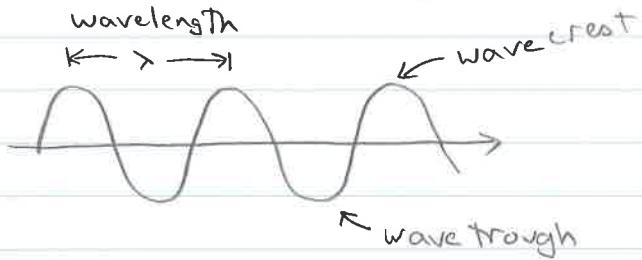


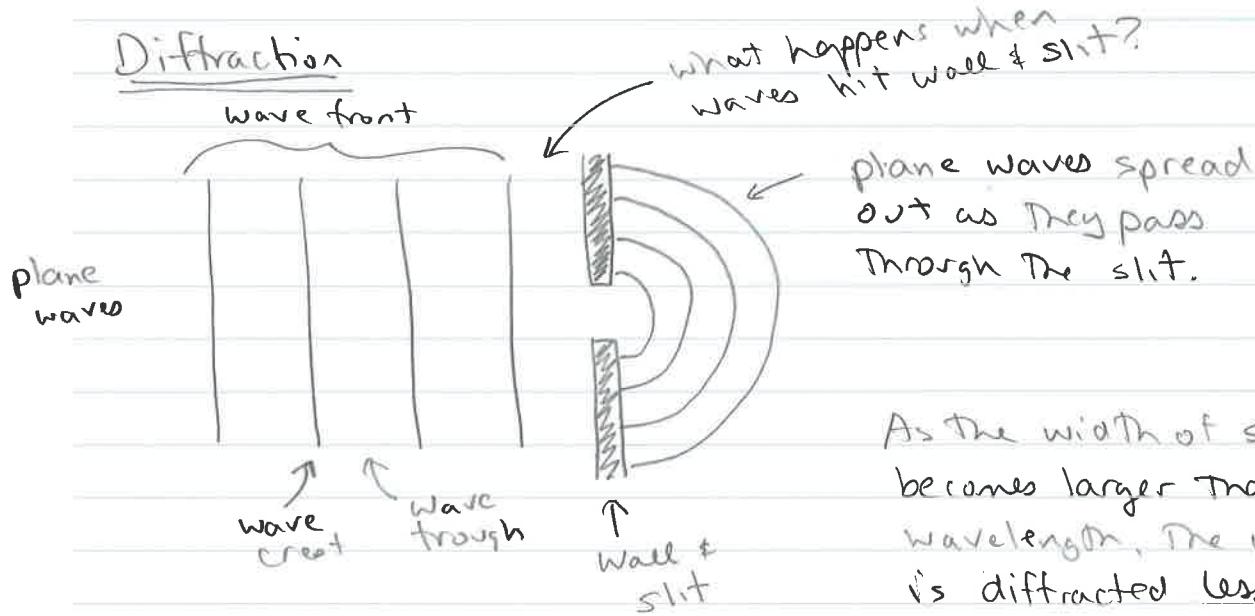
Electricity, Magnetism, and Light

In the 1600's Christiaan Huygens, a Dutch physicist, showed that light behaves like a wave.

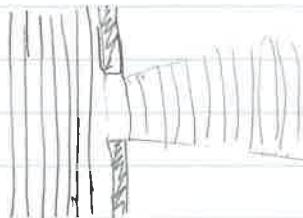
Behavior of Waves



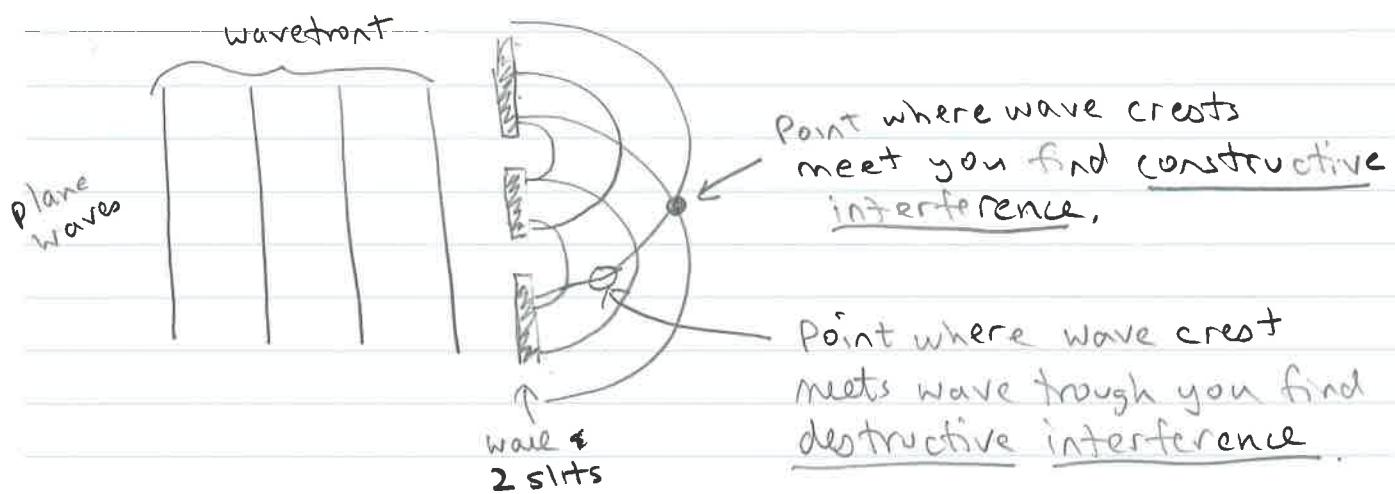
All waves (sound, water, light) exhibit behaviors of Diffraction and Interference



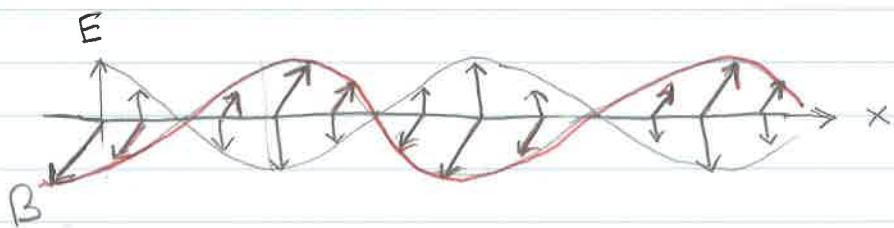
As the width of slit becomes larger than the wavelength, the wave is diffracted less.



Interference



In the 1800's James Clark Maxwell showed that light is a wave of electromagnetic origin, and propagates through space at a speed $c = 3.0 \times 10^8 \text{ m/s}$



Maxwell's equations show that a changing electric field vector generates a perpendicular magnetic field vector and a changing magnetic field generates a perpendicular electric field vector.

The frequency of light is related to its wavelength according to

$$V = \frac{C}{\lambda}$$

\nearrow speed of light
 \searrow wavelength
 \nearrow frequency

The light blue glow given off by mercury street lamps has a wavelength of $\lambda = 436 \text{ nm}$, what is its frequency?

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{436 \text{ nm}} \quad \frac{10^9 \text{ nm}}{\text{m}}$$

$$\nu = 6.88 \times 10^{14} \text{ s}^{-1}$$

The unit s^{-1} has its own unit

$$1 \text{ s}^{-1} = 1 \text{ Hz}$$

← Hertz ← unit for frequency

The region from $\lambda \approx 400 - 750 \text{ nm}$ is visible to the human eye, and it is therefore called the visible region of the electromagnetic spectrum.

Blue light is near the high frequency limit of our eyes

Red light is near the low frequency limit of our eyes.

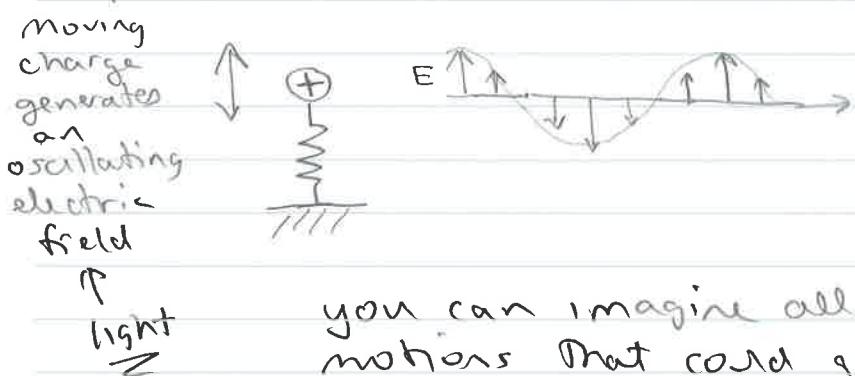
The electromagnetic spectrum is arbitrarily divided into different regions according to wavelength

Radio Waves	Micro Wave	IR - Near IR	Visible	Near U.V.	Vacuum Ultra-violet	Gamma Rays, X-rays	Cosmic Rays
	100mm	300μm	780nm	380nm	200nm	10nm	

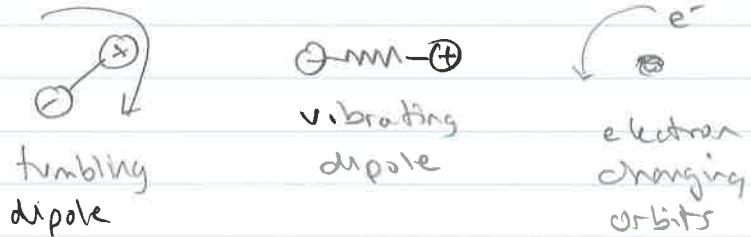
Black body Radiation

Why do objects glow (give off light) when they get hot?

General idea is that heating an object causes an increase in motion of all its microscopic constituents. Since these constituents have electric charges (electrons, cations, anions), or electric dipoles, etc., then their motion generates electromagnetic waves, i.e., light.

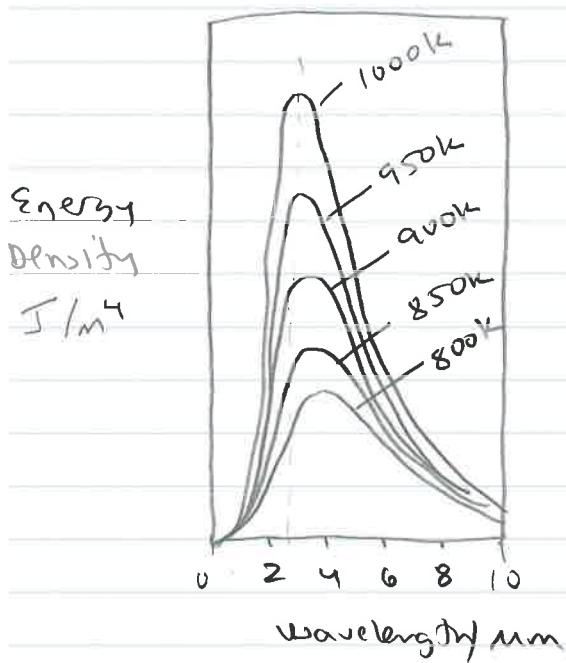


you can imagine all kinds of microscopic motions that could give off electromagnetic radiation.



As object is heated to higher temperature it begins to glow first as red, then orange, yellow, and finally white, as the temperature keeps increasing.

Two observations



(1) The power of light increases with increasing temperature according to

Stefan-Boltzmann Law

$$P = \sigma T^4$$

$$\sigma = 5.67 \times 10^{-8} \frac{W}{m^2 K^4}$$

(2) The most intense light frequency shifts to higher frequencies with increasing temperature according to

Wien's displacement Law

$$\lambda_{max} = \frac{2.9 \text{ K} \cdot \text{mm}}{T}$$

Ultraviolet catastrophe

Remember the equi-partition of energy theorem?

"energy is distributed equally amongst all possible motions"

Well, if any of these motions cause charges or dipoles to fluctuate, then they should give off light.

and if equipartition of energy is correct, then energy distributed to highest frequency motions should emit the most frequencies of light - X-rays! but such high frequency light is never observed.

It was Max Planck in 1900 who proposed that microscopic motion can only create or absorb electromagnetic radiation in quanta called photons whose energy is given by

$$E_{\text{photon}} = h \nu$$

↑
Planck's constant

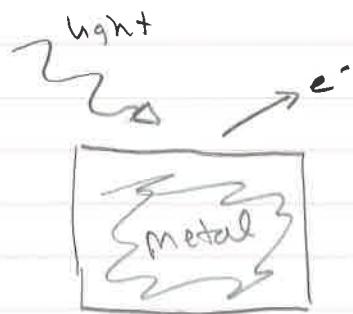
frequency of radiation

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

we also use symbol
 $\hbar = h/2\pi$

With this simple hypothesis Planck could derive the Stefan-Boltzmann law and Wien's displacement law.

The evidence that Planck was right about photons came from the Photoelectric effect.



Light is shined onto a metal and after a certain binding energy was overcome, an electron is emitted from the metal.

An important feature of this experiment is that the electron is emitted from the metal with a specific kinetic energy (i.e., a specific speed).

Anyone who is familiar w/waves knows that the energy of the wave is related to its amplitude or intensity.

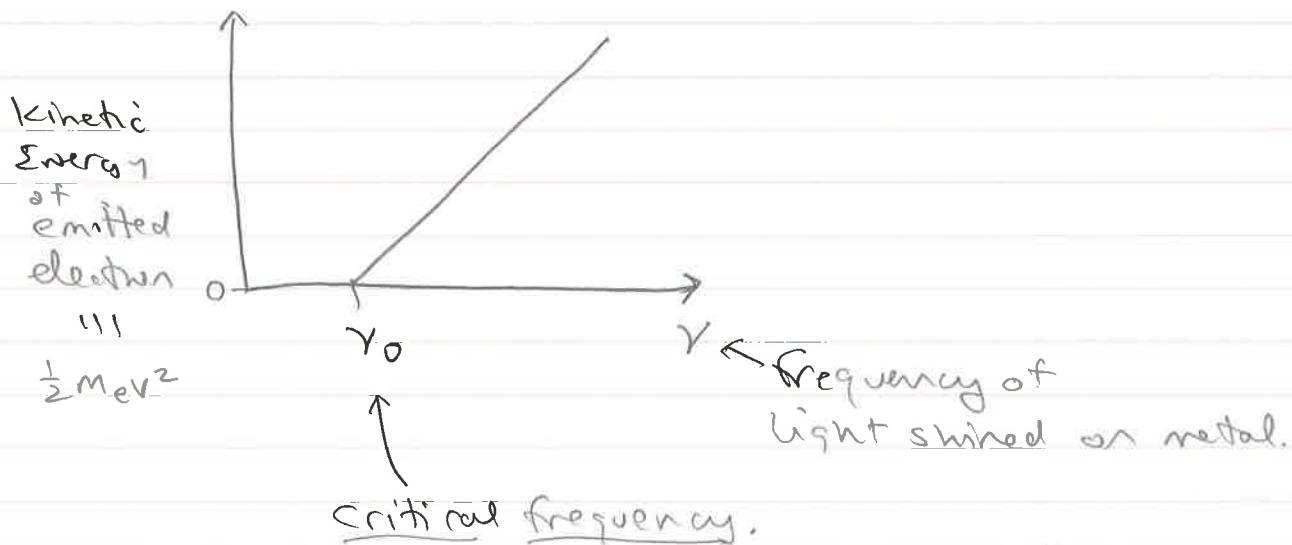
e.g. In the ocean the bigger the wave the higher the energy associated with the wave... you don't get knocked over by the small waves

So, everyone who thought light was a wave were confused when the intensity of the light was increased and the kinetic energy of the emitted electron did not change.

As you make the light brighter more electrons were emitted but all had the same kinetic energy.

Well, they thought the kinetic energy of the emitted electron must depend on something.

So, they varied the frequency of the light and this changed the electron's kinetic energy.



below this frequency no electrons are emitted.

What does all this mean?

The linear relationship suggest that the electron's kinetic energy is equal to the frequency of the light times a constant (the slope).

That constant is Planck's constant

$$h = 6.63 \times 10^{-34} \text{ J-s}$$

$$\text{so } E_{\text{kin}} = h\nu - h\nu_0$$

we define $\Phi = h\nu_0$ as the work function of the metal. It changes from metal to metal, while the slope (h) is constant.

Φ represents the energy that goes toward releasing the e^- from the metal, while the remainder, $(h\nu - \Phi)$, goes into the electron's kinetic energy.

This picture is consistent with one where light is composed of particles, called photons, whose energy is

$$E_{\text{photon}} = h\nu$$

It was Albert Einstein who proposed this explanation of the photoelectric effect, and he received the Nobel Prize for this work.

Conclusion: Light is a particle and also has the behavior of waves.

In 1925, Louis de Broglie hypothesized that if light, which everyone thought for so long was a wave, can also behave like a particle, then...

... particles, like the electron, proton, neutrons, ..., might also behave like waves.

He went further and reasoned that since waves are described by their wavelength, λ ,



λ = wavelength

and particles are described by their momentum, p ,

$$\bullet \rightarrow \vec{p} = \vec{m} \vec{c}$$

momentum mass ↑ velocity

Then perhaps we can relate these two variables...

Quantum Theory says $E = h\nu = hc/\lambda$
and

Relativity Theory says $E = mc^2 = pc$

Then $\frac{hc}{\lambda} = E = pc$ or

$$\boxed{\frac{h}{\lambda} = p} \leftarrow \text{De Broglie Relation}$$

The wavelength of a particle comes from its momentum

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

DeBroglie's idea was experimentally confirmed by Davisson and Germer in 1927.

It was well known that X-rays (light) shined on a crystal would give a diffraction pattern.

Davisson & Germer fired slow moving electrons at crystalline nickel and observed a diffraction pattern, as if they had used X-rays.

Calculate the wavelength of an electron with a velocity of $5.97 \times 10^6 \text{ m/s}$. Mass of e^- is $9.11 \times 10^{-31} \text{ g}$.

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J-s}}{(9.11 \times 10^{-31} \text{ g})(5.97 \times 10^6 \text{ m/s})} \left(\frac{1000 \text{ g-m}^2}{\text{J-s}^2} \right) \left(\frac{10^9 \text{ nm}}{\text{m}} \right)$$

$$\lambda = 0.122 \text{ nm} \quad \leftarrow \text{electron wavelength is similar to X-rays.}$$

Conclusion: Both matter and light are composed of particles that have wave-like properties.

111

wave-particle duality

This weird behavior is usually only observed on the subatomic length scale where the masses are small enough for wavelengths to be large.

The mass of a bowling ball is too large for you to see its wave-like properties.

Quantum Theory tells us that size is not relative.

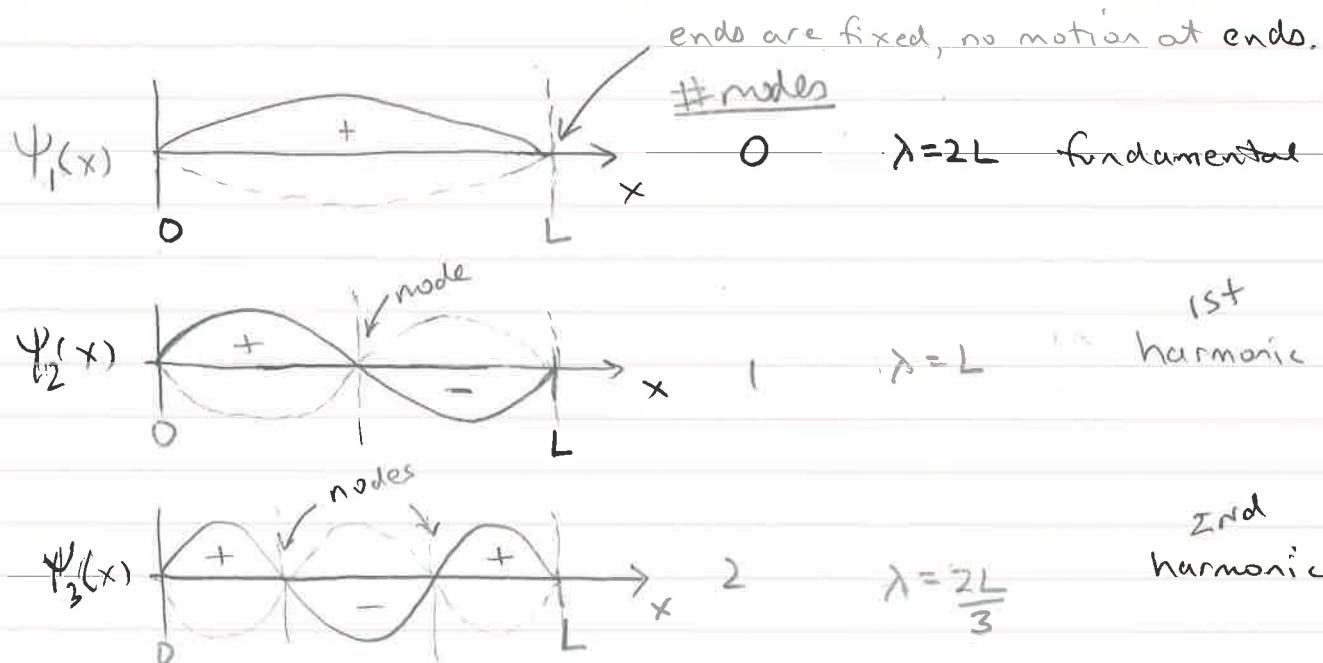
The physical world you experience is not the same experience at the length scale of atomic particles.

In other words, there is an absolute big & absolute small.

What does all this tell us about the structure of atoms and molecules?

To begin answering this question we look at the concept of standing waves.

Whether it's a guitar string fixed at two ends or an e^- trapped between two walls, the behavior is similar.



nodes are where the amplitude changes sign and are always zero.

An important property of standing waves is you can't have any frequency you want because the ends are fixed.

↑
called boundary conditions

With these boundary conditions we can only have discrete wavelengths (frequencies) allowed, which depend on the distance (length of string)

allowed

wavelength are
obtained from...

$$\frac{n\lambda}{2} = L$$

nodes +1

allowed wavelengths

distance between end points

For an e^- trapped in one dimension between 2 walls its wavelength is determined by

- (1) The distance between end points (walls)
- (2.) # nodes (principle quantum #).

Just like the photon, the energy of the electron is proportional to its frequency.

The lowest energy is called the ground state and has the fundamental frequency

The higher energy states are called excited states and occur at the harmonics (multiples) of the fundamental frequency.

So you see how the energy states of the trapped e^- , just like its frequency, are discrete or quantized

"Quantum", "Quantized" \Rightarrow only certain allowed energy levels or frequencies are observed, and nothing in between.

... and this wavelike behavior of e^- , protons, neutrons, also caused them to constructively and destructively interfere with themselves.

What is the physical meaning of the wavefunction?

One interpretation of the wavefunction, $\Psi(x)$, is that

$\Psi^2(x)$ tells us the probability of finding an electron at the point x in space.

$$\text{Probability density of } e^- \text{ at } x = |\Psi(x)|^2$$

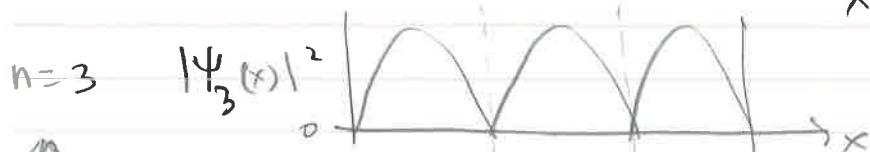
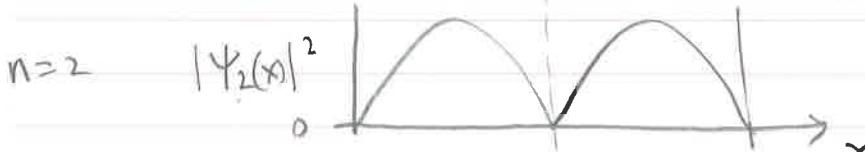
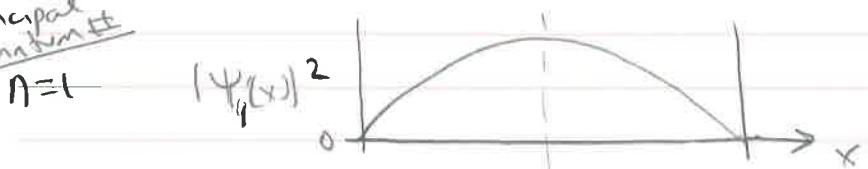
actually $|\Psi(x)|^2 \Delta x$ is probability of e^- at x within Δx .

and since the maximum probability must be 100%. Then $\Psi(x)$ must be defined so

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1$$

What's the probability of finding an e^- trapped between 2 walls in one-dimension?

Principal quantum number



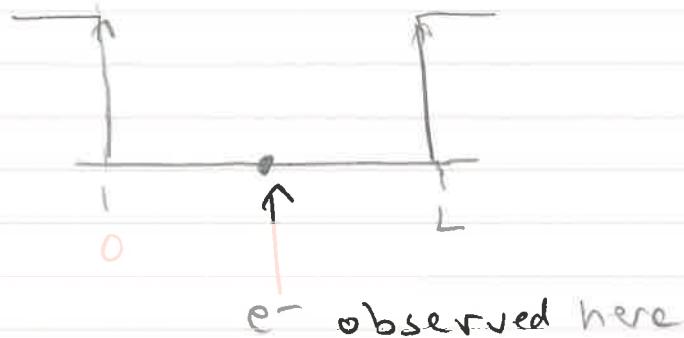
Notice that probability of finding e^- is zero at the nodes, since wavefunction is always zero there.

The principal quantum number, n , fully describes (labels) each possible state of the one-dimensional e^- .

Normally, we operate in 4 dimensions (3 space + 1 time) so we'll need 4 quantum numbers to fully label e^- state.

Of course, this doesn't mean it's difficult to measure the e^- 's position.

We could easily decide to measure its position.



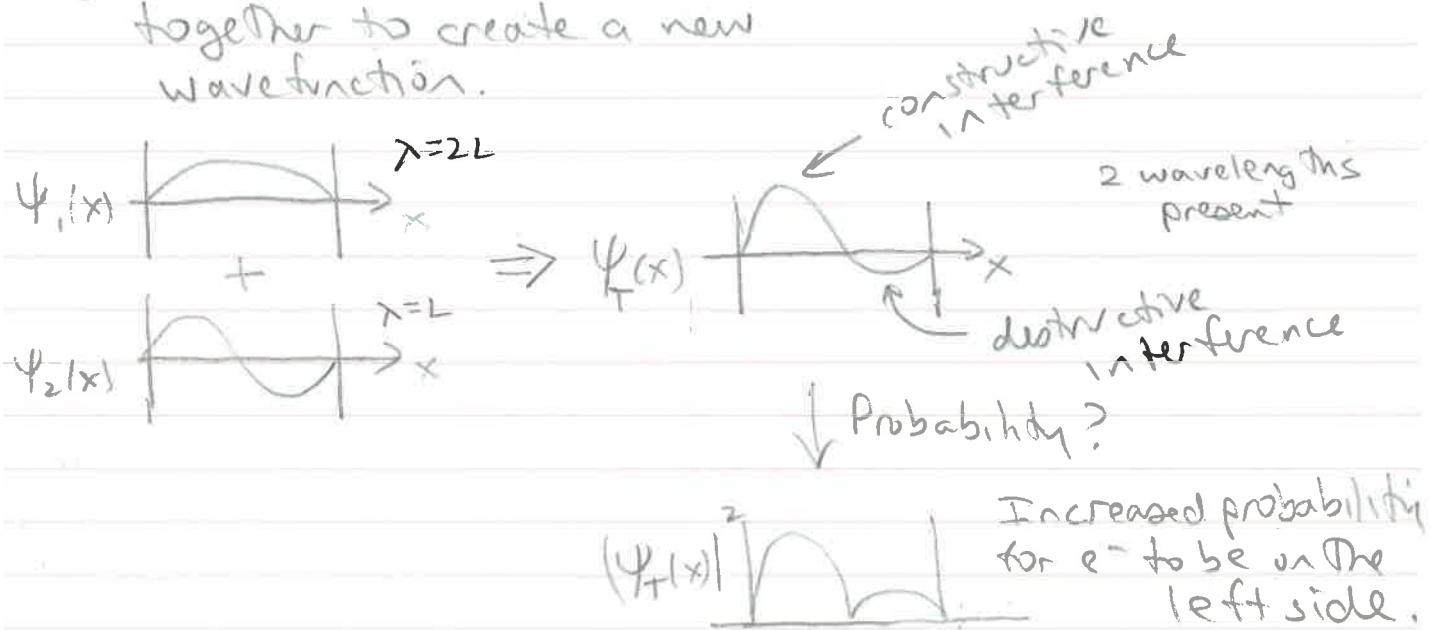
What does such a measurement imply for the wavefunction?

It means that our observation changed the wavefunction of the electron. It is now in a superposition of states.

$$\Psi_{\text{after measurement}} = \sum_{n=1}^{\infty} a_n \psi_n(x)$$

↑
mixing coefficients.

e.g. Mix two wavefunctions together to create a new wavefunction.



Remember that de Broglie said the momentum depended on the wavelength

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

When you add two wavefunctions together to increase the probability that the e^- is on the left side it comes at the expense of knowing the momentum of the e^- .

Observing the e^- at a precise position x , changes the wavefunction by adding together many wavefunctions with different wavelengths in such a way that they all constructively interfere at the spot where the e^- is found, and destructively everywhere else.



To make the wavefunction this localized you would add so many wavelengths that you couldn't say much about the e^- 's momentum anymore.

Big Picture

The more precisely you define a particle's position the less precisely you know its momentum, and vice versa.

} Heisenberg Uncertainty Principle.

Mathematically, this is expressed as

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

Uncertainty in momentum Uncertainty in position

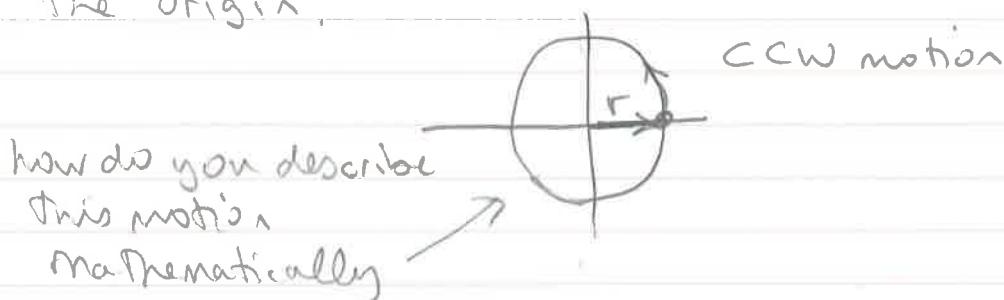
One can also show that $\Delta p \Delta x = \Delta E \Delta t$, so this means

$$\Delta E \Delta t \geq h/4\pi$$

Mathematics of Quantum Mechanics

Complex Numbers are a mathematical tool that can simplify equations that describe oscillations.

Consider an object moving counterclockwise around the origin.



Remember your trigonometry

$$x(t) = r \cos \omega t \quad y(t) = r \sin \omega t$$

x position as function of time

distance from origin

time

angular frequency around path

y position as function of time.

Clearly, we needed 2 equations.

Using complex numbers we can combine these two equations into one.

We define $i = \sqrt{-1}$ and $i^2 = -1$

Then $z(t) = x(t) + iy(t)$

↑
complex number
real part

↑
imaginary part

can also write

$$z(t) = m(t) e^{i\theta(t)}$$

↑
magnitude of complex number

phase of complex number

$$m(t) = \sqrt{x(t)^2 + y(t)^2}$$

$$\tan \theta(t) = \frac{y(t)}{x(t)}$$

Then the counterclockwise motion becomes:

$$z(t) = r \cos \omega t + i r \sin \omega t$$

useful identity: $e^{i\theta} = \cos \theta + i \sin \theta$

$$\text{so } z(t) = r e^{i \omega t} \quad \text{one equation instead of two.}$$

Another useful trick: conjugate of a complex number
 change the sign of imaginary part

if $z = x+iy$ then $z^* = x-iy$

\uparrow
 complex
 conjugate
 of z

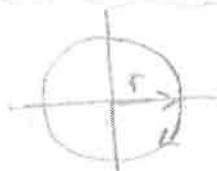
Then

$$zz^* = (x+iy)(x-iy) = x^2 + yx - ixy + y^2$$

$$zz^* = \underbrace{x^2 + y^2}_{\text{square of magnitude}}$$

square of
 magnitude

Describe clockwise motion with complex numbers.



$$x(t) = r \cos \omega t$$

$$y(t) = -r \sin \omega t$$

$$z(t) = r \cos \omega t - i r \sin \omega t$$

use identity $e^{-i\theta} = \cos \theta - i \sin \theta$

so

$$z(t) = r e^{-i \omega t} \quad \text{clockwise motion}$$

To make the mathematical expression of the quantum mechanics wave function simpler we will make the wavefunction a complex quantity.

$\Psi(x)$	$\Psi^*(x)$
↑	↑
complex number	complex conjugate of wavefunction

$$\Psi^*(x) \Psi(x) dx = |\Psi(x)|^2 dx \equiv \text{Probability } e^- \text{ is at } x \text{ within } dx.$$

$$\int_{x_1}^{x_2} \Psi^*(x) \Psi(x) dx = \text{Probability that } e^- \text{ is between } x_1 \text{ and } x_2$$

If we wanted to know the average position of the e^- we perform a weighted average.

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x)|^2 dx$$

In a more general approach we write

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \hat{x} \Psi(x) dx$$

We call \hat{x} the position operator

\hat{x} "operates" on the wavefunction, $\Psi(x)$

In this case operating on the wavefunction simply returns the wavefunction multiplied by x .

On the other hand, if we wanted to calculate the average momentum of the e^- we would write

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \hat{p} \Psi(x) dx$$

↑
momentum operator.

Unlike the position operator, \hat{x} , when the momentum operator "operates" on the wavefunction the calculation is not trivial.

$$\hat{p} = i \frac{\hbar}{2\pi} \frac{d}{dx}$$

The momentum operator.
it takes the 1st derivative
of the wavefunction,
and multiplies that by $i \frac{\hbar}{2\pi}$

From the momentum operator we can create the kinetic energy operator...

recall $T = \frac{p^2}{2m}$, so we define $\hat{T} = \frac{\hat{p}^2}{2m}$

Kinetic Energy expanding this out...

$$\hat{T} = -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}$$

take 2nd derivative
of wavefunction,
then multiply by
 $-\frac{\hbar^2}{8\pi^2 m}$

The Potential Energy
and its operator depend on the problem.

e.g. for an e^- trapped inside a one-dimensional box

Potential $\left\{ \begin{array}{ll} \hat{V}(x) = \infty & \text{if } x < 0 \text{ or } x > L \\ V(x) = 0 & \text{if } 0 \leq x \leq L \end{array} \right.$

Energy Operator $\left\{ \begin{array}{ll} \hat{V}(x) = 0 & \text{if } 0 \leq x \leq L \\ V(x) = \infty & \text{if } x < 0 \text{ or } x > L \end{array} \right.$

To obtain the total energy we sum the kinetic and potential energy operators.

$$\hat{H} = \hat{T} + \hat{V}$$

↑
total
energy
operator

(Hamiltonian)

This brings us to the time independent Schrödinger equation.

$$\hat{H} \Psi(x) = E \Psi(x)$$

↑
Energy
operator ↑
Energy

or

$$\hat{T} \Psi(x) + \hat{V} \Psi(x) = E \Psi(x)$$

using $\hat{T} = -(\hbar^2/8\pi m^2) \frac{\partial^2}{\partial x^2}$

$$-\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} \Psi(x) + \hat{V}(x) \Psi(x) = E \Psi(x)$$

For an electron trapped inside a one-dimensional box we have

inside: $-\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} \Psi(x) = E \Psi(x)$ for $0 \leq x \leq L$

and

outside: $\infty \Psi(x) = E \Psi(x)$ for $x < 0, x > L$

so, only need to focus on solutions inside the box... outside box $E = \infty$

What functions, when differentiated twice, give their original form?

trig. functions ... $\frac{d^2 \cos x}{dx^2} = -\frac{d \sin x}{dx} = -\cos x$

let's start with a generic wavefunction and see if we can fill in the blanks

$$\Psi(x) = A \sin kx + B \cos kx$$

to make this consistent with our boundary conditions we need for

$$\Psi(x) \rightarrow 0 \quad \text{at } x=0 \text{ and } x=L$$

since $\cos kx = 1$ when $x=0$ we must set $B=0$, leaving

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

take 2nd derivative

$$\frac{d\Psi(x)}{dx} = Ak \cos kx$$

$$\frac{d^2\Psi(x)}{dx^2} = -Ak^2 \sin kx = -k^2 \Psi(x)$$

let's rewrite the Schrödinger Eq so it looks like this

$$\frac{-\hbar^2}{8\pi^2 m} \frac{d^2\Psi(x)}{dx^2} = E \Psi(x)$$

becomes

$$\frac{d^2\Psi(x)}{dx^2} = -\frac{8\pi^2 m E}{\hbar^2} \Psi(x)$$

This is k^2 , so $k = \sqrt{\frac{8\pi^2 m E}{\hbar^2}}$

Which brings us to

$$\Psi(x) = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{1/2} x$$

already, at this point we see that the energy is quantized.

Remember $\Psi(x) = 0$ when $x = L$

$$\text{so } \Psi(L) = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{1/2} x = 0$$

This can only be true if

$$\left(\frac{8\pi^2 m E}{h^2}\right)_L^{1/2} = n\pi \quad \begin{array}{l} \text{where } n=1,2,3,\dots \\ \text{since } \sin(n\pi) = 0 \end{array}$$

Thus,

$$E_n = \frac{n^2 h^2}{8 m L^2}$$

Energy levels for electron trapped in a 1-dimensional box

with this we can rewrite $\Psi(x)$ as

$$\Psi(x) = A \sin \frac{n\pi}{L} x$$

and finally, we can solve for A by requiring that the e⁻ has 100% probability to be between 0 & L.

i.e.,

$$\int_0^L |\Psi(x)|^2 dx = 1$$

so

$$A^2 \int_0^L \sin^2 \frac{n\pi}{L} x dx = A^2 \left(\frac{x}{2} - \frac{L}{4n\pi} \sin \frac{2n\pi x}{L} \right) \Big|_0^L$$

$$= A^2 \left(\frac{L}{2} \right) = 1 \quad \text{so} \quad A = \sqrt{\frac{2}{L}}$$

normalization constant

and we finally have

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

wavefunction for e⁻
trapped in a 1D box.

These are
standing waves.

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Energy of e⁻ trapped
in a 1D box

Energy depends on "n",
called principal quantum number.

$$\begin{array}{c} n \\ 4 \\ \hline \end{array} \longrightarrow \frac{E_n}{16h^2/8mL^2}$$

$$\begin{array}{c} 3 \\ \hline \end{array} \longrightarrow \frac{9h^2/8mL^2}{5h^2/8mL^2}$$

$$\begin{array}{c} 2 \\ \hline \end{array} \longrightarrow \frac{4h^2/8mL^2}{3h^2/8mL^2}$$

$$\begin{array}{c} 1 \\ \hline \end{array} \longrightarrow \frac{h^2/8mL^2}{}$$

Unequal
energy
level
spacings

$$\text{lowest possible energy } E_1 = h^2/8mL$$

This is NOT zero, what!?

Every quantum mechanical particle has a zero-point energy. This is a consequence of the wavelike properties of Q.M. particles.

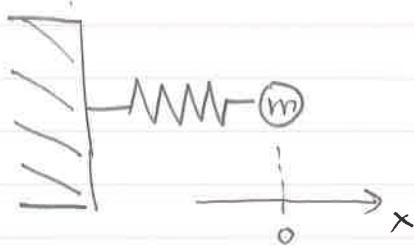
He atom trapped in 1m long 1D box

$$E_1 = 8.257 \times 10^{-42} \text{ J}$$

$$E_2 = 33.029 \times 10^{-41} \text{ J}$$

Quantum Mechanics and Vibrational motion

Harmonic Oscillator



Let's consider a particle attached to a spring as shown here. The restoring force that acts whenever this particle is pushed or pulled away from its equilibrium position, $x=0$, is

$$\vec{F} = -k\vec{x}$$

force constant of the spring

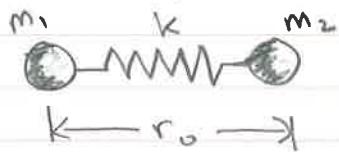
and the potential energy is

$$V(x) = \frac{1}{2}kx^2$$

and the kinetic energy is

$$T = \frac{1}{2}mv^2$$

For our purposes, however, a more interesting problem is where two particles are attached by a spring.



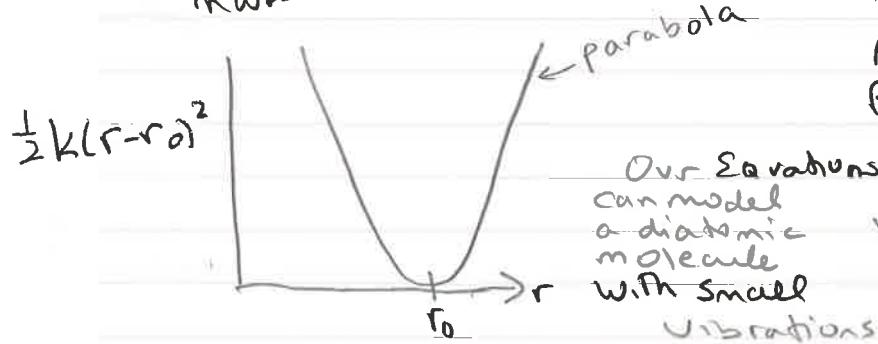
a restoring force acts whenever the two particles are squeezed together or pulled away from their equilibrium separation, r_0 . $F = -k(r - r_0)$

$$\text{or } F = -kx \text{ where } x = r - r_0$$

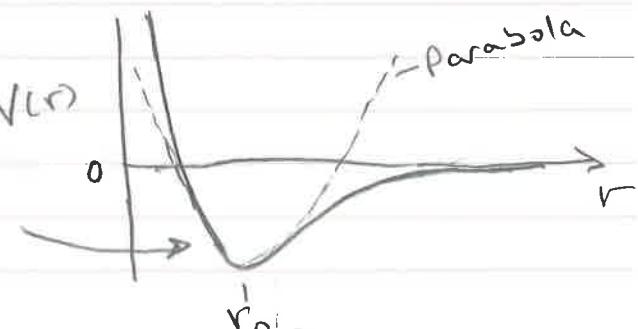
and the potential energy is $V(x) = \frac{1}{2}kx^2$

and the kinetic energy is $T = \frac{1}{2}mv^2$

where $\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2}$
reduced mass



We can pretend this describes the vibration of a diatomic molecule. In reality the potential energy looks like



For a diatomic molecule we can see how Quantum Theory describes vibration with the Schrödinger Eq ...

$$-\frac{\hbar^2}{8\pi^2\mu} \frac{d^2}{dx^2} \Psi(x) + \frac{1}{2} kx^2 \Psi(x) = E \Psi(x)$$

if you're interested this can be solved exactly
(in many pages) to get

$$\Psi_n(x) = N_n H_n(\alpha^{1/2} x) e^{-\alpha x^2/2} \quad \begin{matrix} \text{Principal} \\ \text{Quantum} \\ \# \end{matrix} \quad n=0, 1, 2, \dots$$

$$\text{where } \alpha = (\frac{k\mu}{\hbar^2})^{1/2} \text{ and } N_n = \frac{1}{(2^n n!)^{1/2}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

and $H_n(\xi) \leftarrow$ function called Hermite Polynomial $\begin{matrix} \text{normalization constant} \\ \uparrow \end{matrix}$

More importantly,

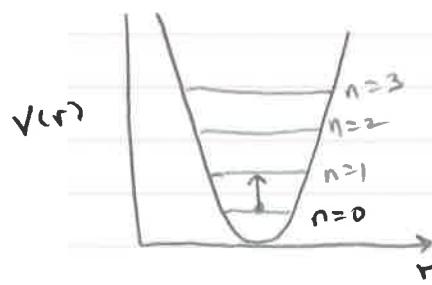
The quantized energy levels are given by

$$E_n = \hbar \left(\frac{k}{\mu}\right)^{1/2} (n + 1/2)$$

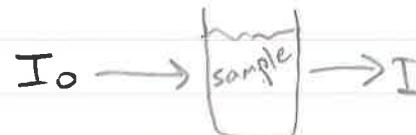
if we define $\omega = (k/\mu)^{1/2}$ \leftarrow angular frequency

or $\nu = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2}$ \leftarrow frequency

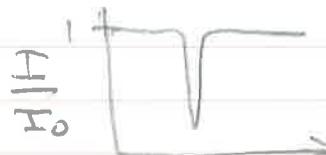
Then we have $E_n = \hbar\nu (n + 1/2)$ $n=0, 1, 2, \dots$



In vibrational spectroscopy we shine light (infrared) onto samples to excite vibrational motion.



some light is absorbed



$$\bar{\nu} = 1/\lambda \quad \text{wavenumber}$$

By measuring the frequency of light absorbed

$$\Delta E = h\nu = E_{n+1} - E_n = \frac{1}{2} \left(\frac{k}{\mu} \right)^{1/2}$$

Then the frequency should be given by

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$$

Since vibrational spectroscopists like to plot their spectra using wavenumbers

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

we have

$$\bar{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2}$$

Since the reduced mass is $\mu = \frac{m_1 m_2}{m_1 + m_2}$

(remember use isotope masses),

then the force constant is $k = (2\pi c \bar{\nu}_{\text{obs}})^2 \mu$

Molecule	$\bar{\nu}/\text{cm}^{-1}$	$k/\text{N/m}$
H_2	4159	520
D_2	2990	530
H^{35}Cl	2886	482
H^{79}Br	2559	385
$^{16}\text{O}^{16}\text{O}$	1556	1140
$^{14}\text{N}^{14}\text{N}$	2331	2260
$^{12}\text{C}^{16}\text{O}$	2140	1870
$^{23}\text{Na}^{35}\text{Cl}$	378	120

$$\text{H}_2 \quad E_n = hc\bar{\nu} (n+1)^{1/2}; \quad E_0 = 4.131 \times 10^{-20} \text{ J}$$

$$E_1 = 12.392 \times 10^{-20} \text{ J}$$

Next, we move to an e^- trapped by the electrostatic attraction to a positively charged nucleus in 3 dimensions.



In 3 dimensions, the position operator is a vector operator

$$\hat{r} = \hat{x}\vec{e}_x + \hat{y}\vec{e}_y + \hat{z}\vec{e}_z$$

and momentum operator is

$$\hat{p} = i\frac{\hbar}{2\pi} \left(\vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z} \right)$$

More importantly, the kinetic energy operator in 3D is

$$\hat{T} = -\frac{\hbar^2}{8\pi^2 m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]$$

and the potential energy operator for an electrostatic attraction to positively charged nucleus is

$$\hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

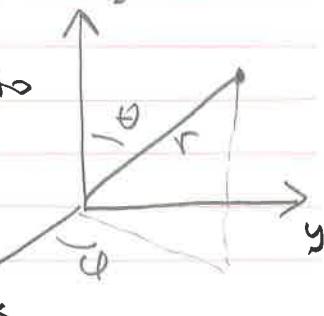
and now the Schrödinger Equation in this problem becomes

$$-\frac{\hbar^2}{8\pi^2 m e} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi$$

Our goal is to find all possible solutions for ψ .

To simplify we convert everything over to spherical coordinates

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}$$



Then The Schrödinger EQUATION becomes

$$\frac{\partial^2 \Psi}{\partial r^2} + \frac{2}{r} \frac{\partial \Psi}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Psi}{\partial \theta} \right] + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \Psi}{\partial \phi^2} + \frac{8\pi^2 me}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \Psi = 0$$

Hmmm, NOT a trivial problem to solve, but nonetheless, it is solvable and the general solution looks like

$$\Psi_{n,l,m}(r, \theta, \phi) = \underbrace{R_{n,l}(r)}_{\substack{\text{radial part} \\ \uparrow \\ \text{3 quantum numbers}}} \underbrace{Y_{l,m}(\theta, \phi)}_{\substack{\text{angular part} \\ \nearrow \\ \text{1st we'll talk about these, and then these}}}$$

Allowed values for 3 quantum numbers: n, l, m

$n = \text{principal quantum number}$
has integral values of $n=1, 2, 3, \dots$

as n increases the electron orbital (wavefunction) extends further out in r , away from the nucleus.

For a single e^- orbiting a nucleus at charge z
the energy depends only on n and z according to...

$$E_n = -\left(2.18 \times 10^{-18} \text{ J}\right) \frac{z^2}{n^2} = -\frac{me^2 c^2 \alpha^2}{2 n^2} z^2$$

for H, $E_1 = -2.18 \times 10^{-18} \text{ J}$
 $E_2 = -0.545 \times 10^{-18} \text{ J}$

$$\alpha = \frac{1}{4\pi\epsilon_0 \frac{qe}{hc}}$$

fine structure const.

$l \equiv$ azimuthal quantum number

has integral values of $l=0$ to $n-1$
for each value of n .

This quantum number defines the total angular momentum of the e^- , and the shape of the orbital.

The total angular momentum is $\sqrt{l(l+1)} \ h$

There are special letters assigned to each l value

$l=0$	S
$l=1$	P
$l=2$	D
$l=3$	F
$l=4$	G

- An e^- with $n=1$ and $l=0$
is in the 1s state (or 1s orbital)
- 2s means $n=2, l=0$
- 2p means $n=2, l=1$
- 3d means $n=3, l=2$

$m_l \equiv$ magnetic quantum number

has integral values of $m_l = -l$ to $+l$

if the x, y, or z component of the electron's angular momentum vector is measured only values of m_l are observed.

if $n=3$ and $l=2$, then possible values of m_l are

$$m_l = -2, -1, 0, +1, +2$$

All 3 quantum numbers, n, l, m_l , specify the electron's wavefunction (or orbital).

The orbital is a standing wave, and when it is squared it gives the probability density for finding the e^- at r, θ, ϕ .

Spectrum of hydrogen

We learned that the e^- 's energy depended only on n & Z

$$E_n = -13.60 \text{ eV} \frac{Z^2}{n^2} = -2.179 \times 10^{-18} \text{ J} \cdot \frac{Z^2}{n^2}$$

$1 \text{ Ry} = 13.605692 \text{ eV} \equiv \text{Rydberg unit of Energy}$

$$\frac{1 \text{ Ry}}{\hbar c} = R_H \leftarrow \text{Rydberg Constant} = 10,973,731.6 \text{ m}^{-1}$$

A few key features of $E_n = -\hbar c R_H Z^2/n^2$

- ① If n increases (holding Z constant), Then E_n increases,
(E_n becomes less negative with increasing n)

In limit that $n \rightarrow \infty$, Then $E \rightarrow 0 \text{ J}$

↗ energy of unbound e^-

- ② If Z increases (holding n constant), The E_n decreases.
(E_n becomes more negative with increasing Z),

makes sense since a higher Z means a more positively charged nucleus, which will hold e^- more tightly.

Energy levels

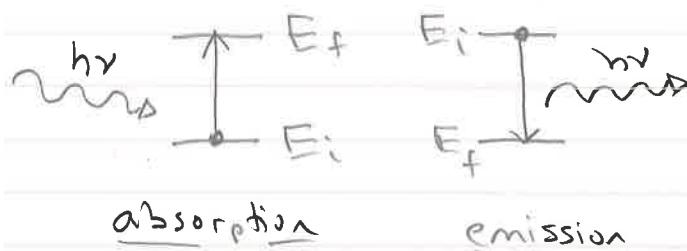
Spacing between levels decreases as n increases,

<u>n</u>	<u>E_n</u>	# orbitals increase as <u>n increases</u> ,
∞	0	
3	-Ry/9	(3s, 3p, 3d orbitals)
2	-Ry/4	(2s, 2p orbitals)

$$1 \quad -\text{Ry} \quad (1s \text{ orbital})$$

all orbitals with same have same energy degenerate ↑

Spectroscopy - analysis of emitted or absorbed light

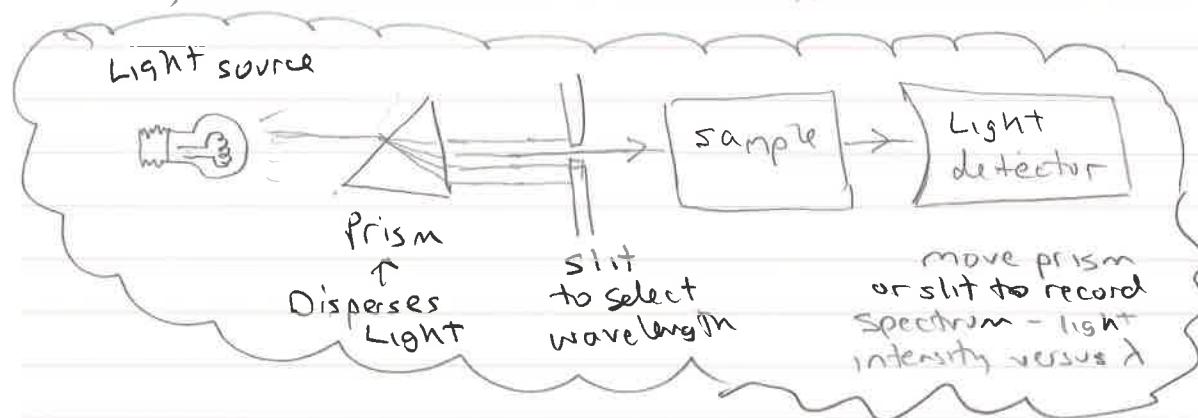


$$\Delta E = E_f - E_i$$

⊕ if absorbed
⊖ if emitted

e.g. an atom absorbs energy of photon to promote e^- to higher energy orbital

e.g. an atom emits energy as photon as e^- falls from higher energy orbital to lower energy orbital



Spectrum of Hydrogen

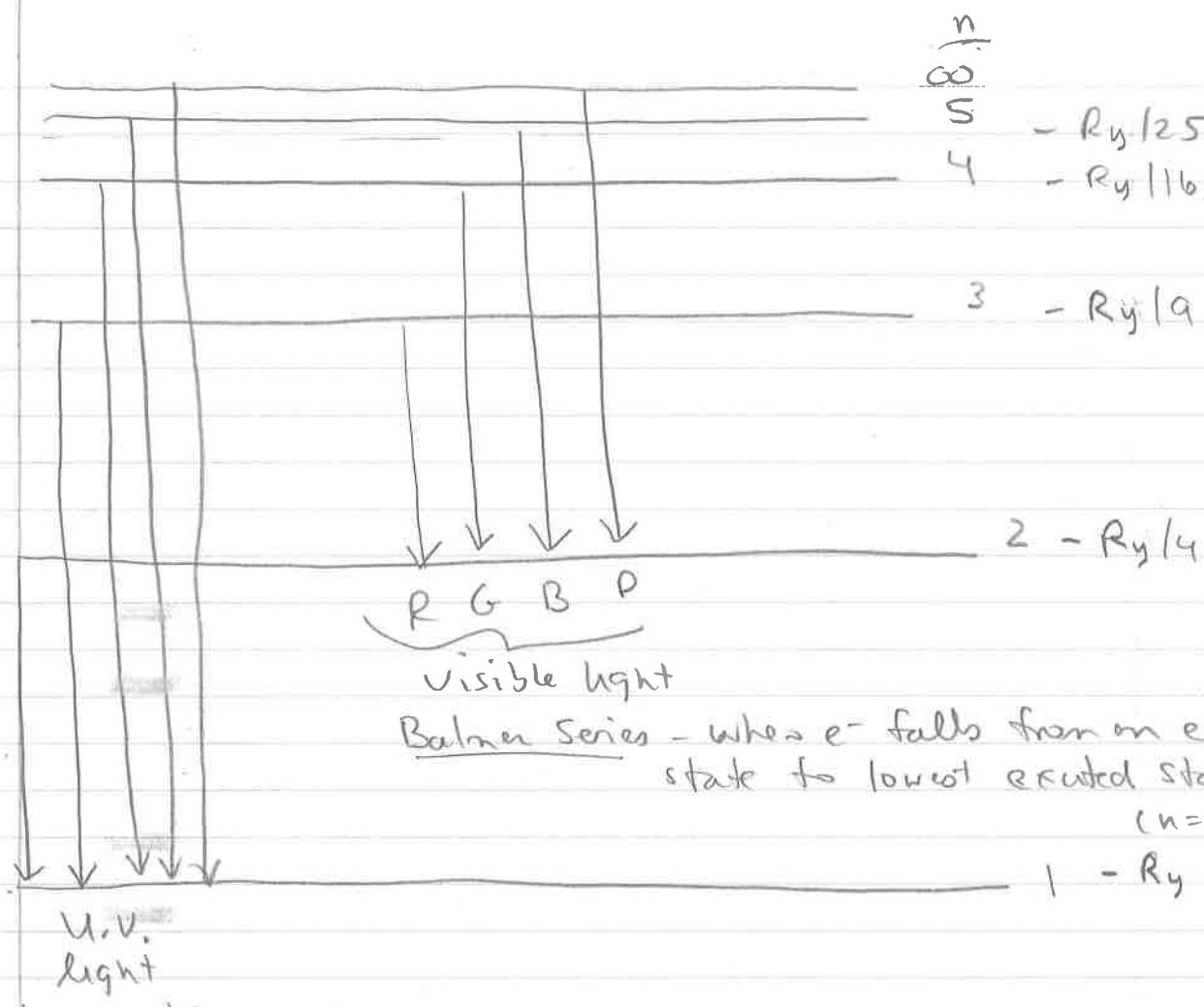
$$\Delta E = E_f - E_i = -hcR_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The frequency of light emitted or absorbed is $\nu = |\Delta E|$

or

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{for hydrogen atom}$$

↑
Principal quantum numbers



Balmer Series - when e^- falls from an excited state to lowest excited state ($n=2$).

$1 - Ry$

We can calc. The wavelength for a given transition using

$$\frac{1}{\lambda} = -R_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$n_i \rightarrow n_f$

$3 \rightarrow 2$ λ 657 nm Red

$4 \rightarrow 2$ 487 nm green

$5 \rightarrow 2$ 435 nm blue

$\infty \rightarrow 2$ 365 nm purple

Energy required to promote e^- to $n=\infty$ is called Ionization Energy.

Now let's dive in and look at the wavefunction for the e⁻ orbiting a positively charged nucleus

$$\Psi_{n,l,m}(r, \theta, \phi) = \underbrace{R_{n,l}(r)}_{\substack{\text{radial} \\ \text{part} \\ \uparrow \\ \text{real}}} Y_{l,m}(\theta, \phi)$$

angular part ↪ complex

Let's start with the radial part.

$$\text{First we define } a_0 = \frac{4\pi \epsilon_0^2}{me^2} = 5.29177 \times 10^{-11} \text{ m}$$

- or -

$$52.9 \text{ pm}$$

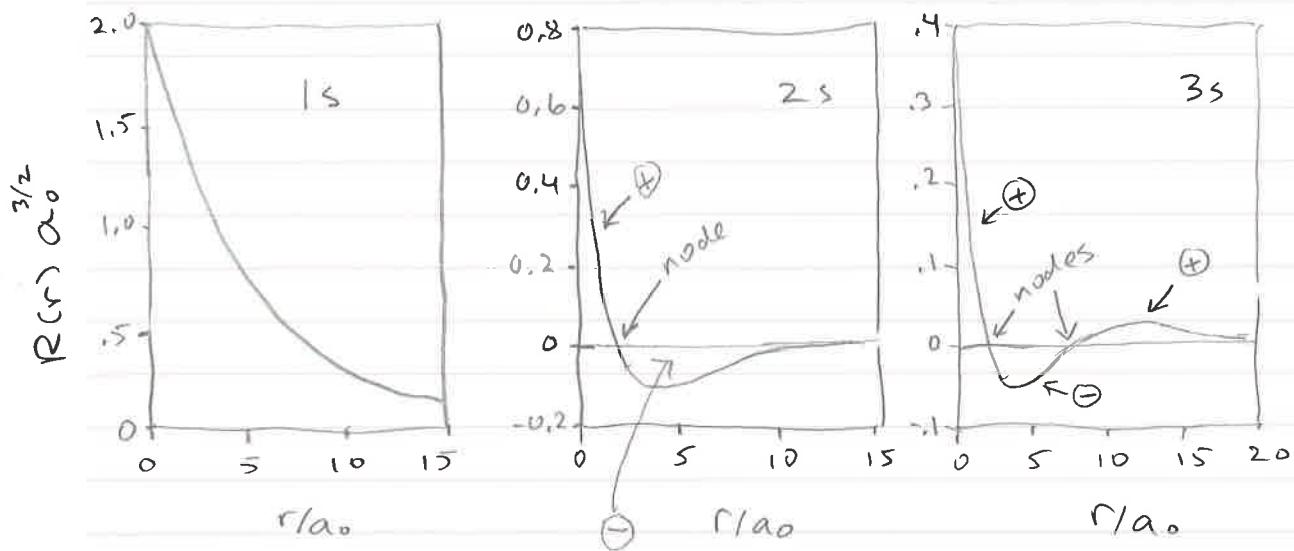
and to simplify our expressions for $R_{n,l}(r)$ we also define $\rho = Zr/a_0$.

<u>Orbital</u>	<u>n</u>	<u>l</u>	<u>$R_{n,l}(r)$</u>
1s	1	0	$2(z/a_0)^{3/2} e^{-\rho}$
2s	2	0	$\frac{1}{2\sqrt{2}} (z/a_0)^{3/2} (2-\rho) e^{-\rho/2}$
2p	2	1	$\frac{1}{2\sqrt{6}} (z/a_0)^{3/2} \rho e^{-\rho/2}$
3s	3	0	$\frac{2}{81\sqrt{3}} (z/a_0)^{3/2} (27-18\rho+2\rho^2) e^{-\rho/3}$
3p	3	1	$\frac{4}{81\sqrt{6}} (z/a_0)^{3/2} (6\rho-\rho^2) e^{-\rho/3}$
3d	3	2	$\frac{4}{81\sqrt{30}} (z/a_0)^{3/2} \rho^2 e^{-\rho/3}$

Pretty intimidating. Let's look at the s-orbitals first where the angular part $Y_{0,0}(\theta, \phi)$ is independent of θ & ϕ ,

That is, $Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$

S-orbitals are spherical symmetric and only vary as a function of r



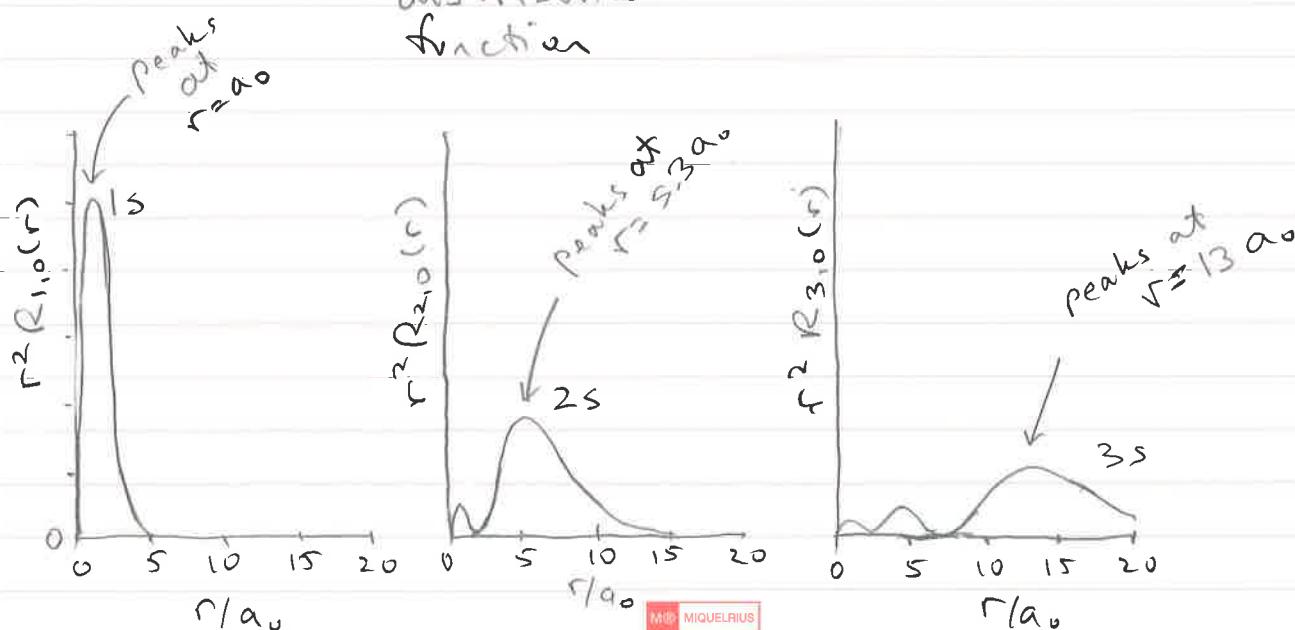
The number of nodes (where sign changes) is $n-1$.

NOTE That the probability amplitude for e^- is not zero at the nucleus ($r=0$).

For S-orbitals, the probability of finding an e^- inside a spherical shell of thickness dr at a distance r from the nucleus is given by

$$\underbrace{r^2 R_{n,l}(r) dr}_{\text{radial distribution}}$$

distribution fraction



$l \quad m$

$\Psi_{l,m}(\theta, \phi)$

0 0

$$\sqrt{1/4\pi}$$

s-orbital

1 0

$$\sqrt{3/4\pi} \cos \theta$$

1 ± 1

$$\mp \sqrt{3/8\pi} \sin \theta e^{\pm i\phi}$$

p-orbitals

2 0

$$\sqrt{5/4\pi} \frac{1}{2}(3\cos^2 \theta - 1)$$

2 ± 1

$$\mp \sqrt{5/4\pi} \sqrt{3/2} \cos \theta \sin \theta e^{\pm i\phi}$$

d-orbitals

2 ± 2

$$\sqrt{5/4\pi} \sqrt{3/8} \sin^2 \theta e^{\pm 2i\phi}$$

The angular part of the wavefunction are harder to visualize than the radial part.

Remember, we used a 2D plot of the wavefunction versus x to visualize the standing wave of an electron trapped in a 1D box.

To visualize the standing wave (orbitals) of an electron bound to a positively charged nucleus in 3D we will need a four-dimensional plot of the wavefunctions (complex) value as a function of $x, y, & z$.

While I can't easily draw the orbitals in these notes, there are a number of excellent web site that illustrate orbital shapes. Here are 2 I recommend:

(1) Winter:group.shef.ac.uk/orbitron

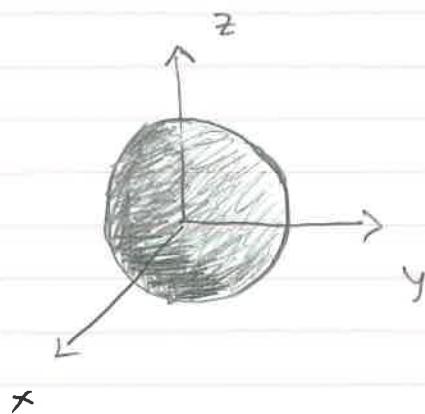
(2) www.falstad.com/gmatom ↗

Java app

I will attempt to draw the variation in the probability of finding the electron. Recall that this is obtained from

$$|\Psi_{n,l,m}(r, \theta, \phi)|^2$$

1s-orbital - e^- probability density is spherically symmetric.

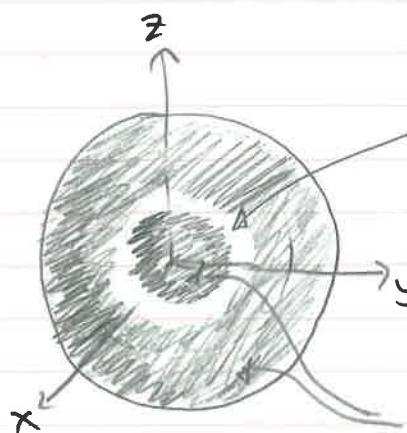


$$n=1, l=0, m_l=0$$

standing wave is all same sign,
no nodal surface where the sign changes.

- In 3D nodes are surfaces
- In 2D nodes are lines
- In 1D node are points

2s-orbital - also spherically symmetric



nodal surface in between regions where wavefunction changes sign. } radial nodal surface

if inside region has positive amplitude, then outside region has negative amplitude.

Generally, all s-orbitals are spherically symmetric.

P-orbitals

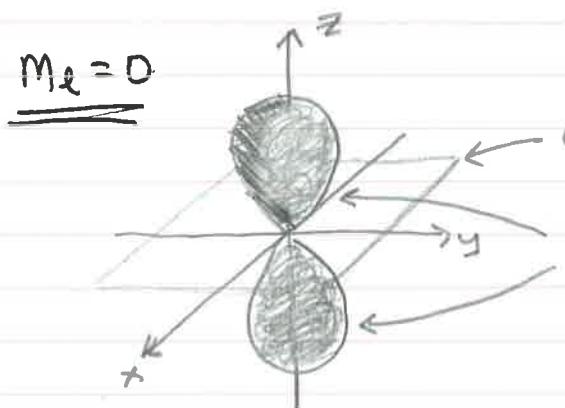
When $n=2$ we have 2 possible values for l .

$l=0$ is the $2s$, which we just saw

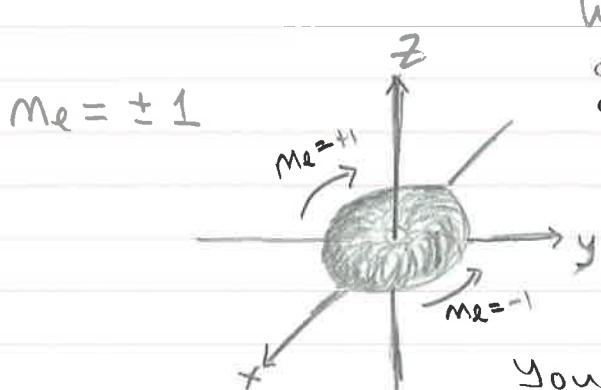
$l=1$ are the $2p$ orbitals.

Remember, for a given l , there are $2l+1$ values of m_l
 $m_l = -1, 0, +1$

These 3 values of m_l correspond to 3 different p-orbitals



$m_l = 0$ angular node in $x-y$ plane.
 The wavefunction above xy plane has the opposite sign of wavefunction below xy plane.



While $m_l = 0$ wavefunctions are always real, $m_l \neq 0$ wavefunctions are complex valued.

$m_l = \pm 1$ orbitals look like donuts with a node line along the z -axis.

You can think of $m_l = +1$ as an e^- orbiting clockwise around z and $m_l = -1$ as an e^- orbiting counter-clockwise around z .

Since the energy of each orbital is a function of only n , then all the $n=2$ orbitals $2s, 2p$ have the same energy - i.e., they're degenerate

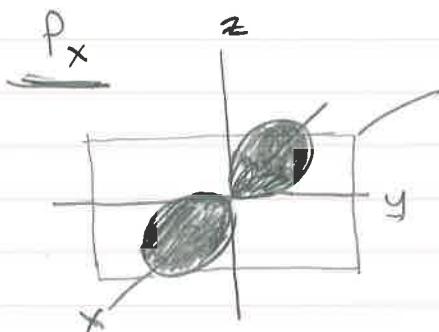
(only true for H-atom).

Chemists are not mathematicians, nor are they physicists, so they can get confused by complex numbers.

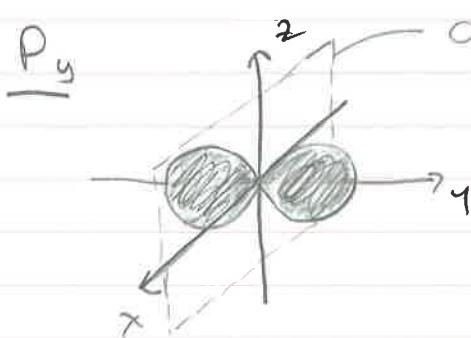
To make it easier for chemists to visualize the p orbitals it is common practice to construct real orbitals by taking the sum and difference of the complex $p_{\pm 1}$ orbitals.

$$\Psi_{p_x}(r, \theta, \phi) = \frac{1}{\sqrt{2}} (\Psi_{p+1}(r, \theta, \phi) + \Psi_{p-1}(r, \theta, \phi))$$

$$\Psi_{p_y}(r, \theta, \phi) = \frac{1}{\sqrt{2}i} (\Psi_{p+1}(r, \theta, \phi) - \Psi_{p-1}(r, \theta, \phi))$$



angular node in yz plane.
wavefunction changes sign across nodal plane.



angular node in xz plane.
wavefunction changes sign across nodal plane.

n=3 and beyond

We can keep going with orbitals having higher n, l, m_l values but you can find better illustrations elsewhere.

for n=3, we have l=0, l=1, l=2
 ↑ ↑ ↑
 s p d orbitals

understand
angular &
radial nodes

Electron spin angular momentum

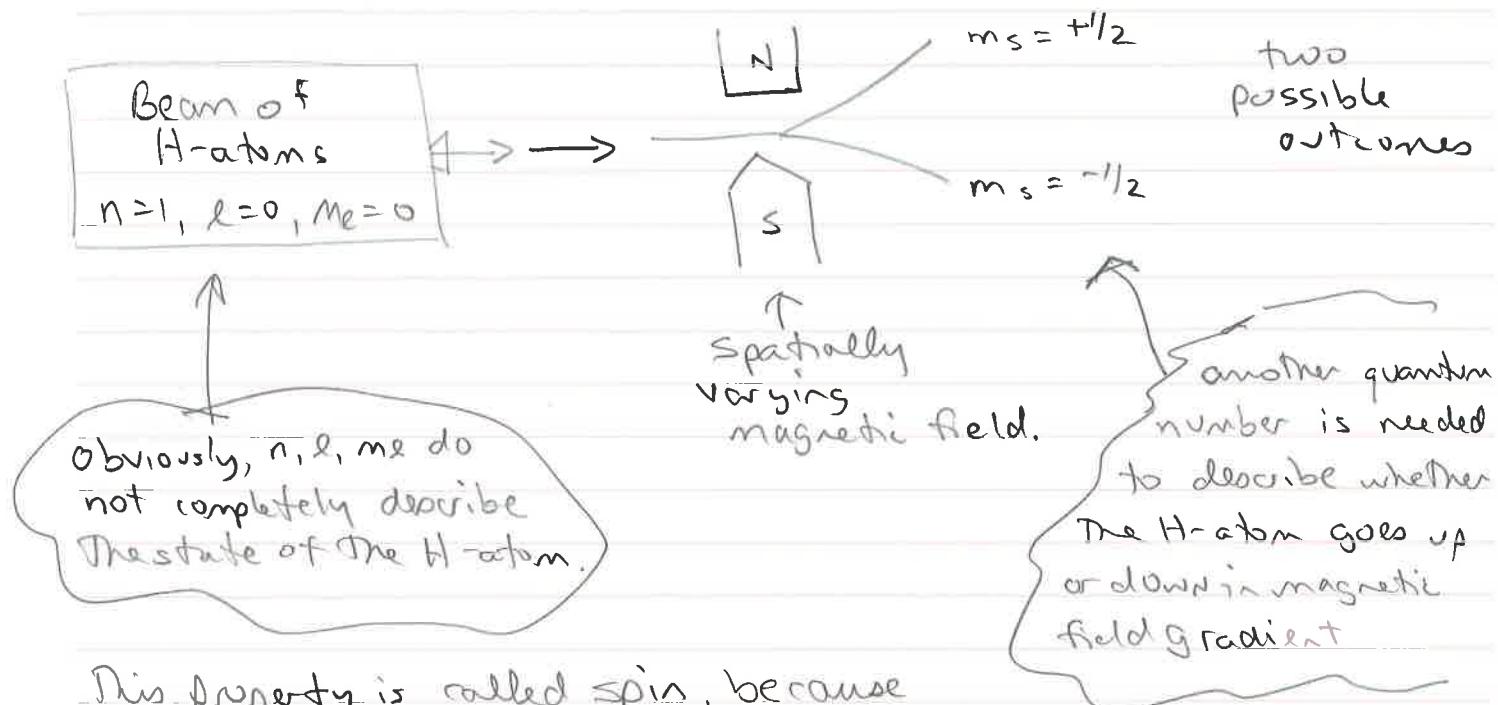
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Earlier I said we would need 4 quantum numbers to describe the state of an electron bound to an atom, and so far we have only seen 3.

The last one is called the spin quantum number and it can only have 2 possible values $m_s = \pm \frac{1}{2}$.

How do we know about spin?

If a beam of hydrogen atoms in their ground state ($1s$) is sent through a region with a spatially varying magnetic field (i.e., a magnetic field gradient), then the beam splits into two beams.



This property is called spin, because if electrons were balls of charge spinning about their own axes then that could explain this behavior, but this picture doesn't correctly explain seeing only two outcomes $m_s = \pm \frac{1}{2}$.

The correct explanation comes from doing a relativistic treatment of the e^- 's wavefunction, i.e., time & space treated the same.

MULTI-ELECTRON ATOMS

While Q.M. has an exact solution for the H-atom, which has only one electron, it runs into problems trying to give exact solutions for an atom with many electrons.

For example, the Hamiltonian for a Helium atom with 2 electrons and a nucleus has a kinetic energy operator

$$\hat{T}_{He} = -\underbrace{\frac{\hbar^2}{8\pi^2m} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right]}_{\hat{T}_H(1)} - \underbrace{\frac{\hbar^2}{8\pi^2m} \left[\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right]}_{\hat{T}_H(2)}$$

+ ↓
Kinetic energy
for single electron
orbiting He nucleus

and has the potential energy operator

$$\hat{V}_{He} = -\underbrace{\frac{ze^2}{4\pi\epsilon_0 r_1}}_{\hat{V}_H(1)} - \underbrace{\frac{ze^2}{4\pi\epsilon_0 r_2}}_{\hat{V}_H(2)} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\text{e}_1 - \text{e}_2 \text{ repulsion}}$$

↑ ↑
Potential energy
for single electron
orbiting He nucleus.
↑
distance between electrons

It is the last electron-electron repulsion term that makes finding an analytical solution for the He wavefunction significantly more complicated.

The simpler approximation for finding the He wavefunction is to ignore the electron-electron repulsion term.

In this simple approximation we write the Hamiltonian as

$$\hat{H}_{He} = \hat{T}_H(1) + \hat{V}_H(1) + \hat{T}_H(2) + \hat{V}_H(2) = \hat{H}_H(1) + \hat{H}_H(2)$$

If the electrons don't "see" each other
then the He wavefunction can be a
product of the single electron wavefunctions
we found for the H atom.

\uparrow \nearrow
Hamiltonian for single
electron orbiting a
He nucleus.

$$\Psi_{He} = \Psi_H(1) \Psi_H(2) \leftarrow \text{this becomes a valid solution}$$

start with...

$$\hat{H}_{He} \Psi_{He} = E \Psi_{He}$$

$$[\hat{H}_H(1) + \hat{H}_H(2)] \Psi_H(1) \Psi_H(2) = E \Psi_H(1) \Psi_H(2)$$

$$\hat{H}_H(1) \Psi_H(1) \Psi_H(2) + \Psi_H(1) \hat{H}_H(2) \Psi_H(2) = E \Psi_H(1) \Psi_H(2)$$

$$E(1) \Psi_H(1) \Psi_H(2) + E(2) \Psi_H(1) \Psi_H(2) = E \Psi_H(1) \Psi_H(2)$$

$$(E(1) + E(2)) \Psi_H(1) \Psi_H(2) = E \Psi_H(1) \Psi_H(2)$$

so the He wavefunction puts each of the two electrons
into H-atom-like orbitals, with total energy

$$E_{He} = E(1) + E(2) = -2.18 \times 10^{-18} J \left(\frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2} \right)$$

In our simple approximation; ignoring $e^- - e^-$ repulsion,
this energy will be too negative.

e.g. $Z=2, n_1=n_2=1$

$$E_{He} = -2.18 \times 10^{-18} J \left(\frac{2^2}{1^2} + \frac{2^2}{1^2} \right) = -6.976 \times 10^{-17} J$$

Predicted J

measured energy of ground state

$$\text{for He } E = -1.266 \times 10^{-17} J$$

One way to account for this difference is to imagine the electrons still don't interact directly, but instead each electron sees a less positive nucleus due to shielding by other e^- .

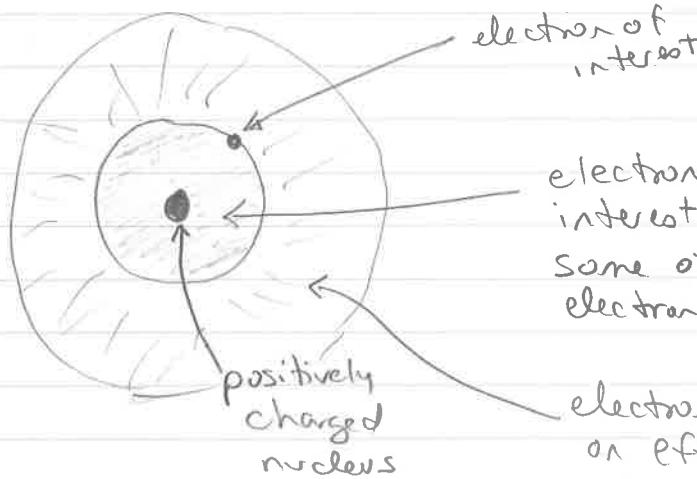
$$E_{He} = -2.18 \times 10^{-18} J \left(\frac{Z Z_{\text{eff}}^2}{r^2} \right) = -\underbrace{1.266 \times 10^{-17} J}_{\text{measured value}}$$

↑
solve for
 Z

$$Z_{\text{eff}} = \sqrt{\frac{1}{2} \left(\frac{-1.266 \times 10^{-17} J}{-2.18 \times 10^{-18} J} \right)}$$

$$Z_{\text{eff}} \approx 1.7 \quad \text{instead of } Z=2$$

For a multi-electron atom we adopt this simple picture



electrons between electron of interest and nucleus. These e^- 's cancel some of the nucleus positive charge for electron of interest

electrons outside have no effect on effective nuclear charge for electron of interest

For electron of interest we write its energy as

$$E(i) = -\hbar c R_H \left(\frac{Z_{\text{eff}}^2}{n^2} \right)$$

effective nuclear charge "seen" by electron of interest

Principal quantum # of e^- of interest

Energy of electron of interest.

The effective nuclear charge equals the number of protons in the nucleus, Z , minus the average number of electrons, σ , between the nucleus and electron of interest.

$$Z_{\text{eff}} = Z - \sigma$$

effective charge
seen by e^-
of interest.

nuclear
charge

average # e^- 's between
nucleus & e^- of interest

In a multielectron atom it turns out that the effective charge, Z_{eff} , decreases with increasing value of l , the azimuthal quantum number, for the e^- of interest.

(σ increases with increasing l)

This is because electrons in the s-orbital have a greater probability of being near the nucleus than a p-orbital, so an electron of interest in an s-orbital sees a greater fraction of the nuclear charge than if it was in a p-orbital.

Likewise, an e^- of interest in a p-orbital sees a greater fraction of the nuclear charge (smaller σ) than if it was in a d-orbital.

In a multielectron atom the energy of an orbital increases with increasing value of l for a given value of n .

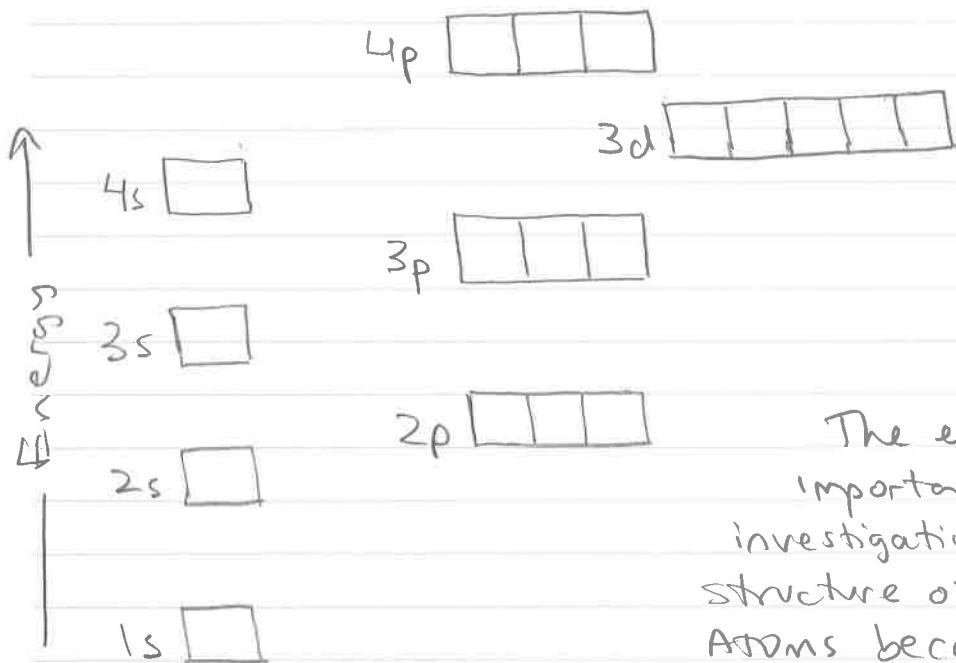
electron shell \Rightarrow all orbitals with same n

electron subshell \Rightarrow all orbitals with same n and l

e^- 's in the same subshell are degenerate

Energy levels for orbitals in MULTIELECTRON ATOM

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This order varies slightly for different atom, particularly when n is high.

The electron spin is important in continuing our investigation of the electronic structure of multielectron atoms because of the Pauli Exclusion Principle.

Pauli Exclusion Principle = No two electrons in an atom can have the same 4 quantum numbers - n, l, m_l, m_s .

Since there are only 2 values for m_s , then any orbital can hold, at most, 2 e⁻s with opposite sign of m_s , otherwise Pauli exclusion principle is violated.

Aufbau Principle - Energy structure of a many-electron atom is obtained by filling the orbitals one electron at a time, in order of increasing energy starting with the lowest energy.

Orbital Diagrams - Each orbital is represented by a box and each e⁻ by a half-arrow
 ↑ up arrow $m_s = +\frac{1}{2}$
 ↓ down arrow $m_s = -\frac{1}{2}$

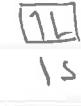
e.g. hydrogen has 1e⁻ so



boron has 5e⁻ so



carbon has 6e⁻ so



Hund's Rule: e⁻s occupy different orbitals of given subshell with spins in same direction before pairing.

Electronic Configuration

Shell or principle quantum number n
 Subshell letter (s, p, d, \dots)
 \leftarrow # e^- 's in subshell

e.g. H has $1e^-$ so $1s^1$

B has $5e^-$ so $1s^2 2s^2 2p^1$

C has $6e^-$ so $1s^2 2s^2 2p^2$

What is electron configuration and orbital diagram for Ne?

C has $10e^-$

1L	1L	1L 1L 1L
1s	2s	2p

$1s^2 2s^2 2p^6$

full shell is why Ne is chemically inert.

Sodium - has $11e^-$

1L	1L	1L 1L 1	1
1s	2s	2p	3s

$1s^2 2s^2 2p^6 3s^1$

This can get tedious beyond $10e^-$, so we abbreviate

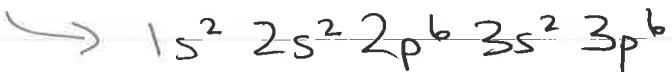
$[Ne] \boxed{1}$ or $[Ne] 3s^1$

Valence electrons - e^- 's in the outermost shell of an atom

Core electrons - e^- 's in the inner closed shells

Atoms in the same group (vertical column) in the periodic table have the same # valence e⁻.

Argon has 18e⁻



Potassium has 19e⁻

\rightarrow where does the 19th e⁻ go?

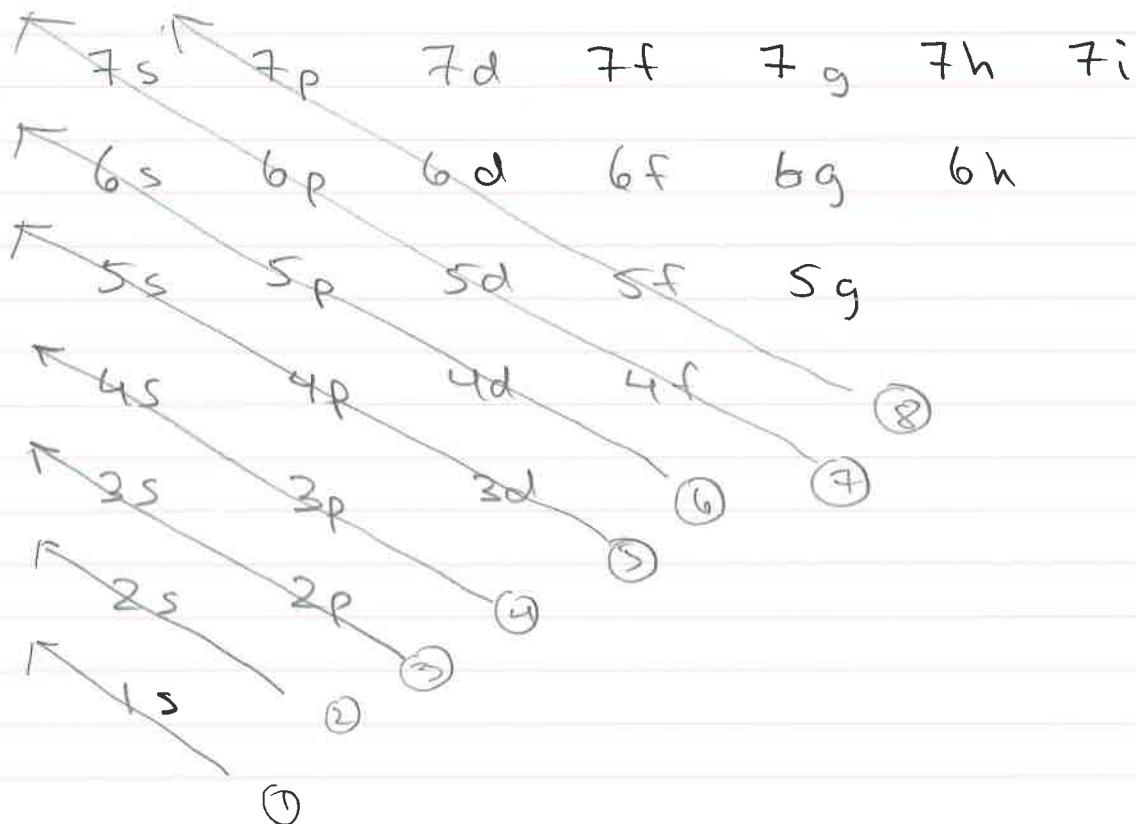
remember our energy level diagram & Aufbau principle
- after 3p the next lowest energy orbital is 4s.

so K has $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

or [Ar] 4s¹

after 4s is full, e⁻'s go to 3d.

Simple Mnemonic for Energy levels



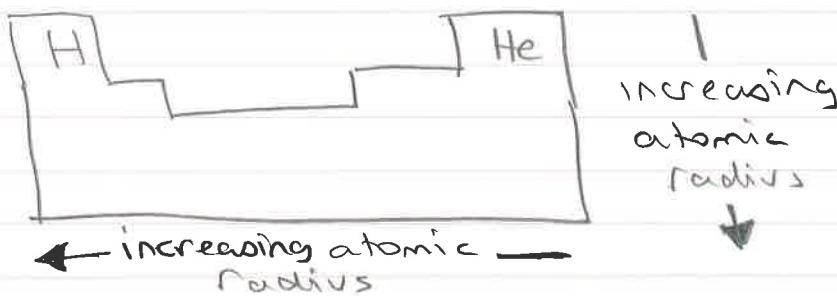
Atomic Radii

In order to talk about atomic radii we have to make an arbitrary decision about where the atom ends.

It is arbitrary because electron orbitals don't end sharply.

Nonetheless, we can choose the radius that the electrons spend 90% of their time inside.

The trend is



(1.) Size increases down a group (column)

The increasing principle quantum number, n , of valence orbitals mean larger orbitals and an increase in atom size.

(2.) Size generally decreases across a period (row)
from left to right

1st realize the more strongly attracted the outermost valence electron is to the nucleus then the smaller the atom will be.

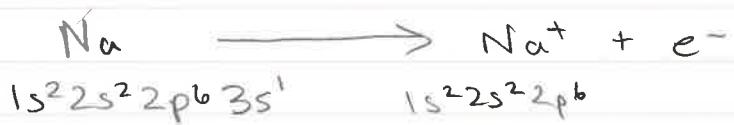
While the number of positively charged protons in the nucleus increases from left to right, the number of negatively charged electrons increase by the same amount. Thus, you might expect no change in radius of outermost e^- orbitals since the increasing charge of the nucleus is cancelled by the increasing number of inner electrons.

However, the ability of inner electrons to cancel nuclear charge depends on the inner electron's orbital. Inner e^- 's in s-orbitals shield better than in p-orbitals. Likewise, inner e^- 's in p-orbitals shield better than in d-orbitals.

As we move across period the ability of inner electrons to cancel the increasing charge of the nucleus diminishes & the outermost e^- becomes more strongly attracted.

Predicting stable anion & cations

When a neutral element loses an e^- it becomes a cation.

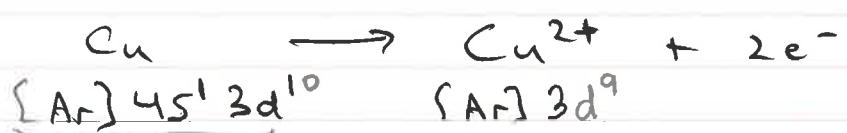
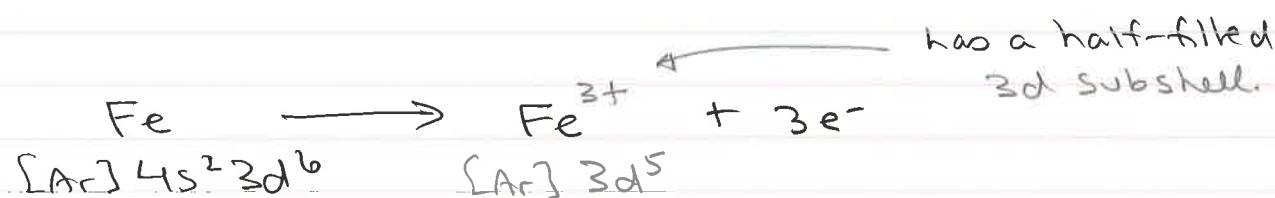
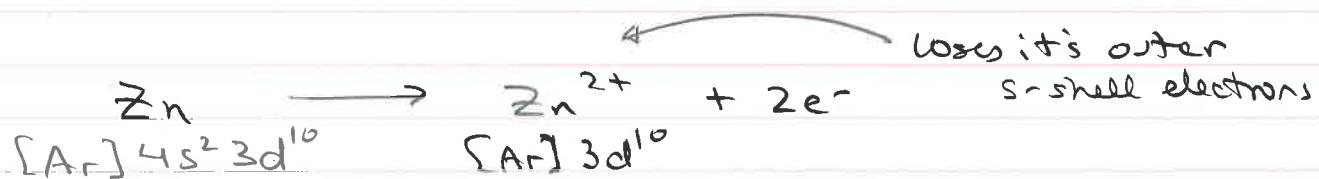


When a neutral element gains an e^- it becomes an anion.



Main group elements (Group A) will gain or lose a minimum number of electrons to obtain a filled shell (noble gas configuration).

Transition group elements (Group B) generally lose outer s-shell electrons. Many also lose electrons to have either a filled or half-filled subshell.



Ionic Radii

A cation is smaller than its neutral parent atom.

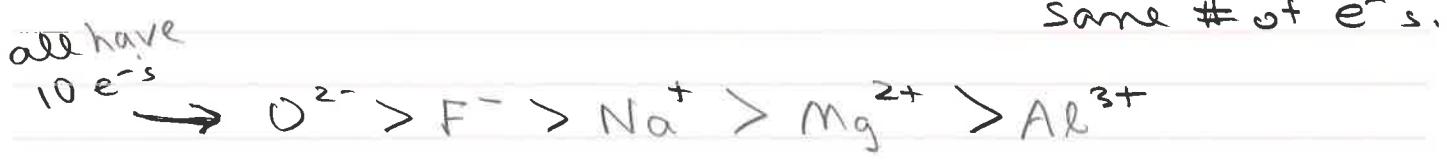
An anion is larger than its neutral parent atom.

	<u>radius</u>		<u>radius</u>
Li	1.52 \AA	Li^+	0.60 \AA
K	2.31 \AA	K^+	1.33 \AA
Cl	0.99 \AA	Cl^-	1.81 \AA
I	1.33 \AA	I^-	2.16 \AA

Generally, ion size increases down a group.

Change in ion size across period is complicated because we change from cations on the left to anions on the right.

However, we can look at relative sizes of isoelectronic ions across a period.



1.40 \AA 1.36 \AA 0.95 \AA 0.65 \AA 0.50 \AA

for isoelectronic ions, radius decreases as nuclear charge increases.

Arrange Se^{2-} , Br^- , Rb^+ , Sr^{2+} in order of increasing radius.

smallest $\text{Sr}^{2+} < \text{Rb}^+ < \text{Br}^- < \text{Se}^{2-}$ largest

$38p$
 $36e^-$

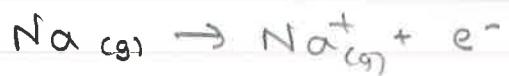
$37p$
 $36e^-$

$35p$
 $36e^-$

Ionization Energy

Amount of energy required to remove an electron from a gaseous atom or ion.

1st ionization energy (I_1) = energy for removing highest energy e^- from neutral gas atom.



$$I_1 = 496 \text{ kJ/mol}$$



Positive quantity,
requires energy

2nd ionization energy (I_2)



$$I_2 = 4560 \text{ kJ/mol}$$

3rd ionization energy



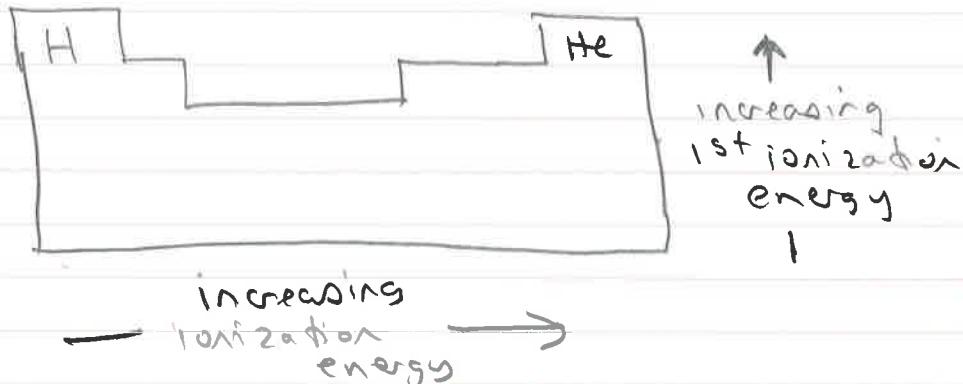
$$I_3 = 6913 \text{ kJ/mol}$$

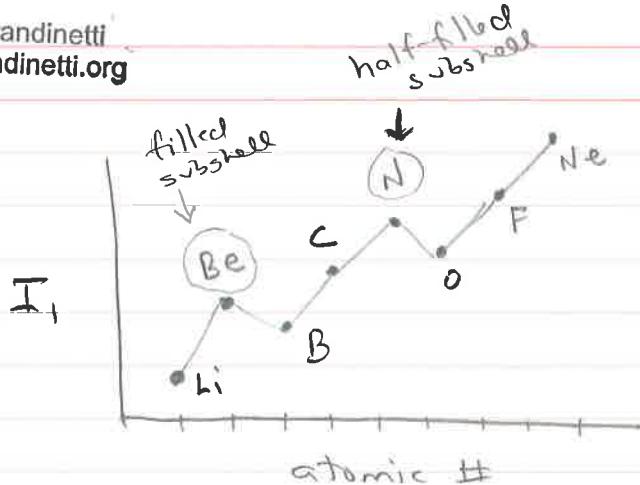
Clearly, it gets progressively harder to remove e^- .

Successive ionization energies increase in magnitude because the number of electrons, which cause repulsion, steadily decrease.

It's not a smooth increase. There's a big jump after an atom loses its last valence electron.

General Trends in 1st ionization Energy





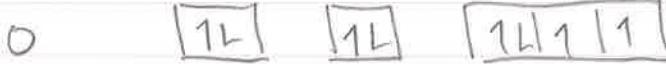
General trend is increasing, but filled and half-filled subshells show a small increase in stability in the same way that filled shells show increased stability



harder to ionize Be than B because Be has filled s-subshell

$$I_1(\text{Be}) > I_1(\text{B})$$

↑ goes against general trend



$$I_1(\text{N}) > I_1(\text{O})$$

yet another...



which has higher I_1 ?

Electron Affinity

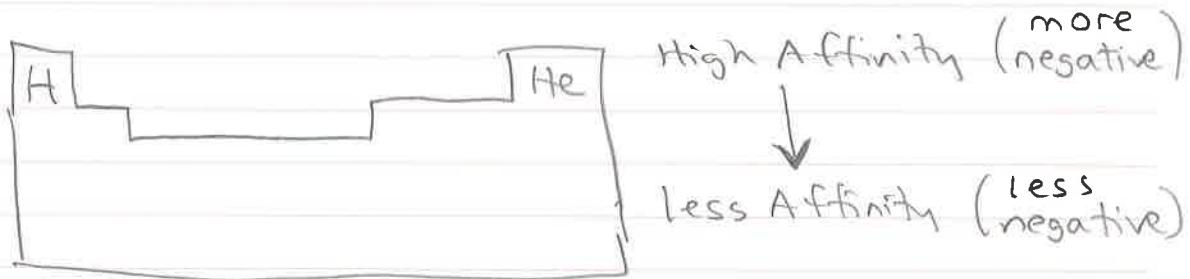
Energy associated w/ addition of e^- to gaseous atom



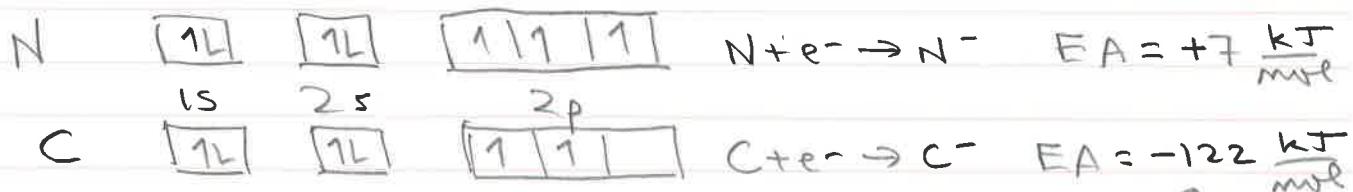
more negative EA means greater e^- attraction to atom.

↑
energy released

General Trends in Electron Affinity



depends on configuration.
hard to predict except when filled/half-filled subshells are involved.



Halogens have the highest affinities

↑
greater e^- affinity

Halogen E.A. / kJ/mol

I	-295.2
Br	-324.5
Cl	-348.7
F	-327.8

break's the trend because smaller atom radius leads to greater $e^- - e^-$ repulsions.