Quantum Mechanics in Three Dimensions

Let's first start of with Schrödinger Equation which describes the time evolution of a certain quantum state $|\psi\rangle$:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H}|\psi\rangle$$

Where $\hat{H}$ is the Hamiltonian operator. For a system constituted of one particle our Hamiltonian would look something like:

$$\hat{H} = \frac{\hat{P}^2}{2m} + \hat{V}(\hat{x})$$

In which $\hat{P}$ corresponds to momentum operator $\hat{P} = -i\hbar \frac{d}{dx}$ in $|x\rangle$ base. $\hat{V}(\hat{x})$ corresponds to the particles's potential energy.

Let's begin by projecting Schröedinger Equation into the configuration space (aka $|\hat{x}\rangle$ basis)

$$i\hbar \frac{\partial}{\partial t} \underbrace{\langle x'|\psi\rangle}_{\psi(x')} = \cancel{\hat{H}\langle x|\psi\rangle} \langle x'|\hat{H}|\psi\rangle$$

Wave Function on configuration space.

The right hand side of our equation will be:

$$\langle x'|\hat{H}|\psi\rangle = \langle x'|\frac{\hat{P}^2}{2m} + V(\hat{x})|\psi\rangle = \langle x'|\frac{\hat{P}^2}{2m}|\psi\rangle + \langle x'|\hat{V}(x)|\psi\rangle$$

We have the following now: $\langle x'|\hat{V}(x) = \langle x'|V(x')$

Operator

function; not an operator anymore.

For a 3D space we have the generalization of the operators:

$$\hat{X} = X \longrightarrow \hat{X} = \vec{X}$$

$$\hat{P} = -i\hbar \frac{d}{dx} \longrightarrow \hat{P} = -i\hbar \vec{\nabla}$$

$$1D \longrightarrow 3D$$

$|x\rangle \longrightarrow |\vec{x}\rangle$

Leading us to:

$$\langle \vec{x}'|\hat{H}|\psi\rangle = \frac{1}{2m}\langle \vec{x}'|\hat{\vec{p}}^2|\psi\rangle + \langle x'|\hat{V}(\vec{x})|\psi\rangle$$

$$= -\frac{\hbar^2}{2m}\langle \vec{x}'|\vec{\nabla}^2|\psi\rangle + \langle \vec{x}'|V(\vec{x})|\psi\rangle$$ with linearity:

$$= -\frac{\hbar^2}{2m}\vec{\nabla}^2\langle \vec{x}'|\psi\rangle + V(\vec{x})\langle \vec{x}'|\psi\rangle$$

$$= -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{x}') + V(\vec{x}')\psi(\vec{x}')$$; therefore:

$$\cancel{i\hbar\frac{\partial}{\partial t}|\psi\rangle}$$

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi(\vec{x},t) = -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)}$$

Schroëdinger Equation for Ondulatory Mechanics (Mecânica Ondulatória)

Schroëdinger Time Independent Equation

~~Le~~ Let's start to imagine now that we prepare our system in such way that we have some stationary state (We had done a measure of an a given operator A which comutes with the Hamiltonean i.e. $[A,H]=0$)

In a given stationary state we know we can describe our state in a given time t with:

$$\langle \vec{x}'|a'(t)\rangle = \langle \vec{x}'|a'\rangle e^{-\frac{iE_{a'}t}{\hbar}}$$

where $E_{a'}$ is eigen value of H and a' eigenvalue of A. If now we throw that state in Schröedinger Equation:

$$i\hbar\frac{\partial}{\partial t}\langle \vec{x}'|a'\rangle e^{-\frac{iE_at}{\hbar}} = -\frac{\hbar^2}{2m}\vec{\nabla}\left(\langle \vec{x}'|a'\rangle e^{-\frac{iE_at}{\hbar}}\right) + V(\vec{x}')\left(\langle \vec{x}'|a'\rangle e^{-\frac{iE_at}{\hbar}}\right)$$

$$\Downarrow$$

$$-i^2E_a\langle \vec{x}'|a'\rangle e^{-\frac{iE_at}{\hbar}} = -\frac{\hbar^2}{2m}\vec{\nabla}\left(\langle \vec{x}'|a'\rangle e^{-\frac{iE_at}{\hbar}}\right) + V(\vec{x}')\left(\langle \vec{x}'|a'\rangle e^{-\frac{iE_at}{\hbar}}\right)$$

Simplifying:

$$E_{a'} \langle \vec{x}' | a' \rangle = \underbrace{-\frac{\hbar^2}{2m} \vec{\nabla}^2 \langle x' | a' \rangle + V(\vec{x}') \langle x' | a' \rangle}_{\hat{H} \langle x' | a' \rangle}$$

Eigen value equation of H; projected into $|x\rangle$ basis

So we can rewrite as:

$$\boxed{-\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi_E(\vec{x}) + V(\vec{x}) \psi_E(\vec{x}) = E \psi_E(\vec{x})}$$

Time independent Schröedinger Equation.

$\boxed{\text{Important:}}$ On sch. Eq. we work with the projection of our state $|\psi\rangle$ into $|x\rangle$ basis. On Time independent; we are working now with the projection of the Hamiltonean eigen vectors (energy basis $|E\rangle$) into $|x\rangle$ basis. $\rightarrow \psi_E$

Given $\psi_E(\vec{x})$ solution; our wave function will be a superposition of our many solutions multiplayed by energy exponential:

$$\psi(\vec{x},t) = \underbrace{\sum c_n \psi_n(\vec{x})\, e^{-iE_n t/\hbar}}$$

determined by initial wave function.

Important: All of this is true when the potential V is time-independent. and the Hamiltonean operator is also time-independent.

One thing we can study now is the case when we use other system of coordinates other than the conventional one such as spherical coordinates (r, θ, φ)

The Time-independent Sch. Eq. is:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi + V\psi = E\psi$$

On spherical coordinates the Laplacian is:

$$\vec{\nabla}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)$$

thus:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\varphi^2}\right)\right] + V\psi = E\psi$$

Using the separation of variables technique we have.

$$\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi) \quad \text{and thus:}$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\dot{R}Y\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta R\frac{\partial Y}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(R\frac{\partial^2 Y}{\partial\varphi^2}\right)\right] + VRY = ERY$$

$$\frac{1}{r^2}Y\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} - \frac{2mV}{\hbar^2}RY = -\frac{2mE}{\hbar^2}RY\left(\times\frac{r^2}{RY}\right)$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right) + \frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} + \frac{2mE}{\hbar^2}r^2 - \frac{2mV}{\hbar^2}r^2 = 0$$

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right)-\frac{2m}{\hbar^2}\left(V(r)-E\right)r^2}_{l(l+1)} + \underbrace{\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right)}_{-l(l+1)}$$

Separation constant

Now we use again the method of separation of constants on $Y(\theta,\varphi)$ where: $Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$ then:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\dot{\Theta}\,\Phi\right)+\frac{1}{\sin^2\theta}\,\Theta\,\ddot{\Phi} = -l(l+1)\,\Theta\,\Phi \qquad \left(\times\frac{\sin^2\theta}{\Theta\,\Phi}\right)$$

$$\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\cdot\frac{d^2\Phi}{d\varphi^2} = -l(l+1)\sin^2\theta$$

$$\Rightarrow \underbrace{\frac{1}{\Phi}\cdot\frac{d^2\Phi}{d\varphi^2}}_{-m^2}+\underbrace{\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)\sin^2\theta}_{m^2} = 0$$

(Second constant separation; not to confund with mass)

Solving Now the first ODE we have:

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi \longrightarrow \lambda^2 = -m^2 \rightarrow \lambda = \pm im$$

$\longrightarrow$ $\Phi = e^{\pm im\varphi}$ if we let m run though negative number our solution simplify to: $\underline{\Phi(\varphi) = e^{im\varphi}}$

φ is a 'measure' of angulation in space which contain the property of returning to its own value over a 2π loop thus:

$$\Phi(\varphi+2\pi) = \Phi(\varphi) \rightarrow e^{im(\varphi+2\pi)} = e^{im(\varphi)} \Rightarrow \underline{e^{i2\pi m} = 1}$$

This is only true ~~when~~ when: $\underline{m = 0, \pm 1, \pm 2, \ldots}$

Looking at the Θ equation now:

$$\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[-m^2+\ell(\ell-1)\sin^2\theta\right]=0$$

Have the associated Legendre Function as solution:

$$\Theta(\theta)=A\,P_\ell^m(\cos\theta)$$

$$P_\ell^m(x)=(1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}P_\ell(x)$$

ℓth Legendre Polynomial

$$P_\ell(x)=\frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell \quad \text{(Rodrigues Formula)}$$

Note that due to the factor $\left(\frac{d}{dx}\right)^{|m|}P_\ell(x)$ in $P_\ell^m(x)$ we will have that if $\Rightarrow$ $|m|>\ell \Rightarrow P_\ell^m=0$

So for any given ℓ ; we have ; $-\ell\le m\le\ell$

$\ell=0,1,2\ldots$; $m=-\ell,-\ell+1,\ldots,-1,0,1,\ldots,\ell-1,\ell$

Important note: Θ equation is a second order diferential equation so it should be able to wild two (2) lineary independent ~~solutions~~ solutions, however the second solution is physically unacceptable due to the fact that the solution blow up at $\theta=0$ and $\theta=\pi$.

For ~~a~~ normalizing the wave function we have:

$$\int d^3x\,|\psi|^2=1$$

On spherical coordinates; $d^3x=r^2\sin\theta\,dr\,d\theta\,d\phi$; and $\psi(r,\theta,\phi)=RY$

So we have:

$$\int d^3x\, |\psi|^2 = \int |\psi|^2 r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

$$\Rightarrow \iiint |R|^2 |Y|^2 r^2 \sin\theta\, dr\, d\theta\, d\varphi = 1$$ we can write this as:

$$\int |R|^2 r^2 dr \iint |Y|^2 \sin\theta\, d\theta\, d\varphi = 1$$ and impose that

$$\int_0^\infty |R|^2 r^2\, dr = 1 \quad \text{and} \quad \int_0^{2\pi}\int_0^{\pi} |Y|^2 \sin\theta\, d\theta\, d\varphi = 1$$

The hole process of normalizing $Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$ will endup given us the so called Spherical Harmonics:

$$\boxed{Y_\ell^m(\theta,\varphi) = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; e^{im\varphi}\, P_\ell^m(\cos\theta)}$$

$$\epsilon = (-1)^m \,;\; m \geq 0 \quad / \quad \epsilon = 1 \,;\; m \leq 0$$

We also have that Spherical Harmonics are orthogonal to each other:

$$\int_0^{2\pi}\int_0^{\pi} [Y_\ell^m(\theta,\varphi)]^* [Y_{\ell'}^{m'}(\theta,\varphi)] \sin\theta\, d\theta\, d\varphi = \delta_{\ell\ell'}\,\delta_{mm'}$$

$\ell \rightarrow$ Azimuthal Quantum number

$m \rightarrow$ magnetic quantum number

Looking at the radial equation:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]R = l(l+1)R$$

Changing variables to $u(r) = rR(r)$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + u\left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] = Eu}$$

Radial Equation which basically takes the same form as 1D Schröedinger Equation changed by the fact our effective potential

$V_{eff} = V + \frac{\hbar^2}{2m} l(l+1)/r^2$ contains an centrifugal term responsible for an expeling force that pushes away the particle from the origin.

We also have normalization uppon u: $\int_0^\infty |u|^2 dr = 1$

Hydrogen Atom

From Coulom's law he have that the potential Energy in the hydrogen Atom is:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{r}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + u\left[-\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] = Eu$$

$$\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} = u\left[-1 - \frac{e^2}{4\pi\epsilon_0 E}\cdot\frac{1}{r} + \frac{\hbar^2}{2mE}\frac{l(l+1)}{r^2}\right]$$

introducing $k = \sqrt{\frac{-2mE}{\hbar^2}} \rightarrow k^2 = -\frac{2mE}{\hbar^2}$ lead us to:

$$\frac{1}{k^2}\frac{d^2u}{dr^2} = u\left[1 - \frac{\overset{\text{mass}}{m}e^2}{2\pi\epsilon_0\hbar^2 k}\cdot\frac{1}{(kr)} + \frac{l(l+1)}{(kr)^2}\right]$$

Also introducing $\rho = kr$; $\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2 k}$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

Analise the assymptotic form of the solutions

⋮

Principal Quantum Number : $\boxed{n = j_{max} + l + 1}$

at the end we have

$$2n = \rho_0 \quad \text{but } \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2 k} \quad \text{and } k = \sqrt{\frac{-2mE}{\hbar}}$$

We can then relate our principal quantum number n with the differents energy levels

Bohr's Formula

$$\boxed{E_n = -\underbrace{\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]}_{\substack{E_1 \\ \text{(ground state energy)}}}\frac{1}{n^2} = \frac{E_1}{n^2} \; ; \; n = 1, 2, 3\ldots}$$

Hydrogen Atom: $V(r) = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r}$ $\quad u = rR(r)$

ground state

$\boxed{E<0}$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + u\left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] = Eu$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + u\left[-\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] = Eu$$

$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} + u\left[-\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{E}\cdot\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{E\, r^2}\right] = u$$

$$\left\{ K = \frac{\sqrt{-2mE}}{\hbar} \qquad K^2 = \frac{-2mE}{\hbar^2} \qquad -\frac{1}{E} = \frac{2m}{\hbar^2 k^2} \right.$$

$$\frac{1}{k^2}\frac{d^2u}{dr^2} + u\left[\frac{e^2}{4\pi\epsilon_0}\cdot\frac{2m}{\hbar^2k^2}\cdot\frac{1}{r} - \frac{1}{k^2}\frac{l(l+1)}{r^2}\right] = u$$

$$\underbrace{\frac{1}{k^2}\frac{d^2u}{dr^2}}_{k^2\frac{d^2u}{d\rho^2}} = u\left[1 - \underbrace{\frac{me^2}{2\pi\epsilon_0\hbar^2k}}_{\rho_0}\cdot\frac{1}{kr} + \frac{l(l+1)}{(kr)^2}\right] ; \quad \rho = kr$$

$$\Rightarrow \boxed{\frac{d^2u}{d\rho^2} = u\left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]}$$

nova EDO em teoria "mais simples"

Análise do comportamento Assintótico:

$\lambda^2=1 \Rightarrow \lambda=\pm1$

$$\rho \to \infty \to \frac{d^2u}{d\rho^2} = u \to u(\rho) = Ae^{\pm\rho} \to \simeq Ae^{-\rho}$$

e^{ρ} explode no ∞ e logo $\to$ não é normalizável.

$$\rho \to 0 \to \frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}$$

(o termo $\frac{1}{\rho^2} \to 0$ muito mais rápido que $1/\rho$ além disso, buscamos apenas comportamentos aproximados)

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u \Rightarrow u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

explode quando $\rho \to 0$

$$\Rightarrow u(\rho) = C\rho^{l+1}$$

Logo nossa solução é do tipo: função a determinar.

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$$

~~Jogando $u(\rho)$ na EDO novamente:~~

$$\frac{du}{d\rho} = (l+1)\rho^{l} e^{-\rho} v(\rho) + \rho^{l+1}\left(-e^{-\rho}v(\rho) + e^{-\rho}\dot{v}(\rho)\right).$$

$$\frac{d^2u}{d\rho^2} = l(l+1)\rho^{l-1}e^{-\rho}v(\rho) + (l+1)\rho^{l}\left(-e^{-\rho}v(\rho) + e^{-\rho}\dot{v}(\rho)\right)$$
$$+ (l+1)\rho^{l}\left(-e^{-\rho}v(\rho) + e^{-\rho}\dot{v}(\rho)\right) + \rho^{l+1}\left(e^{-\rho}v(\rho) - e^{-\rho}\dot{v} - e^{-\rho}\dot{v} + e^{-\rho}\ddot{v}\right)$$

$$= \rho^{l}e^{-\rho}\left\{ l(l+1)\rho^{-1}v(\rho) + (l+1)\left(-v(\rho) + \dot{v}(\rho)\right) + (l+1)\left(-v(\rho) + \dot{v}(\rho)\right) + \rho\left(v(\rho) - \underbrace{\dot{v} - \dot{v}}_{2\dot{v}} + \ddot{v}\right)\right\}$$

$$= \rho^{l}e^{-\rho}\left\{\left(\frac{l(l+1)}{\rho} - (l+1) - (l+1) + \rho\right)v(\rho) + \left((l+1) + (l+1) - 2\rho\right)\dot{v}(\rho) + \rho\ddot{v}(\rho)\right\}$$

$$= \rho^{l}e^{-\rho}\left\{\left(\frac{l(l+1)}{\rho} - 2l - 2 + \rho\right)v(\rho) + \left(2l + 2 - 2\rho\right)\dot{v}(\rho) + \rho\ddot{v}(\rho)\right\}$$

podemos reescrever: $u(\rho) = \rho^{l}e^{-\rho}\left(\rho v(\rho)\right)$

Jogando tudo na EDO novamente teremos:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] u$$

$$\rho\ddot{v} + \dot{v}(2l+2-2\rho) + v\left(\frac{l(l+1)}{\rho} - 2l - 2 + \rho\right) = \rho v\left(1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right)$$

$$v\rho - \rho_0 v + v\frac{l(l+1)}{\rho}$$

$$\rho\ddot{v} + \dot{v}(2l+2-2\rho) + v(\rho_0 - 2l - 2) = 0$$

$$\underbrace{\rho\frac{d^2v}{d\rho^2} + 2\frac{dv}{d\rho}(l+1-\rho) + v(\rho_0 - 2(l+1)) = 0}$$

Supor que v admita solução por série:

$$v(\rho) = \sum_{n=0}^{\infty} C_n \rho^n$$

$$\frac{dv}{d\rho} = \sum C_n n \rho^{n-1} \rightarrow \sum_{m=0}^{\infty} C_{m+1}(m+1)\rho^m$$

usar as duas devido a $\rho\,\frac{d}{d\rho}$

$$\frac{d^2v}{d\rho^2} = \sum C_{m+1} m(m+1)\rho^{m-1} \rightarrow \cancel{\sum_{m=0}^{\infty} C_{m+2}(m+2)(m+1)\rho^m}$$

voltando a EDO temos:

$$\sum_{n=0}^{\infty}\left[C_{n+1}n(n+1)\rho^n + 2(l+1)C_{n+1}(n+1)\rho^n - 2C_n n\rho^n + C_n\rho_0 - 2C_n(l+1)\right] = 0$$

$$\Rightarrow \sum_{n=0}^{\infty}\left[\underbrace{C_{n+1}n(n+1) + 2(l+1)C_{n+1}(n+1) - 2C_n n + C_n\rho_0 - 2C_n(l+1)}_{=0}\right]\rho^n = 0 \quad \forall n$$

$$C_{n+1}n(n+1) + 2(l+1)C_{n+1}(n+1) - 2C_n n + C_n\rho_0 - 2C_n(l+1) = 0$$

$$C_{n+1}\left[n(n+1) + 2(l+1)(n+1)\right] = C_n\left[\rho_0 - 2n - 2(l+1)\right]$$

$$\Rightarrow \underbrace{C_{n+1} = \left(\frac{-\rho_0 + 2n + 2(l+1)}{n(n+1) + 2(l+1)(n+1)}\right)C_n}$$

Relação de Recursão

Trocando os índices $n \to j$

$$C_{j+1} = \left(\frac{2j + 2(l+1) - \rho_0}{j(j+1) + 2(l+1)(j+1)}\right) C_j$$

Entretanto observe que analisando o crescimento dos termo conforme $j \to \infty$:

$$C_{j+1} \simeq \frac{2j}{j(j+1)} C_j \simeq \frac{2}{j+1} C_j$$

Então teríamos aproximadamente:

$$C_j = \frac{2^j}{j!} C_0 \quad ; \quad v(\rho) = \sum_{j=0}^{\infty} C_j \rho^j$$

$$v(\rho) = \sum_{j=0}^{\infty} C_0 \frac{(2\rho)^j}{j!} = C_0 e^{2\rho} \longrightarrow$$ Solução que não queríamos pois explode no ∞ e portanto não é normalizada.

Como contornar isso? $\longrightarrow$ Impor que a série seja Finita!

Ou seja, $\exists !\ j_{max}$; $C_{j_{max}+1} = 0$; temos então:

$$C_{j_{max}+1} = \left(\frac{2j_{max} + 2l + 2 - \rho_0}{\underbrace{j_{max}(j_{max}+1) + 2(l+1)(j_{max}+1)}_{\neq 0}}\right) \underbrace{C_{j_{max}}}_{\neq 0} = 0$$

$$\Rightarrow 2j_{max} + 2l + 2 - \rho_0 = 0$$

$$2(j_{max} + l + 1) - \rho_0 = 0$$

Número Quântico Principal : $\boxed{n \equiv j_{max} + l + 1}$

If we combine everything with K defined before we get an important constant value:

$$K = \underbrace{\left(\frac{m e^2}{4\pi \epsilon_0 \hbar^2}\right)}_{} \cdot \frac{1}{n} = \frac{1}{an} \rightarrow \rho = \frac{r}{an}$$

$a \equiv$ Bohr's Radius
$= 0{,}529 \times 10^{-10}\,m$

And thus we have the Hydrogen atom wave function depends and is labeled after three quantum numbers (n, l, m)

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\, Y_l^m(\theta,\varphi)$$

$\frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho)$ spherical harmonics

polynomial of degree $j_{max} = n-l-1$

In the ground state we have $\underline{n=1}$ but the degree of the ~~polyno~~ polynomial forces that $\overline{l=0}$ and spherical harmonics forces $\underline{m=0}$. Thus the ground state is:

$$\psi_{100}(r,\theta,\varphi) = R_{10}(r)\, Y_0^0(\theta,\varphi)$$

$$\boxed{\psi_{100}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi a^3}}\, e^{-r/a}}$$

with Energy $\underline{E = -13{,}6\,eV}$

For the other values of n $(n>1)$ it will start to appear degenerated states. Different states (depending on values of l, m) but with the same energy.

$\hookrightarrow$ each E_n has n^2 degeneracy

We could also rewrite $v(\rho)$ as a special funtion

$$v(\rho) = L^{2l+1}_{n-l-1}(2\rho) \quad \text{(ignoring normalization)}$$

associated Laguerre Polynomial

$$L^{p}_{q-p}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

Laguerre Polynomial

$$L_q(x) = e^{x} \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

Thus the normalized generic Hydrogen atom wave function is:

$$\boxed{\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n\,[(n+l)!]^3}}\; e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L^{2l+1}_{n-l-1}(2r/na)\right] Y^m_l(\theta,\phi)}$$