QUANTUM MECHANICS $\boxed{2018}$

UESB Official Ementa

- Conceitos e postulados fundamentais da mecânica quântica
- Notação de Dirac
- Espaços vetoriais na mecânica quântica
- Teoria de momento angular
- Sistemas quânticos simples
- Oscilador harmônico quântico
- Teoria de perturbação independente do tempo
- Introdução a técnicas de segunda quantização

Bibliography

Main Textbooks (In order of use and importance for this course)

- Keith Hannabuss "An Introduction to Quantum Theory"
- David Griffiths "Introduction to Quantum Mechanics"
- J. J. Sakurai "Modern Quantum Mechanics"
- Cohen-Tannoudji, Diu, Laloe "Quantum Mechanics"
  (Claude Cohen-Tannoudji, Bernard Diu, Frank Laloe)

Alternative and Complementary Texts
(Interesting somewhat different approaches)

- Steven Weinberg "Lectures on Quantum Mechanics"
- Richard Feynman "The Feynman Lectures on Physics" - vol. 3
- Peter Woit "Quantum Theory, Groups and Representations"
- Ira Levine "Quantum Chemistry
- Oswaldo Pessoa Jr "Conceitos de Física Quântica"
- Ronaldo Thibes "Álgebra Linear e Mecânica Quântica"

Summary

1. Introduction

Plank / Einstein relation:

$$E = h\nu = \frac{h}{2\pi}\overbrace{2\pi\nu}^{\omega} = \hbar\omega$$

De Broglie relation:

$$|\vec{p}| = \frac{h}{\lambda} = \frac{h}{2\pi}\underbrace{\frac{2\pi}{\lambda}}_{|\vec{k}|} = \hbar|\vec{k}|$$

vectorial: $\vec{p} = \hbar\vec{k}$

Consistency with SR:

$$p^\mu = \left(\frac{E}{c}, \vec{p}\right) = \hbar\left(\frac{\omega}{c}, \vec{k}\right)$$

For the case of light, de Broglie relation is not independent because

$$\lambda\nu = c$$

$$\frac{\lambda}{2\pi}\underbrace{2\pi\nu}_{\omega} = c$$

$$\omega = c\underbrace{\frac{2\pi}{\lambda}}_{|\vec{k}|}$$

$$\omega = |\vec{k}|c \quad (\text{light})$$

$$0 = mc^2 = p^2 = \frac{E^2}{c^2} - \vec{p}^2$$

$$E = c|\vec{p}| \quad (\text{light})$$

From $E = \hbar\omega$

$$\cancel{c}|\vec{p}| = \hbar|\vec{k}|\cancel{c}$$

$$\boxed{|\vec{p}| = \hbar|\vec{k}|}$$

consider a plane wave

$$\Psi(t,\vec{x}) = \exp\left[-i(\omega t - \vec{k}\cdot\vec{x})\right]$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \underbrace{i\hbar(-i\omega)}_{\hbar\omega} \underbrace{\exp\left[-i(\omega t - \vec{k}\cdot\vec{x})\right]}_{\Psi}$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \underbrace{\hbar\omega}_{E} \Psi$$

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = E\Psi}$$

$$-i\hbar \vec{\nabla}\Psi = \underbrace{(-i\hbar)(i\vec{k})}_{\hbar\vec{k}} \underbrace{\exp\left[-i(\omega t - \vec{k}\cdot\vec{x})\right]}_{\Psi}$$

$$-i\hbar \vec{\nabla}\Psi = \underbrace{\hbar\vec{k}}_{\vec{p}}\Psi \qquad \therefore \boxed{-i\hbar\vec{\nabla}\Psi = \vec{p}\,\Psi}$$

second derivative:

$$(-i\hbar\vec{\nabla})^2\Psi = (-i\hbar\vec{\nabla})\,\vec{p}\,\Psi$$

$$= \vec{p}\,(\underbrace{-i\hbar\vec{\nabla}\Psi}_{\vec{p}\Psi}) = \vec{p}^{\,2}\Psi$$

Next consider the relation for a particle of mass m in a potential $V(\vec{x},t)$:

$$E = \frac{|\vec{p}|^2}{2m} + V(\vec{x},t)$$

and multiply be $\Psi(t,\vec{x})$:

$$E\,\Psi = \frac{|\vec{p}|^2}{2m}\Psi + V\Psi$$

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi}$$

The complex pde above is known as Schrödinger's wave equation.

Remark: Compare to the more general S.E.

$$i\hbar\frac{d}{dt}|\Psi\rangle = H|\Psi\rangle$$

Sep. of vars: For time-indep. potential $V(\vec{x},t) = V(\vec{x})$, by writing $\Psi(\vec{x},t) = \psi(\vec{x})\,\phi(t)$ we get two ode

$$\begin{cases} i\hbar \dfrac{d\phi}{dt} = E\phi & \Longrightarrow \quad \phi(t) = \phi(0)\, e^{-iEt/\hbar} \\ -\dfrac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi & \end{cases}$$

$$\Psi(\vec{x}, t) = \underbrace{\psi(x)\,\phi(0)}_{\Psi(\vec{x},0)}\, e^{-iEt/\hbar}$$

Def: The pde

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

is known as Schrödinger's time-ind. equation.

Remarks: 1) Both Sch. eqs are linear.

If ψ_1, ψ_2 are two solutions then $c_1\psi_1 + c_2\psi_2$ is also.

2) The time-ind. Sc. eq may be viewed as an eigenvalue equation

$$\left[-\frac{\hbar}{2m} \nabla^2 + V \right] \psi = E\psi$$

Ex.: Find eigenvalues and eigenvectors for $M = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$

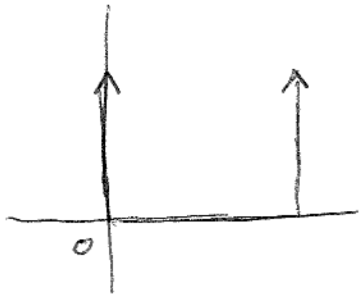
$$\det\left[I - \lambda M \right] = \begin{vmatrix} 1 & -i\lambda \\ i\lambda & 1 \end{vmatrix} = 1 - \lambda^2$$

$\lambda = \pm 1$

$a\begin{pmatrix} 1 \\ -i \end{pmatrix}, \quad a\begin{pmatrix} 1 \\ i \end{pmatrix}$

The Square Well

$$V(x) = 0, \qquad x \in [0, a]$$



$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

For $V = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

boundary condition:

$$\psi(0) = 0 = \psi(a)$$

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0}$$

general solution:

$$\psi_E(x) = \begin{cases} A_E \cosh\left(\sqrt{2m|E|}\, x/\hbar\right) + B_E \sinh\left(\sqrt{2m|E|}\, x/\hbar\right) & (E<0) \\ A_E + B_E x & (E=0) \\ A_E \cos\left(\sqrt{2mE}\, x/\hbar\right) + B_E \sin\left(\sqrt{2mE}\, x/\hbar\right) & (E>0) \end{cases}$$

For all three cases we have

$$0 = \psi(0) \Longleftrightarrow A = 0$$

For $E<0$, we have from the second condition

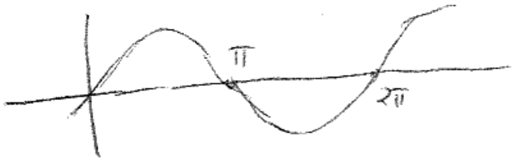
$$\psi(a) = B \sinh\left(\sqrt{2m|E|}\, a/\hbar\right) = 0 \qquad \therefore B = 0$$

For $E = 0$, $\quad 0 = Ba \Longleftrightarrow B = 0$

For $E > 0$

$$\psi(x) = B \sin\left(\sqrt{2mE}\, x / \hbar\right)$$

$$0 = \psi(a) = B \sin\left(\sqrt{2mE}\, a / \hbar\right)$$



$$\frac{\sqrt{2mE}\, a}{\hbar} = n\pi$$

$$\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a}$$

$$\boxed{\psi_n(x) = B \sin\left(\frac{n\pi x}{a}\right)}$$

$$\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a}$$

$$\sqrt{2mE} = \frac{n\pi\hbar}{a}$$

$$2mE = \frac{n^2\pi^2\hbar^2}{a^2}$$

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}}$$

Determination of B_m

$$\psi_m(x) = B_m \sin\left(\frac{m\pi x}{a}\right)$$

$$1 = \int_0^a |\psi(x)|^2 dx = \int_0^a |B_m|^2 \sin^2\left(\frac{m\pi x}{a}\right) dx$$

$$1 = |B_m|^2 \underbrace{\int_0^a \sin^2\left(\frac{m\pi x}{a}\right) dx}_{\frac{1}{2}a}$$

$$\boxed{B_m = \sqrt{\frac{2}{a}}}$$

$$\psi_m(x) = \sqrt{\frac{2}{a}} \sin\frac{m\pi x}{a}$$

Back to the time-evolution, from

$$\psi(t,x) = \psi(x)\,\phi(t) = \psi(x)\,\phi(0)\, e^{-iEt/\hbar}$$

we get the solutions

$$\boxed{\begin{aligned} \psi_m(t,x) &= \sqrt{\frac{2}{a}}\, e^{-iE_m t/\hbar} \sin\frac{m\pi x}{a}, \\ E_m &= \frac{m^2\pi^2\hbar^2}{2ma^2} \end{aligned}}$$

Time Evolution and General Wave Function

A general solution for $\psi(t, x)$ can be expanded as

$$\Psi(t, x) = \sum_{m=1}^{\infty} c_m \Psi_m(t, x)$$

$$= \sqrt{\frac{2}{a}} \sum_{m=1}^{\infty} c_m e^{-\frac{i m^2 \pi^2 \hbar t}{2 m a^2}} \sin \frac{m\pi x}{a}$$

The c_m are constants to be determined. If we know the wave function for $t = 0$

$$\Psi(0, x) = f(x)$$

then we should have

$$\sqrt{\frac{2}{a}} \sum_{m=1}^{\infty} c_m \sin \frac{m\pi x}{a} = f(x)$$

$$f(x) = \sqrt{\frac{2}{a}} \sum_{n=0}^{\infty} c_n \sin \frac{n\pi x}{a}$$

In order to determine the coefficients c_n in terms of the given function $f(x)$ note that

$$f(x) \sin \frac{m\pi x}{a} = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin \frac{n\pi x}{a} \sin \frac{m\pi x}{a}$$

$$\int_0^a f(x) \sin \frac{m\pi x}{a}\, dx = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \underbrace{\int_0^a \sin \frac{n\pi x}{a} \sin \frac{m\pi x}{a}\, dx}_{\delta_{n,m} \frac{a}{2}}$$

$$\int_0^a f(x) \sin \frac{m\pi x}{a}\, dx = \sqrt{\frac{a}{2}}\, c_m$$

$$\boxed{c_n = \sqrt{\frac{2}{a}} \int_0^a f(x) \sin \frac{n\pi x}{a}\, dx}$$

or

$$\boxed{c_n = \int_0^a f(x)\, \phi_n(x)\, dx}$$

Interpretation of the Wave Function

$$\rho(x) = |\psi(x)|^2 \longrightarrow \text{probability density for the position of the particle}$$

If $S \subset \mathbb{R}$ then

$$\int_S |\psi(x)|^2 dx = P(S)$$

gives the probability for the particle to be found within S.

Note that

$$\int_{\mathbb{R}} |\psi(x)|^2 dx = 1$$

probability density

outside the well: zero

inside the well:

$$f_n(x) = |\psi_m(x)|^2$$

$$\psi_m(t,x) = \sqrt{\frac{2}{a}}\, e^{-im^2\pi^2\hbar t/2ma^2} \sin\left(\frac{m\pi x}{a}\right)$$

$$\psi_m^*(t,x) = \sqrt{\frac{2}{a}}\, e^{im^2\pi^2\hbar t/2ma^2} \sin\left(\frac{m\pi x}{a}\right)$$

$$F_m(x) = |\psi_m(t,x)|^2 = |\psi_m(x)|^2$$

$$= \psi_m^*(t,x)\,\psi(t,x)$$

$$= \frac{2}{a}\sin^2\left(\frac{m\pi x}{a}\right)$$

$$= \frac{2}{a}\left[\frac{1-\cos\left(\frac{2m\pi x}{a}\right)}{2}\right]$$

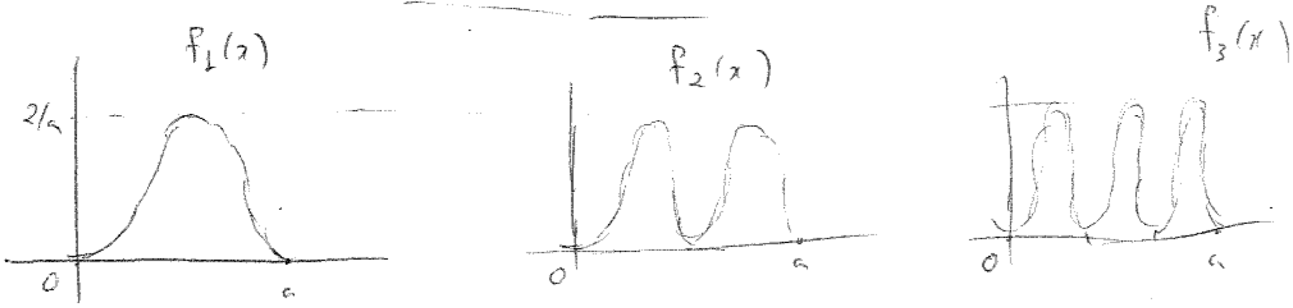
$\cos(a+b) = \cos a\cos b - \sin a\sin b$

$\cos(2a) = \cos^2 a - \sin^2 a$

$\cos(2a) = 1 - 2\sin^2 a$

$\therefore \sin^2 a = \frac{1-\cos(2a)}{2}$

$$\boxed{F_m(x) = \frac{1}{a}\left(1 - \cos\frac{2m\pi x}{a}\right)}$$



Distribution Function

$$F_m(x) = \int_0^x f_m(x)\,dx$$

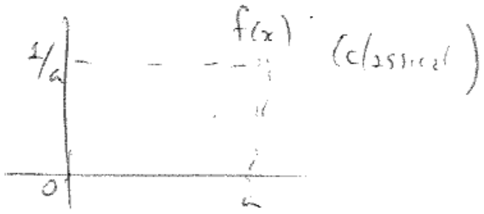
$$= \frac{1}{a}\int_0^x \left(1 - \cos\left(\frac{2m\pi x}{a}\right)\right) dx$$

$$= \frac{1}{a}\left[x - \frac{a}{2m\pi}\sin\left(\frac{2m\pi x}{a}\right)\right]$$

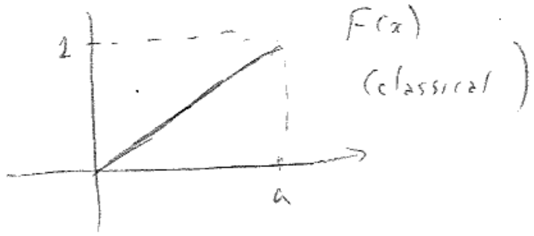
$$= \frac{x}{a} - \frac{1}{2m\pi}\sin\left(\frac{2m\pi x}{a}\right)$$

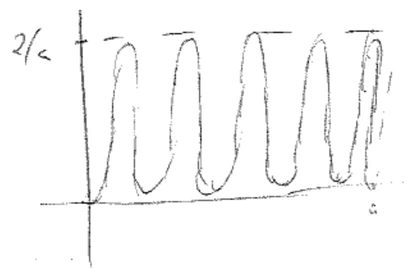
Compare to classical distribution:

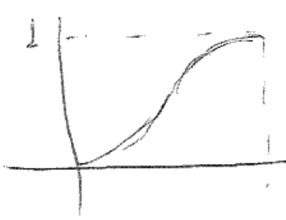
$$f(x) = \frac{1}{a} \quad \text{(classical)}$$

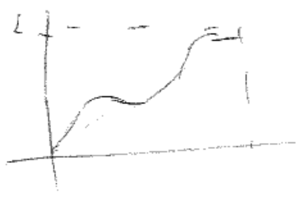


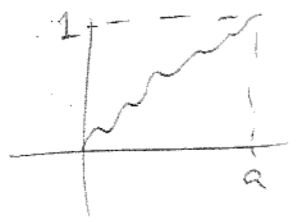
$$F(x) = \int_0^x \frac{1}{a}\,dx = \frac{x}{a} \quad \text{(classical)}$$











Exercise: Compute the probability of finding the particle within $\left[\frac{1}{4}a, \frac{3}{4}a\right]$ as a function of m, for the classical and quantum cases

classical:

$$P = \int_{a/4}^{3a/4} f(x)\,dx = \frac{x}{a}\Bigg|_{a/4}^{3a/4} = \frac{3}{4} - \frac{1}{4} = \frac{1}{2} = 50\%$$

quantum:

$$P = \int_{a/4}^{3a/4} f_m(x)\,dx = \int_0^{3a/4} f_m(x)\,dx - \int_0^{a/4} f_m(x)\,dx$$

$$= F_m\left(\frac{3a}{4}\right) - F_m\left(\frac{a}{4}\right)$$

$$= \left[\frac{3}{4} - \frac{1}{2m\pi}\sin\left(\frac{2m\pi}{a}\left(\frac{3a}{4}\right)\right)\right] - \left[\frac{1}{4} - \frac{1}{2m\pi}\sin\left(\frac{2m\pi}{a}\left(\frac{a}{4}\right)\right)\right]$$

$$= \left(\frac{3}{4} - \frac{1}{4}\right) - \frac{1}{2m\pi}\left[\underbrace{\sin\left(\frac{3m\pi}{2}\right)}_{-\sin\left(\frac{m\pi}{2}\right)} + \sin\left(\frac{m\pi}{2}\right)\right]$$

$$= \frac{1}{2} + \frac{1}{m\pi}\sin\left(\frac{m\pi}{2}\right) = \begin{cases} 1/2, & m \text{ even} \\ \dfrac{1}{2} + \dfrac{(-1)^{\frac{m-1}{2}}}{m\pi}, & m \text{ odd} \end{cases}$$

Mean Value:

$$\bar{x} = \int_0^a \underbrace{x}_{u} \underbrace{f_m(x)\,dx}_{dv} = \underbrace{x}_{u}\underbrace{F_m(x)}_{v}\Big|_0^a - \int_0^a \underbrace{F_m(x)}_{v}\,\underbrace{dx}_{du}$$

$$\bar{x} = a\underbrace{F_m(a)}_{1} - 0\underbrace{F_m(0)}_{0} - \int_0^a \left[\frac{x}{a} - \frac{1}{2m\pi}\sin\left(\frac{2\pi m x}{a}\right)\right]dx$$

$u = x \qquad du = dx$

$dv = f_m(x)\,dx \qquad v = \int f_m(x)\,dx = F(x) + C$

$$\bar{x} = a - \frac{a^2}{2a} - \frac{1}{2m\pi}\cdot\frac{a}{2m\pi}\cos\left(\frac{2m\pi x}{a}\right)\Big|_0^a$$

$$= \frac{a}{2} - \frac{a}{(2m\pi)^2}\left[\underbrace{\cos(2m\pi)}_{1} - \underbrace{\cos 0}_{1}\right]$$

$$= \frac{a}{2} \quad //$$

Current and Probability Conservation

Assume at $t=0$ we have

$$\int_{\mathbb{R}^3} |\psi(0,\vec{x})|^2 d^3\vec{x} = 1$$

then after time evolution by the Schrödinger equation what can we say about

$$\int_{\mathbb{R}^3} |\psi(t,\vec{x})|^2 d^3\vec{x} \qquad \text{for} \quad t>0 \ ?$$

For stationary states we have $\psi_m(t,\vec{x}) = e^{-i\frac{E_m t}{\hbar}} \psi_m(0,\vec{x})$

$$|\psi_m(t,\vec{x})|^2 = \psi_m^*(t,\vec{x})\,\psi_m(t,\vec{x})$$

$$= e^{iE_m t/\hbar}\,\psi_m^*(0,\vec{x})\, e^{-iE_m t/\hbar}\,\psi_m(0,\vec{x})$$

$$= \psi_m^*(0,\vec{x})\,\psi_m(0,\vec{x}) = |\psi_m(0,\vec{x})|^2$$

In the general case we have

$$\rho(t,\vec{x}) \equiv |\Psi(t,\vec{x})|^2$$

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t}\left[\psi^* \psi\right] = \frac{\partial \psi^*}{\partial t}\psi + \psi^* \frac{\partial \psi}{\partial t}$$

From the wave Sch. equation we have

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \quad \text{and} \quad -i\hbar\frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

and we can write

$$\begin{cases} \dfrac{\partial \psi}{\partial t} = \dfrac{i\hbar}{2m}\nabla^2\psi - \dfrac{i}{\hbar}V\psi \\[2ex] \dfrac{\partial \psi^*}{\partial t} = -\dfrac{i\hbar}{2m}\nabla^2\psi^* + \dfrac{i}{\hbar}V\psi^* \end{cases}$$

to obtain

$$\frac{\partial}{\partial t}|\psi(t,\vec{x})|^2 = \left[-\frac{i\hbar}{2m}\nabla^2\psi^* + \frac{i}{\hbar}V\psi^*\right]\psi + \psi^*\left[\frac{i\hbar}{2m}\nabla^2\psi - \frac{i}{\hbar}V\psi\right]$$

$$= \frac{i\hbar}{2m}\left[\psi^*\nabla^2\psi - \nabla^2\psi^*\psi\right]$$

$$= \frac{i\hbar}{2m}\left[\vec{\nabla}\psi^*\vec{\nabla}\psi + \psi^*\nabla^2\psi - \vec{\nabla}\psi^*\vec{\nabla}\psi - \nabla^2\psi^*\psi\right]$$

$$= \frac{i\hbar}{2m}\left[\vec{\nabla}\left(\psi^*\vec{\nabla}\psi\right) - \vec{\nabla}\left(\vec{\nabla}\psi^*\psi\right)\right]$$

$$\frac{\partial \rho}{\partial t} = \frac{i\hbar}{2m}\left[\vec{\nabla}\cdot(\psi^*\vec{\nabla}\psi) - \vec{\nabla}\cdot(\vec{\nabla}\psi^*\psi)\right]$$

$$= \vec{\nabla}\cdot\Big[\underbrace{\frac{i\hbar}{2m}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right)}_{\vec{j}}\Big]$$

Defining

$$\vec{j} \equiv \frac{i\hbar}{2m}\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right)$$

we get the continuity equation

$$\boxed{\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{j} = 0}$$

which expresses local probability conservation.

<u>proposition</u>: Let $\rho(t,\vec{x})$ and $\vec{j}(t,\vec{x})$ be defined in $\mathbb{R}^4$ and differentiable. If $\vec{j}(t,\vec{x})$ tends to zero faster then $|\vec{x}|^{-2}$ as $|\vec{x}| \to \infty$ then the total probability

$$\int_{\mathbb{R}} \rho(t,\vec{x})\, d^3\vec{x}$$

is time-independent.

<u>proof</u>: Let D be a volume enclosed by the closed surface S, then

$$\frac{\partial}{\partial t}\int_D \rho\, d^3\vec{x} = \int_D \frac{\partial \rho}{\partial t}\, d^3\vec{x} = -\int_D (\vec{\nabla}\cdot\vec{j})\, d^3\vec{x} = -\int_S \vec{j}\cdot d\vec{s}$$

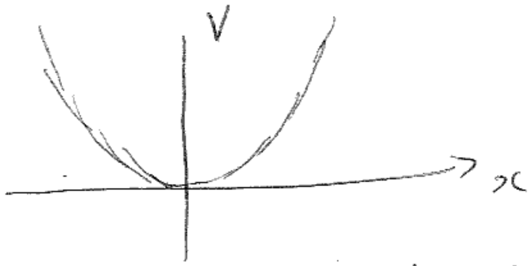
If S is a spherical surface of radius R and we consider the limit $R \to \infty$ we achieve the desired result, i.e.,

$$\frac{\partial}{\partial t}\int_{\mathbb{R}^3} \rho \, d^3\vec{x} = \lim_{R\to\infty} \frac{\partial}{\partial t}\int_D \rho \, d^3\vec{x} = 0$$

The Harmonic Oscillator

Consider the one-dimensional spinless one-particle time-independent Schrödinger equation for the potential

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



Proposition: Given the eigenvalue problem for the harmonic oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi = E\psi$$

the permissible eigenvalues form the sequence

$$E_N = \left(N + \frac{1}{2}\right)\hbar\omega, \qquad N = 0, 1, 2, \ldots$$

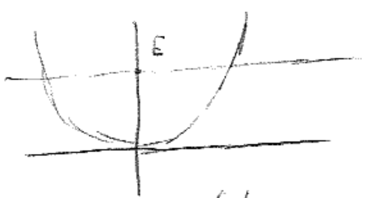
with corresponding eigenfunctions

$$\psi_N(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_n\left(\sqrt{\frac{m\omega}{2\hbar}}\, x\right) e^{-\frac{m\omega x^2}{2\hbar}}$$

where H_N is a N^{th} degree polynomial on its addimensional argument.

The proof will be constructed in an heuristic way by an attempt to directly solve the ode, starting first with an ansatz to factorize the solution and then performing a series expansion. The ansatz from the behaviour of the ode and its solution for large $|x|$

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \left(\frac{1}{2}m\omega^2x^2 - E\right)\psi$$



For large $|x|$, the fixed energy E is neglectible and we may write

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} \simeq \frac{1}{2}m\omega^2x^2\psi \quad , \text{ i.e., } \quad \boxed{\frac{d^2\psi}{dx^2} \simeq \left(\frac{m\omega x}{\hbar}\right)^2\psi}$$

We may try a solution of the form

$$\Phi(x) = \exp\left(\pm\frac{m\omega x^2}{2\hbar}\right)$$

Note that in terms of dimensions we have

$$\left[\frac{m\omega x}{\hbar}\right] = L^{-1} \quad \text{and} \quad \left[\frac{m\omega x^2}{\hbar}\right] = 1$$

Just for completeness note also that

$$[m] = M, \quad [\omega] = T^{-1}, \quad [\hbar\omega] = [\text{energy}] = [E] = ML^2T^{-2}$$

So, considering

$$\phi(x) = e^{\pm \frac{m\omega x^2}{2\hbar}}$$

we get

$$\frac{d\phi}{dx} = \pm \frac{m\omega x}{\hbar} e^{\pm \frac{m\omega x^2}{2\hbar}} = \pm \frac{m\omega x}{\hbar} \phi(x)$$

and

$$\frac{d^2\phi}{dx^2} = \pm \frac{m\omega}{\hbar} \phi(x) + \left(\frac{m\omega x}{\hbar}\right)^2 \phi(x)$$

$$\frac{d^2\phi}{dx^2} = \left[\left(\frac{m\omega x}{\hbar}\right)^2 \pm \frac{m\omega}{\hbar}\right] \phi(x)$$

Again we can check that in terms of dimension,

$$\left[\frac{m\omega x}{\hbar}\right] = L^{-1}, \quad \left[\left(\frac{m\omega x}{\hbar}\right)^2\right] = L^{-2}, \quad \left[\frac{m\omega}{\hbar}\right] = L^{-2}$$

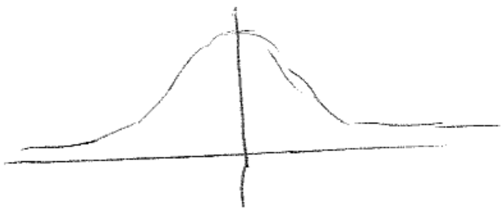
Thus in the domain of large $|x|$ we have

$$\left(\frac{m\omega x}{\hbar}\right)^2 \pm \frac{m\omega}{\hbar} \simeq \left(\frac{m\omega x}{\hbar}\right)^2$$

and $\phi(x) = \exp\left[\pm \frac{m\omega x^2}{2\hbar}\right]$ is an approximate solution for large $|x|$.

Due to normalization requirements we go for

$$\phi(x) = e^{-\frac{m\omega x^2}{2\hbar}}$$



Actually, this happens to be an exact solution for the original ode for a specific eigenvalue E. Let us try:

$$\psi(x) = \phi(x) = e^{-\frac{m\omega x^2}{2\hbar}} \Longrightarrow \left\{ \begin{aligned} \frac{d\psi}{dx} &= -\frac{m\omega x}{\hbar}\psi \\ \frac{d^2\psi}{dx^2} &= -\frac{m\omega}{\hbar}\psi + \left(\frac{m\omega x}{\hbar}\right)^2\psi \end{aligned} \right.$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi =$$

$$= -\frac{\hbar^2}{2m}\left[-\frac{m\omega}{\hbar}\psi + \left(\frac{m\omega x}{\hbar}\right)^2\psi\right] + \frac{1}{2}m\omega^2x^2\psi$$

$$= \left[\frac{\omega\hbar}{2} - \frac{m\omega^2x^2}{2} + \frac{1}{2}m\omega^2x^2\right]\psi$$

$$= \frac{\hbar\omega}{2}\psi \Longrightarrow \boxed{E = \frac{\hbar\omega}{2}}$$

In order to look for the other possible solutions, for different E values, we consider the factorization

$$\psi(x) = f(x)\,\phi(x) \quad \text{with } \phi(x) = \exp\left[-\frac{m\omega x^2}{2\hbar}\right] \text{ as before.}$$

Then, computing derivatives, we get

$$\frac{d}{dx}\psi(x) = \frac{d}{dx}\left[f\phi\right] = \frac{df}{dx}\phi - \frac{m\omega x}{\hbar} f\phi = \left(\frac{df}{dx} - \frac{m\omega x}{\hbar} f\right)\phi$$

$$\frac{d^2\psi}{dx^2} = \left(\frac{d^2f}{dx^2} - \frac{m\omega x}{\hbar}\frac{df}{dx} - \frac{m\omega}{\hbar} f\right)\phi + \left(\frac{df}{dx} - \frac{m\omega x}{\hbar} f\right)\phi'$$

$$= \left[\frac{d^2f}{dx^2} - \frac{m\omega x}{\hbar}\frac{df}{dx} - \frac{m\omega}{\hbar} f - \frac{m\omega x}{\hbar}\frac{df}{dx} + \left(\frac{m\omega x}{\hbar}\right)^2 f\right]\phi$$

$$= \left[\frac{d^2f}{dx^2} - \frac{2m\omega x}{\hbar}\frac{df}{dx} + \frac{m\omega}{\hbar}\left(\frac{m\omega x^2}{\hbar} - 1\right) f\right]\phi$$

Substituting the derivatives $\frac{d\psi}{dx}$ and $\frac{d^2\psi}{dx}$ above back into Schrödinger's equation we get

$$-\frac{\hbar^2}{2m}\left[\frac{d^2f}{dx^2} - \frac{2m\omega x}{\hbar}\frac{df}{dx} + \frac{m\omega}{\hbar}\left(\frac{m\omega x^2}{\hbar} - 1\right) f\right]\phi + \frac{1}{2}m\omega^2x^2 f\phi = E f\phi$$

i.e.,

$$0 = -\frac{\hbar^2}{2m}\left[\frac{d^2f}{dx^2} - \frac{2m\omega x}{\hbar}\frac{df}{dx} + \left(\frac{m^2\omega^2x^2}{\hbar^2} - \frac{m\omega}{\hbar} - \frac{m^2\omega^2x^2}{\hbar^2} + \frac{2mE}{\hbar^2}\right)f\right]\phi$$

or simply

$$\boxed{\frac{d^2f}{dx^2} - \frac{2m\omega x}{\hbar}\frac{df}{dx} + \frac{2m\omega}{\hbar}\left(\frac{E}{\hbar\omega} - \frac{1}{2}\right)f = 0}$$

We may change the independent variable from x to the addimensional

$$\xi = x\sqrt{\frac{m\omega}{\hbar}}$$

with inverse

$$x = \sqrt{\frac{\hbar}{m\omega}}\,\xi$$

such that

$$\begin{cases} \dfrac{d}{dx} = \dfrac{d\xi}{dx}\dfrac{d}{d\xi} = \sqrt{\dfrac{m\omega}{\hbar}}\dfrac{d}{d\xi} \\[2ex] \dfrac{d^2}{dx^2} = \dfrac{m\omega}{\hbar}\dfrac{d^2}{d\xi^2} \end{cases}$$

Substituting these relations into the previous ode we get

$$\frac{d^2f}{dx^2} \longrightarrow \frac{m\omega}{\hbar}\frac{d^2f}{d\xi^2} = \frac{m\omega}{\hbar} f''$$

$$-\frac{2m\omega x}{\hbar}\frac{df}{dx} \longrightarrow -\frac{2m\omega}{\hbar}\overbrace{\xi\sqrt{\frac{\hbar}{m\omega}}}^{x}\sqrt{\frac{m\omega}{\hbar}}\frac{df}{d\xi}$$

$$= -\frac{2m\omega}{\hbar}\xi f'$$

$$\therefore \quad \frac{m\omega}{\hbar} f'' - \frac{2m\omega}{\hbar}\xi f' + \frac{2m\omega}{\hbar}\underbrace{\left(\frac{E}{\hbar\omega} - \frac{1}{2}\right)}_{N} f = 0$$

$$\frac{m\omega}{\hbar}\left[f'' - 2\xi f + 2Nf\right] = 0$$

Defining $N \equiv \frac{E}{\hbar\omega} - \frac{1}{2}$ we get

$$\boxed{f''(\xi) - 2\xi f'(\xi) + 2Nf(\xi) = 0}$$

$$f'' - 2\xi f' + 2Nf = 0$$

Let us try a series solution

$$f(\xi) = \sum_{m=0}^{\infty} a_m \xi^{m+c} \quad , \quad a_0 \neq 0 .$$

$$f'(\xi) = \sum_{m=0}^{\infty} (m+c) a_m \xi^{m+c-1}$$

$$f''(\xi) = \sum_{m=0}^{\infty} (m+c-1)(m+c) a_m \xi^{m+c-2} .$$

$$f'' - 2\xi f' + 2Nf =$$

$$= \sum_{m=0}^{\infty} \Big[(m+c-1)(m+c) a_m \xi^{m+c-2} - 2(m+c) a_m \xi^{m+c} + 2N a_m \xi^{m+c} \Big] = 0$$

$$= \sum_{m=-2}^{\infty} (m+1+c)(m+2+c) a_{m+2} \xi^{m+c} + \sum_{m=0}^{\infty} \Big[-2(m+c) + 2N \Big] a_m \xi^{m+c} = 0$$

$$= (c-1)c\, a_0 \xi^{c-2} + c(c+1) a_1 \xi^{c-1} +$$

$$+ \sum_{m=0}^{\infty} \Big[(m+1+c)(m+2+c) a_{m+2} + 2(N-m-c) a_m \Big] \xi^{m+c} = 0$$

Since $a_0 \neq 0$, from the first term

$$(c-1)c\,a_0\,\xi^{c-2}$$

we have $c=0$ or $c=1$, leading to two possible ind. solutions

$\underline{c=0}$:

$$f(\xi) = \sum_{n=0}^{\infty} a_n \xi^n = a_0 + a_1\xi + a_2\xi^2 + \dots$$

or

$\underline{c=1}$:

$$f(\xi) = \sum_{n=0}^{\infty} a_n \xi^{n+1} = a_0\xi + a_1\xi^2 + a_2\xi^3 + \dots$$

For the case $c=1$, we have $c(c+1)a_1 = 0 \Rightarrow \boxed{a_1 = 0}$.

For the case $c=0$ we can add a term from the other solution to obtain also $a_1 = 0$

$$\begin{array}{rl} f(\xi) = & a_0 + a_1\xi + a_2\xi^2 + \dots \\ + & -\frac{a_1}{\bar{a}_0}\left[\bar{a}_0\xi + \bar{a}_1\xi^2 + \dots\right] \\ \hline & a_0 + \frac{a_2 a_1 \bar{a}_1}{\bar{a}_0}\xi^2 \end{array}$$

without loss of generality we take $a_1 = 0$ and the two solutions read

$$c = 0: \qquad f(\xi) = a_0 + a_2 \xi^2 + a_3 \xi^3 + a_4 \xi^4 + \dots$$

$$c = 1: \qquad f(\xi) = a_0 \xi + a_2 \xi^3 + a_3 \xi^4 + a_4 \xi^5 + \dots$$

Now from the coefficients of ξ^{m+c} we get the recurrence relation

$$(m+1+c)(m+2+c)\, a_{m+2} + 2(N-m-c)\, a_m = 0 \, , \quad m = 0,1,2,3,\dots$$

$$\boxed{a_{m+2} = \frac{2(m+c-N)}{(m+1+c)(m+2+c)} a_m \, , \quad m = 0,1,2,3,\dots}$$

or equivalently, $m \rightarrow m-2$,

$$\boxed{a_m = \frac{2(m-2+c-N)}{(m+c)(m+c-1)} a_{m-2} \, , \quad m = 2,3,4,5\dots}$$

Consider first the case $c = 0$:

$$a_m = \frac{2(m-2-N)}{m(m-1)} a_{m-2} \, , \quad m = 2,3,4,5,\dots$$

$$\underline{\underline{c = 0}}:$$

$\underline{m=2}$:
$$a_2 = \frac{-2N}{2} a_0 = -N a_0$$

$\underline{m=3}$:
$$a_3 = \frac{3(1-N)}{3.2} a_1 = 0 \qquad (\text{recall } a_1 = 0)$$

$\underline{m=4}$:
$$a_4 = \frac{2(2-N)}{4.3} a_2 = \frac{2(2-N)}{4.3} \cdot 2N a_0$$

$\underline{m=5}$:
$$a_5 = \frac{2(3-N)}{5.4} a_3 = 0$$

$\underline{m=6}$:
$$a_6 = \frac{2.(4-N)}{6.5} a_4 = \frac{2.(4-N).\ 2.(2-N).\ 2N}{6.5\ .\ 4.3\ .\ 2} a_0$$

$\underline{m=8}$:
$$a_8 = \frac{2.(6-N)}{8.7} a_6 = \frac{2.(6-N).\ 2(4-N).\ 2(2-N).\ 2N}{8.7\ .\ 6.5\ .\ 4.3\ .\ 2} a_0$$

etc

Similarly, for $c=1$ we have

$$a_m = \frac{2(m-1-N)}{m(m+1)} a_{m-2}, \quad m = 2, 3, 4, \ldots$$

m

The odd coefficients are all null and we may write

$$\begin{cases} c=0: & f(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 + a_6\xi^6 + \dots \\ c=1: & f(\xi) = a_0\xi + a_2\xi^3 + a_4\xi^5 + a_6\xi^7 + \dots \end{cases}$$

(Recall that $\xi = x\sqrt{\frac{m\omega}{\hbar}}$, i.e., ξ is proportional to x, with the advantage of being adimensional)

The complete wave function we are looking for is of the form

$$\begin{aligned} \psi(x) &= f(x)\,\phi(x) \\ &= f(\xi)\exp\left[-\frac{1}{2}\xi^2\right] \end{aligned}$$

and $\psi(x)$ must be normalizable, which means $\int_{-\infty}^{+\infty}|\psi(x)|^2dx = 1$. It is possible to prove that, in order to have convergence for $|x|\to\infty$, equivalently for $|\xi|\to\infty$, the series for $f(\xi)$ must have a finite number of terms. Take a closer look at the recursive formula for the a_m coefficients

$$a_m = \frac{2(m-2+c-N)}{(m+c)(m+c-1)}\,a_{m-2}, \quad m = 2,4,6,\dots$$

Given a fixed value for

$$N = \frac{E}{\hbar\omega} - \frac{1}{2} \in \mathbb{R}$$

there should be a certain even value for $m_{max} = \bar{m}$ such that all subsequent a_m with $m > \bar{m}$ should vanish - such that $f(\xi)$ is a finite polynomial.

Given $N \in \mathbb{R}$, for $c = 0$, there must exist a maximum value for even $m \in \mathbb{N}$, $m \geq 2$, given by $m_{max} = \bar{m}$ (even) such that

$$\bar{m} - 2 - N = 0, \quad \text{i.e.,} \quad \boxed{N = \bar{m} - 2 \quad (\bar{m} \text{ even})}$$

The $a_{\bar{m}} = 0$ and $\boxed{m \geq \bar{m} \Rightarrow a_m = 0}$.

Similarly for $c = 1$, given $N \in \mathbb{R}$, there must exist a maximum even natural $m_{max} = \bar{m} \in \mathbb{N}$, with $m \geq 2$, such that

$$\bar{m} - 1 - N = 0, \quad \text{i.e.,} \quad \boxed{N = \bar{m} - 1 \quad (\bar{m} \text{ even})}$$

Also here we have $\boxed{m \geq \bar{m} \Rightarrow a_m = 0}$.

Considering the fact that $\bar{m}$ can be any even natural number starting at two, we have the following possible values for N:

	$\bar{m}$	2	4	6	8	10	12
$c=0$	N	0	2	4	6	8	10
$c=1$	N	1	3	5	7	9	11

Thus, summarizing, N must be a natural number starting from zero. $N = 0, 1, 2, 3, \dots$

This gives us the energy allowed values.

In fact, from

$$N = \frac{E}{\hbar\omega} - \frac{1}{2}$$

we get

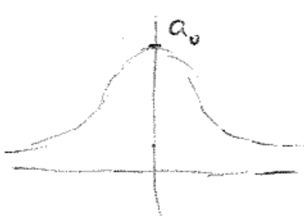
$$N = \frac{E_N}{\hbar\omega} - \frac{1}{2} \longrightarrow N + \frac{1}{2} = \frac{E_N}{\hbar\omega}$$

$$\boxed{E_N = \left(N + \frac{1}{2}\right)\hbar\omega, \quad N = 0, 1, 2, 3, \dots}$$

Examples:

0) $N = 0$: $\boxed{E_0 = \frac{\hbar\omega}{2}}$, $\bar{m} = 2$, $a_2 = 0$

$$f(\xi) = a_0 + \cancel{a_2}\,\xi^2 + \cancel{a_4}\,\xi^4 + \cancel{a_6}\,\xi^6 + \dots$$
$$\quad\quad\quad\;\; \searrow 0 \quad\quad \searrow 0 \quad\quad \searrow 0$$



$$\boxed{f(\xi) = a_0}$$

$$\psi_0(\xi) = f(\xi)\exp\left[-\frac{1}{2}\xi^2\right]$$

$$\boxed{\psi_0(x) = a_0 \exp\left[-\frac{m\omega x^2}{2\hbar}\right]}$$

1) $\underline{N = 1}$ $(c = 1,\ \tilde{n} = 2)$

$$f(\xi) = a_0 \xi + \cancel{a_2} \xi^3 + \cancel{a_4} \xi^5 + \cancel{a_6} \xi^7 + \dots$$

$$f(\xi) = a_0 \xi$$

$$E_1 = \left(1 + \tfrac{1}{2}\right) \hbar\omega \qquad \boxed{E_1 = \tfrac{3}{2} \hbar\omega}$$

$$\psi_1(x) = a_0 \xi \exp\left[-\tfrac{1}{2} \xi^2\right]$$

$$\boxed{\psi_1(x) = a_0 \sqrt{\frac{m\omega}{\hbar}}\, x \exp\left[-\frac{m\omega x^2}{2\hbar}\right]}$$

2) $\underline{N = 2}$ $(c = 0,\ \tilde{n} = 4)$ $E_2 = \left(2 + \tfrac{1}{2}\right) \hbar\omega = \tfrac{5}{2} \hbar\omega$

$$f(\xi) = a_0 + a_2 \xi^2 + \cancel{a_4} \xi^4 + \cancel{a_6} \xi^6 + \dots$$

$$f(\xi) = a_0 + a_2 \xi^2 \qquad a_2 = -N a_0$$

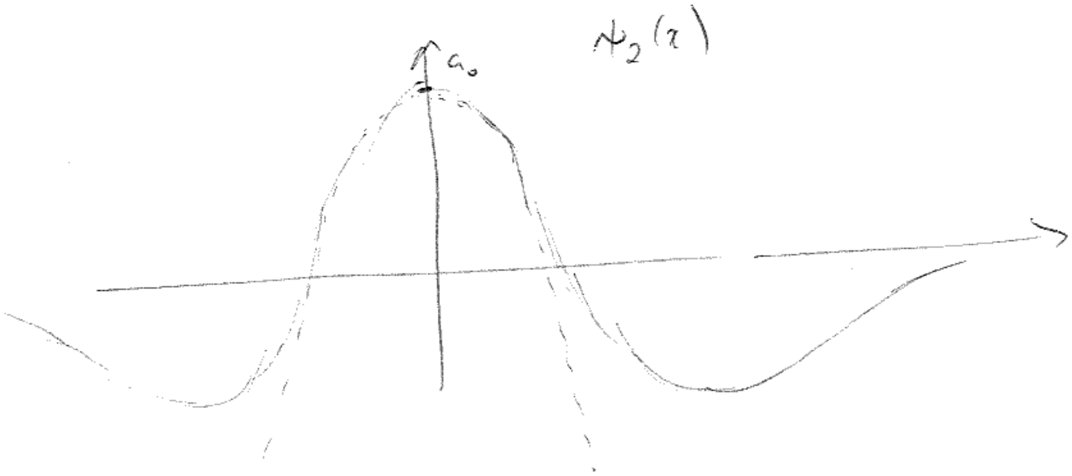
$$f(\xi) = a_0 \left(1 - 2\xi^2\right) \qquad a_2 = -2 a_0$$

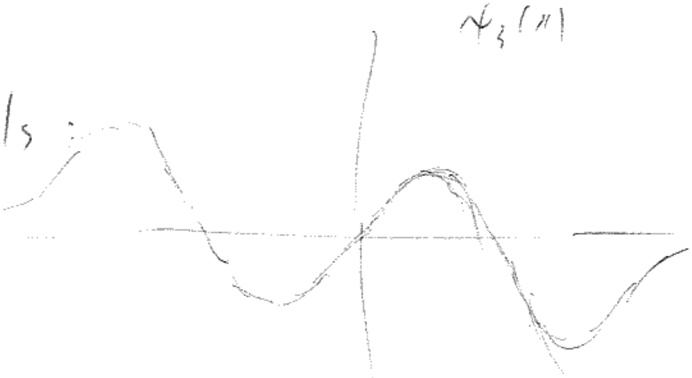
$$f(\xi) = (1 - 2\xi^2)\, a_0$$

$$= a_0 \left(1 - 2 \cdot \frac{m\omega}{\hbar} x^2\right)$$

$$\psi_2(x) = a_0 (1 - 2\xi^2) \exp\left[-\frac{1}{2}\xi^2\right]$$

$$\psi_2(x) = a_0 \left(1 - \frac{2m\omega x^2}{\hbar}\right) \exp\left[-\frac{m\omega x^2}{2\hbar}\right]$$





Hermite Polynomials:

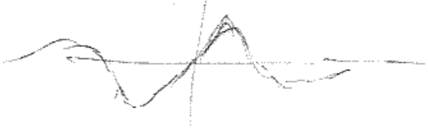
$$H_0 = 1$$

$$H_1 = 2\xi$$

$$H_2 = 4\xi^2 - 2$$

$$H_3 = 8\xi^3 - 12\xi$$

$$H_4 = 16\xi^4 - 48\xi^2 + 12$$



Rodrigues Formula:

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}$$

The general N eigenfunction for the harmonic oscillator takes then the form

$$\psi_N(x) = C_N H_N\left(\sqrt{\frac{m\omega}{2\hbar}}\, x\right) e^{-\frac{m\omega x^2}{2\hbar}}$$

where H_N is a N-degree polynomial and C_N an appropriate constante for normalization purposes. H_N can be chosen to be the Hermite polynomials.

Harmonic Oscillator in Higher Dimensions

Let us consider now two spatial dimensions (x, y), meaning we have

$$\phi = \phi(x, y) \quad , \quad \psi = \psi(t, x, y).$$

In this case, the potential for a two dimensional harmonic oscillator can be written as

$$V(x, y) = \frac{1}{2} m (\omega_1 x^2 + \omega_2 y^2)$$

The time-independent Schrödinger equation can be written as

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2}\right) + \frac{1}{2} m (\omega_1 x^2 + \omega_2 y^2)\phi = E\phi$$

Proposition

Eigenvalues: $$E_{(N_1, N_2)} = \left(N_1 + \frac{1}{2}\right)\hbar\omega_1 + \left(N_2 + \frac{1}{2}\right)\hbar\omega_2$$

Eigenfunctions:

$$\phi_{(N_1, N_2)} = \sqrt{\frac{m}{\pi\hbar}}\,(\omega_1\omega_2)^{1/4}\, H_{N_1}\!\left(\sqrt{\frac{m\omega_1}{\hbar}}\,x\right) H_{N_2}\!\left(\sqrt{\frac{m\omega_2}{\hbar}}\,y\right) \cdot \exp\left[-\frac{m}{2\hbar}(\omega_1 x^2 + \omega_2 y^2)\right]$$

proof: Write $\psi(x,y) = X(x)\,Y(y)$ to obtain

$$-\frac{\hbar^2}{2m} Y \frac{d^2X}{dx^2} - \frac{\hbar^2}{2m} X \frac{d^2Y}{dy^2} + \frac{1}{2}m\left(\omega_1^2 x^2 + \omega_2^2 y^2\right) XY = E\,XY$$

dividing all terms by XY:

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} - \frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{2}m\left(\omega_1^2 x^2 + \omega_2^2 y^2\right) = E$$

separating variables:

$$-\frac{\hbar^2}{2m}\frac{X''}{X} + \frac{1}{2}m\omega_1^2 x^2 = \underbrace{E + \frac{\hbar^2}{2m}\frac{Y''}{Y} - \frac{1}{2}m\omega_2^2 y^2}_{E_1}$$

$$\boxed{-\frac{\hbar^2}{2m} X'' + \frac{1}{2}m\omega_1^2 x^2 X = E_1 X}$$

$$-\frac{\hbar^2}{2m}\frac{Y''}{Y} + \frac{1}{2}m\omega_2^2 y^2 = \underbrace{E + \frac{\hbar^2}{2m}\frac{X''}{X} - \frac{1}{2}m\omega_1^2 x^2}_{E_2}$$

$$\boxed{-\frac{\hbar^2}{2m} Y'' + \frac{1}{2}m\omega_2^2 y^2 Y = E_2 Y}$$

$$E = \underbrace{-\frac{\hbar^2}{2m}\frac{X''}{X} + \frac{1}{2}m\omega_1^2 x^2}_{E_1} \underbrace{- \frac{\hbar^2}{2m}\frac{Y''}{Y} + \frac{1}{2}m\omega_2^2 y^2}_{E_2}$$

$$\therefore \quad \boxed{E = E_1 + E_2}$$

From previous results it follows that

$$\begin{cases} E_1 = \left(N_1 + \frac{1}{2}\right)\hbar\omega_1 \\ E_2 = \left(N_2 + \frac{1}{2}\right)\hbar\omega_2 \end{cases}$$

$$\begin{cases} X_{N_1}(x) = \left(\frac{m\omega_1}{\pi\hbar}\right)^{1/4} H_{N_1}\left(\sqrt{\frac{m\omega_1}{\hbar}}\,x\right) e^{-m\omega_1 x^2/2\hbar} \\ Y_{N_2}(y) = \left(\frac{m\omega_2}{\pi\hbar}\right)^{1/4} H_{N_2}\left(\sqrt{\frac{m\omega_2}{\hbar}}\,y\right) e^{-m\omega_2 y^2/2\hbar} \end{cases}$$

$$\psi_{(N_1, N_2)}(x, y) = X_{N_1}(x)\, Y_{N_2}(y)$$

$$= \sqrt{\frac{m}{\pi\hbar}}\,(\omega_1\omega_2)^{1/4} H_{N_1}\left(\sqrt{\frac{m\omega_1}{\hbar}}\,x\right) H_{N_2}\left(\sqrt{\frac{m\omega_2}{\hbar}}\,y\right) e^{-\frac{m}{2\hbar}\left(\omega_1 x^2 + \omega_2 y^2\right)}$$

That proves the proposition.

Degeneracy:

What happens when w_1 and w_2 coincide? Assume we have for instance

$$w_1 = w_2 \equiv w$$

Then the energy levels are

$$E_{(N_1, N_2)} = E_{1 N_1} + E_{2 N_2}$$

$$= \left(N_1 + \tfrac{1}{2}\right)\hbar w + \left(N_2 + \tfrac{1}{2}\right)\hbar w$$

$$= \left(N_1 + N_2 + 1\right)\hbar w$$

$N_1 + N_2$	N_1	N_2	$E_{(N_1, N_2)}$	wave function
0	0	0	$\hbar w$	$\psi_{00}(x,y)$
1	0	1	$2\hbar w$	$\psi_{01}(x,y)$
	1	0		$\psi_{10}(x,y)$
2	0	2	$3\hbar w$	$\psi_{02}(x,y)$
	1	1		$\psi_{11}(x,y)$
	2	0		$\psi_{20}(x,y)$
3	0	3	$4\hbar w$	$\psi_{03}(x,y)$
	1	2		$\psi_{12}(x,y)$
	2	1		$\psi_{21}(x,y)$
	3	0		$\psi_{30}(x,y)$
4	0	4	$5\hbar w$	$\psi_{04}(x,y)$
	1	3		$\psi_{13}(x,y)$
	2	2		$\psi_{22}(x,y)$
	3	1		$\psi_{31}(x,y)$
	4	4		$\psi_{40}(x,y)$

The Hydrogen Atom

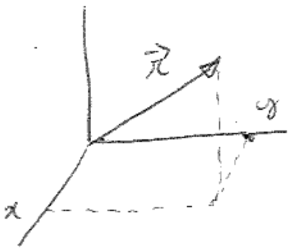
Recall the 3D time-independent Schrödinger equation

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

More precisely, in Cartesian coordinates, we have

$$\psi = \psi(x,y,z), \qquad V = V(x,y,z),$$

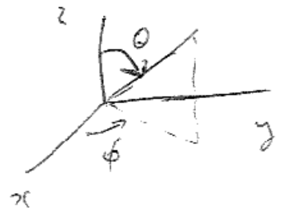
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V(x,y,z)\psi = E\psi$$



For a monoelectronic atom, with fixed nucleous at the origin we may write

$$V(x,y,z) = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$$

or in spherical coordinates



$$r = \sqrt{x^2+y^2+z^2}$$

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

$$\psi = \psi(r,\theta,\phi)$$

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

With the Hyd Atom in mind, we begin by attacking the more general case of a particle in a spherically symmetric potential $V(r)$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{\sin\theta\,\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+$$

$$+\ V(r)\,\psi = E\,\psi$$

By using the separation of variables technique we write

$$\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$$

and then, multiplying by $\dfrac{r^2}{R\,\Theta\,\Phi}$ we get

$$-\frac{\hbar^2}{2m}\left[\frac{r}{R}\frac{d^2}{dr^2}(rR)+\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\frac{\sin\theta\, d\Theta}{d\theta}\right)+\frac{1}{\sin^2\theta\,\Phi}\frac{d^2\Phi}{d\phi^2}\right]+$$

$$+\ r^2 V = r^2 E$$

$$\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\frac{\sin\theta\, d\Theta}{d\theta}\right)+\frac{1}{\sin^2\theta\,\Phi}\frac{d^2\Phi}{d\phi^2} = \overbrace{-\frac{2m}{\hbar^2}(E-V)r^2-\frac{r}{R}\frac{d^2(rR)}{dr^2}}^{\text{depends only on } r}$$

Since the LHS does not depend on r while the RHS depends only on r we must have

$$\frac{1}{\sin\theta\;\Theta}\frac{d}{d\theta}\left(\frac{\sin\theta\, d\Theta}{d\theta}\right)+\frac{1}{\sin^2\theta\,\Phi}\frac{d^2\Phi}{d\phi^2} = -\lambda$$

for λ constant

and

$$\frac{2m}{\hbar^2}(E-V)r^2 + \frac{r}{R}\frac{d^2(rR)}{dr^2} = \lambda$$

$$\frac{r}{R}\frac{d^2(rR)}{dr^2} - \lambda = -\frac{2m}{\hbar^2}(E-V)r^2$$

$$-\frac{\hbar^2}{2m}\left[\frac{r}{R}\frac{d^2(rR)}{dr^2} - \lambda\right] = (E-V)r^2$$

$$-\frac{\hbar^2}{2m}\left[\frac{r}{R}\frac{d^2(rR)}{dr^2} - \lambda\right] + r^2 V(r) = E r^2$$

multiplying by $R(r)$:

$$\boxed{-\frac{\hbar^2}{2m}\left[r\frac{d^2(rR)}{dr^2} - \lambda R\right] + r^2 V R = r^2 E R}$$

For the angular part, depending on θ and ϕ, we have

$$\frac{1}{\Theta \sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2} = -\lambda$$

multiplying by $\sin^2\theta$ we get

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\lambda\sin^2\theta$$

 By changing sides we rewrite

$$\underbrace{\frac{\Phi''}{\Phi}}_{\substack{\text{depends only}\\ \text{on } \phi}} = \underbrace{-\lambda \sin^2\theta - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)}_{\text{depends only on } \theta}$$

Introducing a second separation of variables constant we get

$$\frac{\Phi''}{\Phi} \equiv -\mu^2$$

The choice of sign comes from the fact that $\Phi(\phi)$ must be periodic:

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

thus

$$\Phi'' + \mu^2 \Phi = 0$$

and

$$\Phi(\phi) = A e^{i\mu\phi} + B e^{-i\mu\phi}$$

We are not yet concerned with the integration constant. By demanding periodicity we have

$$\Phi(\phi+2\pi)=\Phi(\phi)$$

$$\therefore\ e^{i\mu\phi}e^{2i\mu\pi}=e^{i\mu\phi}\quad\therefore\ e^{2i\mu\pi}=1\quad\therefore\ \boxed{\mu\in\mathbb{Z}}$$

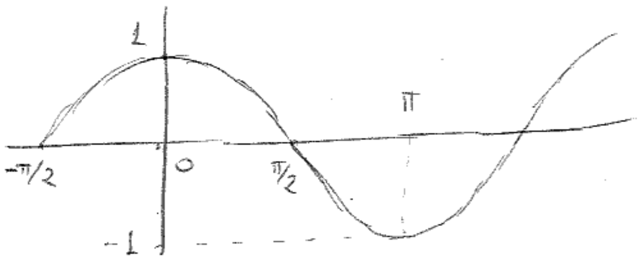
Then the RHS of the angular differential equation leads to

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta=\mu^2$$

with $\mu\in\mathbb{Z}$. This happens to be an ode for each pair (μ,λ). We know that $\mu\in\mathbb{Z}$. Regarding λ, consider the following change of variables:

$$c=\cos\theta$$

$$\frac{d}{d\theta}=\frac{dc}{d\theta}\frac{d}{dc}=-\sin\theta\frac{d}{dc}$$



$$0\le\theta\le\pi\ ,\quad 1\ge c\ge -1$$

Substituting $c=\cos\theta$, $\sin^2\theta=1-c^2$, $\frac{d}{d\theta}=-\sin\frac{d}{dc}$ into the previous ode leads to

$$\frac{\sin\theta}{\Theta}\cdot\sin\theta\frac{d}{dc}\left(\sin\theta.\ \sin\theta\frac{d}{dc}\ \Theta\right)+\lambda(1-c^2)=\mu^2$$

$$\frac{(1-c^2)}{\Theta}\frac{d}{dc}\left((1-c^2)\frac{d}{dc}\Theta\right)+\lambda(1-c^2)=\mu^2$$

multiplying by Θ:

$$\boxed{(1-c^2)\frac{d}{dc}\left[(1-c^2)\frac{d\Theta}{dc}\right]+\left[\lambda(1-c^2)-\mu^2\right]\Theta=0}$$

which is known as (the general) Legendre's equation.

It is possible to prove that the solutions are singular at $c=\pm 1$ unless

$$\boxed{\lambda = \ell(\ell+1)}$$

with ℓ an integer satisfying $\ell \geq |\mu|$. Recalling that $\mu \in \mathbb{Z}$, we have:

$$\left.\begin{array}{l}\mu=0 \Longrightarrow \ell=0,1,2,3,\ldots\\ \mu=\pm 1 \Longrightarrow \ell=1,2,3,\ldots\\ \mu=\pm 2 \Longrightarrow \ell=2,3,4,\ldots\\ \mu=\pm 3 \Longrightarrow \ell=3,4,5,\ldots\end{array}\right\} \Longrightarrow \ell \in \mathbb{N}$$

Or else, reversing:

$$\ell=0 \Longrightarrow \mu=0$$

$$\ell=1 \Longrightarrow \mu=-1,0,1$$

$$\ell=2 \Longrightarrow \mu=-2,-1,0,1,2$$

etc

For each allowed pair (ℓ, μ) we have a corresponding solution

$$(\ell, \mu) \longleftrightarrow P_\ell^\mu$$

$$\begin{array}{lccccccc}
\ell = 0 & & & & P_0^0 & & & \\
\hline
\ell = 1 & & & P_1^{-1} & P_1^0 & P_1^1 & & \\
\hline
\ell = 2 & & P_2^{-2} & P_2^{-1} & P_2^0 & P_2^1 & P_2^2 & \\
\hline
\ell = 3 & P_3^{-3} & P_3^{-2} & P_3^{-1} & P_3^0 & P_3^1 & P_3^2 & P_3^3
\end{array}$$

For $\mu = 0$, the $P_\ell^0 \equiv P_\ell$ are known as the Legendre functions or Legendre polynomials, which happen to be polynomials of degree ℓ. For general μ satisfying $|\mu| \leq \ell$ we have the associated Legendre functions. The Legendre polynomia are solutions to the Legendre equation

$$\boxed{\frac{d}{dc}\left[(1-c^2)\frac{d}{dc} P_\ell\right] + \ell(\ell+1) P_\ell = 0}$$

The Legendre polynomia $P_\ell(c) \equiv P_\ell^0(c)$ can be shown to be generated by the Rodrigues formula

$$P_\ell(c) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dc^\ell}\left[(c^2-1)^\ell\right]$$

More generally, the associated Legendre functions are solutions of the associated Legendre equation

$$\frac{d}{dc}\left[(1-c^2)\frac{d}{dc}P_\ell^\mu(c)\right] + \left[\ell(\ell+1) - \frac{\mu^2}{1-c^2}\right]P_\ell^\mu(c) = 0$$

and can be generated from the Legendre polynomia by

$$P_\ell^\mu(c) = (-1)^\mu (1-c^2)^{\mu/2} \frac{d^\mu}{dc^\mu}\left(P_\ell(c)\right)$$

for positive μ and then using

$$P_\ell^{-\mu}(c) = (-1)^\mu \frac{(\ell-\mu)!}{(\ell+\mu)!} P_\ell^\mu(c)$$

for negative μ.

Alternatively we can generate $P_\ell^\mu(c)$ directly as

$$P_\ell^\mu(c) = \frac{(-1)^\mu}{2^\ell \ell!} (1-c^2)^{\mu/2} \frac{d^{\ell+\mu}}{dc^{\ell+\mu}} (c^2-1)^\ell$$

for $\ell \in \mathbb{N}$, $\mu \in \mathbb{Z}$, with $|\mu| \leq \ell$.

Ex.: $\underline{\ell = 0}$: $P_0(c) = P_0^0(c) = 1$

$\underline{\ell = 1}$. $P_1(c) = P_1^0(c) = \frac{1}{2} \frac{d}{dc} (c^2-1) = c = \cos\theta$

$$P_1^1(c) = -\sqrt{1-c^2} \frac{d}{dc} c = -\sqrt{1-c^2} = -\sin\theta$$

$$P_1^{-1}(c) = \frac{1}{2}\sqrt{1-c^2} = \frac{1}{2}\sin\theta$$

The associated Legendre functions can be proven to be orthogonal

$$\int_{-1}^{1} P_k^m P_\ell^m \, dx = \frac{2(\ell+m)!}{(2\ell+1)(\ell-m)!} \delta_{k,\ell}$$

$$\int_{-1}^{1} \frac{P_\ell^m P_\ell^n \, dx}{1-x^2} = \begin{cases} 0, & m \neq n \\ \dfrac{(\ell+m)!}{m(\ell-m)!}, & m = n \neq 0 \\ \infty, & m = n = 0 \end{cases}$$

<u>Def.</u>: The full angular term

$$\Theta(\theta)\,\Phi(\phi) = P_\ell^\mu(\cos\theta)\, e^{i\mu\phi} \equiv Y_\ell^\mu(\theta, \phi)$$

is called a spherical harmonic of degree ℓ.

<u>theorem</u>: The space of spherical harmonics of degree ℓ has dimension $2\ell+1$.

<u>proof</u>: For each natural $\ell \in \mathbb{N}$, the space is spanned by $Y_\ell^\mu(\theta, \phi)$ with

$$\mu = \underbrace{-\ell, -\ell+1, \ldots, -1}_{\ell}, \underbrace{0}_{1}, \underbrace{1, \ldots, \ell-1, \ell}_{\ell}$$

Let us come back now to the radial equation

$$-\frac{\hbar^2}{2m}\left[r\frac{d^2(rR)}{dr^2} - \lambda R \right] + r^2 V R = E r^2 R$$

As we have seen in the angular part we must have $\lambda = \ell(\ell+1)$ with ℓ natural. Substituting this and dividing by r leads to

$$-\frac{\hbar^2}{2m}\left[\frac{d^2(rR)}{dr^2} - \frac{\ell(\ell+1)\, rR}{r^2} \right] + V rR = E rR$$

We look for approximate solutions for large r.

Assuming $rV(r) \longrightarrow 0$ as $r \to \infty$ we write, for large r:

$$-\frac{\hbar^2}{2m}\frac{d^2(rR)}{dr^2} \simeq E rR$$

$$\frac{d^2}{dr^2}(rR) + \frac{2mE}{\hbar^2} rR = 0$$

$$\therefore \quad \boxed{rR \simeq \exp\left(\pm r\sqrt{2mE}/\hbar \right), \quad \text{for large } r}$$

Note that:

$$\begin{cases} E > 0 \implies \text{real exponential solutions} \\ E < 0 \implies \text{oscillatory solutions} \\ E = 0 \implies \text{straight line solutions } (rR = ar + \ell) \end{cases}$$

However, only the case $E<0$ leads to renormalizable solutions. This can be clearly seen because if $E>0$ we would have

$$|rR| = C \qquad \text{(constant)}$$

and

$$\int_0^\infty |R|^2 r^2 dr = \int_0^\infty |Rr|^2 dr = C\int_0^\infty dr$$

For $E=0$, we would have $|rR| = |ar+b|$

$$\int_0^\infty |R|^2 r^2 dr = \int_0^\infty |ar+b|^2 dr \longrightarrow \text{diverges}$$

Therefore we must have $E<0$.

Defining

$$k^2 \equiv -\frac{2mE}{\hbar^2} > 0, \quad \text{with } k>0,$$

we have

$$E = -\frac{\hbar^2 k^2}{2m}$$

and for large r we get

$$r R \cong \exp(\pm \kappa r)$$

For normalizable solutions we must adopt the negative sign, leading to

$$\boxed{R(r) \cong \frac{\exp(-\kappa r)}{r}, \quad \text{for large } r}$$

<u>Exercise</u>: Verify whether

$$\frac{\exp(-\kappa r)}{r}, \quad \exp(-\kappa r), \quad r\exp(-\kappa r)$$

produce solutions for the radial equation. Which would be $V(r)$ and E?

From these ideas we make an ansatz for $R(r)$ in the general radial equation.

<u>Ansatz</u>:

$$\boxed{R(r) = \frac{f(r)}{r} e^{-\kappa r}}$$

Using the ansatz $R(r) = \frac{f(r)}{r} e^{-\kappa r}$ and substituting into the radial Schrödinger's equation

$$-\frac{\hbar^2}{2m}\left[\frac{d^2}{dr^2}(rR) - \frac{\ell(\ell+1)}{r^2} rR\right] + VrR = ErR$$

leads to

$$-\frac{\hbar^2}{2m}\left[f'' - 2\kappa f' + \kappa^2 f - \frac{\ell(\ell+1)}{r^2} f\right] + Vf = Ef$$

In fact, note that

$$rR = f e^{-\kappa r}$$

$$\frac{d}{dr}(rR) = (f' - \kappa f) e^{-\kappa r}$$

$$\frac{d^2}{dr^2}(rR) = (f'' - \kappa f' - \kappa(f' - \kappa f)) e^{-\kappa r}$$

$$= (f'' - 2\kappa f' + \kappa^2 f) e^{-\kappa r}$$

amounting to

$$-\frac{\hbar^2}{2m}\left[(f'' - 2\kappa f' + \kappa^2 f) e^{-\kappa r} - \frac{\ell(\ell+1)}{r^2} f e^{-\kappa r}\right] +$$

$$+ V f e^{-\kappa r} = E f e^{-\kappa r}$$

Multiplying by $-\frac{2m}{\hbar^2} e^{\kappa r}$ we get

$$\boxed{f'' - 2\kappa f' - \left[\frac{\ell(\ell+1)}{r^2} + \frac{2mV}{\hbar^2} \right] f = 0}$$

which is the ode to be satisfied by $f(r)$ in order for the ansatz $R(r) = \frac{f(r)}{r} e^{-\kappa r}$ to work.

In order to proceed we must consider a specific form for the potential $V(r)$.

The Spectrum of the Hydrogen Atom

For a hydrogen-like atom we have

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

and

$$\frac{m V(r)}{\hbar^2} = -\frac{m Z e^2}{4\pi\epsilon_0 \hbar^2 r} = -Z\left(\frac{me^2}{4\pi\epsilon_0 \hbar^2}\right)\left(\frac{1}{r}\right)$$

defining

$$\boxed{a \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2} \quad (\text{Bohr radius})}$$

we may write

$$\boxed{\frac{m V(r)}{\hbar^2} = -\frac{Z}{ar} \quad \text{(Hydrogen-like atom)}}$$

Proposition:

The allowed band state energies for the Hydrogen-like Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$

are given by

$$\boxed{E_n = -\left(\frac{Z^2e^2}{8\pi\epsilon_0 a}\right)\cdot\frac{1}{n^2}, \quad n = 1, 2, 3, \dots}$$

with corresponding wave functions

$$\boxed{\psi_{n\ell m}(r,\theta,\phi) = C\cdot r^\ell L_n^\ell\left(\frac{Zr}{a}\right) e^{-\frac{Zr}{na}} Y_\ell^m(\theta,\phi)}$$

where L_n^ℓ is a polynomial of degree $n-\ell$, $0 \leq \ell < n$ and $|m| \leq \ell$, and a is the Bohr radius given by $a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$.

In particular, the normalized ground state wave function can be written as

$$\psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a^3}}\, e^{-\frac{Zr}{a}}$$

Proof: As previously shown, by separating variables

$$\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$$

the angular part is indexed by l, m and given by the spherical harmonics $Y_l^m(\theta,\phi)$ so that

$$\psi_{Rlm}(r,\theta,\phi) = R(r)\, Y_l^m(\theta,\phi) \,.$$

Also as previously shown, the radial part can be written as

$$R(r) = \frac{f(r)}{r}\, e^{-\kappa r} \qquad \text{with} \qquad \kappa = \sqrt{\frac{-2mE}{\hbar^2}}$$

and $f(r)$ satisfying

$$f'' - 2\kappa f' - \left[\frac{l(l+1)}{r^2} + \frac{2mV(r)}{\hbar^2}\right] f = 0$$

for

$$\frac{mV(r)}{\hbar^2} = -\frac{Z}{ar}$$

Next we focus on determining f. Substituting the specific Hydrogen-like potential above, the ode for f reads

$$f'' - 2\kappa f' - \left[\frac{\ell(\ell+1)}{r^2} - \frac{2Z}{ar} \right] f = 0$$

Before expanding in power series, we perform the change of variables

$$r \longrightarrow \rho = \frac{Zr}{a}$$

giving

$$r = \frac{a}{Z}\rho, \quad \rho = \frac{Zr}{a}, \quad \frac{d}{dr} = \frac{Z}{a}\frac{d}{d\rho}, \quad \frac{d^2}{dr^2} = \frac{Z^2}{a^2}\frac{d^2}{d\rho^2}$$

$$dr = \frac{a}{Z}d\rho, \quad d\rho = \frac{Z}{a}dr, \quad \frac{d}{d\rho} = \frac{a}{Z}\frac{d}{dr}, \quad \frac{d^2}{d\rho^2} = \frac{a^2}{Z^2}\frac{d^2}{dr^2}$$

The ode changes then to

$$\left[\frac{Z^2}{a^2}\frac{d^2}{d\rho^2} - \frac{2\kappa Z}{a}\frac{d}{d\rho} - \frac{Z^2\ell(\ell+1)}{a^2\rho^2} + \frac{2Z}{a}\frac{Z}{a\rho} \right] f = 0$$

$$\boxed{\frac{d^2 f}{d\rho^2} - \frac{2\kappa a}{Z}\frac{df}{d\rho} - \frac{\ell(\ell+1)f}{\rho^2} + \frac{2f}{\rho} = 0}$$

In order to solve the previous ode we expand $f(r(\rho))$ in powers of ρ:

$$f(\rho) = \sum_{k=0}^{\infty} a_k \rho^{k+c} \quad , \text{ with } \quad a_0 \neq 0 .$$

See that c denotes the first non null power to appear:

$$f(\rho) = a_0 \rho^c + a_1 \rho^{c+1} + a_2 \rho^{c+2} + \cdots$$

Taking derivatives we have

$$\begin{cases} f = \sum_{k=0}^{\infty} a_k \rho^{k+c} \\ \dfrac{df}{d\rho} = \sum_{k=0}^{\infty} (k+c) a_k \rho^{k+c-1} \\ \dfrac{d^2 f}{d\rho^2} = \sum_{k=0}^{\infty} (k+c)(k+c-1) a_k \rho^{k+c-2} \end{cases}$$

Substituting into the previous ode

$$\sum_{k=0}^{\infty} (k+c)(k+c-1) a_k \rho^{k+c-2} - \frac{2aK}{Z} \sum_{k=0}^{\infty} (k+c) a_k \rho^{k+c-1} +$$

$$- \ell(\ell+1) \sum_{k=0}^{\infty} a_k \rho^{k+c-2} + 2 \sum_{k=0}^{\infty} a_k \rho^{k+c-1} = 0$$

i.e.,

$$\sum_{k=0}^{\infty} \left\{ \left[(k+c)(k+c-1) - \ell(\ell+1) \right] a_k \rho^{k+c-2} + 2 \left[1 - \frac{aK}{Z}(k+c) \right] a_k \rho^{k+c-1} \right\} = 0$$

By noting that

$$(k+c)(k+c-1)-l(l+1) = (k+c)(k+c)-(k+c)-l^2-l$$

$$= (k+c)(k+c)-(k+c+l)-l^2$$

$$= (k+c+l)(k+c)-(k+c+l)-l^2-l(k+c)$$

$$= (k+c+l)(k+c)-(k+c+l)-l(k+c+l)$$

$$= (k+c+l)(k+c-1-l)$$

we rewrite

$$\sum_{k=0}^{\infty}\left\{(k+c+l)(k+c-1-l)a_k\rho^{k+c-2}+2\left[1-\frac{a_H}{Z}(k+c)\right]a_k\rho^{k+c-1}\right\}=0$$

In the second sum we may change variables $k \to k-1$, while in the first one we may split into two terms, one for $k=0$ and the other for $k>0$. This leads to

$$(c+l)(c-l-1)a_0\rho^{c-2} +$$

$$+\sum_{k=1}^{\infty}\left[(k+c+l)(k+c-1-l)a_k+2\left[1-\frac{a_K}{Z}(k+c-1)\right]a_{k-1}\right]\rho^{k+c-2}$$

$$=0$$

The first coefficient, of the power ρ^{c-2}, leads to

$$((c+l)(c-l-1)=0 \Longrightarrow \begin{cases} c=-l \\ \text{or} \\ c=l+1 \end{cases}$$

Recall that ℓ is a natural number, $\ell = 0, 1, 2, \ldots$, and that

$$R(r) = \frac{f(r)}{r} e^{-\kappa r}, \qquad \rho = \frac{2r}{a}$$

The radial integration goes like

$$\int_0^\infty |R|^2 r^2 dr = \int_0^\infty |Rr|^2 dr$$

For convergence, in the limit $r \to 0$, $|Rr|^2 = |f|^2$ must remain finite. From

$$f = a_0 \rho^c + a_1 \rho^{c+1} + \ldots$$

we must have then

$$\boxed{c = \ell + 1}$$

(The case $c = -\ell = 0$ leads to the absurd $a_0 = 0$)

Substituting $c = \ell + 1$, we achieve the recurrence relation

$$(k + c + \ell)(k + c - 1 - \ell) a_k = 2\left[\frac{a\kappa}{Z}(k + c - 1) - 1\right] a_{k-1}$$

$$\boxed{k(k + 2\ell + 1) a_k = 2\left[\frac{a\kappa}{Z}(k + \ell) - 1\right] a_{k-1}, \quad k = 1, 2, 3, \ldots}$$

In order to have normalizability, this series must finish. In fact recall

$$rR(r) = f(r)\, e^{-\kappa r}$$

$$= \left[a_0 \rho^{c} + a_1 \rho^{c+1} + a_2 \rho^{c+2} + \dots \right] e^{-\kappa r}$$

$$= \left[a_0 \rho^{\ell+1} + a_1 \rho^{\ell+2} + a_2 \rho^{\ell+3} + \dots \right] e^{-\kappa r}$$

and this diverges for large r unless the series inside the brackets has a finite number of non null terms. Therefore, given ℓ, there must be a minimum natural $\bar{k}$ such that

$$a_{\bar{k}} = 0 \qquad \text{and} \qquad \begin{cases} k > \bar{k} \Rightarrow a_k = 0 \\ k < \bar{k} \Rightarrow a_k \neq 0 \end{cases}$$

From the recurrence relation:

$$(\bar{k} + 2\ell + 1)\,\bar{k}\, a_{\bar{k}} = 2 \left[\frac{a\kappa}{Z} (\bar{k} + \ell) - 1 \right] a_{\bar{k}-1}$$

$$0 = 2 \left[\frac{a\kappa}{Z} (\bar{k} + \ell) - 1 \right] a_{\bar{k}-1}$$

$$\therefore \quad \frac{a\kappa}{Z} (\bar{k} + \ell) - 1 = 0 \quad \therefore \quad \bar{k} + \ell = \frac{Z}{a\kappa}$$

Since $\ell = 0, 1, 2, \dots$ and $\bar{k} \in \mathbb{N}^*$, we have

$$m \equiv \bar{k} + \ell = 1, 2, 3, \dots$$

By definition, the positive integer n is called the <u>principal quantum number</u>. This finally leads to energy quantization:

$$n = \bar{k} + l = \frac{Z}{a\kappa} \Rightarrow \boxed{\kappa = \frac{Z}{na}} \Rightarrow \kappa^2 = \frac{Z^2}{n^2 a^2}$$

$$\Rightarrow \quad -\frac{2mE}{\hbar^2} = \frac{Z^2}{n^2 a^2}$$

$$\Rightarrow \boxed{E_n = -\frac{Z^2 \hbar^2}{2ma^2 n^2}}$$

Recalling the Bohr radius

$$a = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \Rightarrow a^2 = \frac{16\pi^2\epsilon_0^2\hbar^4}{m^2e^4}$$

we can rewrite

$$E_n = -\frac{Z^2\hbar^2}{2mn^2} \cdot \frac{m^2e^4}{16\pi^2\epsilon_0^2\hbar^4} = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} \quad //$$

or else

$$E_n = -\frac{Z^2\cancel{\hbar^2}}{2\cancel{m}an^2} \cdot \frac{\cancel{m}e^2}{4\pi\epsilon_0\cancel{\hbar^2}} = -\frac{Z^2e^2}{8\pi\epsilon_0 a n^2}$$

This finishes the proposition of page 56 $\longrightarrow$ $\boxed{E_n = -\frac{1}{2}\left(\frac{Z^2e^2}{4\pi\epsilon_0 a}\right)\cdot\frac{1}{n^2}}$

The radial solutions are indexed by $n = \bar{k} + l$ and l.

$n = 1$, $\bar{k} = 1$, $\boxed{a_1 = 0}$ $l = 0$, $c = l+1 = 1$, $\boxed{f(r) = a_0 \rho e^{-kr}}$

$$f_{10} = a_0 \rho e^{-kr} = a_0 \frac{Zr}{a} e^{-kr}$$

$$R(r) = \frac{f(r)}{r} e^{-kr}$$

$$R_{10}(r) = a_0 \frac{\cancel{Z}}{a} e^{-kr}$$

$$R_{10}(r) = C e^{-kr}$$

$$\int |R_{10}(r)|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi = 1$$

$$\left[\int_0^\infty |C e^{-kr}|^2 r^2 dr\right] \underbrace{\left[\underbrace{\int_0^\pi \sin\theta \, d\theta}_{2} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}\right]}_{4\pi} = 1$$

$$|C|^2 \int_0^\infty e^{-2kr} r^2 dr = \frac{1}{4\pi}$$

$$\int_0^\infty e^{-2\kappa r} r^2 dr = \frac{1}{4}\frac{d^2}{d\kappa^2}\underbrace{\int_0^\infty e^{-2\kappa r} dr}_{\left.\frac{-e^{-2\kappa r}}{2\kappa}\right|_0^\infty}$$

$$= \frac{1}{4}\frac{d^2}{d\kappa^2}\left[\frac{1}{2\kappa}\right] = \frac{1}{8}\left(\frac{d}{d\kappa}\left(-\frac{1}{\kappa^2}\right)\right)$$

$$= \frac{1}{4}\cdot\frac{1}{\kappa^3} = \frac{1}{4\kappa^3}$$

$$|c|^2 \cdot \frac{1}{4\kappa^3} = \frac{1}{4\pi} \Rightarrow \boxed{|c|^2 = \frac{\kappa^3}{\pi}}$$

From $\kappa = \frac{Z}{na}$ and $n=1$, i.e., $\kappa = \frac{Z}{a}$, we

get

$$|c|^2 = \frac{Z^3}{a^3\pi} \quad \text{and choose} \quad c = \sqrt{\frac{Z^3}{a^3\pi}}$$

$$R_{10}(r) = \sqrt{\frac{Z^3}{a^3\pi}}\, e^{-\frac{Z}{a}r}$$

$$\psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{a^3\pi}}\, e^{-\frac{Zr}{a}}\underbrace{Y_0^0(\theta,\phi)}_{1}$$

<u>Exercise</u>: Write the nonormalized wave functions for the states corresponding to $n = 2$.

<u>theorem</u>: The energy levels E_n for the hydrogen-like atom has degeneracy n^2.

<u>pre-proof</u>:

Note that we have the following possibilities:

$n = \bar{k} + l$

n	$\bar{k}$	l	m	
1	1	0	0	1
2	1	1	-1, 1, 1	4
2	2	0	0	
3	1	2	-2, ~~-1~~, 0, 1, 2	9
3	2	1	-1, 0, 1	
3	3	0	0	
4	1	3	-3, -2, -1, 0, 1, 2, 3	16
4	2	2	-2, -1, 0, 1, 2	
4	3	1	-1, 0, 1	
4	4	0	0	

proof:

The space of spherical harmonics of degree l has dimension $2l+1$. For each natural n, l can take the values $0, 1, \dots, n-1$ (because $n = \bar{k} + l$, $\bar{k} \in \mathbb{N}^*$). Thus, given n the total number of linear ind. functions which characterize the same energy E_n is

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

$$= \sum_{l=1}^{n} l^2 - \sum_{l=0}^{n-1} l^2$$

$$= n^2 + \sum_{l=1}^{n-1} l^2 - \sum_{l=1}^{n-1} l^2 = n^2 \;//$$

or else

$$\sum_{l=0}^{n-1} (2l+1) = 2 \sum_{l=0}^{n-1} l + \underbrace{\sum_{l=0}^{n-1} 1}_{n}$$

$$= 2 \frac{(n-1)n}{2} + n = n^2 - n + n = n^2 \;//$$

Summarizing, we have shown that the energy levels of the Hydrogen atom are given by

$$E_n = -\left(\frac{Z^2 e^2}{8\pi\epsilon_0 a}\right)\cdot\frac{1}{n^2}, \qquad n = 1, 2, 3, \ldots$$

and each level n has energy degenerescence of n^2. That means for each natural n we have n^2 independent eigenfunctions spaning a n^2 dimensional eigensubspace. For each n, the corresponding eigenfunctions are given by products of spherical harmonics $Y_\ell^m(\theta, \phi)$ with r^ℓ times a Laguerre polynomial $L_n^\ell\left(\frac{Zr}{a}\right)$ (a polynomial of degree $n-\ell$). More explicitly, as stated in page 56, the eigenfunctions for $n \in \mathbb{N}^*$ are

$$\psi_{n\ell,m}(r,\theta,\phi) = C\, r^\ell L_n^\ell\left(\frac{Zr}{a}\right) e^{-\frac{Zr}{na}}\, Y_\ell^m(\theta,\phi)$$

with

$$\ell = 0, 1, 2, \ldots, n-1$$

and

$$m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell.$$

Note that n, ℓ are natural numbers, $n \neq 0$ and m is an integer. We shall later see that ℓ refers to angular momentum.