Dawn of Quantum Theory
Mid 19th century, scientists began playing with gas discharge tubes
Thermal radiation problem

Heated object

Record intensity of radiation as function of $\lambda$. 

detector
Results of experiments

1. $R(\lambda)$

- 1250 K
- 1000 K
2. Total intensity radiated by object over all wavelengths increases as temperature increases

\[ I = \int R(\lambda) d\lambda \propto T^4 \]

\[ I = \sigma T^4 \]

Known as Stefan’s Law

\[ \sigma = 5.670399 \times 10^{-8} \text{ W/m}^2 \text{ K}^4 \]
3. Maximum wavelength is proportional to $1/T$

$$\lambda_{\text{max}} T = 2.898 \times 10^{-3} \text{ mK}$$

Known as Wein’s Displacement Law
Question is: can results be explained by theory

Electromagnetic radiation is a wave

Model for thermal radiation – blackbody

amount of radiation emitted by solid object
  - temperature
  - surface properties

Consider a blackbody
  reflects zero radiation (eliminates surface effects)
Must also consider what the blackbody cavity really is

- Radiation enters and cannot escape except after many reflections
- Any radiation escaping is in thermal equilibrium with the inside of the box
Classical wave analysis leads to

\[ R(\lambda) = \frac{c}{4} U(\lambda) \]

\( U(\lambda) \) is energy density as a function of wavelength

\[ U(\lambda) = \# \text{ waves per unit volume} \times \text{energy/standing wave} \]
Classical wave theory

\[ \nabla^2 f(x, y, z, t) = \frac{1}{v^2} \frac{\partial^2 f(x, y, z, t)}{\partial t^2} \]

Where \( f(x, y, z, t) \) represents components of the oscillating E and B fields

Okay, how do we solve this guy?

First assume that we can write \( f(x, y, z, t) = X(x)Y(y)Z(z)T(t) \)

or simply as \( XYZT \)
Then

\[
\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)_{XYZT} = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \cdot_{XYZT}
\]

\[
\left( YZT \frac{\partial^2 X}{\partial x^2} + XZT \frac{\partial^2 Y}{\partial y^2} + XYT \frac{\partial^2 Z}{\partial z^2} \right) = \frac{1}{v^2} \cdot_{XYZ} \frac{\partial^2 T}{\partial t^2}
\]

To proceed, we apply separation of variables.

divide through by \(XYZT\)
\[ \frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = \frac{1}{v^2 T} \frac{\partial^2 T}{\partial t^2} \]

At this point, we can separate variables to solve the differential equation for each degree of freedom

\[ \frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -\frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} + \frac{1}{v^2 T} \frac{\partial^2 T}{\partial t^2} \]

\[ \Rightarrow \frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -\text{cons tan } t = -k_x^2 \]
\[ \Rightarrow \frac{1}{X} \frac{d^2X}{dx^2} = -\text{const} \tan t = -k_x^2 \]

\[ \Rightarrow \frac{1}{X} \frac{d^2X}{dx^2} + k_x^2 = 0 \]

\[ \Rightarrow \frac{d^2X}{dx^2} + k_x^2 X = 0 \]

At this point, you probably recognize this differential equation and can guess what the solution will be. No? Look back at our math review slides. Remember

\[ \frac{d^2y}{dx^2} + k^2 y = 0 \]
Several solutions to this differential equation. We have already seen the series solution. Lets try a different approach here. Start by rewriting expression as

\[(D^2 + k^2)X(x) = 0\]

where \(D = d/dx\)

1. Trivial solution is \(X(x) = 0\).
2. Non-trivial solution is \(D^2 + k^2 = 0\).

How do you solve?

Must find roots for \(D^2 + k^2 = 0\).

\[D^2 + k^2 = 0\]

\[\Rightarrow D^2 = -k^2\]

\[\Rightarrow D = \sqrt{-1}\sqrt{k^2} = \pm ik\]
In other words, \( DX(x) = \pm ikX(x) \) or \( \frac{d}{dx}X(x) = \pm ikX(x) \)

Now, lets evaluate one root at a time. Does not matter which one we start with, so …

\[
\frac{dX(x)}{dx} = -ikX(x)
\]

Rearranging …

\[
\frac{dX(x)}{X(x)} = -ikdx
\]

Then integrate

\[
\int \frac{dX(x)}{X(x)} = \int -ikdx
\]
These are actually very easy integrals to evaluate.

\[ \int \frac{dX(x)}{X(x)} = \int -i k dx \]

\[ \ln(X(x)) = -i k x + C \]

\[ e^{\ln X(x)} = e^{-i k x + c} = e^c e^{-i k x} = Ce^{-i k x} \]

\[ X(x) = Ce^{-i k x} \]

Other root will give \[ X(x) = C'e^{i k x} \]
Thus the general solution for this particular problem is

\[ X(x) = Ce^{-ikx} + C'e^{ikx} \]

We can put this into a more familiar form using Euler’s relations, i.e.,
\[ e^{ix} = \cos x + i \sin x \text{ and } e^{-ix} = \cos x - i \sin x \]

\[ X(x) = C (\cos kx + i \sin kx) + C'(\cos kx - i \sin kx) \]

\[ X(x) = (C+C') \cos kx + (C-iC') \sin kx \]

\[ X(x) = A \cos kx + B \sin kx \]

This solution represents what is known as the general solution. To obtain the specific solution to this problem, we need to apply the boundary conditions that the solution only exits inside the cavity.
What these boundary conditions imply is that the E&M standing waves are localized in the cavity or mathematically we would say

\[ X(0) = X(L) = 0 \]

At \( X(0) \)

\[ X(0) = 0 = A \cos k_x 0 + B \sin k_x 0 \]

\[ = A(1) + B(0) \]

\[ \Rightarrow A = 0 \]
\[\begin{align*}
\text{at } X(L) & \quad X(L) = 0 = B \sin k_x L \\
\Rightarrow \sin k_x L &= 0 \\
\Rightarrow k_x L &= n\pi \\
\Rightarrow k_x &= \frac{n\pi}{L} \\
X(x) &= B \sin \left( \frac{n_x \pi}{L} x \right)
\end{align*}\]
If we examine YZT in the same way, we will get

\[ Y(y) = D \sin\left(\frac{n_y \pi}{L} y\right) \]

\[ Z(z) = F \sin\left(\frac{n_z \pi}{L} z\right) \]

\[ T(t) = H \sin(2\pi \omega t) = H \sin\left(\frac{2\pi c}{\lambda} t\right) \]
The overall solution will be of the form

\[
f(x, y, z, t) = C \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \\
\times \sin\left(\frac{n_z \pi}{L} z\right) \sin\left(\frac{2\pi c}{\lambda} t\right)
\]
The relationship between \( \lambda \) and size of the cavity can be determined by putting this function back into the original differential equation.

\[
\nabla^2 f(x, y, z, t) = \frac{1}{c^2} \frac{\partial^2 f(x, y, z, t)}{\partial t^2}
\]

\[
\Rightarrow \left( \frac{n_x \pi}{L} \right)^2 + \left( \frac{n_y \pi}{L} \right)^2 + \left( \frac{n_z \pi}{L} \right)^2 = \left( \frac{2\pi}{\lambda} \right)^2
\]

\[
\Rightarrow n_x^2 + n_y^2 + n_z^2 = \frac{4L^2}{\lambda^2}
\]
Now, how many standing waves are in the cavity?

Question really is, what is total # of modes contained in volume of sphere with radius $r$?

$$\# \text{ waves} = \frac{1}{8} \frac{4}{3} \pi (n_x^2 + n_y^2 + n_z^2)^{\frac{3}{2}}$$

$$\Rightarrow \# \text{ waves} = \frac{\pi}{3} (n_x^2 + n_y^2 + n_z^2)^{\frac{3}{2}} = \frac{\pi}{3} \left( \frac{4L^2}{\lambda^2} \right)^{\frac{3}{2}} = \frac{8\pi L^3}{3\lambda^3}$$
Okay, so we have an expression for the total # of waves. How many modes are there as a function of wavelength?

$$\frac{d(#\text{waves})}{d\lambda} = -\frac{8\pi L^3}{\lambda^4}$$

Interesting. The # of normal modes or standing waves decreases with increasing values of $\lambda$. Now, how many modes/wavelength/unit volume?

$$\frac{\#\text{modes}}{\text{wavelength}} = -\frac{1}{L^3} \frac{d(#\text{modes})}{d\lambda} = \frac{8\pi}{\lambda^4}$$
So, in terms of energy density as function of wavelength …

\[ U(\lambda) = \text{# waves per unit volume x energy/standing wave} \]

we still need to get average energy per standing wave. From classical statistical mechanics (pchem II) we will show that

\[ \langle E \rangle = \int_{0}^{\infty} EP(E)dE = kT \]

And so …

\[ \Rightarrow U(\lambda) = \frac{8\pi}{\lambda^4} kT \]
And, with the definition of Radiance

\[ R(\lambda) = \frac{c}{4} U(\lambda) \]

We can write

\[ R(\lambda) = \frac{c \cdot 8\pi}{4 \cdot \lambda^4} kT \]

This expression is known as the Rayleigh-Jeans Law. How does it compare with experiment?
$$R(\lambda) = \frac{c \, 8\pi}{4 \lambda^4} kT$$
Solution Proposed by Max Planck

- Walls of cavity do not simply reflect radiation
- Atoms, at the interior surface, actually absorb and then reemit the radiation
- Atoms are essentially oscillating at the frequency corresponding to the absorbed radiation
Solution Proposed by Max Planck

- Each oscillator (atom) can only absorb radiation if $E=n\epsilon$ where $n$ is an integer and $\epsilon$ is directly proportional to the frequency of the radiation. The proportionality constant later became known as Planck’s constant.
How does this effect \( R(\lambda) \)?

Well, the average energy per standing wave will be different.

\[
E = \sum_{n=0}^{\infty} n\hbar \nu N
\]

Where \( N \) represents the \# oscillators with energy \( n\hbar \nu \)

\[
N = N_0 e^{-\frac{n\hbar \nu}{kT}}
\]

\[
E = \sum_{n=0}^{\infty} n\hbar \nu N_0 e^{-\frac{n\hbar \nu}{kT}}
\]
\[ E = \sum_{n=0}^{\infty} n\hbar v N_0 e^{-n\hbar v/kT} \]

\[ = N_0 \hbar v \left( e^{-\hbar v/kT} + 2e^{-2\hbar v/kT} + 3e^{-3\hbar v/kT} + \ldots \right) \]

\[ = N_0 \hbar v e^{-\hbar v/kT} \left( 1 + 2e^{-\hbar v/kT} + 3e^{-2\hbar v/kT} + \ldots \right) \]

You may well recognize this series from your calculus days as being similar to

\[ \left(1 + 2x + 3x^2 + \ldots \right) = (1 - x)^{-2} \]
Thus the energy can be written as

\[ E = N_0 h v e^{-\frac{h v}{k T}} \left( 1 - e^{-\frac{h v}{k T}} \right)^{-2} \]

And the average energy per oscillator then is

\[ \langle E \rangle = \frac{E}{N} = \frac{N_0 h v e^{-\frac{h v}{k T}} \left( 1 - e^{-\frac{h v}{k T}} \right)^{-2}}{N_0 \left( 1 - e^{-\frac{h v}{k T}} \right)^{-1}} \]

Where \( N \) is defined as

\[ N = \sum_{n=0}^{\infty} N_n = N_0 \left( 1 + e^{-\frac{h v}{k T}} + e^{-2 \frac{h v}{k T}} + \ldots \right) \]
Putting this together, Planck was able to derive the expression for average energy per normal mode

\[
\langle E \rangle = \frac{E}{N} = \frac{h\nu e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}}
\]

Which yields for the radiancy

\[
R(\lambda) = \frac{c}{4} \frac{8\pi}{\lambda^4} \left[ \frac{hc}{\lambda} \left( e^{\frac{hc}{\lambda kT}} - 1 \right) \right]
\]
\[ R(\lambda) = \frac{c}{4} \frac{8\pi}{\lambda^4} \left[ \frac{hc}{\lambda} \left( e^{\frac{hc}{\lambda kT}} - 1 \right) \right] \]

with Planck’s constant having a value of

\[ h = 6.626 \times 10^{-34} \text{ Js} \]
Interestingly, ... when \( \frac{h\nu}{kT} \ll 1 \)

\[
e^{\frac{h\nu}{kT}} = 1 + \frac{h\nu}{kT} + \left( \frac{h\nu}{kT} \right)^2 + \ldots
\]

\[
e^{\frac{h\nu}{kT}} - 1 = 1 + \frac{h\nu}{kT} + \left( \frac{h\nu}{kT} \right)^2 + \ldots - 1
\]

\[
\approx \frac{h\nu}{kT}
\]
Which implies that

\[
\frac{\frac{\hbar \nu}{ekT}}{e^{\frac{\hbar \nu}{kT}} - 1} \approx \frac{\hbar \nu}{kT} \approx kT
\]

for \( \hbar \nu \ll kT \). Again, \( kT \) represents the classical result. What is the major difference between Planck’s theory and Rayleigh-Jeans? It is simply the manner in which energy is partitioned!

Origin of Quantum Theory – in some cases, you cannot ignore the small (or very small) contributions to energy.
Extension of Planck’s Idea

Photoelectric effect

$hv$

e$^-$

$V$

$A$
Observations of Phillpe Leonard
(student of Heinrich Hertz)

1) Electrons are emitted from a surface that is illuminated.
2) Emission is instantaneous, even for low intensity light
3) There is a threshold frequency below which no emission is observed.
4) For $\nu > \nu_{\text{threshold}}$, the KE of emitted photoelectrons is a linear function of frequency.
5) For $\nu > \nu_{\text{threshold}}$, the number of $e^-$ emitted per unit time is directly proportional to the intensity of radiation.
Einstein’s Interpretation

See Ann. der Physik, 20, 199 (1905).

1) E&M radiation is also quantized,

quantum of light => photon

photons have energy and momentum

2) Matter absorbs photons of energy. Absorption causes oscillators/electrons in matter to change energy levels

\[ E_{\text{photon}} = E_{n+1} - E_n = (n+1)\nu - n\nu = \nu \]
Metals

Drude Model

Outer/conduction electrons free to move

“sea of electrons”

\[ + \quad + \quad + \quad + \quad + \quad + \quad + \quad + \]

- electron absorbs a photon if \( \varepsilon = h\nu \) is sufficient
- electron leaves metal

KE of electron given by

\[ KE = h\nu - \phi \]
Photoelectric Effect

E&M radiation is incident upon a sheet of lead. What is maximum \( \lambda \) of light that can cause an electron to be ejected from the metal?

In order to eject electron \( h\nu > \phi \)

\[
\frac{hc}{\lambda} > \phi \quad \Rightarrow \quad \lambda < \frac{hc}{\phi}
\]

For lead, \( \phi = 4.3 \text{ eV} \)

\[
\lambda_{\text{max}} = \frac{hc}{\phi} = \frac{1240 \text{ eV} \cdot \text{nm}}{4.3 \text{ eV}} = 288 \text{ nm}
\]
Photoelectric Effect

KE determined by applying voltage to stop the flow of electrons. If UV light at 200 nm is incident upon an aluminum cathode, how much voltage is needed to stop the flow of electrons?

For aluminum $\phi = 4.3$ eV

$$E = \frac{hc}{\lambda}; \quad KE_{\text{max}} = \frac{hc}{\lambda} - \phi$$

$$V_{\text{stopping}} = \frac{KE_{\text{max}}}{e} = \frac{1}{e} \left( \frac{hc}{\lambda} - \phi \right) = \frac{1}{e} \left( \frac{1240 \text{ eV} \cdot \text{nm}}{200 \text{ nm}} - 4.3 \text{ eV} \right)$$

$$= 1.9 \text{ V}$$
Reverse Photoelectric Effect

- High energy electrons are accelerated toward target
- Electrons pass through material and interact with nuclei
- Electrons lose energy via collisions

Bremsstrahlung ("braking") radiation
Rutherford Scattering Experiment

α source

Thin gold foil
Rutherford Scattering Experiment

Thin gold foil

α source

Observations of Geiger and Marsden
1) Most particles go straight through foil
2) Some particles experience a slight deflection (most probable angle of deflection is less than a degree)
3) A few actually bounce straight back (1 in 8000 will experience a deflection greater than 90 degrees)
Rutherford Scattering Experiment

Rutherford Hypothesis
1) Atoms consist of a small nucleus at center of atom. Most of the mass and all of the positive charge is contained in the nucleus.
2) Large angle scattering is result of an encounter with a single atomic nucleus.
3) Smaller angle deflections due to Coulomb’s Law repulsion between alpha particle and nucleus.
Spectroscopy of Gas Discharges
To understand line spectra in a quantitative sense
Look for regularities in the spectra
Balmer in 1885

Observations for hydrogen discharge

\[ \lambda = b \frac{n^2}{n^2 - 4} \]

With \( b = 346.56 \text{ nm} \)

\( n \) integer starting with 3

\( n = 3, 4, 5, 6 \text{ etc.} \)
Balmer predicted a series of 9 lines. The value of 346.56 nm represented an empirical limit for the series

\[ \lambda = b \frac{n^2}{n^2 - 4n} \rightarrow b \frac{n^2}{n^2} = b \]
Other series for hydrogen discharge tube

Lyman \((n_o = 1)\)

Paschen \((n_o = 3)\)

Brackett \((n_o = 4)\)

Pfund \((n_o = 5)\)

\[
\lambda = b \frac{n^2}{n^2 - n_o^2}
\]
General Expression for Line Spectra

\[
\frac{1}{\lambda} = R \left( \frac{1}{n_0^2} - \frac{1}{n_1^2} \right)
\]

\[R = 1.097 \times 10^{-7} \text{ m}^{-1}\]
Hydrogen Atom: A Quantum Theory

1913 – Neils Bohr

Treat electron-proton system as a miniature planetary system.

1) Dynamical equilibrium
2) Electrons can exist only in certain orbits
Minimum Allowed Orbit?

\[ KE = \frac{p^2}{2m} ; \quad PE = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} \]

\[ \Rightarrow E = \frac{p^2}{2m} - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} \]

Assuming the Heisenberg Uncertainty Relationship

\[ \Delta p \Delta r \propto \hbar \]
Minimum Allowed Orbit?

\[ \Delta p \Delta r \propto \frac{h}{r} \approx p \cdot r \]

\[ \Rightarrow E = \left( \frac{\hbar}{r} \right) + \frac{1}{2m} \frac{e^2}{4\pi \varepsilon_0 r} \]

To get the minimum orbit, we need to evaluate the max-min problem

\[ \frac{dE}{dr} = 0 \]
Minimum Allowed Orbit?

\[
\frac{dE}{dr} = 0 = -\frac{2\hbar^2}{2mr^3} + \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r^2}
\]

\[\Rightarrow \frac{\hbar^2}{mr^3} = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r^2}\]

Solving for \(r_{\text{min}}\) yields …

\[r_{\text{min}} = \frac{\hbar^2 4\pi\varepsilon_0}{me^2} = 0.0529 \text{ nm} = a_0\]
General Situation …

Classically, we know that $E = KE + PE$!

For a Coulomb Force …

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

This attractive force will in turn produce a centripetal acceleration of $a=v^2/r$. 
Given an acceleration, we know from freshman physics that we can immediately write a force associated with the acceleration. In this case, the force is a centripetal force.

\[ F_{\text{centripetal}} = m\ddot{a}_{\text{centripetal}} = \frac{mv^2}{r} \]

And since this system is in dynamical equilibrium, the two forces, Coulomb and Centripetal, must be equal to one another.

\[ F_{\text{centripetal}} = F_{\text{Coulombic}} \]

\[ \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r^2} = \frac{mv^2}{r} \]
If we rearrange the equality and solve for $mv^2$...

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

The reason for the rearrangement is obvious if we are trying to solve for total energy ($KE + PE$). Thus, we now have a way to express the kinetic energy for the electron in terms of fundamental constants viz

$$KE_{\text{electron}} = \frac{1}{2} mv^2 = \frac{1}{8\pi \varepsilon_0} \frac{e^2}{r}$$
The potential energy for a particle in a Coulomb potential is simply

$$PE = -\frac{1}{4\pi \varepsilon_0} \frac{e^2}{r}$$

Thus, the total energy for the electron-proton particle is given by

$$E = KE + PE$$

$$E = \frac{1}{8\pi \varepsilon_0} \frac{e^2}{r} - \frac{1}{4\pi \varepsilon_0} \frac{e^2}{r} = -\frac{1}{8\pi \varepsilon_0} \frac{e^2}{r}$$
Now, if we only knew what the acceptable values for \( r \) were, we could calculate what the total energy for the proton-electron system is in the hydrogen atom. Curiously, this is the point where Bohr made a rather startling assumption. To determine the angular momentum in the various orbits or stationary states, he assumed that the angular momentum was quantized such that

\[
L = \hbar, 2\hbar, 3\hbar, 4\hbar, \ldots n\hbar
\]

How does this assumption help us determine a value for \( r \)?

Well, classically angular momentum is defined as

\[
L = mvr = n\hbar \Rightarrow v = \left( \frac{n\hbar}{mr} \right)
\]
Given that kinetic energy is

\[ KE_{\text{electron}} = \frac{1}{2} mv^2 = \frac{1}{8\pi\varepsilon_0} \frac{e^2}{r} \]

Now, if we solve for \( r \)

\[
\frac{1}{2} m \left( \frac{n\hbar}{mr} \right)^2 = \frac{1}{8\pi\varepsilon_0} \frac{e^2}{r}
\]

\[
r = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} n^2
\]
Again, the minimum orbit corresponds to the case with \( n=1 \).

\[
r = \frac{4\pi\varepsilon_o \hbar^2}{me^2} n^2 = 0.0529 \text{ nm}
\]

This value of \( r \) is known as the Bohr radius and is given the symbol \( a_o \). Now with an expression for \( r \) in hand, we can simply plug into the corresponding expression for the energy

\[
E = -\frac{\frac{1}{8\pi\varepsilon_o} \frac{e^2}{r}}{\frac{1}{8\pi\varepsilon_o} \frac{4\pi\varepsilon_o \hbar^2 n^2}{me^2}} = -\frac{\frac{me^4}{32\pi^2\varepsilon_o^2 \hbar^2 n^2}}{\frac{1}{n^2}} = -\frac{13.6 \text{ eV}}{n^2}
\]
For the ground state of hydrogen, \( n=1 \), thus

\[ E_{\text{ground state}} = -13.6 \text{ eV} \]

For the first excited state, \( n=2 \)

\[ E_{n=2} = -3.4 \text{ eV} \]

And so on. In case you are interested, this work was published as two separate articles in Phil. Mag., 26, 476 and 857 (1913).
While Bohr’s model is compelling, is there an experimental test of the model? Well, the answer is, yes. Consider the line spectra problem. What is the physical interpretation of the quantum number \(n\)? In the Bohr model, the \(n\) values represent the orbits of the electron. A spectroscopic transition within the Bohr model corresponds to an electron “hopping” from one allowed orbit to another. In order that energy be conserved, the electron must give off or emit a photon when hopping to an orbit of lower energy and absorb a photon when hopping to an orbit representing higher energy.

\[
E_{\text{photon}} = E_{n_{\text{final}}} - E_{n_{\text{initial}}} = h\nu
\]

\[
= \frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2} \left( \frac{1}{n_o^2} - \frac{1}{n_1^2} \right)
\]
In terms of wavelength

\[ h\nu = h\frac{c}{\lambda} = \frac{me^4}{32\pi^2 \varepsilon_o^2 \hbar^2} \left( \frac{1}{n_o^2} - \frac{1}{n_1^2} \right) \]

\[ \frac{1}{\lambda} = \frac{1}{hc} \frac{me^4}{32\pi^2 \varepsilon_o^2 \hbar^2} \left( \frac{1}{n_o^2} - \frac{1}{n_1^2} \right) \]

Note the collection of constants on the right have a value of

\[ \frac{me^4}{32\pi^2 \varepsilon_o^2 \hbar^2} = 1.09730 \times 10^{-7} \text{ m}^{-1} \]

This value is within 0.05% of the experimental Rydberg constant, \( R \)
In other words, Bohr’s model is able to reproduce all of the line spectra for the hydrogen atom and give a physical interpretation for the phenomena. For other atomic species, the Bohr model can be generalized viz

\[ r_n = \frac{a_0 n^2}{Z}; \quad E_n = -13.6 \text{ eV} \frac{Z^2}{n^2} \]
One of Rutherford’s students, Harry Moseley, observed regularity in x-ray spectra for different atomic species

\[ \sqrt{\nu} = b(Z - a) \]

Where \( b \) and \( a \) are determined from slope and intercept.

Harry Moseley fought in WWI as an infantryman and was KIA at Gallipolli. In any event, beyond the broad generalizations shown here, Bohr’s model proved difficult to extend to atomic systems with more complexity than hydrogen.
Problem with Bohr Model

1. Model useful for 1 electron systems only!

2. More serious problem concerns the prediction of angular momentum of the hydrogen atom

   Bohr ⇒ L = h/2π

   Experiment ⇒ L = 0

3. Model also violates Heisenberg Uncertainty Principle.
Development of Quantum Mechanics

1924 – Louis DeBroglie

1. Nature loves symmetry

2. Suggests that two great physical entities, matter and energy, should be mutually symmetrical.

3. If radiant energy exhibits both wave and particle behavior

    $\Rightarrow$ matter should also exhibit a similar dual nature behavior
Development of Quantum Mechanics

Starting with the Einstein concept for a photon, light will obey the relationships, \( E = pc \) and \( E = hv = \frac{hc}{\lambda} \).

Now, if we simply set these two equal to one another …

\[
p c = \frac{hc}{\lambda}
\]

And solve for \( \lambda \)

\[
\lambda = \frac{h}{p}
\]

Planck’s constant fixes the scale in quantum domain!!!
Development of Quantum Mechanics

Seems almost too simple, right? $\lambda$ here represents the wavelength for the object under consideration.

But, matter waves????

Seem far-fetched?

Consider an electron in a hydrogen atom (Bohr model).

DeBroglie reasoned

1. \( \lambda \) in classical mechanics was related to spatial dimensions of the vibrating system. 
   e.g., Standing waves on strings

2. Electron in orbit about proton should have similar resonance condition!
In order to maintain standing wave over the circumference of the orbit

\[ n\lambda_n = 2\pi r_n \]

Now, by inserting the DeBroglie relationship

\[ n\lambda_n = n\frac{h}{p_n} = n\frac{h}{mv_n} = 2\pi r_n \]

Simple rearrangement of this expression yields

\[ \frac{n}{2\pi} \frac{h}{\hbar} = n\hbar = mv_n r_n \]
Remembering that $mvr$ is a classical expression for angular momentum leads to …

$$n\hbar = mv_r r_n = L$$

In other words,

DeBroglie hypothesis able to link quantization of $L$ in Bohr model to classical ideas.

Significance of quantum # $n$ also includes the number of DeBroglie wavelengths needed to fit into the circumference of Bohr’s stationary orbits.
DeBroglie ideas are compelling, although experimental evidence did not exist at this time. However, the idea of matter waves does help us deal with one shortfall of the Bohr model.

Question about DeBroglie waves:

Do they have same characteristics as other waves, i.e., wavelength and amplitude? If so, what does it mean? How do we describe these waves?
DeBroglie Waves

For example, can we use cosine waves?

\[ Y = A \cos kx \]

Where is such a wave localized?
DeBroglie Waves

Where is such a wave localized?

Answer: not localized anywhere!!

Unfortunately, in order to represent the attributes of a particle, the matter wave must be localized (an electron cannot be simultaneously everywhere). Well then, what about a sum of cosine waves such as

\[ y = A \cos k_1x + B \cos k_2x \]

Where A and B are constants and the \( k_i \) differ by a small \%.
DeBroglie Waves

<table>
<thead>
<tr>
<th>X</th>
<th>k1</th>
<th>cos k1X</th>
<th>k2</th>
<th>cos k2X</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1.25869</td>
<td>0</td>
<td>0.30737</td>
<td>0.9625</td>
</tr>
<tr>
<td>2</td>
<td>-0.0807</td>
<td>-0.07533</td>
<td>1</td>
<td>0.41513</td>
<td>1.20522</td>
</tr>
<tr>
<td>3</td>
<td>-0.77364</td>
<td>-0.10004</td>
<td>1</td>
<td>0.77364</td>
<td>1.74768</td>
</tr>
<tr>
<td>4</td>
<td>0.60982</td>
<td>0.10004</td>
<td>1</td>
<td>0.77364</td>
<td>1.74768</td>
</tr>
<tr>
<td>5</td>
<td>0.90528</td>
<td>0.30737</td>
<td>1</td>
<td>0.90528</td>
<td>1.81265</td>
</tr>
<tr>
<td>6</td>
<td>-0.28366</td>
<td>-0.5403</td>
<td>-0.82396</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-0.83907</td>
<td>0.01427</td>
<td>-1.25522</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-0.75969</td>
<td>-0.98999</td>
<td>-1.74968</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.408082</td>
<td>-0.65364</td>
<td>-0.24556</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.991203</td>
<td>0.283662</td>
<td>1.274865</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.154251</td>
<td>0.96017</td>
<td>1.114422</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-0.90369</td>
<td>0.753902</td>
<td>-0.14979</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>-0.66694</td>
<td>-0.1455</td>
<td>-0.81244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.525322</td>
<td>-0.91113</td>
<td>-0.38581</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.964966</td>
<td>-0.83907</td>
<td>0.125894</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.022127</td>
<td>0.004426</td>
<td>0.026552</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>-0.95241</td>
<td>0.843854</td>
<td>-0.10856</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>-0.56245</td>
<td>0.907447</td>
<td>0.344993</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>0.633319</td>
<td>0.136737</td>
<td>0.770056</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.921751</td>
<td>-0.75969</td>
<td>0.162063</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>-0.11039</td>
<td>-0.95766</td>
<td>-1.06805</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>-0.98438</td>
<td>-0.27516</td>
<td>-1.25954</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>-0.44807</td>
<td>0.660317</td>
<td>0.212243</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.730174</td>
<td>0.988705</td>
<td>1.718878</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.862319</td>
<td>0.408082</td>
<td>1.270401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>-0.24096</td>
<td>-0.54773</td>
<td>-0.78869</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>-0.99902</td>
<td>-0.99996</td>
<td>-1.99898</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>-0.32581</td>
<td>-0.53283</td>
<td>-0.85864</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>0.814181</td>
<td>0.424179</td>
<td>1.23836</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.787715</td>
<td>0.991203</td>
<td>1.778917</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>0.367319</td>
<td>0.525322</td>
<td>0.892641</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>-0.975623</td>
<td>-0.266643</td>
<td>-1.242266</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>-0.487188</td>
<td>-0.66694</td>
<td>-0.17975</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>0.996085</td>
<td>0.300593</td>
<td>1.299615</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.240827</td>
<td>0.964966</td>
<td>1.205954</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>-0.8623</td>
<td>0.742154</td>
<td>-0.12015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>-0.73029</td>
<td>-0.16299</td>
<td>-0.89318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>0.448047</td>
<td>-0.91828</td>
<td>-0.47024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>0.984382</td>
<td>-0.82931</td>
<td>0.155072</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.11039</td>
<td>0.022127</td>
<td>0.132544</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>-0.92174</td>
<td>0.85322</td>
<td>-0.06852</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>-0.63334</td>
<td>0.999867</td>
<td>0.266524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>0.562429</td>
<td>0.11918</td>
<td>0.681609</td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>0.952422</td>
<td>-0.77108</td>
<td>0.181342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>-0.0221</td>
<td>-0.95241</td>
<td>-0.97451</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>0.937995</td>
<td>-0.84857</td>
<td>0.089424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>0.598484</td>
<td>-0.30737</td>
<td>-0.26532</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>-0.00003</td>
<td>-0.12596</td>
<td>-0.12596</td>
<td></td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>0.999022</td>
<td>0.300593</td>
<td>1.300593</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.93801</td>
<td>-0.765414</td>
<td>-0.17259</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>-0.598462</td>
<td>-0.90369</td>
<td>-0.30521</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>-0.12796</td>
<td>-0.72642</td>
<td>-0.852642</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>0.814181</td>
<td>0.424179</td>
<td>1.23836</td>
<td></td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>0.787715</td>
<td>0.991203</td>
<td>1.778917</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>0.367319</td>
<td>0.525322</td>
<td>0.892641</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>-0.996085</td>
<td>0.300593</td>
<td>-1.299615</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>-0.862319</td>
<td>0.742154</td>
<td>-0.12015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>-0.73029</td>
<td>-0.16299</td>
<td>-0.89318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>0.448047</td>
<td>-0.91828</td>
<td>-0.47024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.984382</td>
<td>-0.82931</td>
<td>0.155072</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
DeBroglie Waves

Two waves add together in such a way as to produce regions of constructive and destructive interference. For values of $k$ that are similar, we refer to this phenomena as “beats”. If two cosine terms with slightly different $k_i$ produces a more localized pattern, what will a large number of cosine terms do??

$$y = \sum_{k_i} A(k_i) \cos k_i x$$
**DeBroglie Waves**

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>-0.004170216</td>
</tr>
<tr>
<td>-49</td>
<td>0.024131141</td>
</tr>
<tr>
<td>-48</td>
<td>-0.030721028</td>
</tr>
<tr>
<td>-47</td>
<td>0.012945178</td>
</tr>
<tr>
<td>-46</td>
<td>0.011987257</td>
</tr>
<tr>
<td>-45</td>
<td>-0.017902844</td>
</tr>
<tr>
<td>-44</td>
<td>0.000401938</td>
</tr>
<tr>
<td>-43</td>
<td>0.016976397</td>
</tr>
<tr>
<td>-42</td>
<td>-0.009599988</td>
</tr>
<tr>
<td>-41</td>
<td>-0.018856885</td>
</tr>
<tr>
<td>-40</td>
<td>0.039362496</td>
</tr>
<tr>
<td>-39</td>
<td>-0.030863497</td>
</tr>
<tr>
<td>-38</td>
<td>0.005759809</td>
</tr>
<tr>
<td>-37</td>
<td>0.003259319</td>
</tr>
<tr>
<td>-36</td>
<td>0.01869431</td>
</tr>
<tr>
<td>-35</td>
<td>-0.049840742</td>
</tr>
<tr>
<td>-34</td>
<td>0.055669249</td>
</tr>
<tr>
<td>-33</td>
<td>-0.029474415</td>
</tr>
<tr>
<td>-32</td>
<td>0.001986303</td>
</tr>
<tr>
<td>-31</td>
<td>-0.006745208</td>
</tr>
<tr>
<td>-30</td>
<td>0.039960243</td>
</tr>
<tr>
<td>-29</td>
<td>-0.062575534</td>
</tr>
<tr>
<td>-28</td>
<td>0.04481219</td>
</tr>
<tr>
<td>-27</td>
<td>-0.002633294</td>
</tr>
<tr>
<td>-26</td>
<td>-0.018178813</td>
</tr>
<tr>
<td>-25</td>
<td>-0.005016271</td>
</tr>
<tr>
<td>-24</td>
<td>0.042586584</td>
</tr>
<tr>
<td>-23</td>
<td>-0.044198833</td>
</tr>
<tr>
<td>-22</td>
<td>-0.002011504</td>
</tr>
<tr>
<td>-21</td>
<td>0.051613202</td>
</tr>
<tr>
<td>-20</td>
<td>-0.052496189</td>
</tr>
<tr>
<td>-19</td>
<td>0.007357694</td>
</tr>
<tr>
<td>-18</td>
<td>0.024054989</td>
</tr>
<tr>
<td>-17</td>
<td>0.008302735</td>
</tr>
<tr>
<td>-16</td>
<td>-0.082480084</td>
</tr>
<tr>
<td>-15</td>
<td>0.122595677</td>
</tr>
<tr>
<td>-14</td>
<td>-0.084816238</td>
</tr>
<tr>
<td>-13</td>
<td>0.015479764</td>
</tr>
<tr>
<td>-12</td>
<td>-0.007183374</td>
</tr>
<tr>
<td>-11</td>
<td>0.091705743</td>
</tr>
<tr>
<td>-10</td>
<td>-0.190097687</td>
</tr>
<tr>
<td>-9</td>
<td>0.189707019</td>
</tr>
<tr>
<td>-8</td>
<td>-0.077209381</td>
</tr>
<tr>
<td>-7</td>
<td>-0.021993102</td>
</tr>
<tr>
<td>-6</td>
<td>-0.035735721</td>
</tr>
<tr>
<td>-5</td>
<td>0.238861789</td>
</tr>
<tr>
<td>-4</td>
<td>-0.381482791</td>
</tr>
<tr>
<td>-3</td>
<td>0.230511328</td>
</tr>
<tr>
<td>-2</td>
<td>0.238693499</td>
</tr>
<tr>
<td>-1</td>
<td>-0.768177419</td>
</tr>
<tr>
<td>0</td>
<td>0.238693499</td>
</tr>
<tr>
<td>1</td>
<td>0.230511328</td>
</tr>
<tr>
<td>2</td>
<td>0.238861789</td>
</tr>
<tr>
<td>3</td>
<td>-0.381482791</td>
</tr>
<tr>
<td>4</td>
<td>0.230511328</td>
</tr>
<tr>
<td>5</td>
<td>0.238861789</td>
</tr>
<tr>
<td>6</td>
<td>-0.035735721</td>
</tr>
<tr>
<td>7</td>
<td>-0.021993102</td>
</tr>
<tr>
<td>8</td>
<td>-0.077209381</td>
</tr>
<tr>
<td>9</td>
<td>0.189707019</td>
</tr>
</tbody>
</table>

8/13/2008 SWR 81
DeBroglie Waves

Note, as we increased the number of waves (essentially increasing $\Delta k$), the uncertainty in $x$ ($\Delta x$) decreased. In other words, there is an uncertainty relationship such that

$$\Delta k \Delta x \approx 1$$
DeBroglie Waves

What does this argument have to do with anything?

Remember from freshman physics ….

\[ k = \frac{2\pi}{\lambda} \]

Or the position of the wavepacket can only be determined at the expense of our knowledge of the wavelength!

\[ \Delta k \Delta x \approx 1 \]
DeBroglie Waves

If we now further make use of the DeBroglie relation …

\[ \lambda = \frac{h}{p} = \frac{2\pi}{k} \]

\[ p = \frac{hk}{2\pi} = \hbar k \]

Which implies that \( \Delta k \) can be expressed in terms of the momentum as

\[ \frac{\Delta p}{\hbar} \Delta x \approx 1 \]
DeBroglie Waves

Of course, this expression can be rearranged into the Heisenberg Uncertainty relationship as shown below.

\[ \Delta p \Delta x \approx \hbar \]

And, if we consider motion along the other axes, we can derive similar expressions for y and z.
DeBroglie Waves

However, there are still a couple of serious issues with the Bohr model (particularly the issues surrounding L). Nonetheless, DeBroglie was in the process of presenting his idea to the physics community and at one of these presentations in the fall of 1925, Erwin Schrodinger just happened to be in the audience.
Schroedinger Equation

Justification:

Consider again the classical wave equation

\[ \nabla^2 f(x, y, z, t) = \frac{1}{v^2} \frac{\partial^2 f(x, y, z, t)}{\partial t^2} \]

Let's assume that we can write \( f(x, y, z, t) \) as a product wavefunction of the form

\[ f(x, y, z, t) = \psi(x, y, z) \cos \omega t \]
Schroedinger Equation

Then ....

\[ \nabla^2 f(x, y, z, t) = \frac{1}{v^2} \frac{\partial^2 f(x, y, z, t)}{\partial t^2} \]

\[ \nabla^2 \psi(x, y, z) \cos \omega t = \frac{1}{v^2} \psi(x, y, z) \frac{\partial^2}{\partial t^2} \cos \omega t \]

\[ \nabla^2 \psi(x, y, z) \cos \omega t = -\frac{1}{v^2} \psi(x, y, z) \omega^2 \cos \omega t \]

\[ \nabla^2 \psi(x, y, z) = -\frac{1}{v^2} \omega^2 \psi(x, y, z) \]
Schroedinger Equation

As an aside, for a plane wave with

$$f(x, t) = Ae^{i(kx - \omega t)}$$

phase velocity is

$$v = \frac{\omega}{k} \Rightarrow \omega = vk$$

$$\Rightarrow \nabla^2 \psi = -\frac{1}{v^2} (vk)^2 \psi$$

$$\Rightarrow \nabla^2 \psi = -k^2 \psi$$
Schrodinger Equation

From classical physics, \( k = \frac{2\pi}{\lambda} \), thus the time dependent equation for a classical wave becomes

\[
\nabla^2 \psi = -\left( \frac{2\pi}{\lambda} \right)^2 \psi
\]

Now, in terms of the classical total energy, we can write

\[
E = KE + PE \text{ or } KE = E - PE = E - V
\]
Schroedinger Equation

And, in terms of momentum, we can write the KE as

\[ KE = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mKE} \]

\[ \Rightarrow p = \sqrt{2m(E - V)} \]

Finally, if we employ the DeBroglie relation

\[ \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mKE}} \]
Schroedinger Equation

Using this relationship

$$\nabla^2 \psi = -\left(\frac{2\pi}{\lambda}\right)^2 \psi$$

Becomes in 1D
Schrodinger Equation

\[ \frac{\partial^2}{\partial x^2} \psi(x) = -\left( \frac{2\pi}{\hbar} \right)^2 \psi(x) \]

\[ \frac{\partial^2}{\partial x^2} \psi(x) = -\frac{2m}{\hbar^2} (E - V)\psi(x) \]

\[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = (E - V)\psi(x) \]

\[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V\psi(x) = E\psi(x) \]
Schroedinger Equation

Thus the time independent SE for a particle of mass \( m \) moving under a potential energy \( V \) is

\[
\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V\psi(x) = E\psi(x)
\]

Schroedinger Equation

Procedure for solving any SE type problem:

1. Write equation using appropriate potential.
2. Find general solution for $\psi(x)$.
3. Apply boundary conditions to obtain particular solutions for $\psi(x)$.
4. Evaluate and determine constants.
Postulates of Quantum Mechanics

• Postulate 1:
The state of a quantum mechanical system is completely specified by a function $\Psi(r,t)$ that depends upon the coordinates of the particle and time. This function is called the wavefunction and has the property that $\Psi^*\Psi$ represents the probability the particle can be found in a volume element located at $r$ at a particular time $t$. 
Postulates of Quantum Mechanics

• Postulate 2:
For every observable in classical mechanics there corresponds an operator in quantum mechanics

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r, \theta, \phi) \]
Postulates of Quantum Mechanics

• Postulate 3:
In any measurement of an observable associated with an operator, the ONLY values that will ever be observed are the eigenvalues which satisfy, for the case of energy,

\[ \hat{H}\Psi = E\Psi \]
Postulates of Quantum Mechanics

• Postulate 4:

If a system is in a state described by a normalized wavefunction $\Psi$, then the average value of the observable $E$ say, is given by

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{H} \Psi \, d\tau = \langle \Psi | \hat{H} | \Psi \rangle$$
Postulates of Quantum Mechanics

• Postulate 5:

The wavefunction of a system evolves in time according to the time-dependent SE viz

\[ \hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \]
Postulates of Quantum Mechanics

How do we deal with this time-dependent part?

Assume that $\Psi$ can be written as

$$\Psi(r, t) = \psi(r)e^{-\frac{iEt}{\hbar}}$$

Time independent part

“stationary states”

Time dependent part

We will come back to this issue later when investigating selection rules associated with spectroscopy!
Postulates of Quantum Mechanics

Finally, there are some properties that all acceptable wavefunctions must possess including:

• Must be single valued everywhere.
• Must be finite: $\psi(x) \to 0$ as $x \to +/- \infty$
• Must be continuous.
• And, ideally first derivative must be continuous.