, electron diffraction became an extraordinary tool in analytical measurements of molecules.

THE UNCERTAINTY PRINCIPLE

The wave-particle duality of both EMR *and* matter brought an end to the idea that classical physics could be used to precisely identify trajectories or locations of electrons.

Consider these notions:

- Where is a wave?
    - Pluck a guitar string. Where is the wave it makes? – Its location is not well identified.
- What about the continuum of mass and energy?
    - Classical physics predicted that, on the atomic level, matter is discrete (i.e., behaves *only* as a particle). – This turned out not to be the case, as shown by the discovery of matter's wave-particle duality.

Interestingly, it turns out that there are **complementary pairs** of physical **parameters** that allow us to **quantify uncertainty**. Here is an equation of a famous complementary pair from quantum mechanics:

$\Delta p \Delta x \geq \frac{1}{2}\hbar$ where $\Delta \boldsymbol{p}$ = **momentum** and $\Delta \boldsymbol{x}$ = **location**

(These variables are the complementary pair.)

(Side note about the constant $\hbar = \dfrac{h}{2\pi} \equiv 1.05 \times 10^{-34}$ Js – this is simply an adaptation of Planck's constant (*h*) – it's ***h*** **divided by 2*π***.)

Another famous one in spectroscopy is:

$\Delta \nu \Delta t \geq \frac{1}{2}\hbar$ where $\Delta \boldsymbol{\nu}$ = **frequency** and $\Delta \boldsymbol{t}$ = **time**

Says that the longer you look at something, the narrower (more defined) the peak.

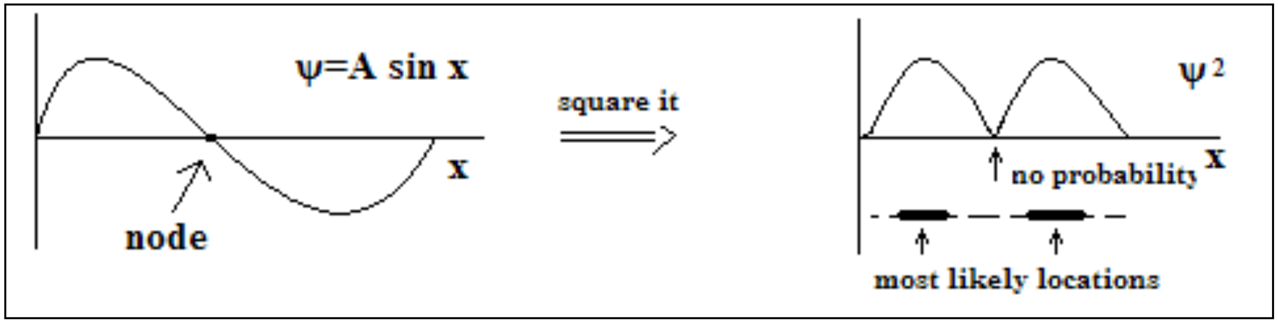
WAVE FUNCTIONS AND ENERGY LEVELS

Schrödinger decided it would be a good idea to develop a method for generating wave functions. This was the beginning of **quantum mechanics**.

$\boldsymbol{\psi}$ = psi = is the **wave function** he wanted to identify.

The reason to bother with ψ:

$\boldsymbol{\psi^2}$ = psi squared = yields the **probability** that a particle will be in a **certain area (volume)** of an atom.



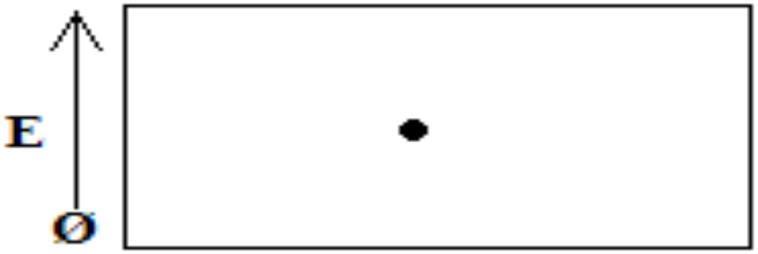
To do this, Schrödinger's method was to generate a differential equation:

$$-\underbrace{\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}}_{\text{2nd derivative of }\psi}+\underbrace{V(x)\Psi}_{\text{Potential energy function}}=\underset{\text{System energy}}{\underset{\uparrow}{E}}\Psi$$

<-------- Taking a differential equations course would let you solve this, a great reason to become an engineer!

PARTICLE IN A BOX: SOLVED BY QUANTUM MECHANICS

As a first application of the Schrödinger equation, consider the hypothetical situation of a **particle in a box**: imagine having a two-dimensional box with an electron (or proton) in it. Everywhere in the box, the potential is $V(x) = 0$ (i.e., no potential energy). Here's a depiction:

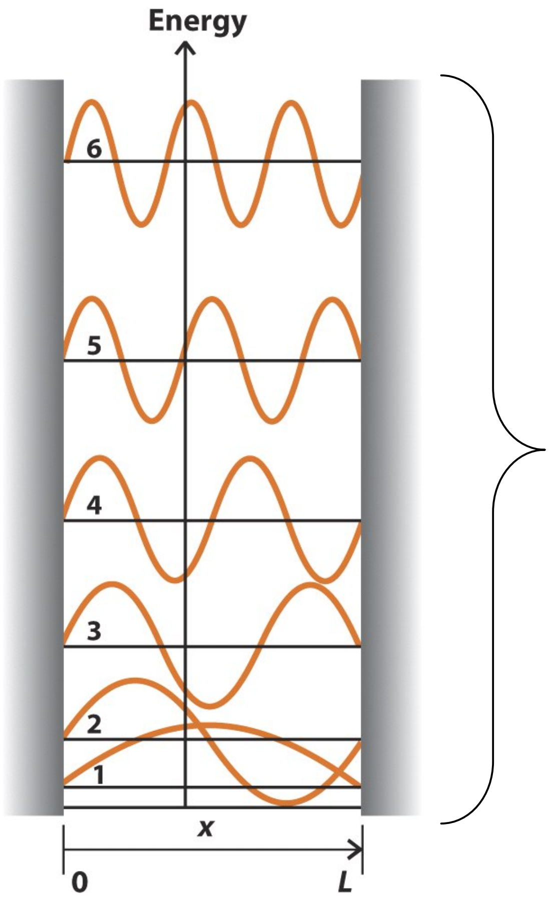


Without potential energy, Schrödinger’s equation can be simplified:

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi}$$

Now we must solve the equation to find ψ.

To better understand the particle in a box scenario, think of a model system of a standing wave in physics – this will represent the particle moving between sides of the box. One example of this is a plucked guitar string:



We need the wave to start and end on the horizontal line on both sides of the box. Note that there are only **specific λ’s** that make that happen. These particular λ’s are **functions of *L***, the **length** of the box, just like standing waves in physics.

Just as in physics, solving a standing wave requires the wave function, and we'll use it the same way for particle in a box:

$$\boxed{\Psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad \text{where } n = 1, 2, \ldots}$$

And using previous equations to find E_k: $\boxed{E_k = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}}$

Recall: all kinetic E – no potential E in box.

Note that half-integers for λ also work: $\boxed{\lambda = \frac{2L}{n}}$

So, combining the last two equations: $\boxed{E_n = \frac{n^2h^2}{8mL^2}}$

Now we have multiple equations that give us different ways to solve for a particle in a box:

$$\boxed{\Psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)} \quad \text{and} \quad \boxed{E = \frac{n^2h^2}{8mL^2} \quad \text{where } n = 1, 2, \ldots} \quad \text{and} \quad \boxed{\Delta E = h\nu = \frac{(2n+1)h^2}{8mL^2}}$$

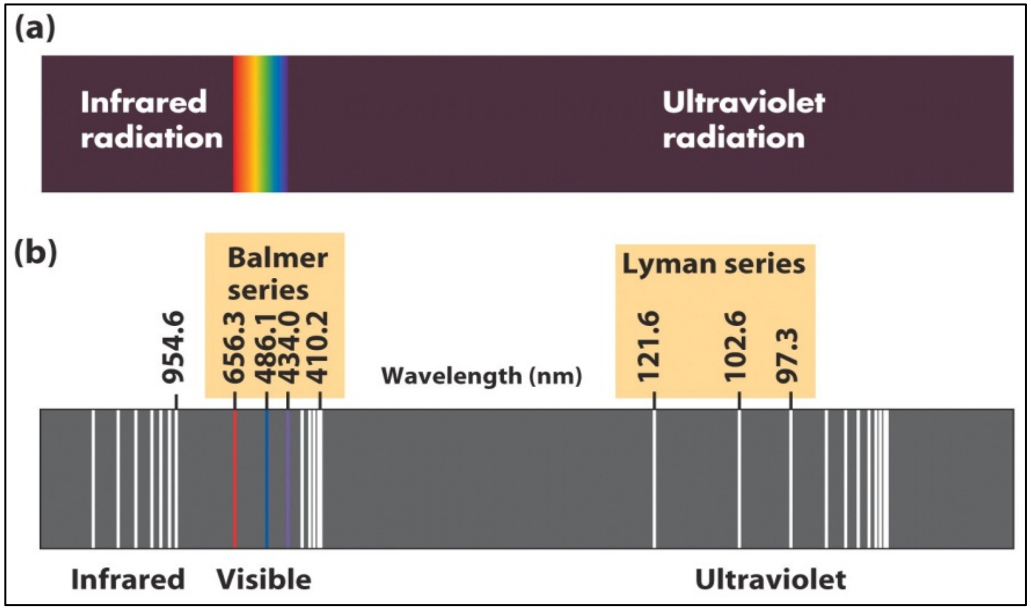
What do we see from this?

- ***E* can't be zero**, which makes sense. – The uncertainty principle doesn't permit a particle to lose all its energy and become fixed in space.
- As ***L***, length of box, **increases**, **Δ*E* gets smaller.** – This is why a macroscopic *L* (i.e., we can see it) has energy levels that are too small to distinguish.
- We have **quantized energy levels**! (n = 1, 2, 3, …) – And this was done using a classical physics model of a standing wave.
- What made the quantized levels? **Boundary conditions**. – At the edges of the box, the fixed points (represented by the horizontal line in our model system) determine which ψ are possible.

With these equations, we can find the Δ*E* between energy levels 1 and 2 by sticking in n = 2 and n = 1, getting *E* for each, and subtracting the 2 *E*'s.

ATOMIC SPECTRA AND ENERGY LEVELS

As if blackbodies and photoelectric effects weren't bad enough for classical physics, some school teacher named Balmer started electrocuting gases. The **emission spectra** he saw were not continuous, but rather **discrete** lines:



A guy named Rydberg then came up with an empirical equation to describe the separation in frequency between the lines:

$$\boxed{\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_u^2}\right) \qquad \text{with } R = 3.3\times10^{15}\,\text{Hz}}$$

Believe it or not, he decided the constant (R) should be the first letter of his last name!

Rydberg's equation $\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_u^2}\right)$ allows a quick calculation of discrete values of ***E*, *ν*, or λ** for an electron. The whole reason we're interested in ν is because it tells us the region of the EMR spectrum (IR vs. visible vs. UV) into which an emission line will fall. To do this, the electron's starting (upper) and ending (lower) energy levels must be known:

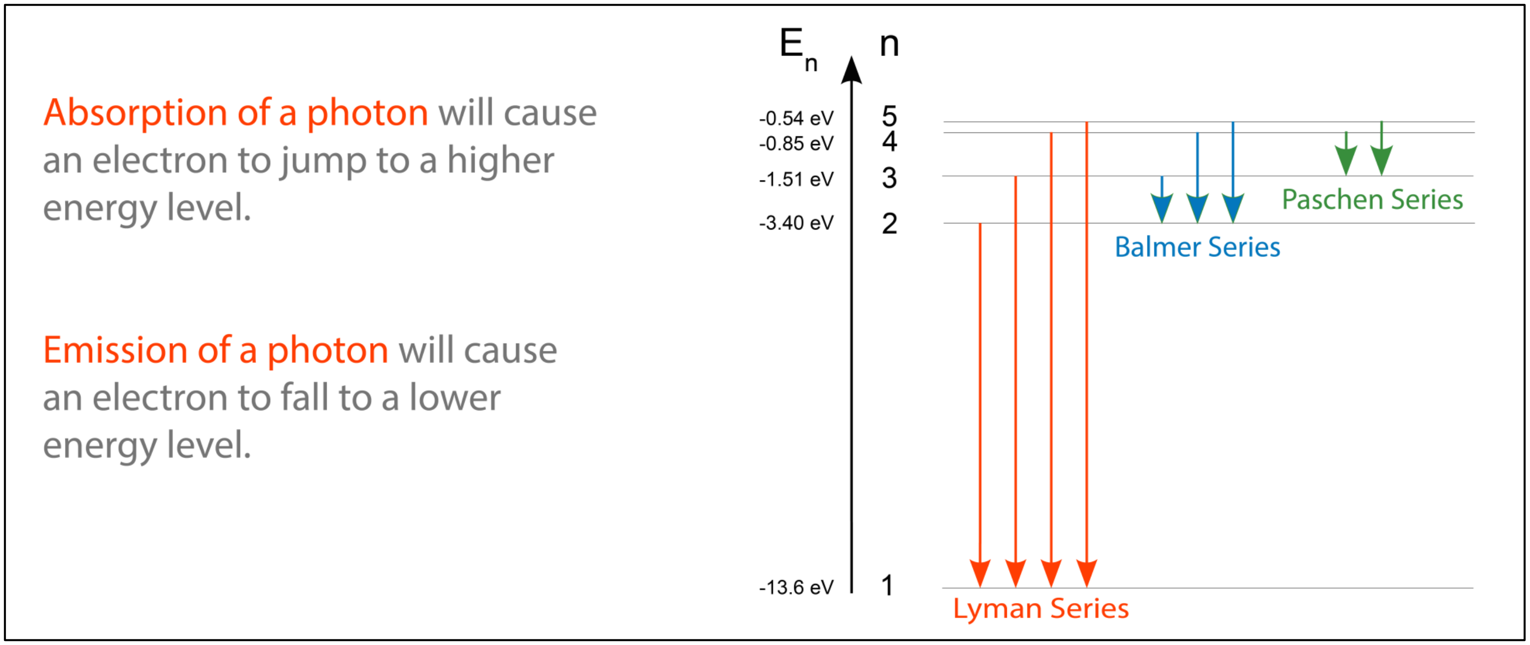
$\boldsymbol{n_\ell}$ = the lower energy level of the electron

$\boldsymbol{n_u}$ = the upper energy level of the electron

If $\boldsymbol{n_\ell}$ is ***n*=1**, the emission lines show up in the **UV** region (**<u>Lyman</u>** series).

If $\boldsymbol{n_\ell}$ is ***n*=2**, the emission lines show up in the **visible** region (**<u>Balmer</u>** series).

If $\boldsymbol{n_\ell}$ is ***n*=3**, the emission lines show up in the **IR** region (**<u>Paschen</u>** series).



Absorption of a photon will cause an electron to jump to a higher energy level.

Emission of a photon will cause an electron to fall to a lower energy level.

Important note: only the $\boldsymbol{n_\ell}$ (lower energy level) matters in determining the EMR region where emission lines fall.

Principal Quantum Number (*n*): Energy Level and Distance from Nucleus

The **principal quantum number, *n***, describes both the **energy level** of an electron and its **distance** from the atom's nucleus.

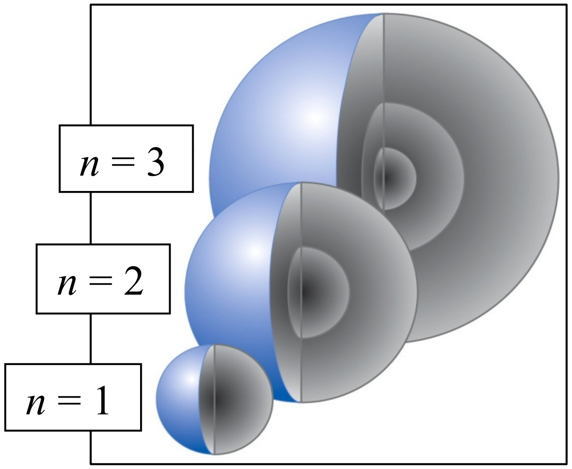
What a great chance for Schrödinger to test his equation! He could try to mimic what Balmer and Rydberg saw. The test: can quantum mechanics yield $v = 3.3\times10^{15}\left(\frac{1}{n^2}\right)$?

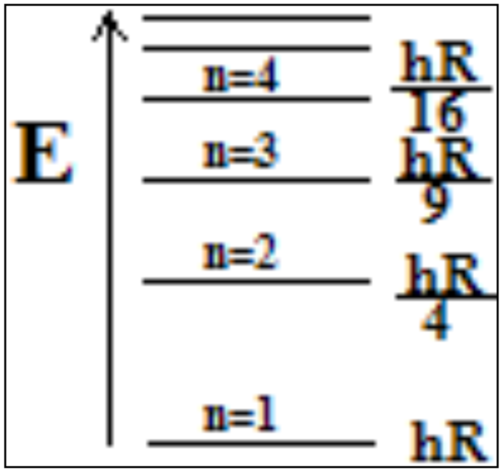
To find out, he had to solve: $-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi$ with $V(x)$ for an H atom, which is: $V(x) = \frac{(-e)(+e)}{4\pi\varepsilon_o r}$ (with r = radius of electron's distance, and ε_o = vacuum permittivity).

And the solution is…

$$\boxed{E_n = \frac{hR}{n^2} \qquad \text{with} \quad R = 3.29\times10^{15}\ \text{Hz}}$$

So… Schrödinger did it! He generated the same solution with his equation that Rydberg had experimentally. Therefore, ***n*** turns out to be the **principal quantum number** and tells us the **distance of electrons from the nucleus**.





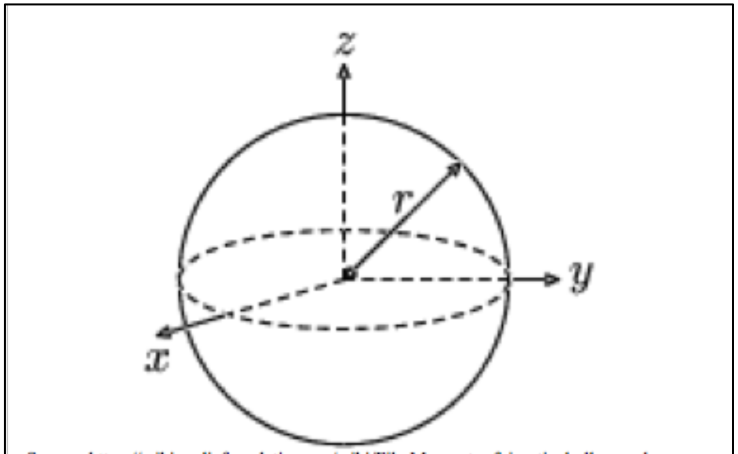
LECTURE 3: ATOMIC ORBITALS AND FINDING THE ELECTRONS

In one sentence I will tell you the most important idea in this lecture:

Wave equation solutions generate atomic orbitals that define the electron distribution around an atom.

SPHERICAL COORDINATES

To start, we need to simplify the math by switching to **spherical polar coordinates** (everything = spherical; needed for 3D spaces) rather than Cartesian coordinates (everything = at right angles; used for 2D spaces). So the wave equations generated will now be of the form **$\psi(r, \theta, \Phi) = R(r)Y(\theta, \Phi)$**, where **R(r)** describes how far out something is on a **radial trajectory** from the nucleus.



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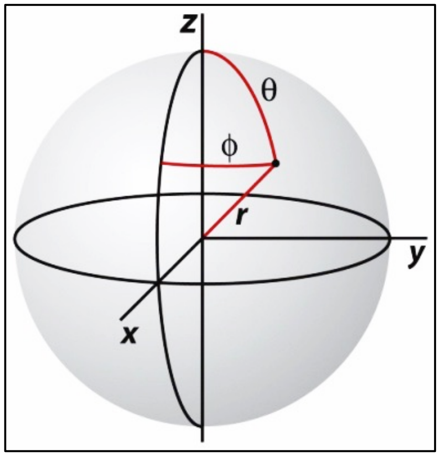
Now that we are extended radially on ψ, we need to ask where we are on the sphere carved out by R(r). Think of blowing up a balloon and asking what is going on at the surface of each new R(r). To cover the entire surface at projection R(r), we need two angles, **θ** ("theta") and **Φ** ("phi"), that get us around the sphere in a manner similar to knowing the latitude and longitude on the earth.



These two angles yield **Y(θ, Φ)**, which is the **angular wave function**.

A FIRST SOLUTION: GENERATING THE "1S" ORBITAL

So what answers did Schrödinger get for $\psi(r, \theta, \Phi)$? He found that it depended on **four quantum numbers** that bounded the system:

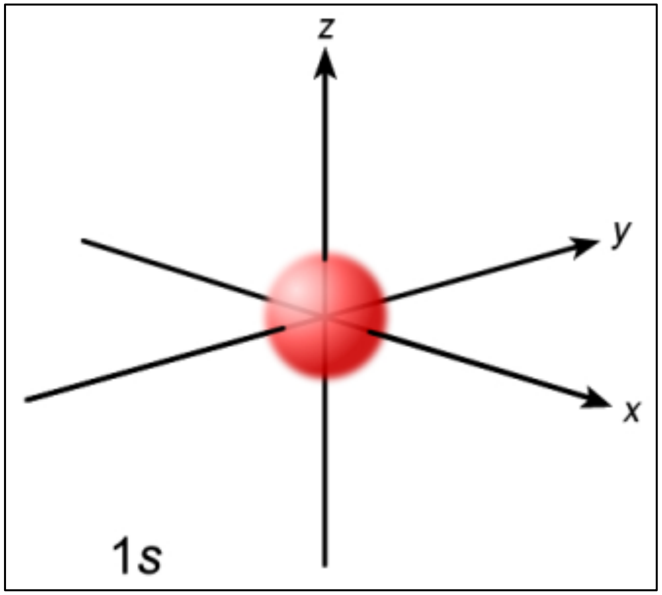
n, ℓ, m_ℓ and m_s

Recall from last chapter that ***n*** is the **principal quantum number**, and describes an electron's **energy level** and **distance** from the nucleus. We will learn about the other three quantum numbers in this chapter.

So, for example, when Schrödinger used $n = 1$ and $\ell = 0$ in his equation, his solution was:

$$R(r) = 2(Z/a_0)^{1/2} * e^{-Zr/a0} \quad \text{and} \quad Y(\theta, \Phi) = (1/4\pi)^{1/2}$$

This is the wave function for a **ground state** electron in a "**1s orbital**" and has the famous **spherical shape** that was described in the Bohr atom and in elementary school Styrofoam models across the world:



ANGULAR MOMENTUM HAPPENS

Things get a lot more complicated for ψ mathematically at even the next principal energy level, ***n*** **= 2**, as shown in the table below. Specifically, note that **when ℓ = 0, there was no θ or Φ component**; however, **when ℓ = 1, there *is* a Y(θ, Φ) term (in the form of "sinθcosΦ")**. **Y(θ, Φ)** describes the **angular momentum** of an electron.

When **ℓ = 0 → wave function equation has no Y(θ, Φ) term → no angular momentum →** We have a simple blob-like distribution of aimless electrons in a spherical area (i.e., **s orbital**).

But when **ℓ ≥ 1 → wave function equation has a Y(θ, Φ) term → angular momentum is present →** There is the **acceleration of electrons** around a non-spherical area (i.e., **p, d, or f orbital**).

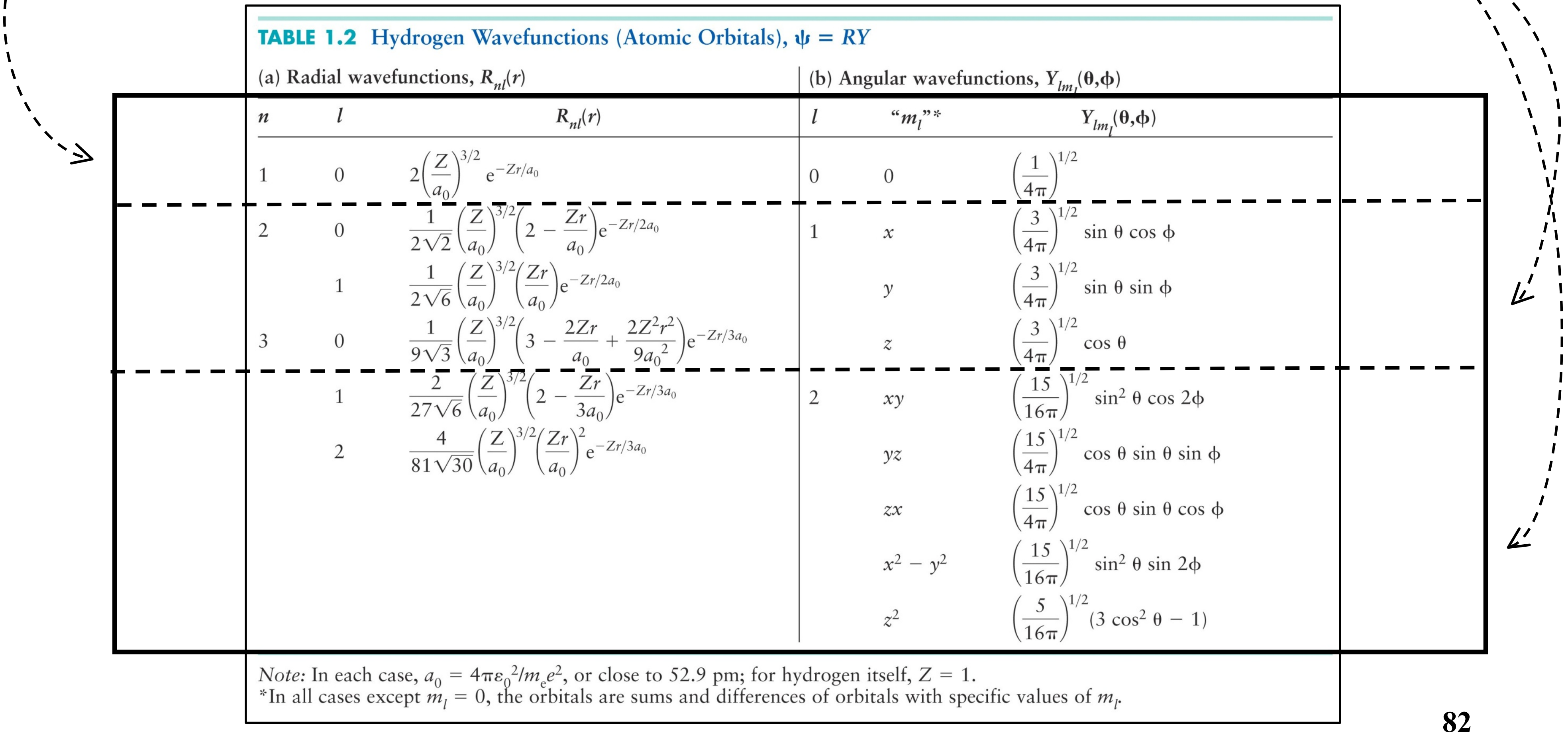


TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

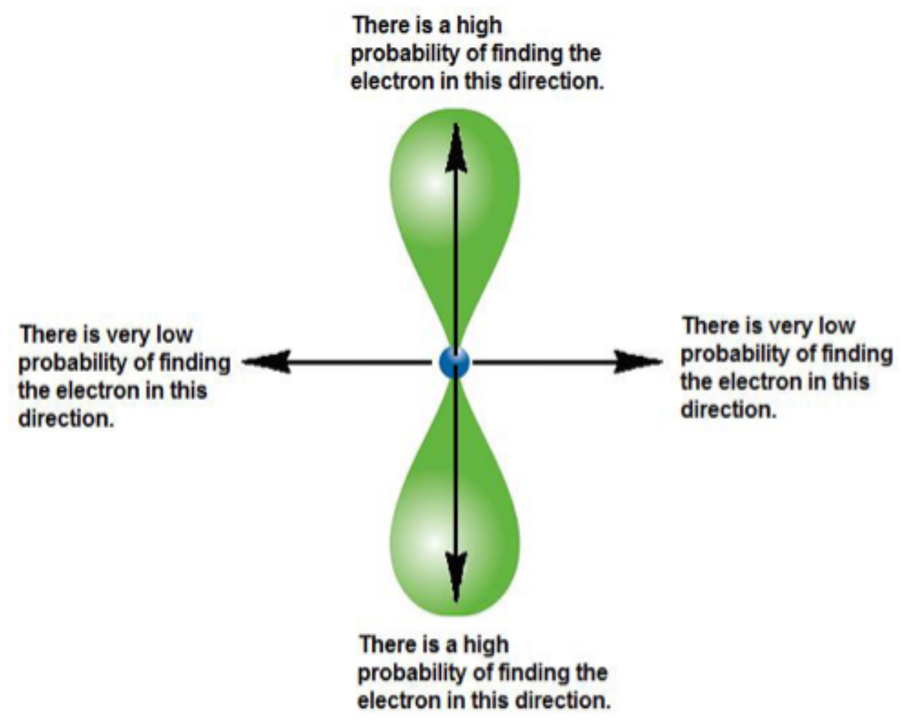
(a) Radial wavefunctions, $R_{nl}(r)$			(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$		
n	l	$R_{nl}(r)$	l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$		y	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3	0	$\frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3-\frac{2Zr}{a_0}+\frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$		z	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	1	$\frac{2}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$
				zx	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$
				x^2-y^2	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$
				z^2	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$

Note: In each case, $a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.
*In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

Ψ^2 Is What We’re After

While it’s great to have a table of wave functions (ψ), what we’re really after is **ψ^2(r, θ, Φ)**, which (recall from last chapter) tells us the probability of finding an electron in a small volume (ΔV) now defined by r, θ, and Φ.

For example, ψ^2(r, θ, Φ) for ***n* = 2, ℓ = 1** generates the famous “**p orbital**” shape that has a nodal plane at the nucleus:



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

Note: in this diagram, the x- and y-axes have the same orientation as usual (horizontal and vertical), but since we’re working in three dimensions now, there is another axis – the **z-axis** –coming in and out of the page perpendicularly.

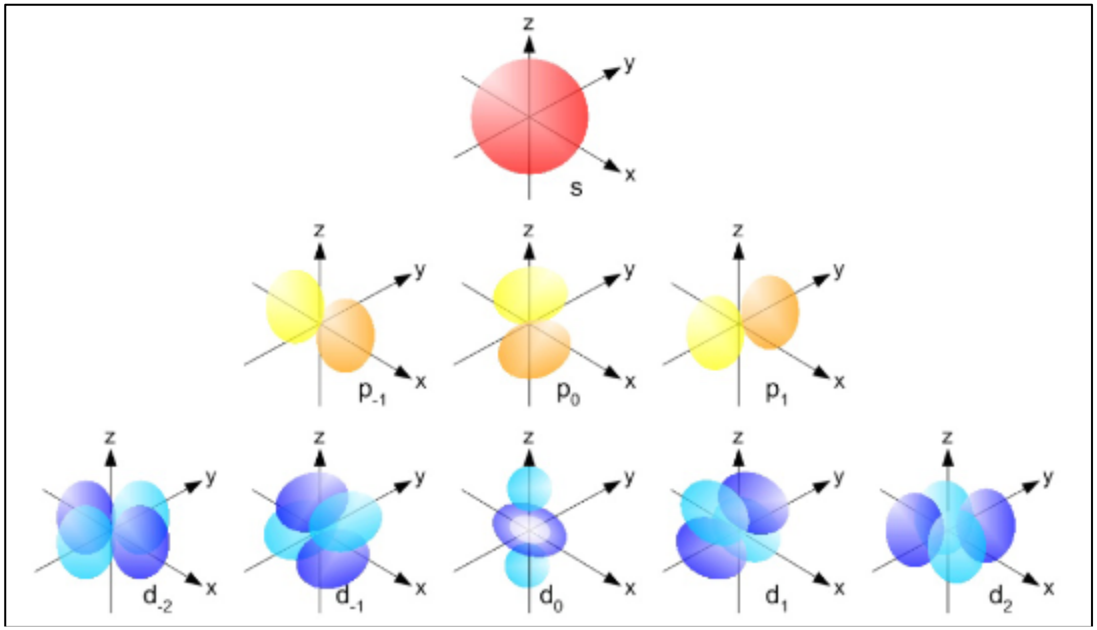
ψ^2 tells us the probability of electron density in any volume we carve around the nucleus. Simply stick in ψ^2(r, θ, Φ), and it tells you the probability of e^- density in those volumes. Thus, for example, with the quantum numbers that describe the dumbbell shape above, most of the electron density lies along the y-axis.

AZIMUTHAL QUANTUM NUMBER (ℓ): DESCRIBES THE SHAPE

The **second quantum number**, called the **azimuthal quantum number, ℓ**, tells us the **shape of orbitals**. Its boundary conditions are:

$$\ell = 0, 1, 2, \ldots, (n - 1)$$

If we calculate ψ^2 for various values of ℓ – the orbital angular momentum – we end up with shapes like:



Note that any time you have **ℓ = 0**, the orbital looks spherical, and it's called an "**s orbital**."

Any time you have **ℓ = 1**, the orbital looks like a dumbbell, and it's called a "**p orbital**."

Any time you have **ℓ = 2**, the orbital looks like two overlapping dumbbells, and it's called a "**d orbital**."

These are the famous shapes that we will draw over and over again to represent "where the electrons are" around a nucleus.

THIRD QUANTUM NUMBER (m_ℓ): DESCRIBES THE ORIENTATION

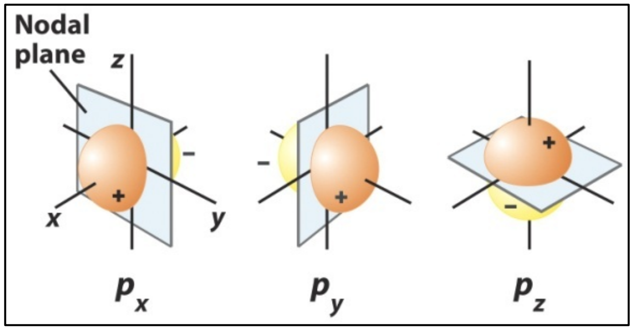
Falling out of the wave equations for $\psi(r, \theta, \Phi)$ is a **third quantum number**, **m_ℓ**, defining the **direction/orientation** of an orbital. The number of possible directions is determined by the boundary conditions, which are determined by the orbital's azimuthal quantum number (ℓ):

Given ℓ → **$m_\ell = -\ell, \ldots, 0, \ldots, +\ell$**

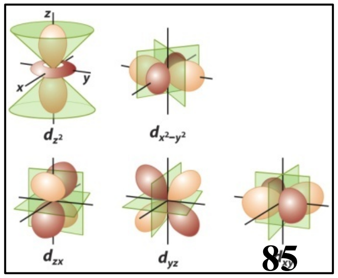
So when:

- **$\ell = 0$** → There is only **one orientation for the s orbital**.
  - Because, given **$\ell = 0$** → **$m_\ell = 0$**
  - This makes sense, because a sphere has only one orientation – it looks the same from every direction.
- **$\ell = 1$** → There are **three orientations for the p orbital**.
  - Because, given **$\ell = 1$** → **$m_\ell = -1, 0, 1$**
  - This makes sense, because a figure a couple pages ago showed a dumbbell-shaped p orbital – you could orient that dumbbell along any of the three axes.
- **$\ell = 2$** → There are **five orientations for the d orbital**.
  - Because, given **$\ell = 2$** → **$m_\ell = -2, -1, 0, 1, 2$**

The orientations are not usually easy to define given our unfamiliarity with spherical polar coordinates. But fortunately we can easily identify the three directions of p orbitals (produced when $\ell = 1$) in Cartesian system:

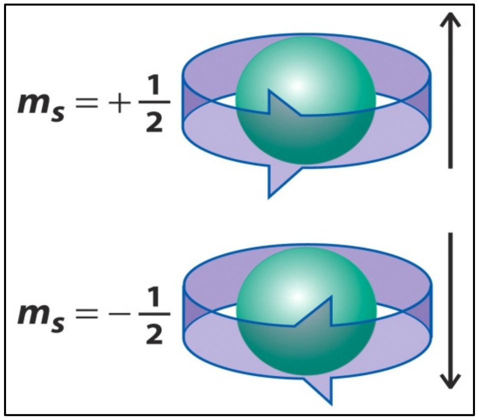


As you look at the five orientations of d orbitals (figure to the right), it is apparent that a lot more is going on with those than you will be taught in this course.



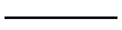
FOURTH QUANTUM NUMBER (m_s): DESCRIBES THE SPIN DIRECTION

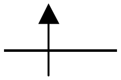
The **fourth quantum number**, **m_s**, describes the **direction of spin** of an electron. The really good news is that there are only **two ways** an electron can spin: **up and down**. They are assigned the values of **plus and minus ½**, but we don't need to be concerned with that value – just that there are two directions. (Note: the fact that m_s must be plus or minus ½ is its version of **boundary conditions**.) We can show off these two directions by picturing a cheerleader doing a handstand and spinning clockwise, next to Dr. Laude standing upright and spinning counterclockwise – or we can do it with an electron.

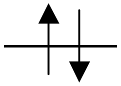


ORBITAL SHORTHAND: WRITING POSSIBLE m_s CONDITIONS

That last quantum number (m_s) is actually the one that gets depicted most often as we start to build up our electron configurations. Rather than the pretty picture above, we simply draw a short horizontal line to represent an orbital. The boundary conditions for the **m_s** quantum number say that there are only two possible electron spins – up and down. So, putting these ideas together, we end up having just **three** possible allowed states for an **orbital**: **empty**, **half-filled**, and **filled**, as depicted below.







SUMMARY OF BOUNDARY CONDITIONS

The end result of Schrödinger's solution to the wave equations for a multi-electron system surrounding a positive nucleus is the set of four boundary conditions in the table below. The allowed combinations of these quantum numbers determine the distribution of electron density around atoms and – consequently – the basis for the chemical bonding that defines matter in the universe. Learn to apply these boundary conditions and then compare them to what you see in the periodic table. They are the same. Wow. Summarizing:

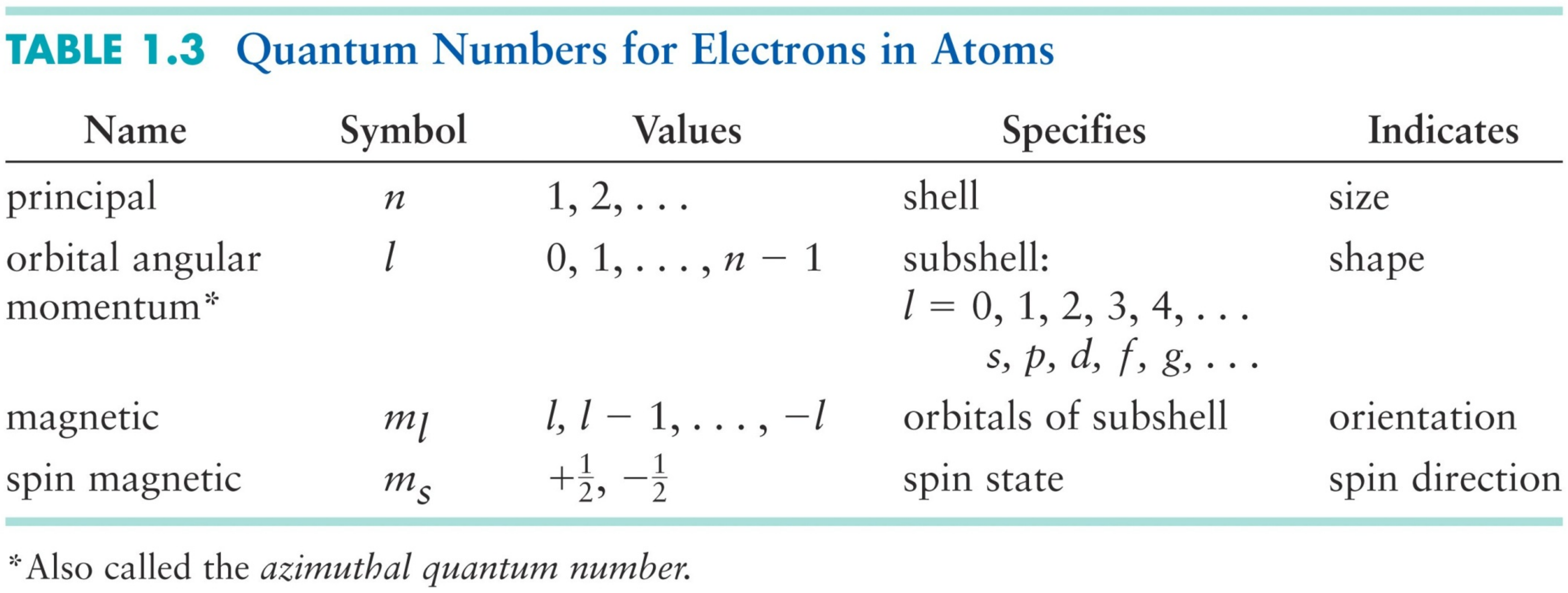


TABLE 1.3 Quantum Numbers for Electrons in Atoms

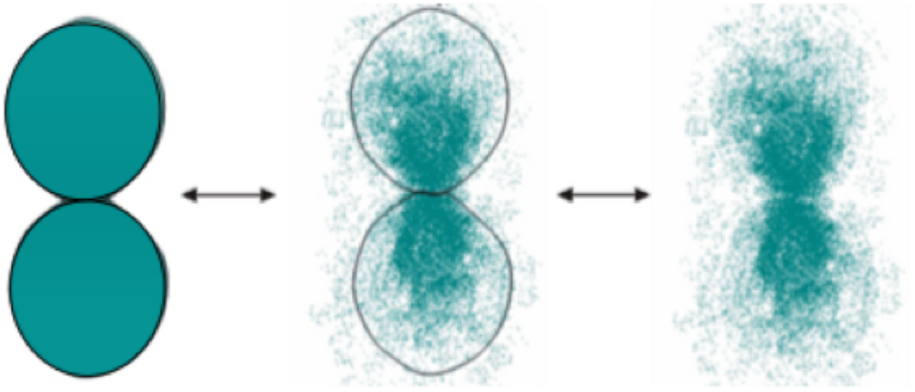
Name	Symbol	Values	Specifies	Indicates
principal	n	$1, 2, \ldots$	shell	size
orbital angular momentum*	l	$0, 1, \ldots, n-1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ $s, p, d, f, g, \ldots$	shape
magnetic	m_l	$l, l-1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the *azimuthal quantum number.*

And now onto one final idea before we leave quantum mechanics and start building electronic configurations…

RADIAL DISTRIBUTION FUNCTION

We've been thinking of orbitals as spheres and lobes that have an even distribution of electron density (after all, the orbitals we've seen were constructed with ψ^2, which gives the probability of electrons being in a certain volume of space), but it turns out that the e^- density is not evenly distributed throughout an orbital – within the same orbital, different distances from the nucleus can have different e^- densities, as seen in the p orbital to the right.



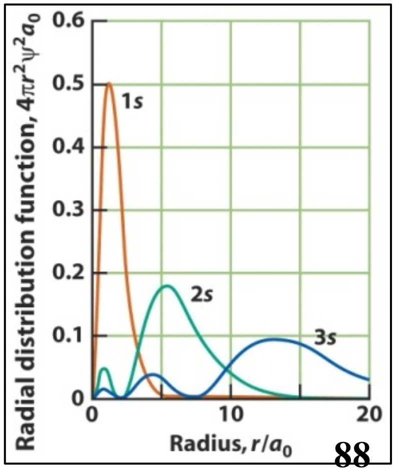
Source: https://wikimediafoundation.org/wiki/File:Electron_density_balloons.png

A way to quantify these variations in electron density is with **<u>P(r)</u>**, a **radial distribution** along a **single axis**:

<u>P(r)</u> = <u>radial distribution</u> = probability of finding an e^- at any location on the sphere carved out along r

Why are P(r) distributions valuable? Well, they tell us exactly how e^- densities vary along radial distributions. In other words, they indicate layers of differing electron density within orbitals.

The P(r) graph to the right shows how, over multiple energy levels (n = 1, 2, 3), radial distributions of s orbitals reveal that there are lots of complexities we might not have seen otherwise. For example, the larger s orbitals are not single uniform spheres – they actually have waves of increased spherical density extending out from the nucleus.



LECTURE 4: HOW TO GENERATE ELECTRONIC CONFIGURATIONS FOR ATOMS AND IONS

We are about to do something incredibly useful – create the **electronic configurations** for every kind of neutral or charged atom we can find in the periodic table. And we will do it by applying the **boundary conditions (quantum rules)** for n, ℓ, m_ℓ and m_S. We will also need to implement three rules for how one "builds up" the electrons in an atom.

Important note for this lecture and the rest: another term we use for "**orbital**" is "**subshell**." There is technically a subtle difference, but you will hear us use them interchangeably. The same goes for "**energy level**" and "**shell**."

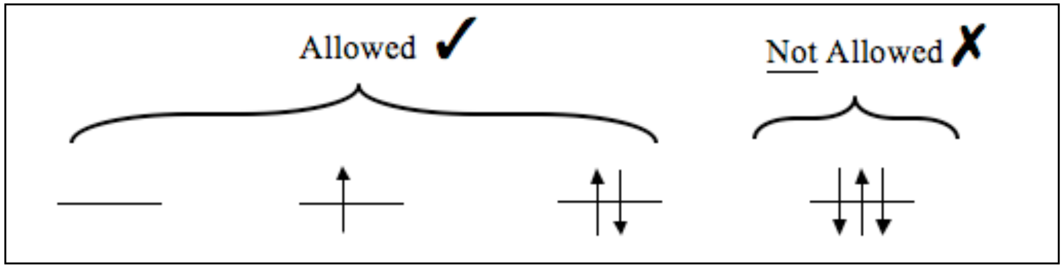
THREE RULES FOR BUILDING UP THE ELECTRONIC CONFIGURATION FOR AN ATOM

Rule 1: Aufbau Principle

Always fill electron orbits starting with the orbits that are closest to the nucleus. This is the **lowest energy** or **ground state** configuration. What are the lowest energy orbits? Look at the periodic table. You will see that the $n = 1$, $\ell = 0$ orbit (1s) comes first. The $n = 2$, $\ell = 0$ orbit (2s) comes second, and the $n = 2$, $\ell = 1$ orbit (2p) comes third. So according to Aufbau, you **fill the 1s first, then the 2s, then the 2p, and so on**.

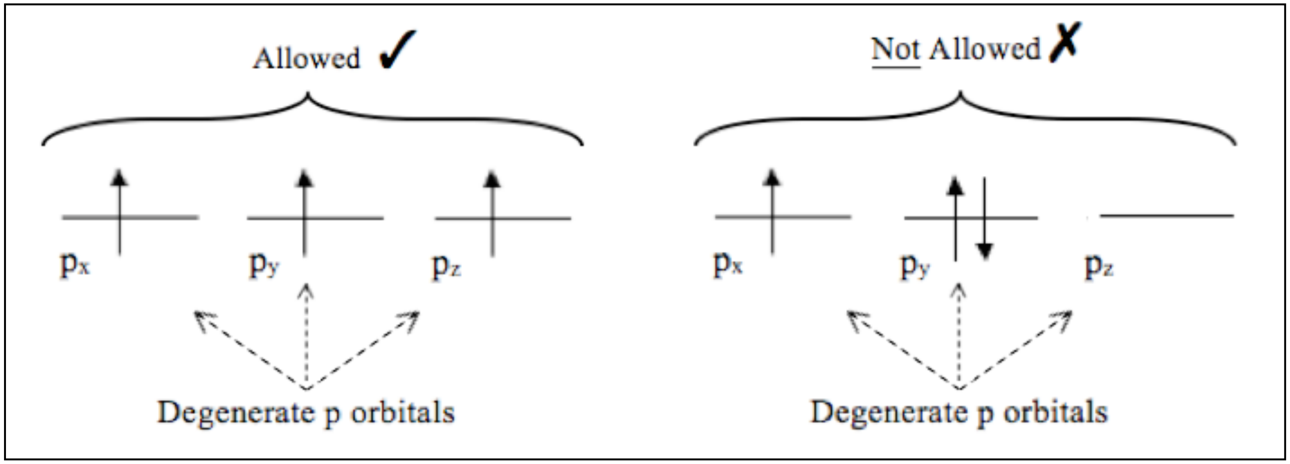
Rule 2: Pauli Exclusion Principle

Never put **more than 2** electrons in a single orbit. This is actually the consequence of a larger idea promoted by Pauli that **no two electrons** can have the **same four quantum numbers**. So, since the m_S boundary conditions only allow up to **two electrons** of **opposite spin** per orbital, you can't add a third electron to an orbit without it taking on either the +½ or -½ spin number, which violates Pauli. And I trust none of us wants to violate Pauli.



Rule 3: Hund’s Rule

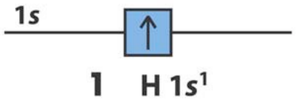
The quantum rules produce energy levels (n) that are the same (**degenerate**) for **p and higher** orbitals. In building up the electrons in an orbit, you must **distribute** the electrons **between degenerate** orbitals as much as possible to minimize electron repulsion effects.



PUTTING IT ALL TOGETHER FOR THE SMALLER ATOMS

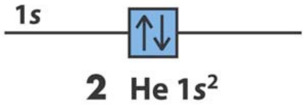
Following Aufbau, Hund, and Pauli, we can get under way with building up electronic configurations, **beginning with the lowest-energy** orbitals. We’ll start by placing a single electron into the very first orbital – the one with the lowest energy of all orbitals: the 1s orbit, with quantum numbers $n = 1$ and $\ell = 0$. Note that among the various possible charged and uncharged atoms, the first and simplest is the hydrogen atom, which has a single electron in an orbit.

The **neutral hydrogen** electronic configuration:



We can now add a second electron and again follow Aufbau, Hund, and Pauli to put another opposite-spin electron in that same 1s orbit. A helium atom is the obvious example of this electronic configuration, since it is the neutral atom with two electrons.

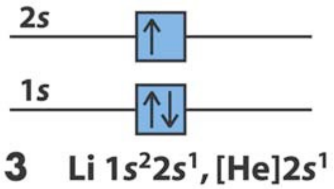
The **neutral helium** electronic configuration:



LARGER ATOMS: PAULI AND HUND SPRING TO ACTION

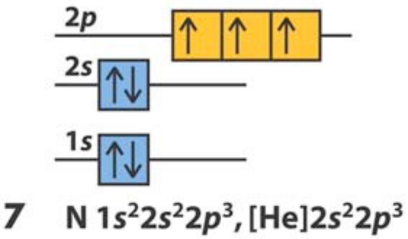
As we add a third electron, we get really excited because we can use one of our rules, the Pauli Exclusion Principle, that doesn't let us put a third electron into a single orbital. So we have to use the next lowest-energy orbital created by the boundary conditions. Recall from last chapter: when $n = 1$, there is no $\ell = 1$ (or greater), so for this next step we're going to have to move to $n = 2$ and $\ell = 0$. This is the 2s orbital, which will house our third and fourth electrons.

The **neutral lithium** electronic configuration**:**



An obvious progression through the first several neutral atoms will take us into the **2p** orbitals, where, for the first time, we are dealing with **ℓ equal to something other than zero**. Recall that when $\ell = 1$ we have a p orbital, and there are **three degenerate (equal) energy levels** for it that we can write as three horizontal dashes on the same line. With these three lines, we can now apply Hund's Rule by spreading out the electrons across the equal orbits as much as possible.

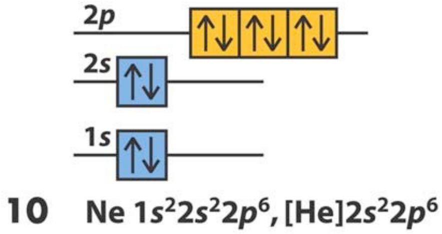
The **neutral nitrogen** electronic configuration:



THE IDEA OF FILLED AND HALF-FILLED SHELL STABILITY: A HARBINGER OF THINGS TO COME

I don't really know what a harbinger is, but it sounded like a good word to use here. Anyway, the nitrogen example above and the neon electronic configuration below are examples of what are called **half-filled** (**three electrons in a six-electron subshell**) and **filled** (**eight electrons in the n = 2 shell**) electronic configurations. It will turn out that filled and half-filled shells and subshells have **added stability**. Because of this, all kinds of physical and chemical consequences are realized. You know, for example, that neon is unreactive. The reason? It has a filled shell configuration. There is much more to come on this concept, since it is at the root of just about everything in this course.

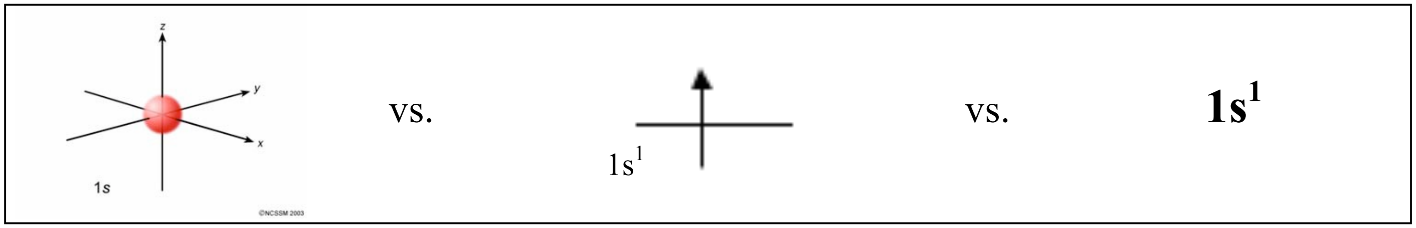
The **neutral neon** electronic configuration – a VERY stable atom:



I don't feel like doing this "building up" routine for 100 atoms. So why don't you. Meanwhile, some other related concepts.

WHAT'S THAT SHORTHAND UNDER THOSE ELECTRONIC CONFIGURATION PICTURES?

Excellent question. Chemists are lazy, and except for organic chemists, we can't draw very well either. So rather than draw all those three-dimensional pictures of ψ^2, or even those orbitals with the up/down arrows, we would rather create some **line notation** that says the same thing. So, very simply, rather than draw this or that to show you **two electrons** in a **1s** orbital, we would rather simply write "**$1s^2$**." Check out all the ways of writing the same thing:



So when you see line notation like: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$, it's just lazy chemists at work.

GETTING LAZIER

Actually, since there is so much repetition to our electronic configurations thanks to the Aufbau Principle, we can even decide to **substitute** chunks of filled orbitals with **noble gas symbols**, like [He] or [Ne]. Thus:

$1s^2 = [He]$ and $1s^2\ 2s^2\ 2p^6 = [Ne]$ and $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 = [Ar]$ …and so on.

KNOWING THE SEQUENCE OF ORBITALS

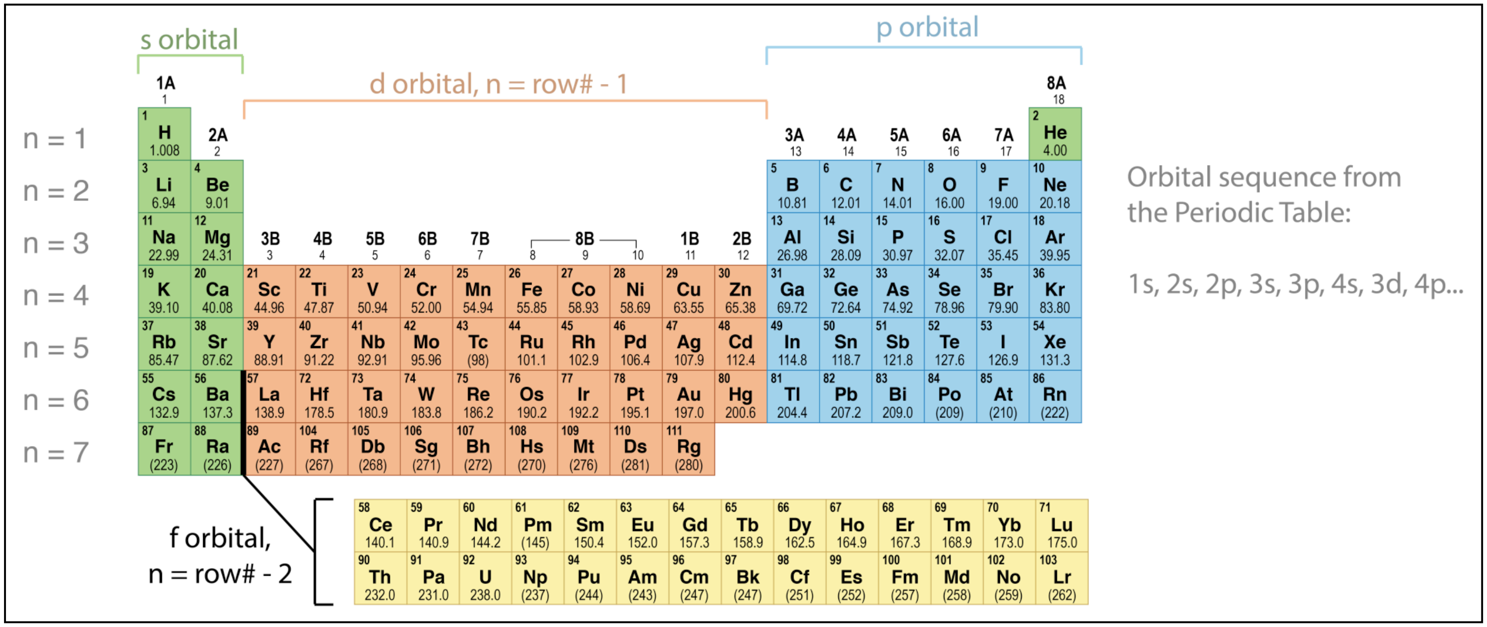
We don't get to violate Aufbau, which means we have to make sure we use the correct **order of increasing energy levels**. Is it simply what we get from following the boundary conditions for the quantum numbers? This would be:

1s → 2s, 2p → 3s, 3p, 3d → 4s, 4p, 4d, 4f → …and so on.

Sadly, no. It's actually what falls out of the energy calculations from the wave functions. Unfortunately, it's something of an increasingly arbitrary-looking sequence:

1s → 2s, 2p → 3s, 3p → 4s → 3d → 4p → …and so on.

Do we have to memorize this order? No! Why? It is found in the way the **periodic table is sequenced** (pay attention to the light font at the top of each block):



	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
n = 1	1 H 1.008																	2 He 4.00
n = 2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
n = 3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
n = 4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
n = 5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
n = 6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
n = 7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (267)	105 Db (268)	106 Sg (271)	107 Bh (272)	108 Hs (270)	109 Mt (276)	110 Ds (281)	111 Rg (280)							

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

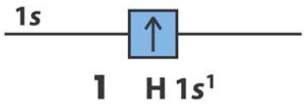
Orbital sequence from the Periodic Table:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p...

CHARGED ATOMS' CONFIGURATIONS: ONLY THE NUMBER OF ELECTRONS MATTERS

As you will soon come to learn, when drawing electronic configurations, the number of protons in the nucleus is not all that important, except in determining the distance from the nucleus to the electrons. But besides that, all that matters is the **number of electrons**. (Flashback to high school: a **charged atom** is called an **ion**.)

For example, the ions He^{+} and C^{5+} and Po^{83+} all have one electron, so their electronic configurations will all be the same as:



→ or, equivalently → $1s^1$

How about Si^{2-} and P^{-} and Cl^{+}? Note that each of the three ions has 16 electrons, so they all have the same electronic configuration as neutral S:

$\mathrm{S} = \mathrm{Si}^{2-} = \mathrm{P}^{-} = \mathrm{Cl}^{+} = 16e^{-}$ → or, equivalently → $[\mathrm{Ne}]\ 3s^2\ 3p^4$

What are the electronic configurations for Bi, Tl^{2-} and Po^{+}? In each case there are 83 e^-. So to write your configuration in shorthand, find the highest noble gas with **fewer** e^- than your atom or ion – [Xe] in this case –, and then, for the remaining e^- needed to reach the total of 83, put them in orbitals according to our three rules.

Bi electronic configuration = $[\mathrm{Xe}]\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$

You can now create electronic configurations for charged and neutral atoms. Congratulations.

As we finish the first four lectures, a great thing to remember amidst all this grief is that there is real payoff in understanding Wien's Law, particle in a box, Schrödinger, orbital angular momentum, and radial probability densities. Being able to generate electronic configurations just by staring at a periodic table sets the table (no pun intended) for you to be able to do the most important thing in all of chemistry:

Create bonds between atoms.

LECTURE 5: PERIODIC TRENDS EXPLAINED BY EFFECTIVE NUCLEAR CHARGE

Chapter Summary

The periodic table was created as a consequence of the boundary conditions imposed by the quantum mechanical solutions to Schrödinger's wave equations for multi-electron systems. What we will learn in this lecture is that, in defining the properties of atoms in the table, there will turn out to be periodic trends that go along with those properties. Specifically, we will see that as we go across the table from left to right, or down the table from top to bottom, a systematic increase or decrease in the quantitative measure of a property is observed. This is good for two reasons: first, allows us to cement into place the important ideas that explain the properties; and second, it keeps us from having to do much memorization since we can make nice sweeping generalizations.

What are the trends we'll be able to explain? There are a lot of them. But here are six you will see over the next several lectures:

- **Atomic radii**
- **Ionization energy**
- **Electron affinity**
- **Metallic character**
- **Ionic radii**
- **Electronegativity**

And what are the two big ideas that explain the trends for these six properties? They are the titles of the next two lectures:

Rule 1: **Effective nuclear charge (ENC)** will explain the relative size of atoms, as well as electrons' interest in them. As will be shown, for example, as ENC↑, size↓, and as ENC↓, size↑. A similar trend can be defined for how much an atom wants an electron. **ENC arguments** are the most important arguments in explaining the **overall trends** in the periodic table.

Rule 2: **Filled and half-filled shells have additional stability.** As mentioned when drawing the electronic configurations of atoms, whenever a filled shell or half-filled shell can be created, it will have **more stability** than **expected by our ENC** arguments. **Filled-shell** stability, for example, is the root of the idea behind the **octet rule** in explaining chemical bonds. We will also see it impact the fine structure in many of our trends, such as creating **exceptions to the Aufbau principle** for trends for ionization energy and electron affinity.

THE MULTI-ELECTRON SCHRÖDINGER EQUATION

Recall that when we had a single e^- (and nucleus), there was a simple potential energy term to stick into the Schrödinger equation:

When there is one e^- → $V(x) = \dfrac{(-e)(+e)}{4\pi\varepsilon_o r}$ → which yields the solution → $E_n = \dfrac{hR}{n^2}$

But what happens with more than one e^-? Things quickly get more complicated: we have to account for the **electrons repulsing each other**, so, in addition to the attraction term, a **repulsion term** must be added to the equation:

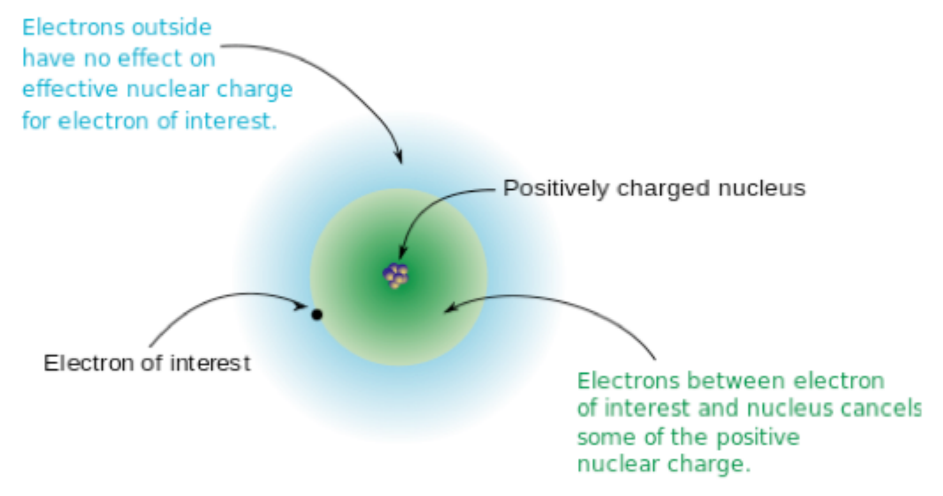
When there is more than one e^- → $$V(x) = \underbrace{\frac{-2e^2}{4\pi\varepsilon_o r}}_{\text{Attraction of } e^-_1 \text{ to the nucleus}} - \underbrace{\frac{2e^2}{4\pi\varepsilon_o r}}_{\text{Attraction of } e^-_2 \text{ to the nucleus}} + \underbrace{\frac{e^2}{4\pi\varepsilon_o r}}_{\text{Repulsions between } e^-_1 \text{ and } e^-_2}$$

The key thing to note is that in addition to the simple attractions between protons in the nucleus and each electron, there are **repulsions between electrons**. This repulsive effect – called **electron shielding** – has a profound implication in that it **keeps atom sizes from getting smaller** and smaller as the **number of protons increases**. We'd live in a very different world if an atom with 100 protons was smaller than an atom with one proton just because attractive forces ruled everything.

SHIELDING AND EFFECTIVE NUCLEAR CHARGE

The calculation of *V(r)* to determine the extent of repulsion is not something we'll bother with in this course, so we'll simplify it and make a nice freshman-chemistry definition of **shielding**: **a singly-charged electron has just as much repulsive effect as a singly-charged proton has an attractive effect**.

Let's put this into context. For innermost-shell electrons ($\boldsymbol{n = 1}$; max. of two e^-), nothing stands between them and the protons in the nucleus, so their attractive forces are in full effect. However, the same cannot be said about electrons in any shell behind that innermost shell. This is because electrons closer to the nucleus interfere (or, **shield**) the **attractive** forces **between more distant electrons and the nucleus**. In other words, all electrons are (obviously) attracted to the nucleus, *but* electrons in $\boldsymbol{n > 1}$ shells are also **repulsed** by the electrons standing **between** themselves and the nucleus, and the ultimate result is that their **attraction to the nucleus is diminished**.



Source: https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/periodic-properties-8/electron-configuration-68/the-shielding-effect-and-effective-nuclear-charge-319-7515/

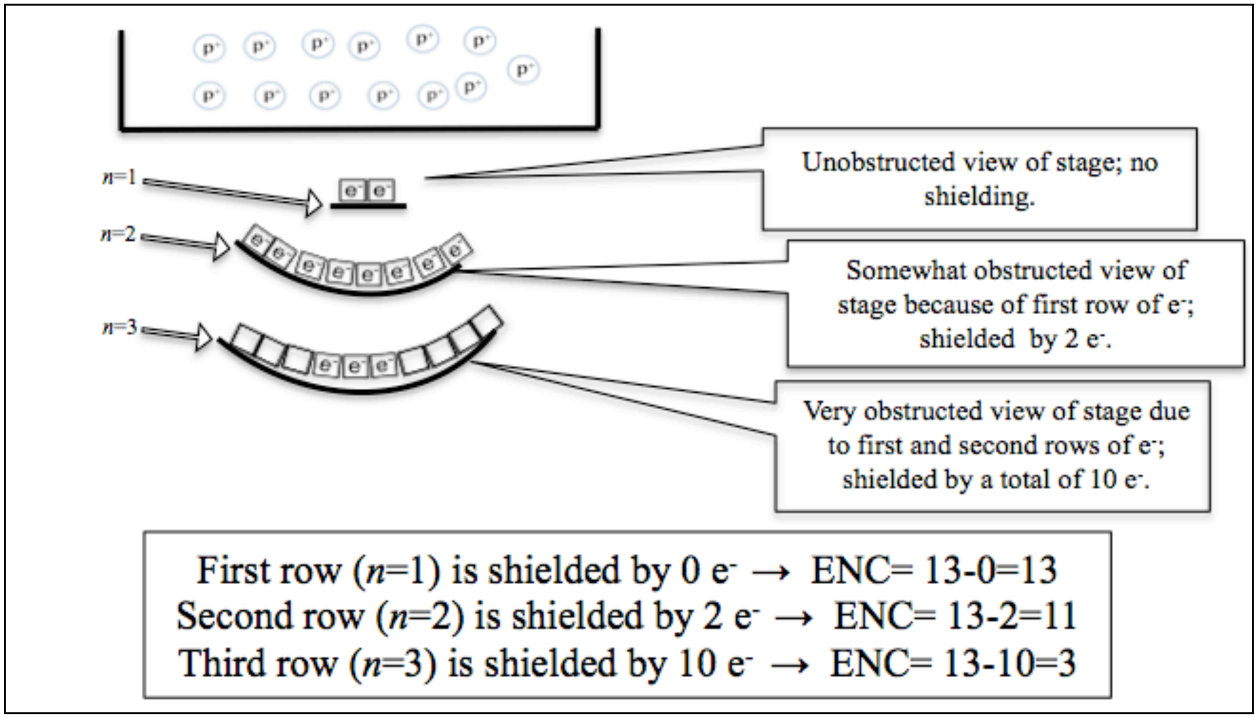
While this argument is certainly an oversimplification, it is remarkably useful in providing a semi-quantitative measure of shielding. The equation below determines the **effective nuclear charge**: the **nucleus'** pull on its electrons, taking into account any **attractions weakened** by shielding. As mentioned before, ENC explains all of the **trends in the periodic table**, so be able to do this calculation:

ENC = effective nuclear charge = (# of protons in nucleus) – (# of shielding inner-shell electrons)

ENC CALCULATIONS ANALOGY: GETTING GOOD SEATS AT A CONCERT

A better understanding of ENC might come from creating an analogy to attending a concert. The protons are the band, and the people in the audience are the electrons. Which electrons get to see the band best (i.e., experience highest ENC)? The people in front row, of course – they see all of the show. What about people in back rows? Their views of the stage aren't as good, because people in front of them block – shield – their view. They see less of the show (i.e., experience lower ENC).

So let's imagine a 13-person band (note: this equals 13 protons, which means 13 e^-, which equals 13 concert-goers) and think about the values of ENC for the first three rows of the theatre. It's also important to know that this theatre has 2 seats in the front row, 8 seats in the second row, and 10 seats in the third row. (The architect was somewhat eccentric.)



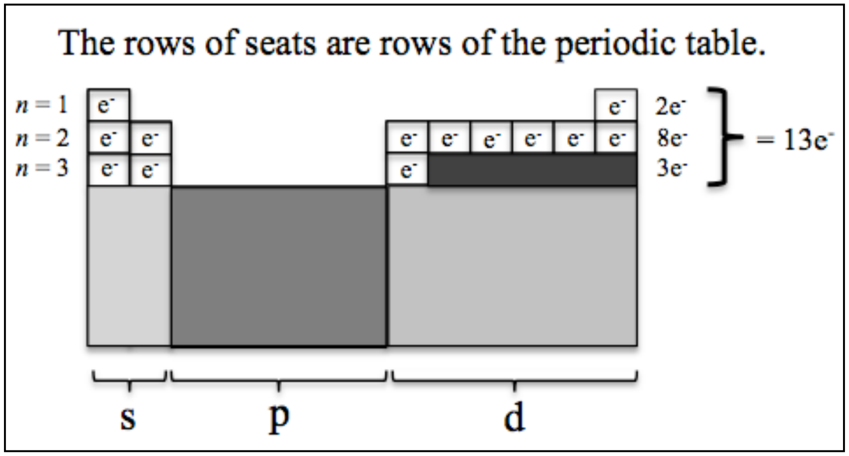
Unobstructed view of stage; no shielding.

Somewhat obstructed view of stage because of first row of e^-; shielded by 2 e^-.

Very obstructed view of stage due to first and second rows of e^-; shielded by a total of 10 e^-.

First row (n=1) is shielded by 0 e^- → ENC= 13-0=13
Second row (n=2) is shielded by 2 e^- → ENC= 13-2=11
Third row (n=3) is shielded by 10 e^- → ENC= 13-10=3

Unless you haven't been paying attention, you'll see that I can straighten out the rows in the theatre above, and you're staring at the periodic table – specifically the 13th element, Al:

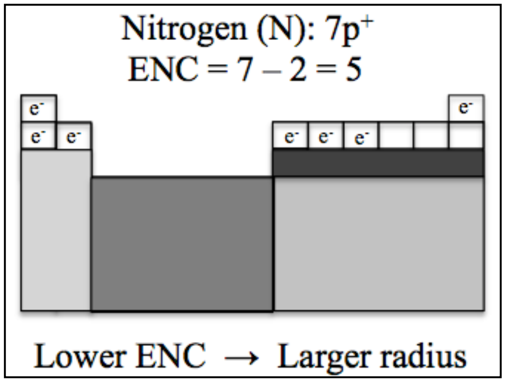

The rows of seats are rows of the periodic table.

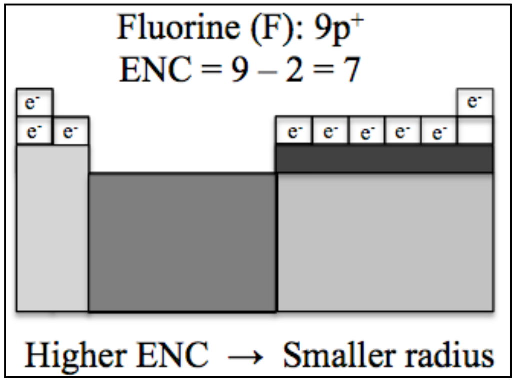
Important note: as we've been showing, each shell of an atom has its own ENC; however, when we talk about *the* ENC of an atom (which we'll be doing from now on), we're referring to the e^-'s in its **outermost shell** (AKA **valence electrons**).

ENC TRENDS IN THE TABLE: DOWN AND ACROSS

Now we can see why it is that as we go **down** the periodic table, **electrons** are **not getting closer** to the nucleus. New protons are being added, but there are an equivalent number of electrons to shield them. So **ENC doesn't increase**.

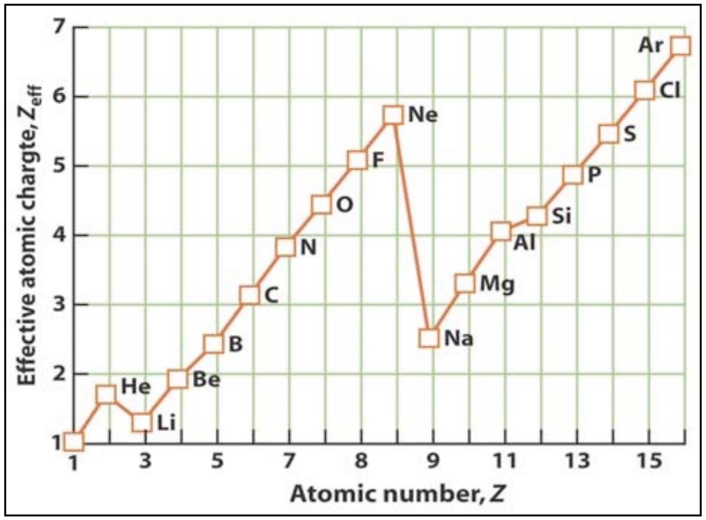
But what happens to ENC across the same row?





So going to the **right across the row**, ENC actually **increases**. This makes sense: moving to the right means getting both a new proton and a new electron, but the new electron is a valence electron, which doesn't count towards shielding (because people in your own row can't shield you). In terms of our ENC equation, this means that the left-hand term (# of protons) is increasing, while the right-hand term (# of shielding electrons) being subtracted is staying the same – this results in an ENC decrease.

So how well do our pictures correspond with the actual data? Perfectly. Study the nice zigzag shape:

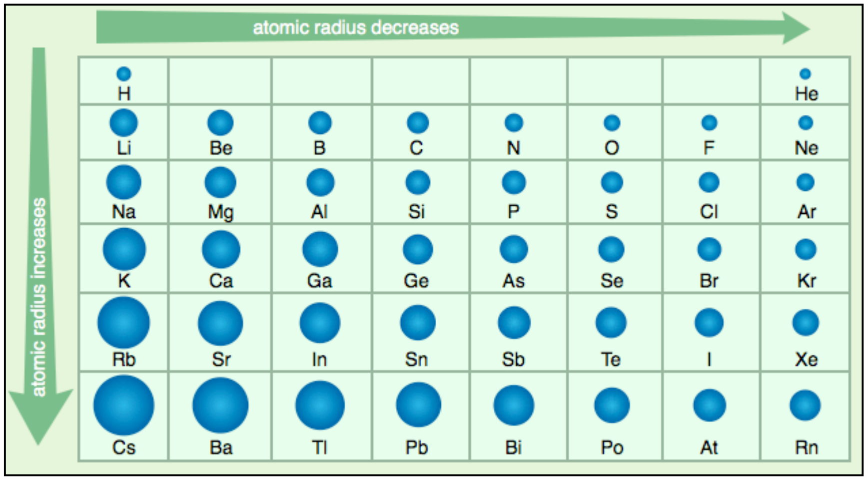


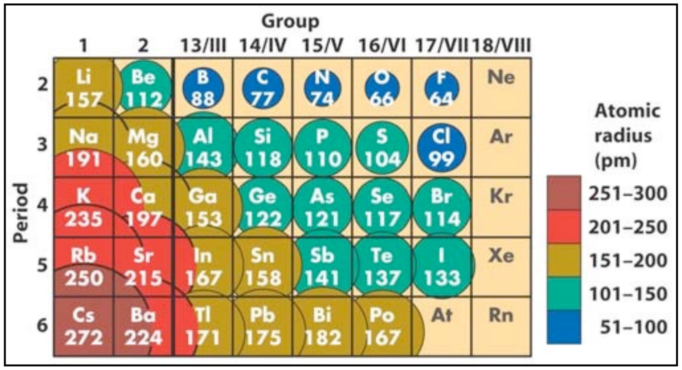
Now, what impact do these observations have on the trends in periodicity? They determine what our trends will do as we move across and down the periodic table.

TRENDS IN SIZE: ATOMIC RADIUS

The trend for **atomic radius** follows the ENC arguments closely and without exception. The arguments are simple: the **bigger the ENC**, the **greater the electrons' attraction** to the nucleus, and the **smaller the atom**; conversely, the smaller the ENC, the smaller the attraction, and the larger the atom.

Atomic radius is easy to understand, and a simple cartoon drawing fits the actual data perfectly:





Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
2	Li 157	Be 112	B 88	C 77	N 74	O 66	F 64	Ne
3	Na 191	Mg 160	Al 143	Si 118	P 110	S 104	Cl 99	Ar
4	K 235	Ca 197	Ga 153	Ge 122	As 121	Se 117	Br 114	Kr
5	Rb 250	Sr 215	In 167	Sn 158	Sb 141	Te 137	I 133	Xe
6	Cs 272	Ba 224	Tl 171	Pb 175	Bi 182	Po 167	At	Rn

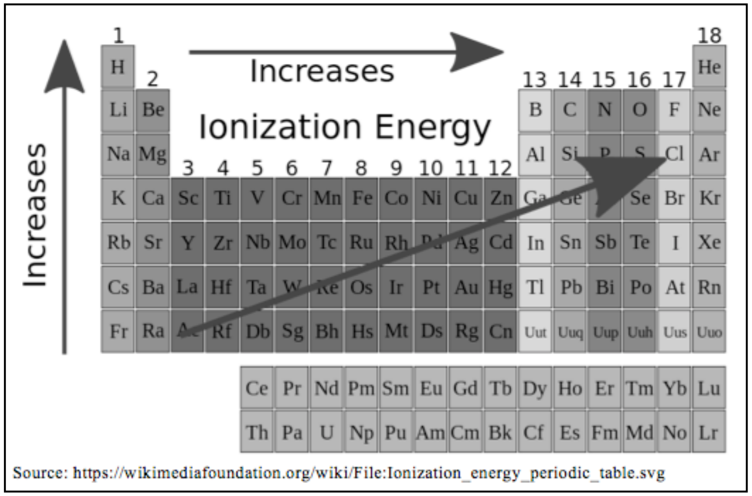
TRENDS IN ELECTRONS' INTEREST: IONIZATION ENERGY AND ELECTRON AFFINITY

What is important to see is that the trend based on **ENC** is the **same** as that of **atomic radius** – **larger going up and to the right**. ENC arguments can also be used to explain the primary trends associated with how easily an **electron is removed** from an atom (**ionization energy**) and how easily an **electron is attracted** to an atom (**electron affinity**).

Ionization Energy:	First Ionization Energy:	$M \rightarrow M^{+} + e^{-}$
	Second Ionization Energy:	$M^{+} \rightarrow M^{++} + e^{-}$
Electron Affinity (applies to gases only):		$X_{(g)} + e^{-} \rightarrow X_{(g)}^{-}$

So what should we expect?

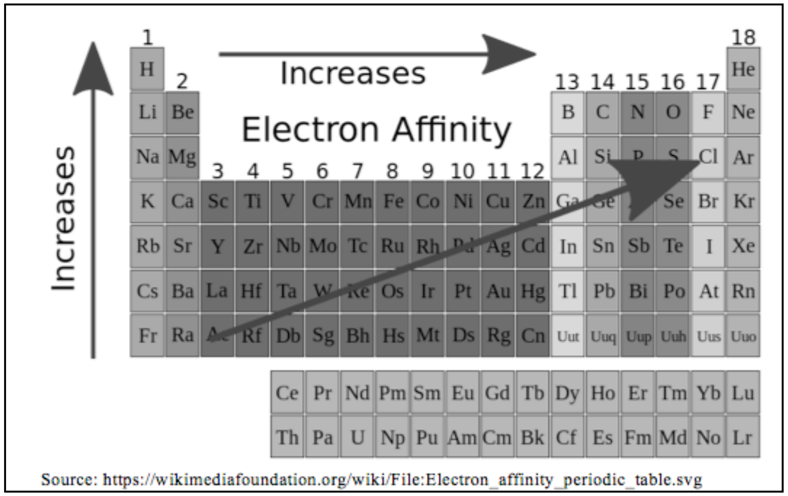
For **<u>ionization energy</u>**, getting rid of an electron should be **easiest** when **ENC is low**. So IE should be **lowest in the lower left** of the periodic table.



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

Sneak peak of upcoming lecture: ionization energy vs. atomic radius: the trend for IE isn't as smooth as the trend for atomic radius. This is due to the stability of filled and half-filled subshells.

For **<u>electron affinity</u>**, coveting an electron should be **greatest** when **ENC is highest**, which is the **upper right** of the periodic table. The trends are generally correct as predicted:



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

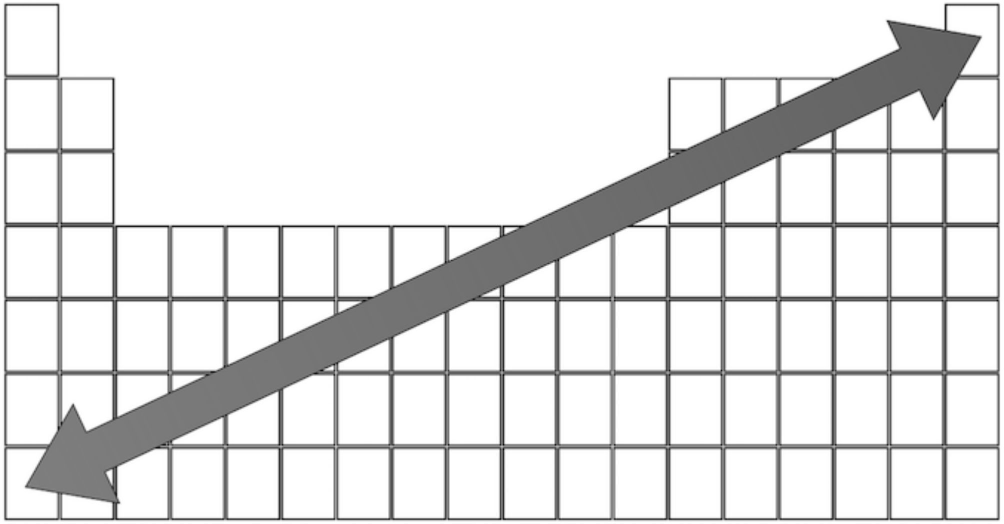
“To the Right and Up, to the Right and Up.”

If you’ve ever seen the movie “JFK,” maybe you remember that Kevin Costner kept saying the phrase: “Back and to the left... back and to the left... back and to the left,” over and over as proof that there were two gunmen who shot JFK. Most of that has faded from my memory, but the cadence he used remains, because it is the same way to remember how ENC is related to **ALL** six trends of interest to us. It is the creation of a **diagonal that starts in the lower left-hand corner and works its way to the upper right-hand corner.**

Summarizing our six trends – all described as they go **up and to the right**:

- Atomic radius decreases
- Electron affinity increases
- Ionization energy increases
- Electronegativity increases
- Metallic character decreases

These trends are discussed in the next lectures.



Area of highest:
- ENC
- Ionization energy
- Electron affinity

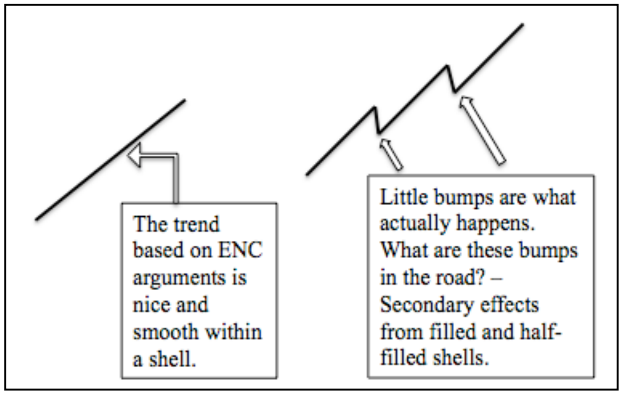
Area of highest:
- Atomic radius

LECTURE 6: PERIODICITY'S FINE POINTS – FILLED AND HALF-FILLED SHELL STABILITY

Chapter Summary

If ENC was all we needed to explain trends in the periodic table, then life would be easy. But we all know it's not. And in fact, if we scratch too much at the surface of things, we uncover an underbelly that we probably wish we hadn't seen.

So if we let the surface be the nice smooth trends of ENC and the underbelly be **filled and half-filled shell stability**, we're staring at the real data for electronic configurations and periodic trends. See, rules like Aufbau and ENC are pretty and give us straight lines, but in reality, most of the data has a bunch of bumps in it that create secondary effects we need to explain:



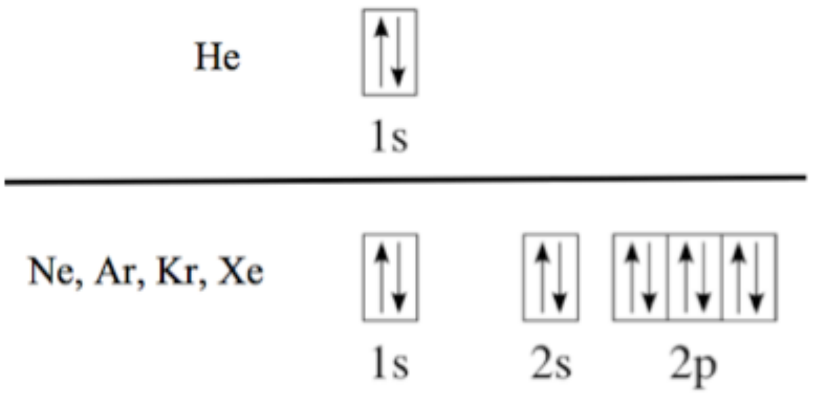
So what are some of these secondary bumps that need to be explained?

- Electronic configurations of atoms don't always follow Aufbau.
  - Example: Cu is s^1d^{10}, not s^2d^9.
- Electronic configurations of ions don't always follow Aufbau.
  - Example: Tl^{3+} is d^{10}, not s^2d^8.
- Ionization energy trends are not smooth across a row of the periodic table.
  - Example: IE of O < IE of N.
- Electron affinity trends not smooth across a row of the periodic table.
  - Example: EA for C is > EA for N.

The good news is that once we understand the concept behind filled and half-filled shell stability, we can rationalize the examples above – and others like them – with confidence.

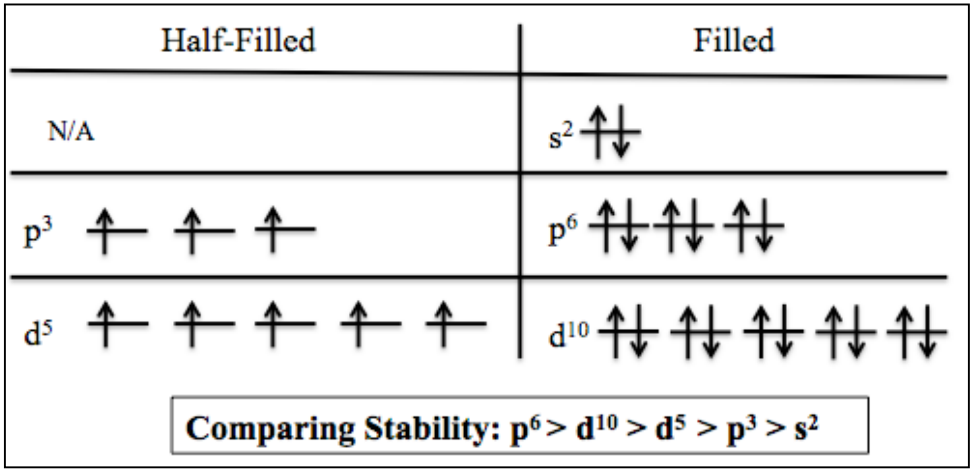
STABLE FILLED AND HALF-FILLED SHELLS

We all know that the **noble gas** elements (He, Ne, Ar, Kr, Xe) are “**stable**” – they’re unreactive because they have **low-energy orbitals** that don’t like to change. The property they have in common with each other is a **filled s or p subshell**, which puts them at the end of a row on the periodic table.



Source: https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/periodic-properties-8/electron-configuration-68/hund-s-rule-318-3668/

Although the noble gases are the most stable group, a few other groups have a similar enhanced stability due to their electronic configurations; these groups are considered “**islands of stability**” in the periodic table, and their common trait is a filled or half-filled outer subshell:



Half-Filled	Filled
N/A	s^2 ↑↓
p^3 ↑ ↑ ↑	p^6 ↑↓ ↑↓ ↑↓
d^5 ↑ ↑ ↑ ↑ ↑	d^{10} ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

Comparing Stability: $p^6 > d^{10} > d^5 > p^3 > s^2$

While you examine the periodic table, you should start to see certain groups or columns as being special. In the same way you'll learn to look at the last column of the periodic table – the s^2p^6 group, or the noble gases – as being special, you will learn to look at all groups with electronic configurations of:

s^2 **and** **p^3 and p^6** **and** **d^5 and d^{10}**

as being special, too. **Not as special as p^6**, but more special than the other groups. It is these especially stable columns in which the glitches of the ENC argument will be found. So it you are working a problem and find yourself in the vicinity of one of these groups, pay attention!

SHELL STABILITY MESSES WITH ELECTRONIC CONFIGURATION

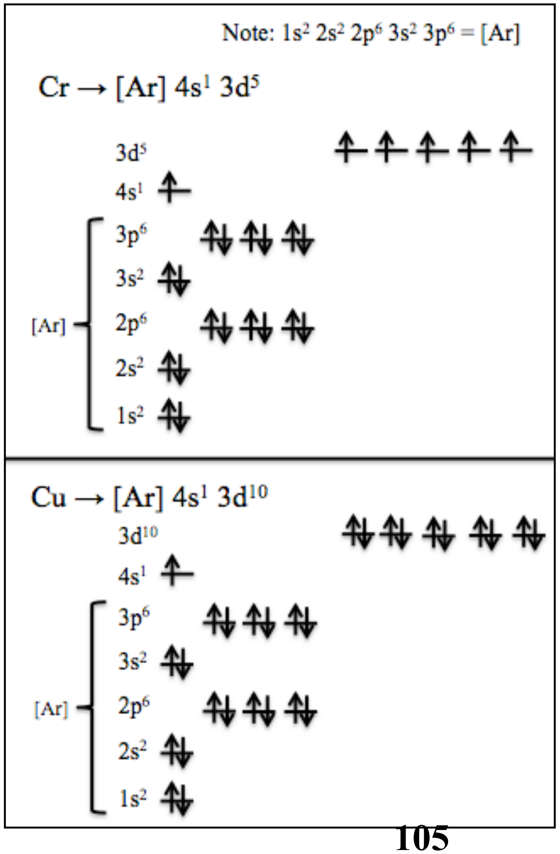
Case #1: The d^4 and d^9 columns

Certainly the most famous example of the **ENC argument being messed up** by increased shell stability is when we use the **Aufbau principle** to fill an electronic configuration. For example, all the **d^4 and d^9** electron configurations change because of filled/half-filled shells; in each case, a single electron that originated in the **s^2** orbital gets **relocated** to the **d orbital**, converting what had been a d^4 or d^9 orbital into a new, lovable **d^5 or d^{10} orbital**, all because of the increased stability in filling or half-filling a large d subshell. Reasonably, this results in the **s^2 becoming s^1**.

Note: this exception applies to both atoms *and* ions with the same number of electrons.

Examples of this exception:

- Cr, Mo, W, and ions like Fe^{2+}, Ru^{2+}, and Ir^{3+} all move an electron from s^2 to create an s^1d^5 electronic configuration.
- Cu, Ag, Au, and ions like Tl^{2+}, Au^- all move an electron from s^2 to create an s^1d^{10} electronic configuration.



Case #2: Large metals with p^1 to p^4 valence electrons

You may or may not have noticed that there are a collection of metals at the bottom right of the periodic table. They aren't the famous transition metals like iron or copper, but they are pretty important and actually possess some pretty remarkable properties. They include some of the "softer metals," like tin, indium, and lead, among others.

The **cations** of these soft metals want to **lose** electrons, and the question is: from what subshell are they removed? According to Aufbau, they should come from the valence p orbits, but in reality, the subshells for these larger ions are so far from the nucleus, that Aufbau's simple rules about energy fall apart. So the question turns into: should they come from an s, or a p, or a d subshell?

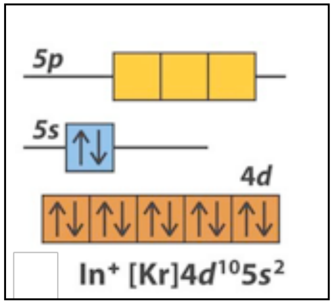
The answer? – Remove them from wherever necessary to **create a filled d^{10} orbital** as soon as possible.

So we have a new rule: electrons lost from large atoms come off in the following order:

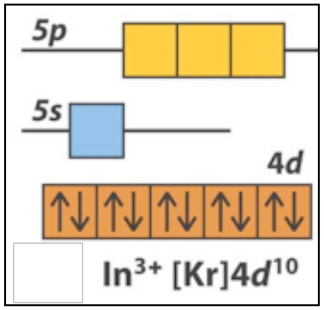
p first → s second → d last

Examples of this exception:

- In$^+$ lost its electron from the 5p orbital, thus making a new configuration of [Kr]$5s^2 4d^{10}$.



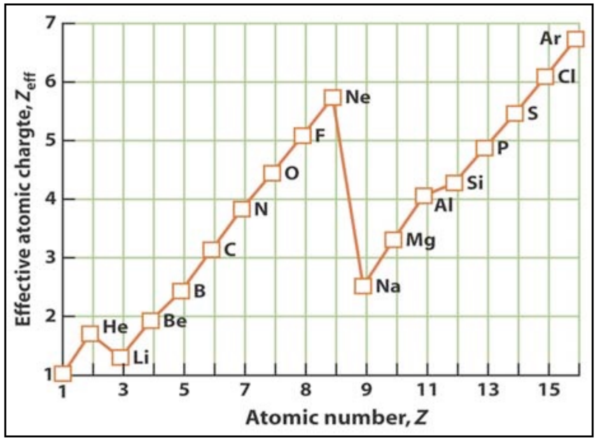
- In^{3+} lost its three electrons from two different places: the first was taken from its 5p orbital, and the second two were taken from the 5s orbital, so the ion ends up with an electron configuration of [Kr]$4d^{10}$.



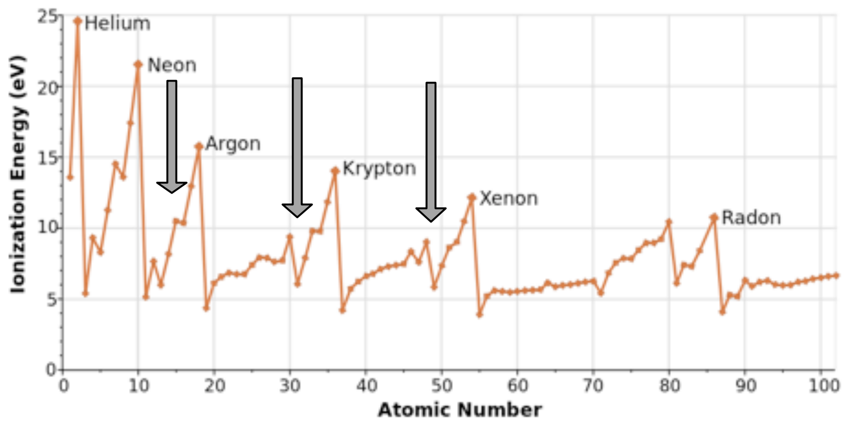
Remember, all of this is because we love d^{10}!

SHELL STABILITY MESSES WITH PERIODIC TRENDS

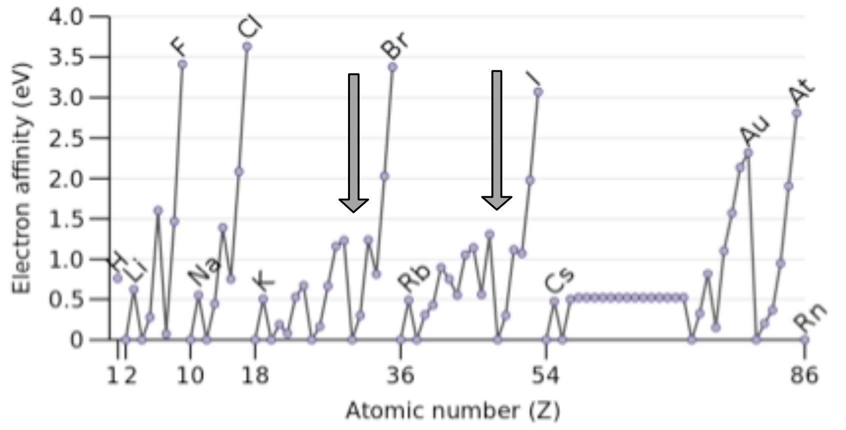
Recall the phrase: “to the right and up.” It suggested that we should see beautifully smooth trends that follow ENC, like the atomic radii trend, shown on the right.



The reality is that except for atomic radii, this kind of smoothness in the trends just doesn’t happen. Instead we see a lot of jaggedness in the pictures of ionization energy and electron affinity. Can we explain this jaggedness? Well since we are in the section on shell stability, this had better be the reason. So here’s something exciting to do – try staring really closely at the wiggles in the IE and EA data below (some are pointed out):



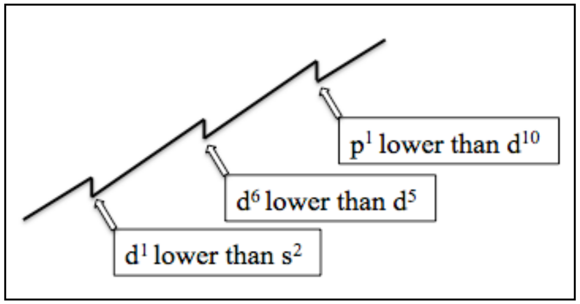
Source: https://wikimediafoundation.org/wiki/File:Ionization_energies.svg



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

What you should notice is that the seemingly random up-and-down areas actually occur around islands of stability – the filled and half-filled shells and subshells.

In the blow up below of IE data, notice that the group to the right of a stable group is higher in energy (less stable).



Example of ranking ionization energy around an island of stability – comparing C, N, and O:

The famous examples of an IE bump (often found on exams) occur for the stable half-filled p^3 subshell. Consider what is going on with electron configuration around **p^2, p^3, and p^4**, and ask: how would you **rank IE** for C, N, and O?

The answer is **C<O<N** — *not* — **C<N<O**:

C is *lower* than N because N has a higher ENC.
N is *higher* than O because its p^3 orbital doesn't want to lose an electron.
O is *lower* than N because its p^4 orbital wants to become a p^3 orbital to offset ENC.

Example of ranking electron affinity around an island of stability – comparing C, N, and O:

Famous examples of an EA bump (found on exams) also occur for the stable half-filled p^3 subshell. Consider what is going on with electron configurations around **p^2, p^3, and p^4**, and ask: how would you **rank EA** for C, N, and O?

The answer is **N<C<O** — *not* — **C<N<O:**

C has a *more positive* EA because adding an electron makes a p^3 orbital.
N has a *more negative* EA because adding an electron makes a p^4 orbital.
O has the *most positive* EA due to the highest ENC.

And if you want to see the numerical proof of these examples, it's presented below:

	C	**N**	**O**	**F**
IE	1090	1400	1310	1680
EA	+122	-7	+141	+328

As mentioned earlier, the **hiccup** in the trend is directly attributed to the **islands of stability around** $\mathbf{p^3}$.

RANKING THE ISLANDS OF STABILITY

No doubt you will wonder sometimes whether the magnitude of the exceptions' increased stability is going to matter. Is there a way to quantify how much extra stability is realized? Of course – just program a computer with the Schrödinger equation. But barring that, can we come up with a ballpark idea of how important the added stability is? Sure. Obviously the noble gas configuration is way more stable than anything else. And based on the examples we have seen, the relative extent of filled and half-filled shell stability is:

$$\mathbf{p^6 \quad >>>>>>> \quad d^{10} \quad >>>> \quad d^5 \; > \; p^3 \; >> \; s^2}$$