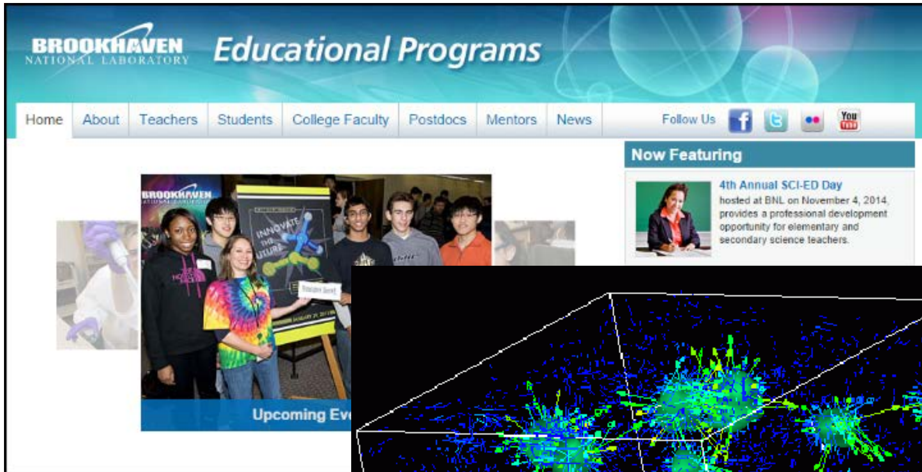
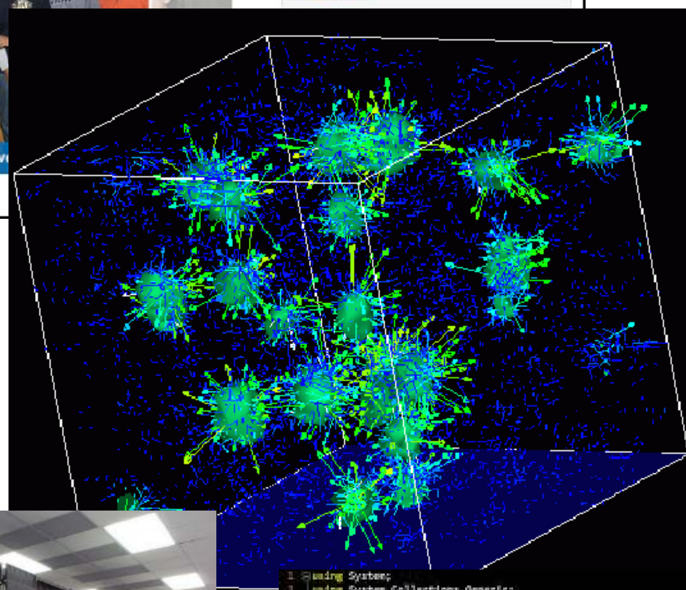
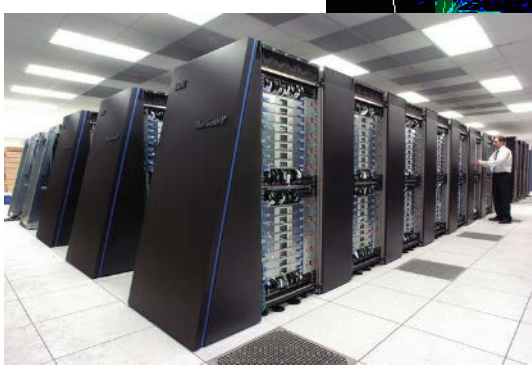






Survey of Scientific Computing

(SciComp 301)

Dave Biersach
Brookhaven National Laboratory
dbiersach@bnl.gov

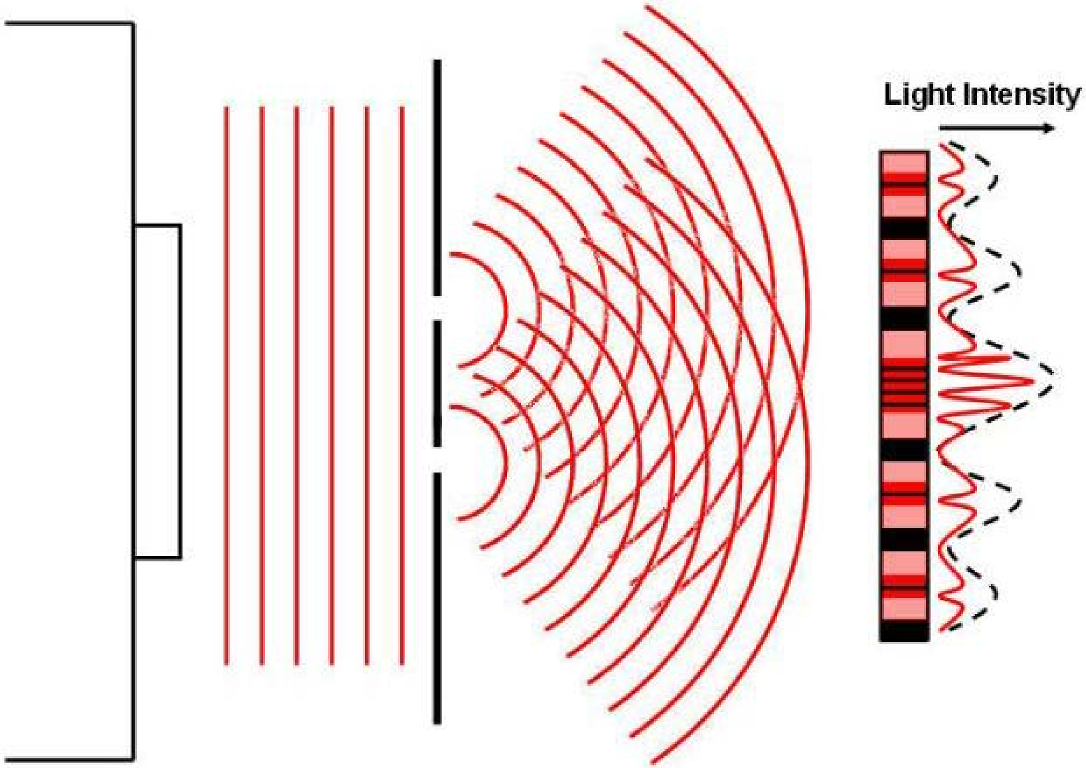
Session 25

Early Quantum Mechanics

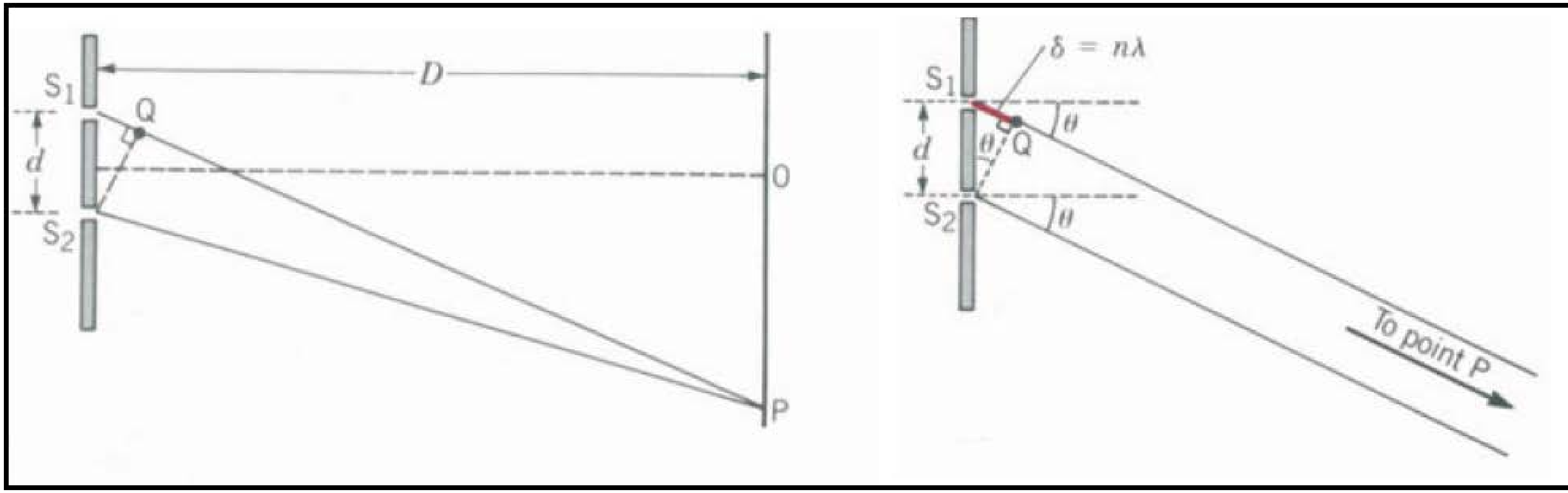
Session Goals

- Understand how **double-slit diffraction** enables measurement of wavelengths
- Predict the **spectral emission lines** of Hydrogen using the **Rydberg Formula**
- Discuss the evolution of the early atomic models
- Develop the **Bohr Atomic Model** for Hydrogen
- Calculate spectral lines using the Bohr Atomic Model
- Compare the Rydberg Formula to the Bohr Model

Double Slit Diffraction



Double Slit Diffraction



$$D \ggg d \Longrightarrow \overline{S_1P} \parallel \overline{S_2P} \therefore \delta = d\sin\theta$$

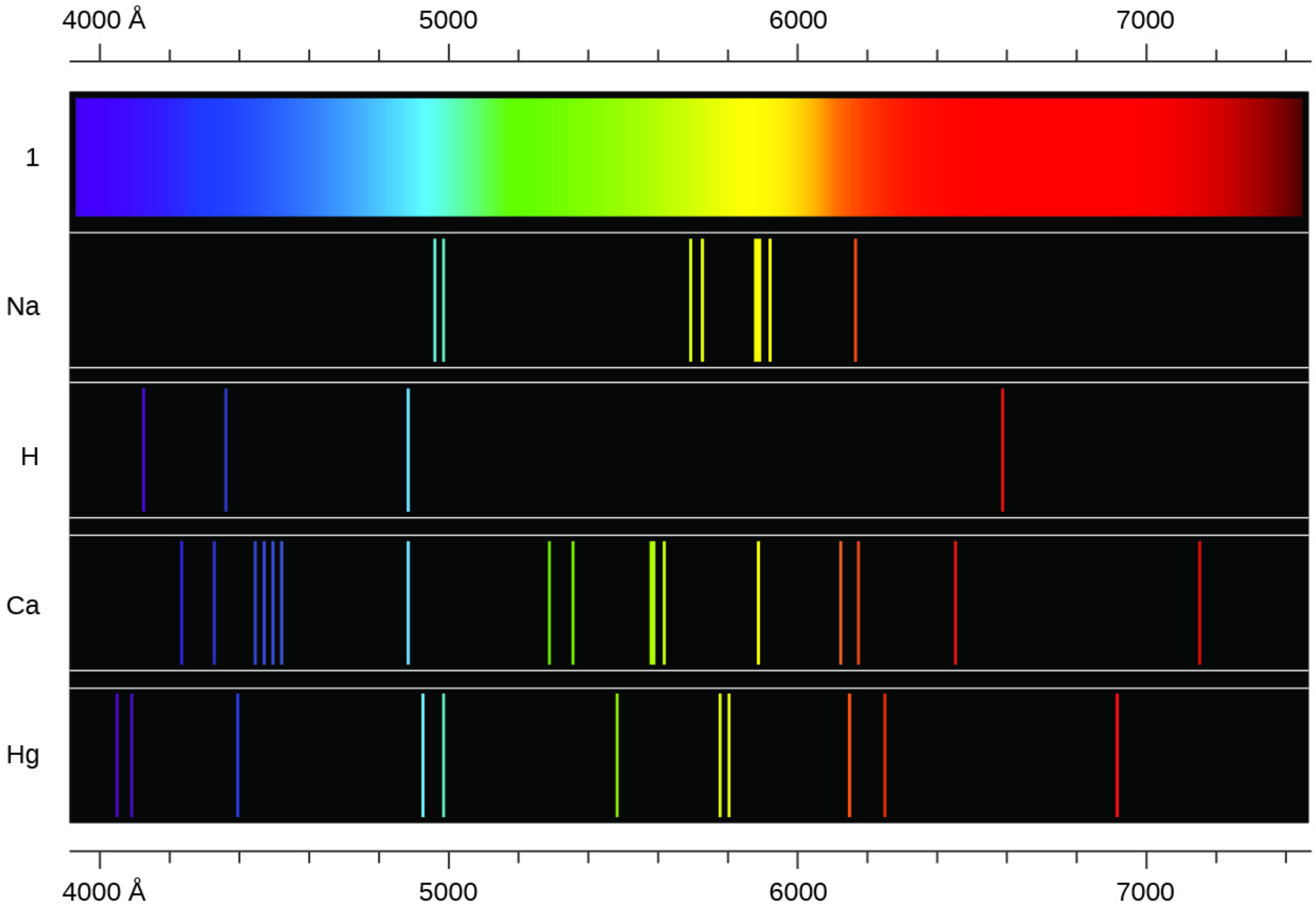
For constructive interference:

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

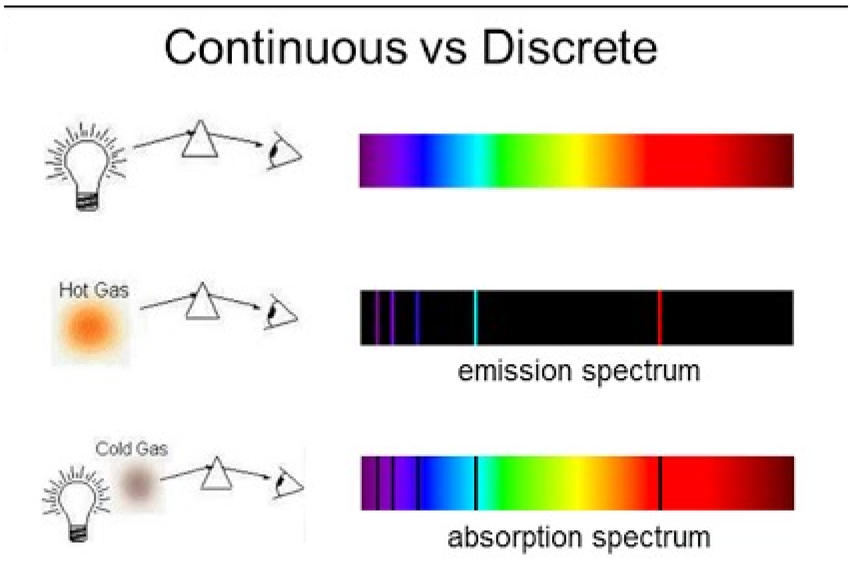
$$\lambda = \frac{d\sin\theta}{n}$$

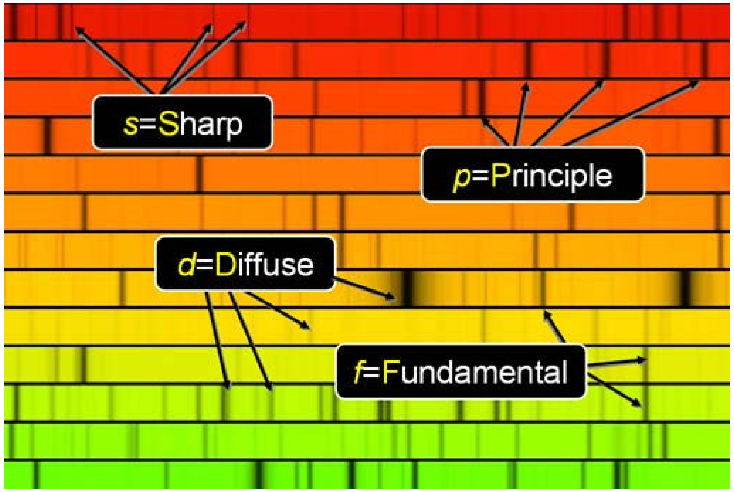
Wavelengths (λ) of four visible emission lines after heating pure Hydrogen

Spectral Emission Lines



Spectral Emission Lines





Spectral Emission Lines

Spherical harmonics

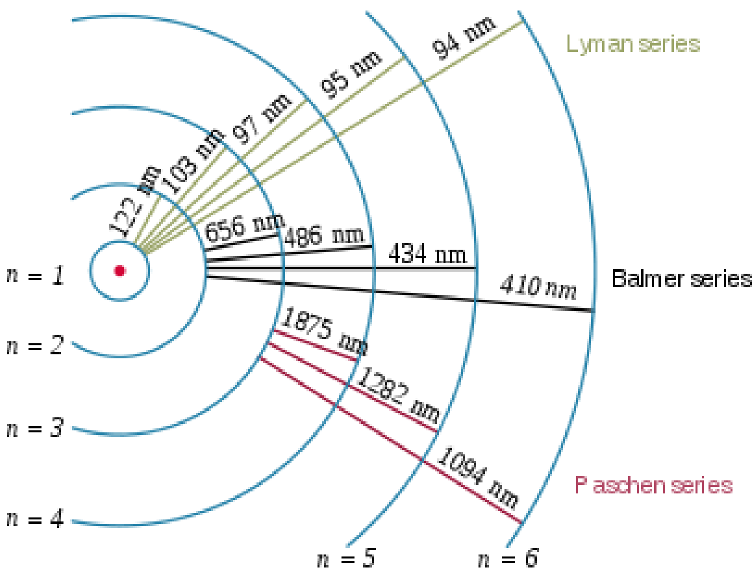
Despite their name, spherical harmonics take their simplest form in Cartesian coordinates, where they can be defined as homogeneous polynomials of degree ℓ in (x, y, z) that obey Laplace's equation. Functions that satisfy Laplace's equation are often said to be harmonic, hence the name spherical

A specific set of spherical harmonics, denoted $Y_\ell^m(\theta, \varphi)$ or $Y_\ell^m(\mathbf{r})$, are called Laplace's spherical harmonics, as they were first introduced by Pierre Simon de Laplace in 1782.[1] These functions form an orthogonal system, and are thus basic to the expansion of a general function on the sphere as alluded to above.

Spherical harmonics are important in many theoretical and practical applications, e.g., the representation of multipole electrostatic and electromagnetic fields, computation of atomic orbital electron configurations, representation of gravitational fields, geoids, fiber reconstruction for estimation of the path and location of neural axons based on the properties of water diffusion from diffusion-weighted MRI imaging for streamline tractography, and the magnetic fields of planetary bodies and stars, and characterization of the cosmic microwave background radiation. In 3D computer graphics, spherical harmonics play a role in a wide variety of topics including indirect lighting (ambient occlusion, global illumination, precomputed radiance transfer, etc.) and modelling of 3D shapes.

Spectral Emission Lines

Hydrogen Emission Lines



Rydberg Formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_k^2} - \frac{1}{n_j^2}\right)$$

$$k, j \in \mathbb{Z}^+ \; and \; j > k$$

$$Rydberg\ Constant$$
$$R = 1.0967757 \times 10^7 m^{-1}$$

Initial orbit

	k	j	j	j	j	j
	1	2	3	4	5	6
Lyman		122	103	97	95	94

Final orbit

	2	3	4	5	6	7
Balmer		656	486	434	410	397

	3	4	5	6	7	8
Paschen		1876	1282	1094	1005	955

	4	5	6	7	8	9
Brackett		4052	2626	2166	1945	1818

$$nm = 1 \times 10^{-9} m$$

$$Å = 1 \times 10^{-10} m$$

Open Lab 1 - Rydberg Spectra for Hydrogen

https://en.wikipedia.org/wiki/Hydrogen_spectral_series

- Update a C++ console application to generate the anticipated wavelengths of the spectral emission of Hydrogen using the **Rydberg formula**
- For each family from the **Lyman** to the **Brackett** series, display the **first five** (5) wavelengths (nm) in each series

If $n_k = 1$, then $n_j = 2, 3, 4, \cdots$	This family is known as the Lyman series
If $n_k = 2$, then $n_j = 3, 4, 5, \cdots$	This family is known as the Balmer series
If $n_k = 3$, then $n_j = 4, 5, 6, \cdots$	This family is known as the Paschen series
If $n_k = 4$, then $n_j = 5, 6, 7, \cdots$	This family is known as the Brackett series

Edit Lab 1 – Rydberg Spectra for Hydrogen

spectrum-rydberg.cpp

```cpp
// spectrum-rydberg.cpp

#include "stdafx.h"

using namespace std;

int main()
{
    const double R = 1.0967757e7;

    cout << "Rydberg Formula Hydrogen Spectral Lines" << endl;

    for (int k{ 1 }; k < 5; ++k) {
        for (int j{ k + 1 }; j < k + 6; ++j) {
            double lambda = 0;
            cout << setw(3) << j;
            cout << setw(10) << setprecision(0) << fixed;
            cout << lambda * 1e9 << "nm" << endl;
        }
        // Skip a line between families
        cout << endl;
    }

    return 0;
}

```

Enter the correct formula

Run Lab 1 – Rydberg Spectra for Hydrogen

spectrum-rydberg.cpp

```
// spectrum-rydberg.cpp

#include "stdafx.h"

using namespace std;

int main()
{
    const double R = 1.0967757e7;

    cout << "Rydberg Formula Hydrogen Spectral Lines" << endl;

    for (int k{ 1 }; k < 5; ++k) {
        for (int j{ k + 1 }; j < k + 6; ++j) {
            double lambda = 1 / (R * (1 / pow(k, 2) - 1 / pow(j, 2)));
            cout << setw(3) << j;
            cout << setw(10) << setprecision(0) << fixed;
            cout << lambda * 1e9 << "nm" << endl;
        }
        // Skip a line between families
        cout << endl;
    }

    return 0;
}
```

Check Lab 1 – Rydberg Spectra for Hydrogen

spectrum-rydberg

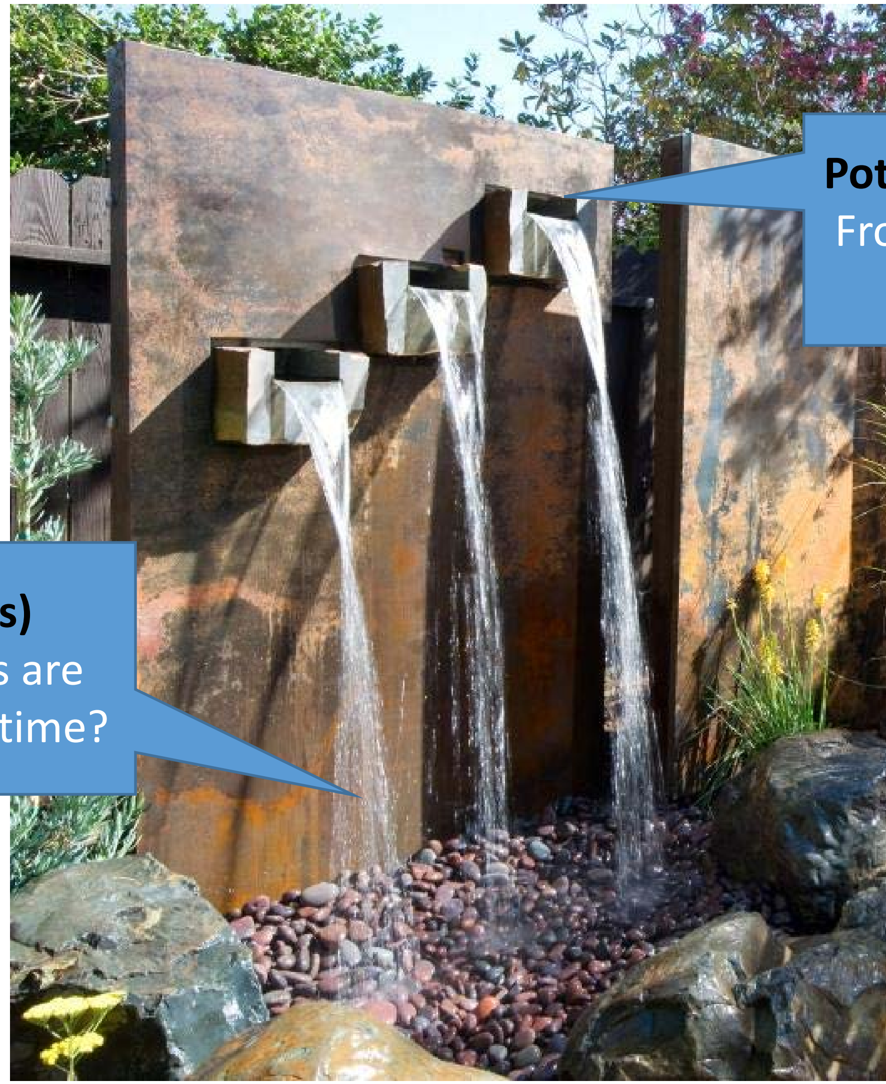
File Edit View Terminal Tabs Help

```
Rydberg Formula Hydrogen Spectral Lines
  2       122nm
  3       103nm
  4        97nm
  5        95nm
  6        94nm

  3       656nm
  4       486nm
  5       434nm
  6       410nm
  7       397nm

  4      1876nm
  5      1282nm
  6      1094nm
  7      1005nm
  8       955nm

  5      4052nm
  6      2626nm
  7      2166nm
  8      1945nm
  9      1818nm


Process returned 0 (0x0)   execution time : 0.014 s
Press ENTER to continue.
```

Formulas $\neq$ Physics

- Rydberg developed his formula in **1888** and it was later extended by Ritz to account for all known atoms
- But it is still only an empirical formula – there was no explanation given as to ***why*** the formula worked
- Fitting a curve mathematically and then making accurate predictions **is still not physics** if you don't understand the underlying physical laws that lead to the equation
- It took the next 50 years for science to understand the true nature of the formula and to realize the source of **Rydberg's constant**

Physics Intuition: Voltage vs. Current



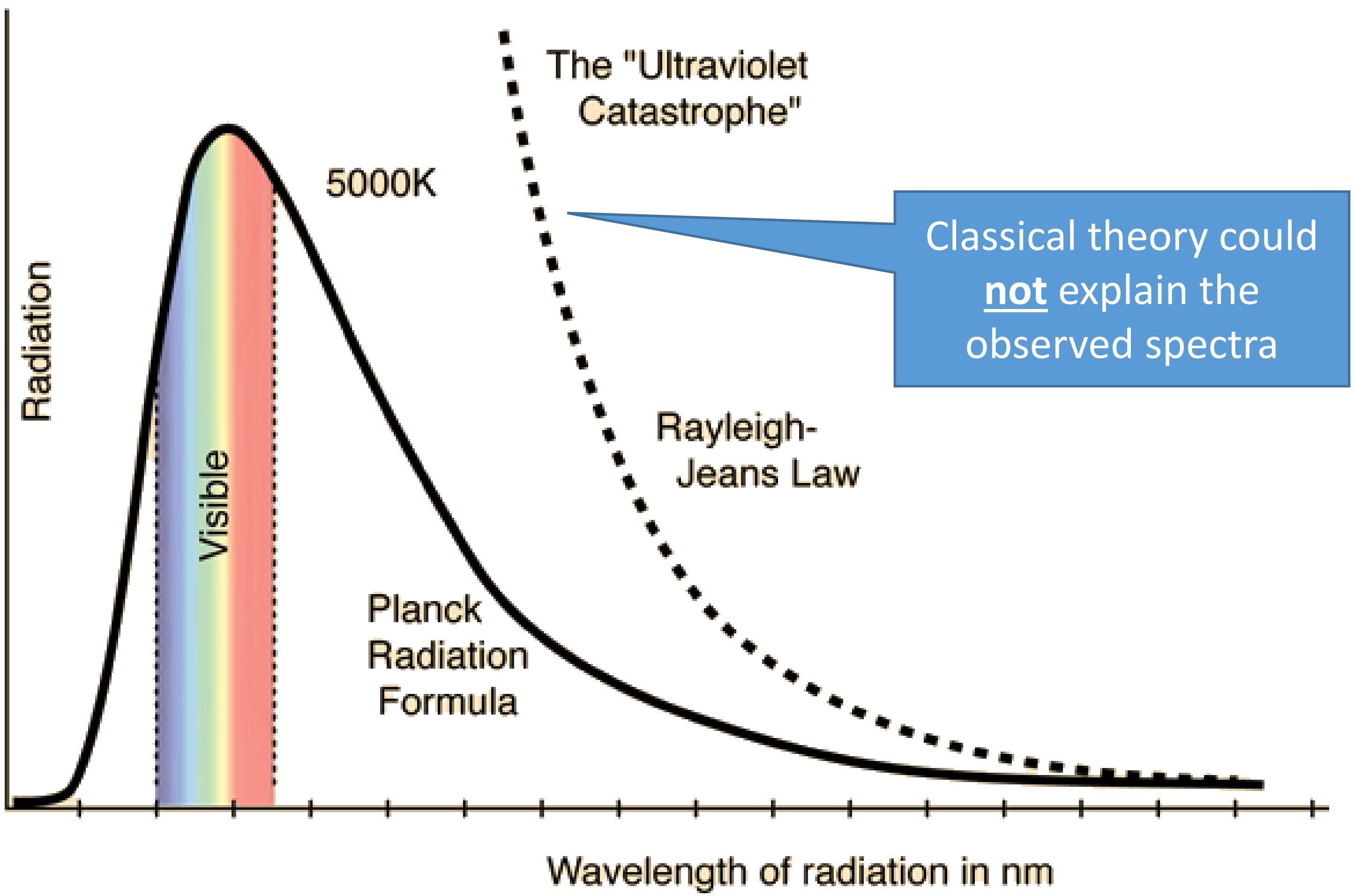
Potential Energy (Volts)
From how *high* are the drops falling?

Current (Amps)
How ***many*** drops are falling per unit of time?

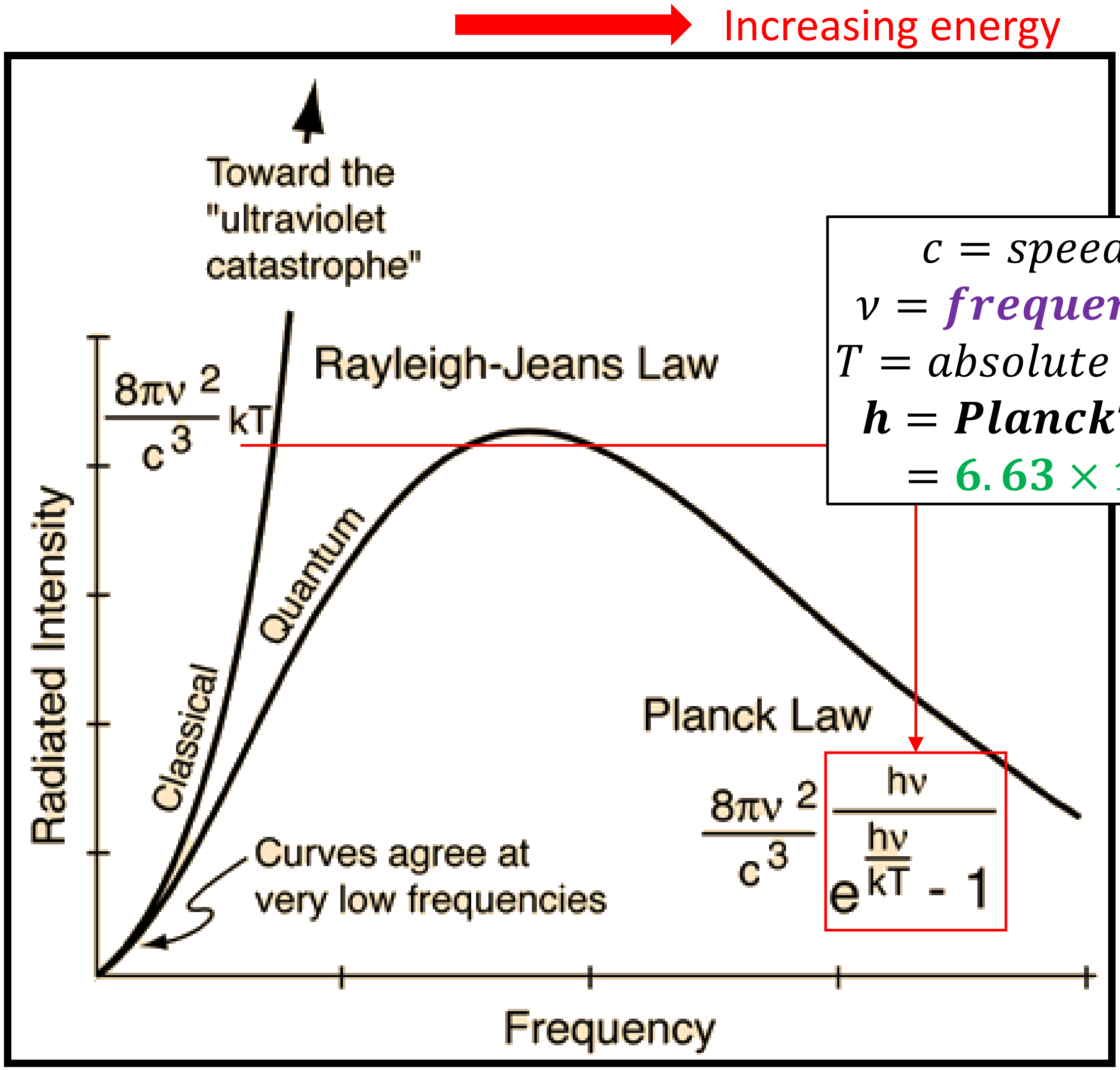
It is neither the size nor the speed of the drops

The Ultraviolet Catastrophe

Increasing energy



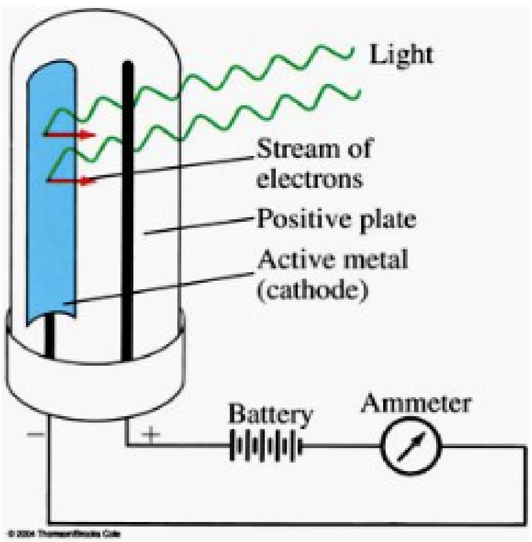
Max Planck's Law - 1900



$c = speed\ of\ light$
$\nu = \boldsymbol{frequency}\ of\ wave$
$T = absolute\ temperature$
$\boldsymbol{h = Planck's\ constant}$
$= \mathbf{6.63 \times 10^{-34} Jsec}$

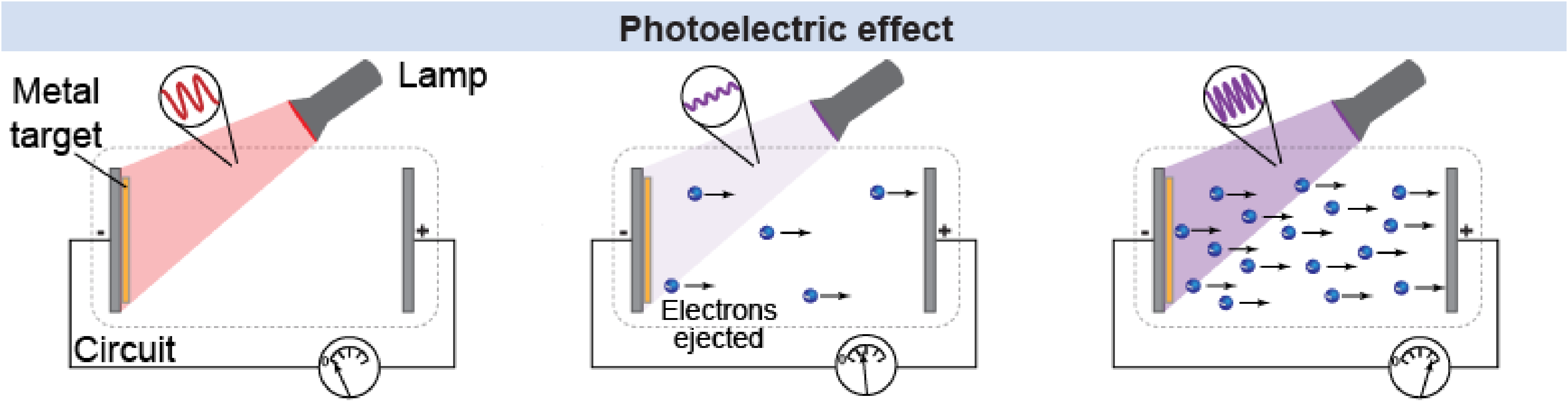
Energy is **quantized!** It comes in packets of $\boldsymbol{h\nu}$

Einstein's Photon Quantum - 1905



- Light can strike the surface of some metals causing an electron to be ejected
  - No matter how brightly the light shines, electrons are ejected only if the light has sufficient energy (sufficiently short wavelength)
  - After the necessary energy is reached, the current (# electrons emitted per second) increases as the intensity (brightness) of the light increases
  - The current, however, does not depend on the wavelength

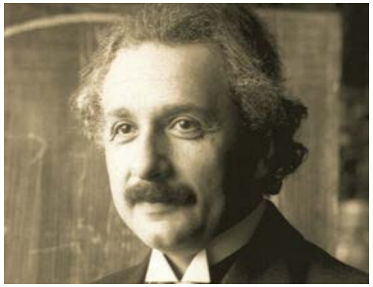
Einstein's Photon Quantum - 1905



Light frequency too low; no electrons ejected from metal; no electric current flows.

Low-intensity light above threshold frequency; some electrons ejected from metal; small current.

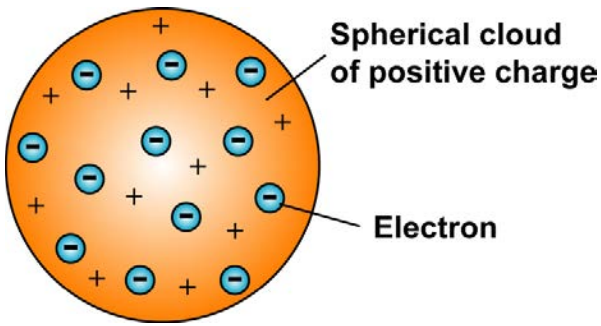
High-intensity light above threshold frequency; many ejected electrons; high current.



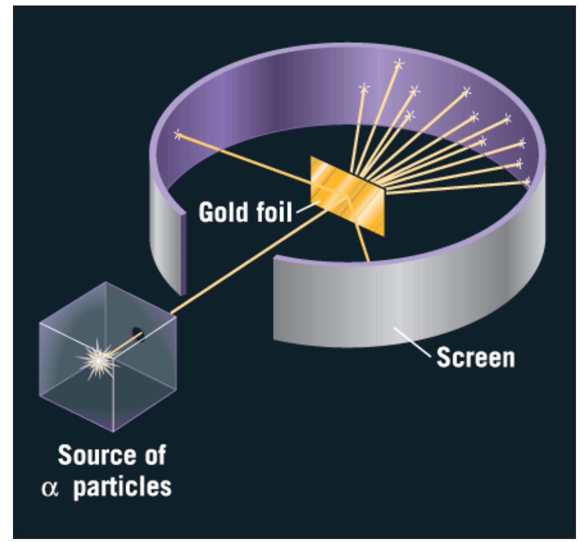
$$E_{photon} = \frac{hc}{\lambda}$$

Early Atomic Models

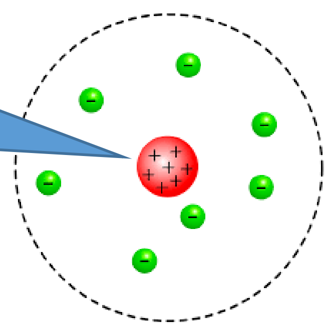
J.J Thomson (1904)



E. Rutherford Experiment (1911)

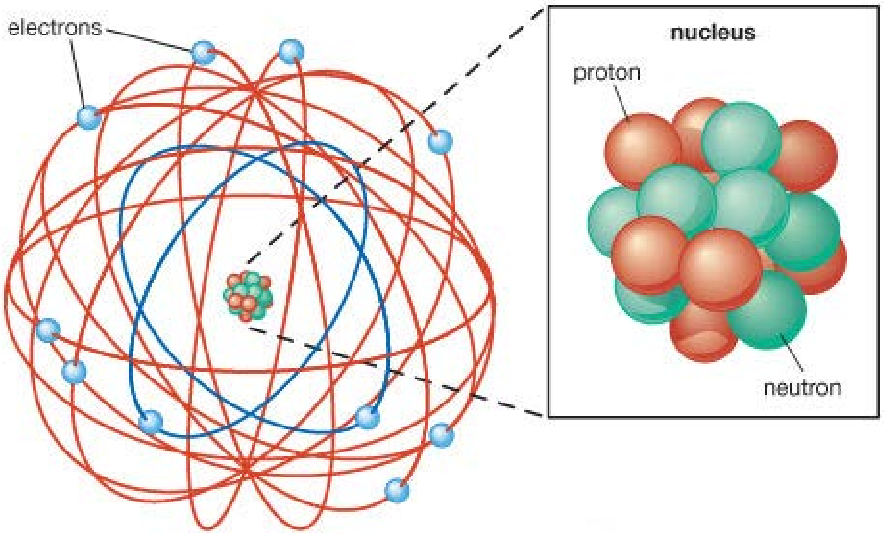


But if like charges repel, then what keeps the protons close together?

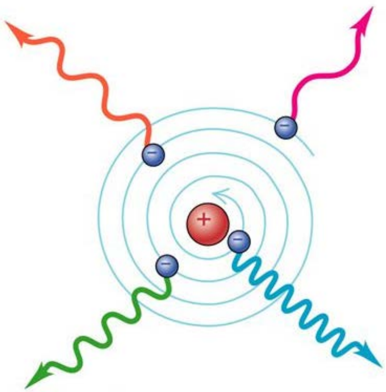


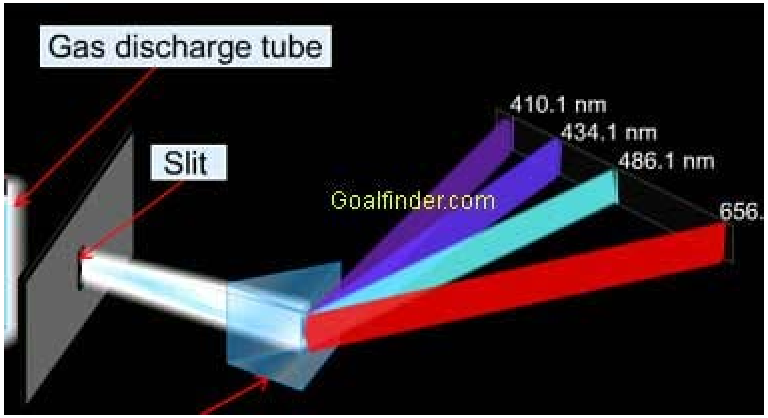
Rutherford scattering indicated atoms have a heavy & compact nucleus

Early Atomic Models

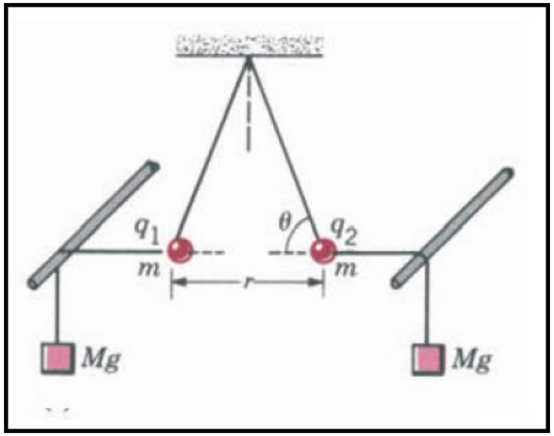


The Rutherford model required even *stable* atoms to constantly emit radiation (but they don't) and it could not explain discrete spectral emission lines





Electric Field Potential



Coulomb's Law

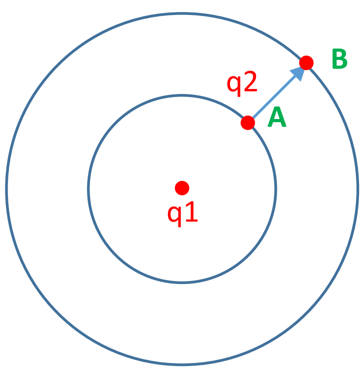
$$F \propto \frac{q_1 q_2}{r^2} \Longrightarrow F = k\frac{q_1 q_2}{r^2}$$

$$k = \frac{1}{4\pi\varepsilon_0}\ (Coulomb's\ constant)$$

Eq 1 $\boxed{F = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}}$

q = Electric charge
$\mathcal{E}_0$ = Permittivity of free space

Electric Field Potential



$$W_{A\rightarrow B} = \int_A^B F\,ds$$

$$E(r) = \frac{q_1 q_2}{4\pi\varepsilon_0}\int_A^B \frac{1}{r^2}dr$$

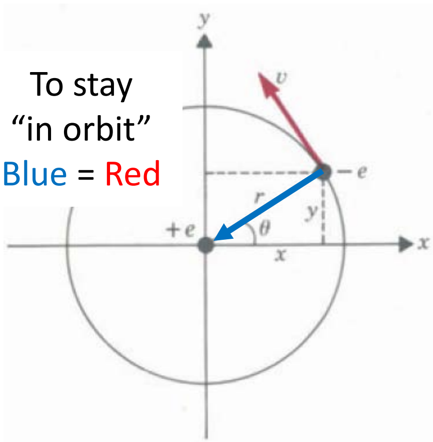
$$\int \frac{1}{r^2} = -\frac{1}{r}$$

$$E = \frac{q_1 q_2}{4\pi\varepsilon_0}\left[\frac{1}{r_A} - \frac{1}{r_B}\right]$$

A as reference point $\therefore r_B = \infty$

Eq 2 $\boxed{E_A = \frac{q_1 q_2}{4\pi\varepsilon_0 r_A}}$

Atomic Model – N. Bohr - 1913



$$F = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$$ Eq 1

$$q_{electron} = -e$$
$$q_{proton} = +e$$

$$F_{radial} = m * a_{radial}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\frac{v^2}{r}$$

Eq 3

$$L = mvr = n\hbar \qquad v = n\frac{\hbar}{mr}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{m}{r}n^2\frac{\hbar^2}{m^2r^2}$$

$$r = n^2\frac{4\pi\varepsilon_0\hbar^2}{e^2m}$$ Eq 4

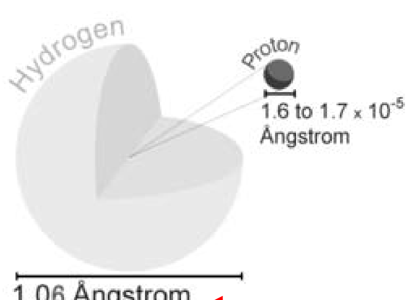
Bohr: Angular momentum L is **quantized** and a multiple n of Plank's constant $\hbar$

$$\hbar = \frac{h}{2\pi}$$

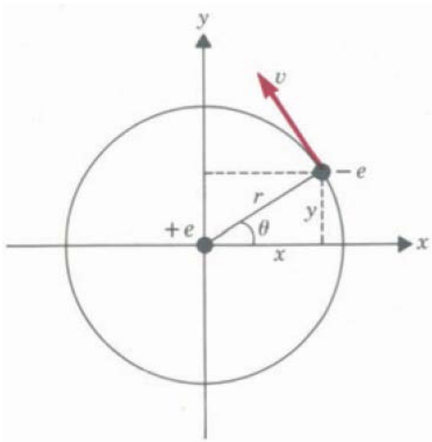
$$r = \frac{(1.11 \times \frac{10^{-10}C^2}{Nm^2})(1.05 \times 10^{-34}Jsec)^2}{(1.6 \times 10^{-19}C)^2(9.1 \times 10^{-31}kg)}$$

$$n = 1$$

$$r = 0.53 \times 10^{-10} = 0.53\ \text{Å}$$



Atomic Model – N. Bohr - 1913



Eq 2 $$E = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

$$E_{TOTAL} = kinetic + potential$$

$$E_{TOTAL} = \frac{1}{2}mv^2 \boxed{-} \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

Potential is negative because $q_1 = -e$ & $q_2 = e$

$$E_{TOTAL} = \frac{1}{2}\left[\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right] - \left[\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right]$$

$$E_{TOTAL} = -\frac{1}{2}\left[\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right]$$

Eq 3 $$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\frac{v^2}{r}$$

$$\frac{r}{2}\left[\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2}\right] = \frac{r}{2}\left[m\frac{v^2}{r}\right]$$

$$\frac{1}{2}mv^2 = \frac{1}{2}\left[\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right]$$

Eq 4 $$r = n^2\frac{4\pi\varepsilon_0\hbar^2}{e^2 m}$$

$$h = 2\pi\hbar$$

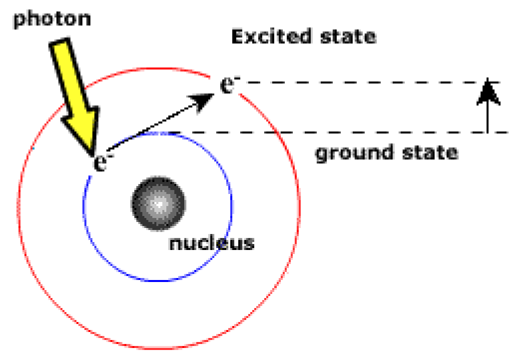
Eq 5 $$E_n = -\frac{e^4 m}{8\varepsilon_0^2 h^2}\frac{1}{n^2}$$

Atomic Model – N. Bohr - 1913

Eq 5 $$\boxed{E_n = -\frac{e^4 m}{8\varepsilon_0^2 h^2}\frac{1}{n^2}}$$

$$E_0 = \frac{e^4 m}{8\varepsilon_0^2 h^2}$$

E_0 = The constants



$$E_n = -\frac{E_0}{n^2}, n = 1,2,3,\ldots$$

$$E_{final} - E_{initial} = \frac{hc}{\lambda}$$

Einstein's Photon Energy Quantum

$$\lambda = \frac{hc}{E_{final} - E_{initial}}$$

When an electron falls back to its ground state, it will emit a photon at the wavelength associated with the corresponding energy delta

Open Lab 2 – Bohr Spectra for Hydrogen

- Update a C++ console application to generate the anticipated wavelengths of the spectral emission of Hydrogen (for the same series as Lab 1) using Bohr's Atomic model

$$E_0 = \frac{e^4 m}{8\varepsilon_0^2 h^2}$$

$$E_n = -\frac{E_0}{n^2}, n = 1,2,3, \ldots$$

$$\lambda = \frac{hc}{E_{final} - E_{initial}}$$

$$e = 1.6 \times 10^{-19} C$$
$$m = 9.1 \times 10^{-31} kg$$
$$\varepsilon_0 = 8.84 \times 10^{-12} C^2/Nm^2$$
$$h = 6.63 \times 10^{-34} Jsec$$
$$c = 3 \times 10^8 m/sec$$

Note: The SI unit for distance is meters (m) but we want the results shown in nanometers (nm)

Edit Lab 2 – Bohr Spectra for Hydrogen

spectrum-bohr.cpp

```cpp
// spectrum-bohr.cpp

#include "stdafx.h"

using namespace std;

int main()
{
    const double eCharge = 1.6e-19;
    const double eMass = 9.1e-31;
    const double permittivity = 8.84e-12;
    const double hPlank = 6.63e-34;
    const double speedLight = 3e8;

    const double E0 = (pow(eCharge, 4)*eMass) /
        (8 * pow(permittivity, 2) * pow(hPlank, 2));

    cout << "Bohr Model Hydrogen Spectral Lines" << endl;

    for (int i{ 1 }; i < 5; ++i) {
        for (int f{ i + 1 }; f < i + 6; ++f) {
            double Ei = 0;
            double Ef = 0;
            double lambda = 0;
            cout << setw(3) << f;
            cout << setw(10) << setprecision(0) << fixed;
            cout << lambda << "nm" << endl;
        }
        // Skip a line between families
        cout << endl;
    }

    return 0;
}
```

Enter the correct formulas

Run Lab 2 – Bohr Spectra for Hydrogen

spectrum-bohr.cpp

```
// spectrum-bohr.cpp

#include "stdafx.h"

using namespace std;

int main()
{
    const double eCharge = 1.6e-19;
    const double eMass = 9.1e-31;
    const double permittivity = 8.84e-12;
    const double hPlank = 6.63e-34;
    const double speedLight = 3e8;

    const double E0 = (pow(eCharge, 4)*eMass) /
                      (8 * pow(permittivity, 2) * pow(hPlank, 2));

    cout << "Bohr Model Hydrogen Spectral Lines" << endl;

    for (int i{ 1 }; i < 5; ++i)
    {
        for (int f{ i + 1 }; f < i + 6; ++f)
        {
            double Ei = -E0 / pow(i, 2);
            double Ef = -E0 / pow(f, 2);
            double lambda = hPlank * speedLight / (Ef - Ei) * 1e9;
            cout << setw(3) << f;
            cout << setw(10) << setprecision(0) << fixed;
            cout << lambda << "nm" << endl;
        }
        // Skip a line between families
        cout << endl;
    }

    return 0;
}
```

Check Lab 2 – Bohr Spectra for Hydrogen

spectrum-bohr

File Edit View Terminal Tabs Help

```
Bohr Model Hydrogen Spectral Lines
  2       122nm
  3       103nm
  4        98nm
  5        95nm
  6        94nm

  3       660nm
  4       489nm
  5       436nm
  6       412nm
  7       399nm

  4      1885nm
  5      1289nm
  6      1100nm
  7      1010nm
  8       960nm

  5      4073nm
  6      2640nm
  7      2177nm
  8      1955nm
  9      1827nm


Process returned 0 (0x0)   execution time : 0.015 s
Press ENTER to continue.
```

Atomic Model – N. Bohr - 1913

Eq 5 $$\boxed{E_n = -\frac{e^4 m}{8\varepsilon_0^2 h^2}\frac{1}{n^2}}$$

$$E_{initial} - E_{final} = \frac{hc}{\lambda}$$

$$E_n = -\frac{E_0}{n^2}, n = 1,2,3, \dots$$

$$\left(-\frac{E_0}{n_i^2}\right) - \left(-\frac{E_0}{n_f^2}\right) = \frac{hc}{\lambda}$$

$$E_0 = \frac{e^4 m}{8\varepsilon_0^2 h^2}$$

$$i, f \in \mathbb{Z}^+ \ and\ f > i$$

$$\frac{1}{\lambda} = \frac{E_0}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Rydberg Formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_k^2} - \frac{1}{n_j^2}\right)$$

$$R_{Bohr} = \frac{E_0}{hc} = \frac{e^4 m}{8\varepsilon_0^2 h^3 c}$$

$$Rydberg\ Constant$$
$$R = 1.0967757 \times 10^7 m^{-1}$$

$$R_{Bohr} = 1.09740 \times 10^7 m^{-1}$$

Atomic Model – N. Bohr - 1913

Rydberg Formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_k^2} - \frac{1}{n_j^2}\right)$$

$$where\ k, j \in \mathbb{Z}^+\ and\ j > k$$

$$Rydberg\ Constant$$
$$R = 1.0967757 \times 10^7 m^{-1}$$

Bohr Formula

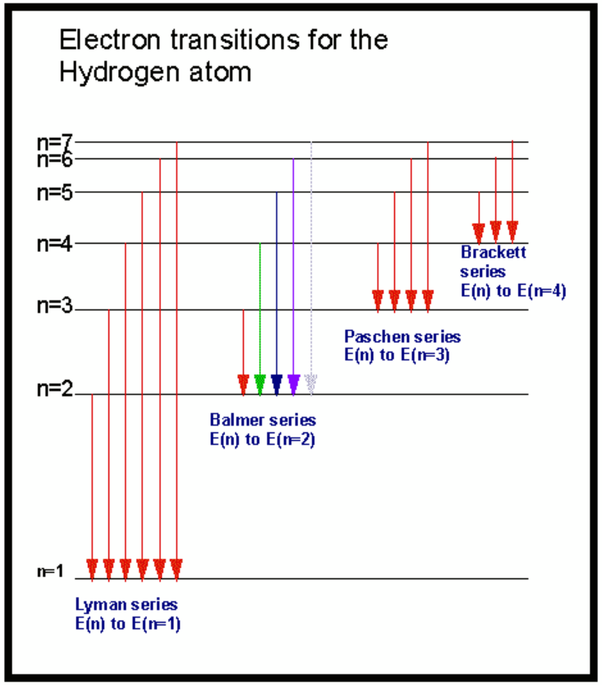
$$\frac{1}{\lambda} = R_{Bohr}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

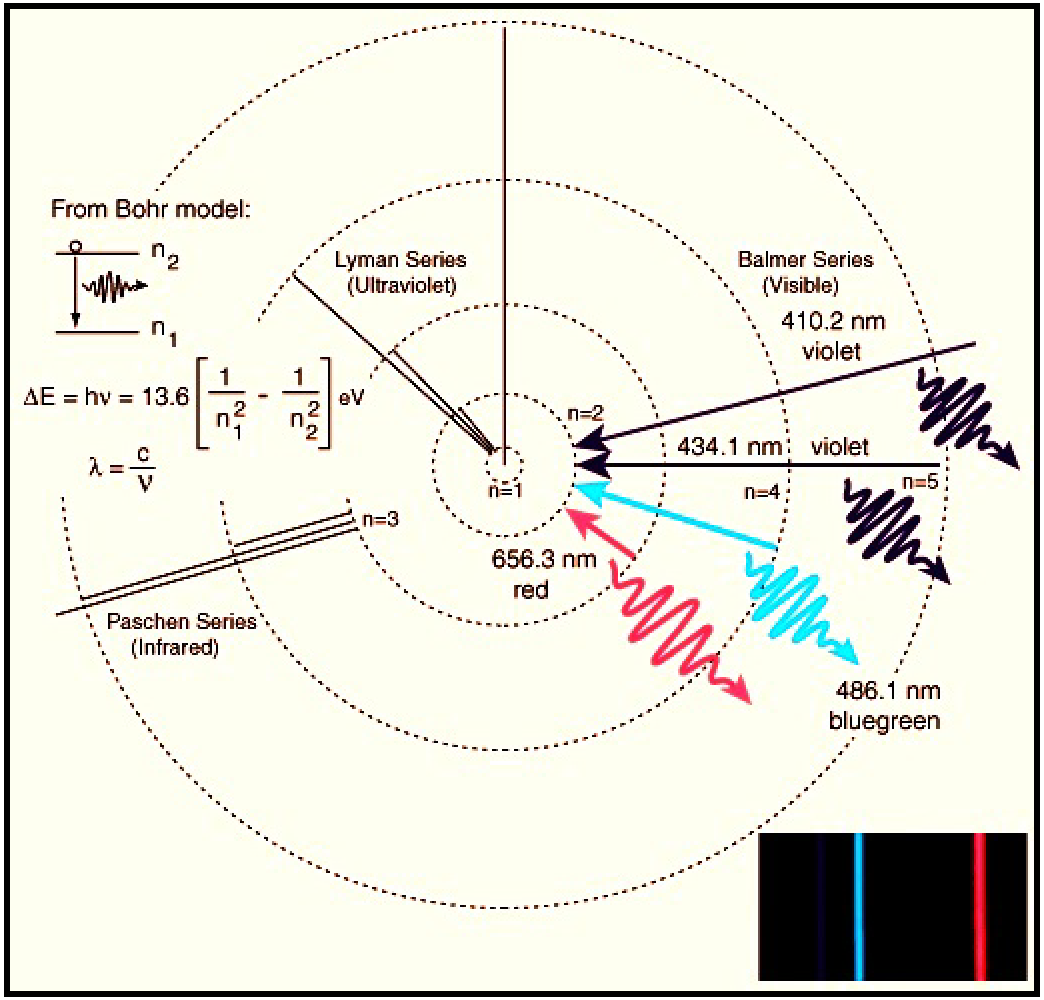
$$where\ f, i \in \mathbb{Z}^+\ and\ f > i$$

$$Bohr\ Constant$$
$$R_{Bohr} = 1.09740 \times 10^7 m^{-1}$$

Now we are doing physics! With Bohr's model we can assemble a logical sequence of physical laws to derive an empirical rule!

Atomic Model – N. Bohr - 1913





Atomic Model – N. Bohr - 1913

Rydberg Formula

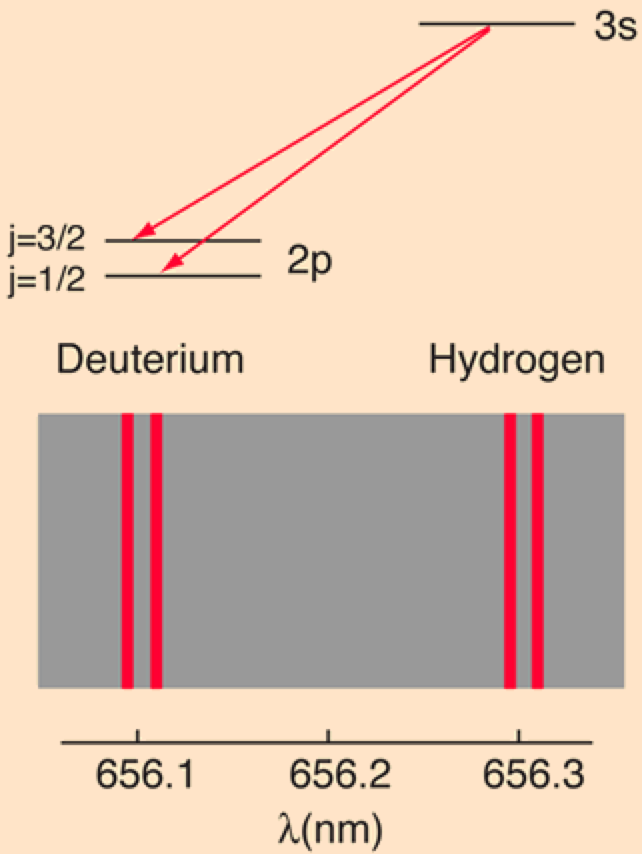
```
spectrum-ryd
File  Edit  View  Terminal  Tabs  Help
Rydberg Formula Hydrogen Spectral Lines
  2       122nm
  3       103nm
  4        97nm
  5        95nm
  6        94nm

  3       656nm
  4       486nm
  5       434nm
  6       410nm
  7       397nm

  4      1876nm
  5      1282nm
  6      1094nm
  7      1005nm
  8       955nm

  5      4052nm
  6      2626nm
  7      2166nm
  8      1945nm
  9      1818nm
```

Bohr Formula

```
spectru
File  Edit  View  Terminal  Tabs  Help
Bohr Model Hydrogen Spectral Lines
  2       122nm
  3       103nm
  4        98nm
  5        95nm
  6        94nm

  3       660nm
  4       489nm
  5       436nm
  6       412nm
  7       399nm

  4      1885nm
  5      1289nm
  6      1100nm
  7      1010nm
  8       960nm

  5      4073nm
  6      2640nm
  7      2177nm
  8      1955nm
  9      1827nm
```

The Bohr Model still had problems!

Bohr Didn’t Include Electron “Spin”



The familiar red H-alpha line of hydrogen is a single line according to the Bohr theory. The straight application of the Schrodinger equation to the hydrogen atom gives the same result. If you calculate the wavelength of this line using the energy expression from the Bohr theory, you get 656.11 nm for hydrogen, treating the nucleus as a fixed center. If you use the reduced mass, you get 656.47 nm for hydrogen and 656.29 nm for deuterium. The difference between the hydrogen and deuterium lines is about 0.2 nm and the splitting of each of them is about 0.016 nm, corresponding to an energy difference of about 0.000045 eV. This corresponds to an internal magnetic field on the electron of about 0.4 Tesla.

Now you know…

- Double-slit diffraction enables measurement of **wavelengths**
- The **Rydberg Formula** indicated an underlying model existed, but an equation without an explanation is just **a nifty observation**
- Consider the plight of early atomic models – how do you measure something you cannot possibly see?
- At the atomic level, Mother Nature is **quantized** – this violates common experience with *continuous* spectrums
- Don't be scared off by a soup of complex looking symbols and a long series of equations – learn to **glide with them**!