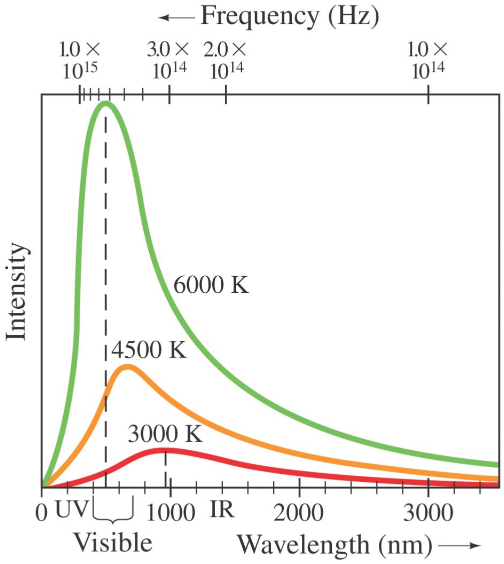
PH2233 Fox : Lecture 21
Chapter 37 (bits) : Early Quantum Theory and Models of the Atom
(mostly sections 37-1, 37-2, 37-10 and 37-11

Classical mechanics (PH2213) and Electricity and Magnetism (PH2223) were exceptionally accurate ways of modelling and predicting outcomes, from mechanical structures to circuits, but by the early part of the 20th century, experiments were yielding results that couldn't be explained by these classical approaches.

Black-body Radiation (bits of 37-1)

When a sample is heated up, it radiates energy in a predictable way, called **blackbody radiation**. In 1900, Max Planck applied ideas from thermodynamics (basically statistics when vast numbers of entities are involved) and derived that this was a statistical result if he assumed that energy could be treated as a vast number of entities called photons, each carrying an energy that depended on it's frequency or wavelength: $\boxed{E = hf = hc/\lambda}$, where $\boxed{h = 6.6261 \times 10^{-34}\ J\ s}$ (now called Planck's constant), from which he showed that the curve was correctly fit using the expression: $I(\lambda, T) = \frac{2\pi hc^2\lambda^{-5}}{e^{hc/(\lambda kT)}-1}$, now called the Planck radiation formula. (NOTE: the k here isn't the Coulomb constant we used back in PH2223, it's an unrelated constant called the Boltzmann constant that appears in thermodynamics.)



This expression peaks at a wavelength λ_p such that $\lambda_p T = 2.90 \times 10^{-3}\ m\ K$, where the temperatures here are all in absolute degrees (degrees Kelvin).

This was controversial at the time due to the introduction of the idea of photons, but they helped explain other phenomenon as well.

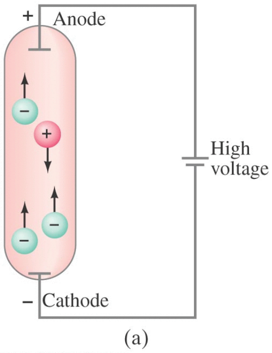
The fact that h exists is what splits the classical physics world we normally live in from the weird quantum mechanical world that exists down at atomic and subatomic scales.

Let's use $E = hf = hc/\lambda$ to look at how much energy the photons involved in visible light must have.

- Violet: $\lambda = 390\ nm$ so $E = hc/\lambda = \frac{(6.63\times10^{-34}\ J\ s)(3\times10^{8}\ m/s)}{390\times10^{-9}\ m} = 5.1 \times 10^{-19}\ J$ Converting to electron volts: $E = (5.1 \times 10^{-19}\ J) \times \frac{1\ eV}{1.602\times10^{-19}\ J} = 3.18\ eV$.
- Shortcut: since at this scale we're working with wavelengths in nm and energies in eV, pre-applying those conversions yields $\boxed{E = \frac{1240\ eV\ nm}{\lambda}}$ (with λ in nm, yielding E in eV directly)
- Red: $\lambda = 750\ nm$ so $E = (1240\ eV\ nm)/(750\ nm) = 1.65\ eV$
- Each photon of **visible light** then carries energy around 2 to 3 eV.
- **X-ray** photons each carry energies around 100 eV to 100 keV.
- **Gamma rays** can carry energies well into the MeV range.

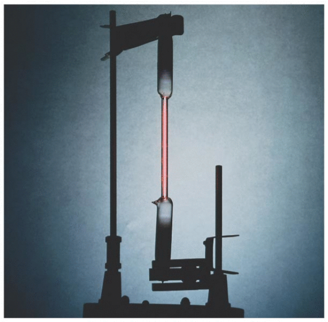
Atomic Spectra (bits of 37-10)

Even so, there were situations where this blackbody spectrum did not occur at all, going back to at least the 1850's (Geissler). When currents were passed through gasses (or any material vaporized into a gas or plasma), the spectrum instead took on very specific frequencies.



(a)

Gas discharge tube (schematic)



(b)

Gas discharge tube (actual)

Here, we see the colors emitted by hydrogen (top) and helium (bottom) gasses

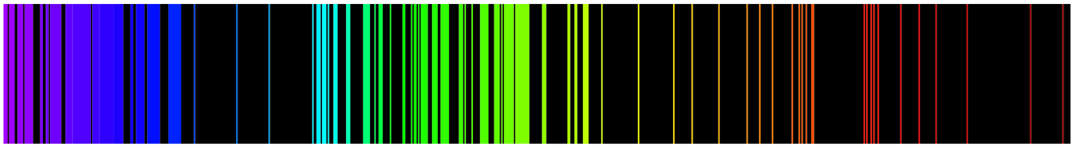
(a)

Spectrum of hydrogen gas.

(b)

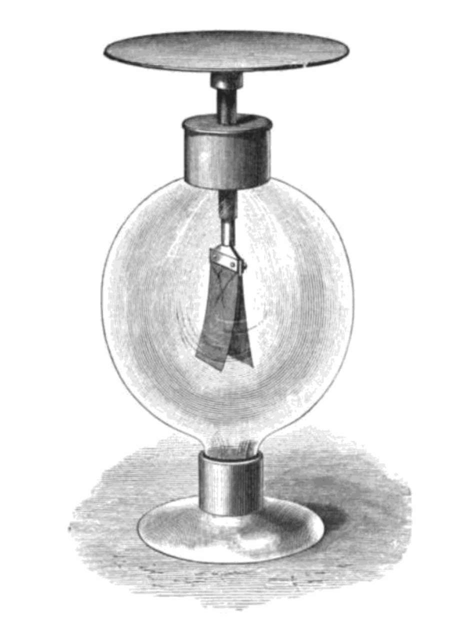
Spectrum of helium gas.

Heavier elements have dramatically more complicated spectra. Here we see the light given off by iron:



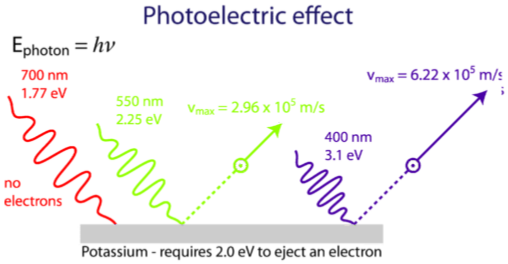
Why should the atoms emit only these specific wavelengths (of frequencies), and no others?

Photo-electric Effect (bits of 37-2)



Gadgets like the **electroscope** shown on the right were used to measure electric charge, even before charge was well understood. If what we now know as voltage or current were applied to the electrode at the top, the charges would build up on the 'leaves' and cause them to separate. It was noticed however that just exposing the device to ultraviolet light would also cause the leaves to separate, indicating the light was inducing a charge on the leaves somehow.

Later, it was observed that some materials (usually metals) had the odd behaviour of emitting electrons when exposed to light.

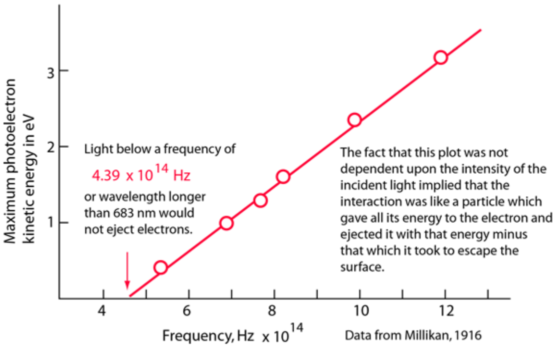


If that weren't enough, it was found that this would only occur if the frequency of the light was higher than a certain value, which was different for each type of metal. If light of a lower frequency (longer wavelength) than this threshhold were applied, no current would be generated, no matter how intense the light was.

This result was in conflict with the wave theory of light. If some amount of energy was required to eject these electrons from the metal, then increasing the intensity should be enough: there should be no dependence on the wavelength.

These experiments hinted that light was acting like a particle, with an energy related to its frequency, and that each atom was 'holding onto' its electrons with a particular amount of energy. The incoming photon had to have enough energy to break the electron free and if it didn't, no electron would be released, no matter how intense the light.

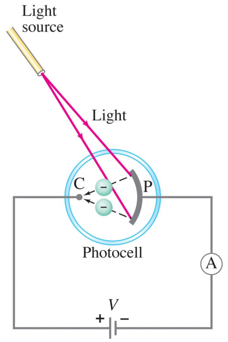
Here's an actual experimental result from 1916 where metallic sodium was exposed to light of various frequencies (or wavelengths, since $f = c/\lambda$). Below a certain frequency (corresponding to a wavelength of 683 nm, or red) no current was created, but as the frequency increased (i.e. as the wavelength got shorter, moving through orange, green, blue, etc), electrons were being released with higher and higher kinetic energies.



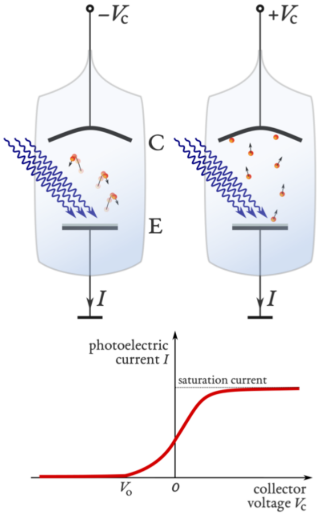
The model here is that the incoming photon has some amount of energy E_γ which goes first into breaking the electron free of the metal (called the 'work function' of the metal) and then whatever was left would go into the kinetic energy K of the freed electron: $E_\gamma = W + K$

Let's look at experiments like this in more detail.

In the 'circuit' shown, there is no complete path for electrons to flow (note the gap in the photocell) but light appeared to cause electrons to be ejected from the metal plate on the right, which were then attracted to the plate on the left (at the higher voltage due to the battery), resulting in a current flow.



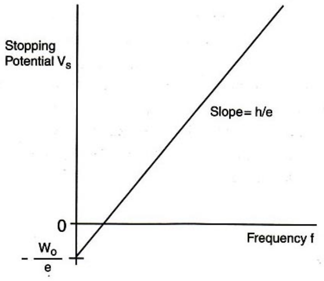
Here's a better figure illustrating what's going on. Photons strike the plate labelled **E**, causing electrons to be released with some kinetic energy K. If no external voltage is provided, some fraction of these electrons will reach the plate labelled **C**, resulting in a low current. If we apply a voltage such that plate **C** has a positive voltage, more and more of the electrons will be attracted towards it. If the positive voltage is high enough, essentially ALL the electronc released by **E** will arrive at **C** resulting in a maximum amount of current flowing. If instead we apply a slight **negative** voltage to **C**, electrons will tend to be repelled by it, BUT if their kinetic energy is high enough, some will still make it there, resulting in a small current.



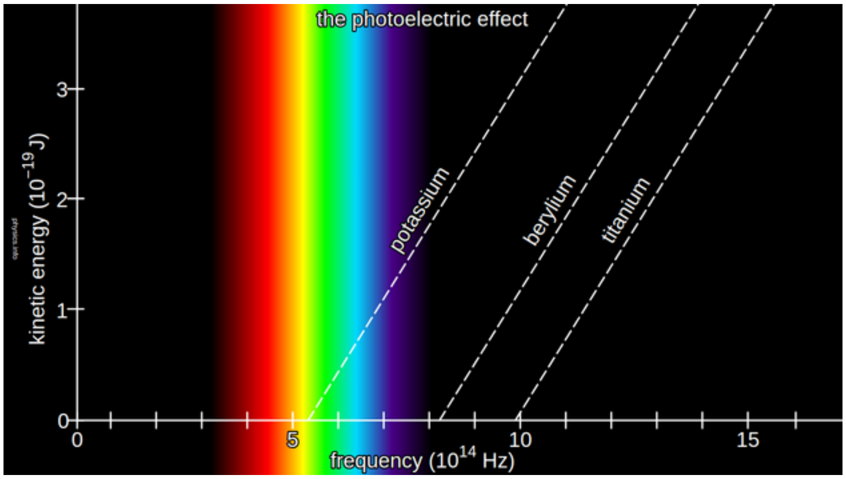
Once the voltage reaches a certain value though, the electrical potential energy barrier between **E** and **C** is too high and NO current will flow. At that point, the kinetic energy of the released electrons must be an exact match for the $U = eV_o$ electric potential energy barrier.

By adjusting the voltage carefully and looking at the resulting graph of current vs applied voltage, the exact kinetic energy of the released electrons can be determined: $K = eV_s$. (The subscript s here refers to the 'stopping potential' : the voltage that 'stops' the current from flowing.)

The experiments indicated that the photon is carrying some amount of energy $E_\gamma = hf$ (using Planck's idea of photons) that depends on the frequency. When a photon strikes an atom, some of that energy is 'used up' is separating the electron from the atom (the 'work function' for that material), and the rest goes into the kinetic energy of the electron:
$E_\gamma = hf = W + K$ and with $K = eV_s$.
We can rewrite this then as $hf = W + eV_s$ or rearranging: $V_s = (\frac{h}{e})f - (\frac{1}{e})W$



This experiment was done with many different elements, mostly in metallic forms, and all had the exact same slope h/e, but each element had a different 'work function' : i.e. each element seemed to 'hold onto' its easiest-to-free-up electron by different amount of energy.



We can relate the threshhold frequency (the frequency below which NO current will be created) and wavelength to the work function. No electron will be released until the photon energy $E = hf$ exceeds the work function, so we need $hf > W$ and $f = c/\lambda$ so we can write this also as $\frac{hc}{\lambda} > W$ or rearranging: $\lambda < hc/W$.

For **potassium**, the work function is about 2.30 eV, corresponding to a wavelength of 539 nm (green). That color and any shorter wavelengths (blue, violet, etc) will have enough energy to kick electrons free.

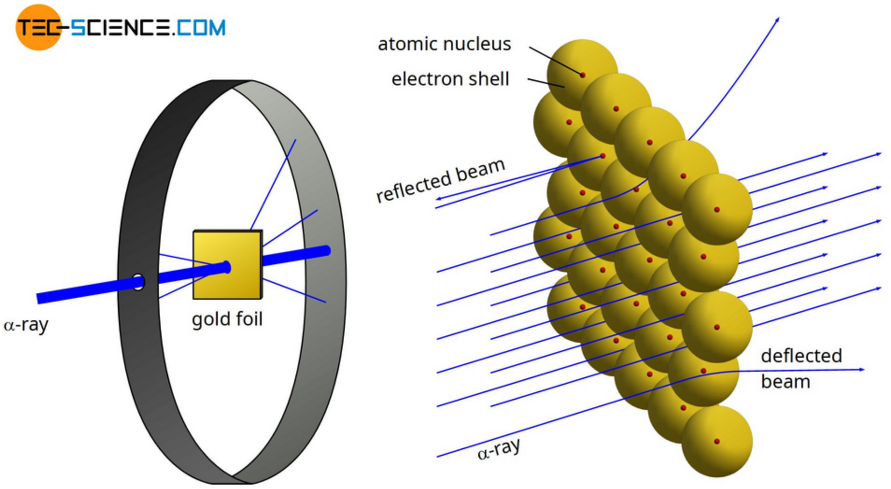
For **berylium**, the work function is higher, at about 5.0 eV which means it will require more energetic photons (higher frequencies, and thus shorter wavelengths). For this element, the photons have to have wavelengths shorter than about 250 nm, which is in the ultraviolet range and not visible.

The element with the **lowest** (smallest) work function I could find is **cesium** with $W = 2.1\ eV$, corresponding to a photon with a wavelength of 590 nm or lower (the yellow/orange boundary).

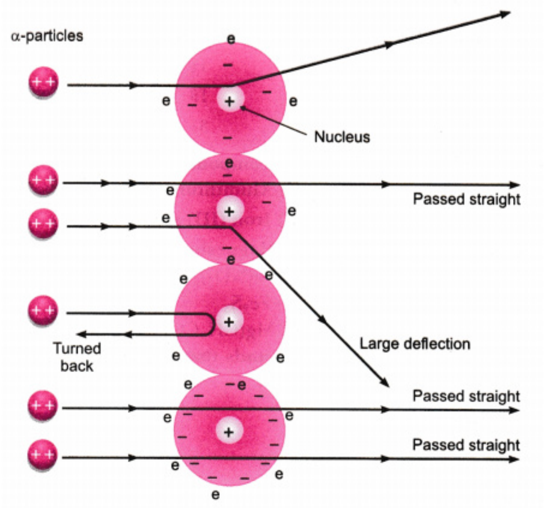
ADDENDUM : in PH2223 we looked at cathode ray tubes (CRT's). The emitter (the cathode) is made of a metal oxide with a low 'work function' so that heat alone is enough to cause it to emit electrons. In section 37-11 it's noted that the average kinetic energy of individual atoms or molecules is given by $K = \frac{3}{2}kT$ where T is the temperature in degrees K (Kelvin), and $k = 1.38 \times 10^{-23}\ J/K$ (called the Boltzmann constant) and again the symbol K in the units there is also 'degrees Kelvin'. A common cathode might emit electrons at a temperature of $1000^o\ F$ or about $600^o\ C$, which would be $600 + 273 = 873^o\ K$, so at that temperature the atom would have a kinetic energy of $K = (1.5)(1.38 \times 10^{-23})(873) = 1.8 \times 10^{-20}\ J$. Converting, that's only about 0.1 eV, so these cathode materials hold onto their outermost electrons very weakly.

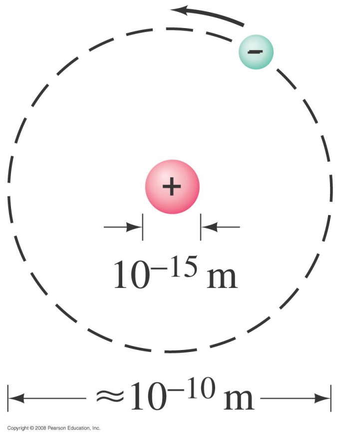
Rutherford Experiment (section 37-02)

Back in the late 1890's (before we understood really what an atom was), a beam of alpha particles (generated via the radioactive decay of uranium) was passed through a thin gold foil. The vast majority of the alpha particles went straight through, but occasionally one would be deflected, in some cases nearly bouncing straight back off the foil. One comment often associated with this experiment is that it was like firing a cannon ball at tissue paper and occasionally having it bounce back.



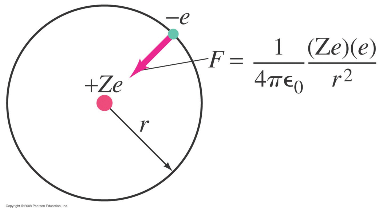
To explain the experiment, Rutherford proposed that atoms consisted mostly of empty space with most of the mass concentrated in a **very** small 'nucleus':





Even if the thin layer of foil consisted of many layers of gold atoms, most alpha particles would pass straight through, never coming close enough to any nuclei to be deflected, implying that the positively charged nucleus must be VERY much smaller than the overall atom, as shown in the figure on the right above.

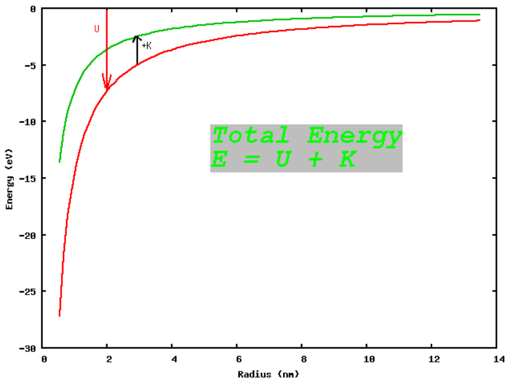
Classical (Bohr) Model of the Atom (bits of 37-11)



The usual high school model of the atom has a nucleus with some number (Z) of protons (and some number N of neutrons), with electrons orbiting around the nucleus due to the electrical force attracting the protons and electrons, mathematically equivalent to how planets orbit the Sun due to gravity. Both of those are central forces that drop off as $1/r^2$.
$F_E = kq_1q_2/r^2 = ma_r$

NOTE: in what follows, we're going to assume we have a nucleus of any atom BUT only a SINGLE ELECTRON in orbit about that nucleus. So this model applies to hydrogen, singly-ionized helium, double-ionized lithium, and so on.

The nucleus has a charge of $q_1 = Ze$ and the electron has a charge of $q_2 = -e$ leading to a radially inward force. Setting our radial direction to be positive inward, we have $F_E = \frac{1}{4\pi\epsilon_o}Ze^2/r^2 = mv^2/r$ where m is the mass of the electron.



If this electron is orbiting at a radius r from the nucleus, it will have a kinetic energy of $K = \frac{1}{2}mv^2$ but we can use the previous equation (which also involves mv^2 on the RHS) to find that: $\boxed{K = \frac{1}{8\pi\epsilon_o}Ze^2/r}$.
There is also electrical potential energy here: $U_E = kq_1q_2/r$ which here will be $\boxed{U_E = -\frac{1}{4\pi\epsilon_o}Ze^2/r}$.
NOTE that this is exactly twice the kinetic energy and the opposite sign, which means that the total mechanical energy of the electron will be: $\boxed{E = -\frac{1}{8\pi\epsilon_o}\frac{Ze^2}{r}}$.

This **begins** to explain the photoelectric effect since the electron is 'bound' to the proton by this amount of energy: we'll need to provide at least this much energy before we can eject the electron and start to see current flowing, but why the very specific energy (voltage) that we needed?

It also **begins** to explain spectra since an electron moving from a given radius to one closer to the nucleus represents a decrease in it's energy, which can be accounted for by a photon being emitted. But again, r could be anything, so why do we only see very specific energies (wavelengths) being emitted?

Based on the actual wavelengths emitted by hydrogen, Bohr concluded that we could reproduce everything perfectly if we assumed that the **angular momentum** of the electron was **quantized**: that is, it can only take on specific values that were integer multiples of the same h parameter (divided by 2π) that Planck had introduced.

Recall that angular momentum is the rotational variant of linear momentum ($p = mv$): $L = I\omega$. For a point mass, $I = mr^2$, so $L = (mr^2)\omega = mr^2\frac{v}{r} = mvr$.

Bohr's quantum condition then was that the electron could only take on values of L such that $L = n\frac{h}{2\pi}$ which implies that

$L = mvr = n\frac{h}{2\pi} = n\hbar$ where $\hbar = h/(2\pi)$ is often used.

Quantized Angular Momenta : Impact on Real World Scales

Consider a spinning golf-ball. In class, I spun a golf-ball so that it was rotating at about $f = 2\ Hz$. What angular momentum does that represent? How many $h/(2\pi)$ units is it? As the golf ball slows down, it has to jump from one L to the next 'allowed' value for L. Can we 'see' this happening?

- $L = I\omega$
- For a solid sphere $I = \frac{2}{5}MR^2$
- Golf-ball parameters: $M = 46\ grams = 0.046\ kg$, $R = 2.134\ cm = 0.02134\ m$
- $I = \frac{2}{5}(0.046\ kg)(0.02134\ m)^2 = 8.4 \times 10^{-6}\ kg\ m^2$
- $\omega = 2\pi f = 2\pi(2\ Hz) = 12.6\ s^{-1}$
- $L = I\omega \approx 1 \times 10^{-4}\ kg\ m^2\ s^{-1}$

According to Bohr, angular momenta will be multiple of $h/(2\pi)$ which is $(6.626 \times 10^{-34}\ J\ s)/(2\pi) = 1.055 \times 10^{-34}\ J\ s$.

If the golf ball's angular momentum is $L = n\frac{h}{2\pi}$ what is n?

$n = (1 \times 10^{-4})/(1.055 \times 10^{-34}) = 9.5 \times 10^{29}$.

What does this imply? As the golf ball slows down and comes to a stop, it has to 'jump' from one allowed angular momentum value to the next, but it does so in nearly 10^{30} steps, so it appears to be continuous to us (and to any way we have of measuring it).

These 'quantized' angular momenta play a huge role down at the atomic and molecular level, but are invisible to us up here at the macro scale.

Getting back to where we were, Bohr found that the angular momenta of the electrons in the various (allowed) orbits in the Hydrogen atom were such that $L = mvr = n\frac{h}{2\pi}$.

We started with Newton's Law applied to the electrical force between the electron and the nucleus:

$F = ma$ or $k\frac{(Ze)(e)}{r^2} = m\frac{v^2}{r}$

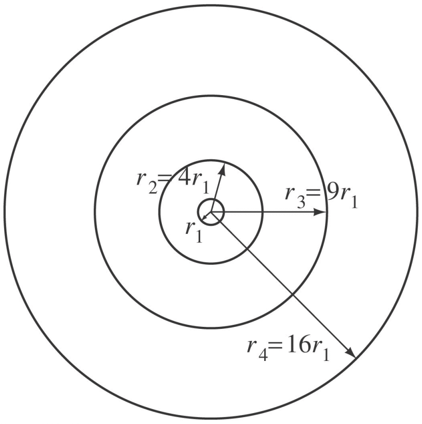
Cancelling one of the r's and rearranging: $r = \frac{kZe^2}{mv^2}$ (a)

The angular momentum must be $mvr = n\frac{h}{2\pi}$ which we can rearrange into: $v = \frac{nh}{2\pi mr}$. (b)

Replacing v in equation (a) using this expression and rearranging to solve for r, we arrive finally at:

$r_n = \frac{n^2h^2\epsilon_o}{\pi mZe^2}$ or simply $\boxed{r_n = \frac{n^2}{Z}r_1}$ where $r_1 = \frac{h^2\epsilon_o}{\pi me^2}$, called the **Bohr radius**.

For the hydrogen atom, this is $\boxed{r_1 = 0.529 \times 10^{-10}\ m}$ and represents the closest orbit the electron is allowed to be in around the proton, and since the total energy of the electron varies as $-1/r$, it represents the lowest possible energy state for the electron.
The next allowed orbit ($n = 2$) will be $r_2 = (2)^2r_1 = 4r_1$ and so on.
Now that we know the specific orbits the electron must occupy, we can find the specific energies it can take on:

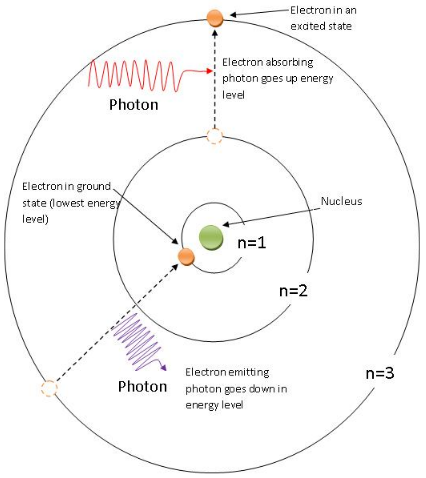


Copyright © 2008 Pearson Education, Inc.

$E_n = -(\frac{Z^2e^4m}{8\epsilon_o^2h^2})\frac{1}{n^2}$, and with judicious units conversions we can write this as:

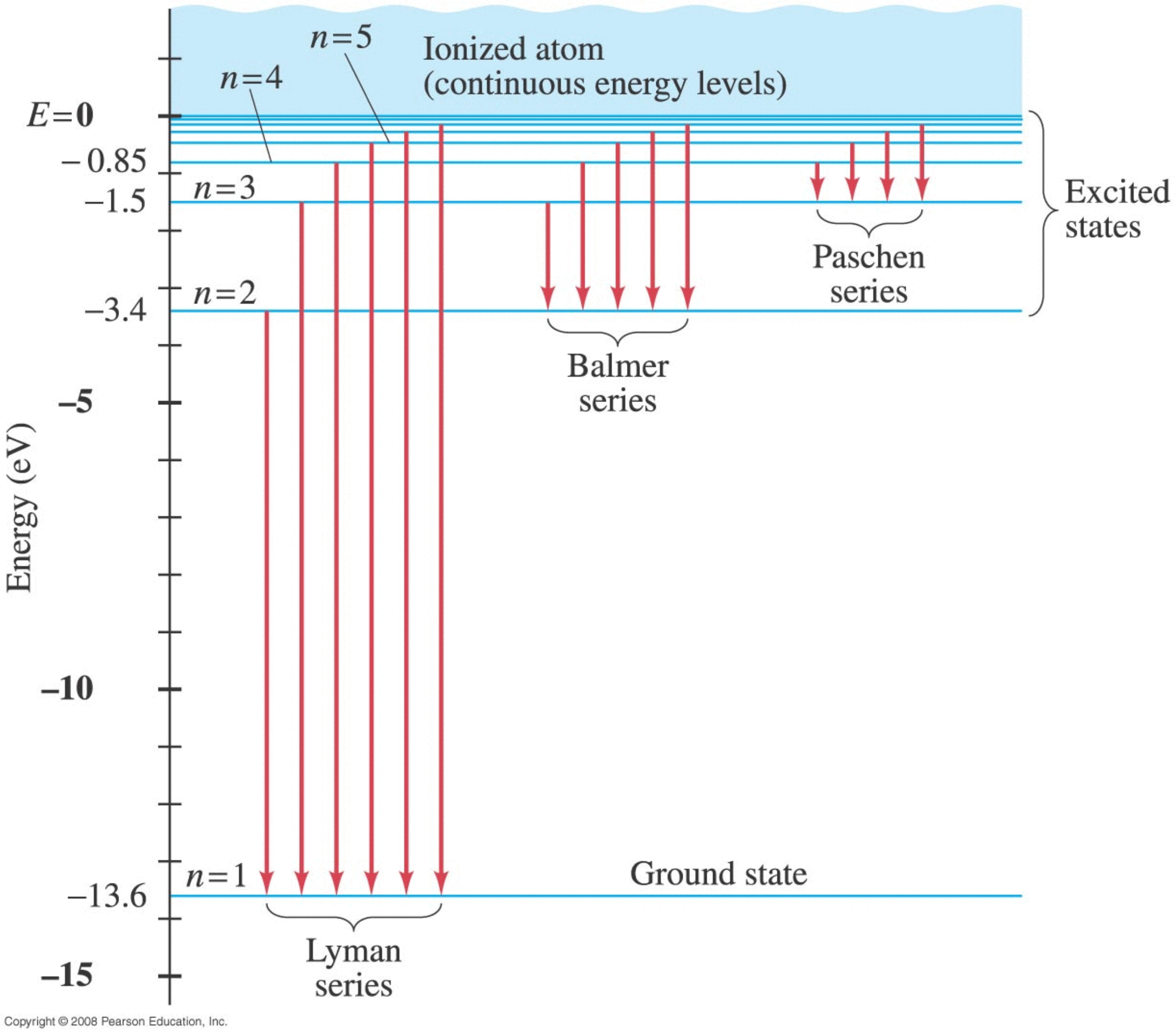
$\boxed{E_n = -(13.6\ eV)\frac{Z^2}{n^2}}$ **(Reminder: the nucleus has Z protons, but this model assumes there's only a SINGLE electron orbiting this nucleus. This equation does not apply to atoms with more than one electron present.)**

This now explains why hydrogen (and other atoms) only have specific 'lines' in their spectra. **The electrons can only move from one orbit to another, and those represent very specific changes in energy**, so very specific wavelengths of light emitted (or **absorbed** so this also explains the absorption spectra of elements also).



These transitions can occur between any pairs of orbits though, each one representing the emission or absorption of a photon.

Here we see the full series of transitions in a hydrogen atom.



- The **Lyman series** (electron dropping to $n = 1$ from some higher orbit) represents energy changes from 13.6 eV to 10.2 eV and using $E = (1240\ eV\ nm)/\lambda$ this implies light wavelengths between 91 nm and 121 nm, meaning they're in the **ultraviolet** (not visible) range.

- The **Balmer series** (electron dropping from some higher orbit to $n = 2$) involves ΔE between 3.4 eV and 1.9 eV corresponding to wavelengths between 365 nm and 653 nm and most of those transitions create light in the visible range.

- The **Paschen series** represents ΔE between 1.5 eV and 0.65 eV, corresponding to wavelengths between 827 nm and 1908 nm, which are in the infrared range.

It's worth noting that it's the UV photons from the Sun (and tanning beds) that can cause damage to our skin and retinas, due to their much higher energies.

Light-emitting Diodes : lab this week

A diode is a particular type of electronic circuit element that we usually don't cover and won't do so here (they're usually used to limit currents to only flowing one direction, preventing any current from flowing in the opposite direction). Some of these will emit light once a certain voltage is reached. Basically the voltage is creating a strong enough electric field to strip electrons from some of the atoms in the device, and when those electrons are re-captured, they emit this energy as photons. The LED's you'll be (virtually) using emit photons that represent visible light.

For a given LED, nothing happens until the voltage reaches some critical level though. At that point, the electron has acquired an energy of $E = (q)(V) = (e)(V)$, which must be enough to pull the electron from the atom. The electron in the atom has a certain (negative) total mechanical energy, so nothing will happen (no light will be emitted) until our supplied energy (eV) is **just** enough to allow the electron to escape. At which point it gets recaptured and releases that energy as light.

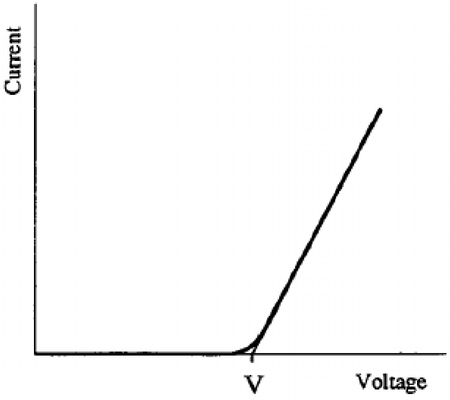
At that exact threshhold then, the energy we provided (eV) is exactly the energy in the light (hf) so:

$eV = hf = hc/\lambda$.

This gives us a way to experimentally determine the value of h: we apply a voltage and gradually increase it until the LED suddenly starts emitting light. The LED's in the lab are labelled as to their specific wavelength, so we can use $(e)(V) = hc/\lambda$ (with the critical voltage V we just found) to determine h.

In practice this is a bit difficult since the LED at the critical voltage will only be emitting a little light and we might not be able to see it easily.

Another potential path is available though (which unfortunately we **don't** do in the lab). As we increase the voltage this higher energy is enough to free up more and more electrons (i.e. a higher current flowing), so another way of doing this is to graph the current flowing in the circuit vs the voltage applied. We end up with a graph like the one at the right and we can fit a line to our data and project backward to determine the voltage at which the current would just start flowing - that is the threshhold voltage we're looking for and we can use that value in the $(e)(V) = hc/\lambda$ equation to again determine h.



The LED is putting out visible light, which means the voltage where light starts to be emitted will only be a couple of volts as we found earlier.

(It's a little troublesome that our nice linear $V = IR$ relationship from PH2223 is failing here, but we can thank quantum mechanics for that...)