Introduction to Quantum Mechanics

Haoyu Zhen

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1 The Wave Function

What we are looking for is the **wave function $\boldsymbol{\Psi}$**.

Law 1.1 (Schrodinger Equation).

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

For simplicity, we always rewrite it as:

$$i\hbar\partial_t\Psi = -\frac{\hbar^2}{2m}\partial_x^2\Psi + V\Psi.$$

Born's statistical interpretation:

$$\int_a^b |\Psi(x,t)|^2 \,\mathrm{d}x = \text{probability of finding the particle between } a \text{ and } b \text{ at time } t.$$

Law 1.2 (Normalization).

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \,\mathrm{d}x = 1.$$

Proposition 1.1. The wave function will always stay NORMALIZED.

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \,\mathrm{d}x = 0.$$

Proof. By Schrodinger EQ.,

$$\text{LHS} = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\Bigg|_{-\infty}^{+\infty}.$$

□

Definition 1.1.

$$\langle x\rangle \xlongequal{def} \int_{-\infty}^{\infty} x|\Psi|^2 \,\mathrm{d}x$$

and

$$\langle p\rangle \xlongequal{def} m\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t}.$$

Theorem 1.1.

$$\langle x\rangle = \int \Psi^*(x)\Psi \,\mathrm{d}x$$

and

$$\langle p\rangle = \int \Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi \,\mathrm{d}x.$$

Remark 1.1 (Operator)**.** We say that the operator x represents position, and the operator $-i\hbar\,\partial/\partial x$ represents momentum. Also,

$$\langle Q(x,p)\rangle = \int_{-\infty}^{\infty} \Psi^* \left[Q(x, -i\hbar \frac{\partial}{\partial x}) \right] \Psi \,\mathrm{d}x.$$

Property 1.1. Operators do **NOT**, in general, commute. For example, $\hat{x}\hat{p} \neq \hat{p}\hat{x}$, i.e.,

$$\exists \text{ a function } f, \text{ s.t. } (\hat{x}\hat{p})f \neq (\hat{p}\hat{x})f.$$

Theorem 1.2 (de Broglie formula)**.** The wave length is related to the momentum of the particle:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}.$$

Theorem 1.3 (Heisenberg's uncertainty principle)**.**

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}.$$

2 Time-independent Schrodinger Equation

2.1 Stationary states

We look for solutions that are simple products,

$$\Psi(x,t) = \psi(x)\varphi(t).$$

Theorem 2.1. By the method of separation of variables,

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

and

$$\varphi(t) = e^{-iEt/\hbar}.$$

The first is called the **time-independent Schrodinger equation**.

Definition 2.1 (Hamiltonian)**.** In classical mechanics, the total energy (kinetic plus potential) is called Hamiltonian:

$$H(x,p) = \frac{p^2}{2m} + V(x).$$

Now we introduce **Hamiltonian operator**:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

Thus the time-independent Schrodinger EQ. can be written

$$\hat{H}\psi = E\psi$$

which is **IMPORTANT**.

Remark 2.1. Intriguingly and intuitively,

$$\langle H \rangle = E.$$

Also, if the equation yields an infinite collection of solutions $(\psi_1(x), \psi_2(x), \cdots)$, each with its associated value of the separation constant $(E1, E2, \cdots)$; thus the wave function is:

$$\Psi(x,t) = \sum_{n=1}^{+\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}.$$

Particularly,

$$E_n \geq 0 \text{ for all } n$$

2.2 The infinite square well

Suppose

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases}.$$

Theorem 2.2. Inside the well, we have

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

and

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right).$$

Property 2.1. $\psi_n(x)$ has some interesting and important porperties:

1. They are alternately even and odd, with the respect to the center of the well.
2. They are mutually orthogonal (i.e., $\int \psi_m(x)^* \psi_n(x) \, \mathrm{d}x = \delta_{mn}$) where δ_{mn} is **Kronecker delta**:

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n \\ 1, & \text{if } m = n \end{cases}.$$

3. They are complete by Dirichlet's theorem.

2.3 The harmonic oscillator

Let

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

Here I will introduce 2 entirely different approaches to this problem. The first is a diabolically clever algebraic technique and the second is a straitforward "brute force" solution.

2.3.1 Algebraic method

To begin with, let's rewrite the EQ. in a more suggestive form:

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

The idea is to factor the term in square brackets:

$$u^2+v^2=(u-iv)(u+iv).$$

Definition 2.2 (Ladder operator).

$$\hat{a}_\pm=\frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p}+m\omega x).$$

Definition 2.3 (Commutator). The commutator of operators $\hat{A}$ and $\hat{B}$ is

$$\left[\hat{A},\hat{B}\right]\xlongequal{def}\hat{A}\hat{B}-\hat{B}\hat{A}.$$

Property 2.2.

$$[\hat{a}_-,\hat{a}_+]=1.$$

Theorem 2.3. If ψ satisfies the Schrodinger's EQ. with energy E, then $\hat{a}_+\psi$ satisfies the Schrodinger's EQ. with energy $E+\hbar\omega$:

$$\hat{H}\psi=E\psi\Longrightarrow\hat{H}(\hat{a}_+\psi)=(E+\hbar\omega)(\hat{a}_+\psi).$$

Similarly,

$$\hat{H}\psi=E\psi\Longrightarrow\hat{H}(\hat{a}_-\psi)=(E-\hbar\omega)(\hat{a}_-\psi).$$

Proof.

$$\hat{H}=a_+a_-+\frac{1}{2}\hbar\omega.$$

□

Here, then, is a wonderful machine for generating new solutions—if we could just find one solution. Thus, we call $\hat{a}_+$ raising operator and $\hat{a}_-$ lowering operator.
But what if I apply the lowering operator **repeatly**? We will reach a state with energy less than zero. By 2.1, there is **NO** guarantee that it will be normalized.

Proposition 2.1. Thus, there occurs a "lowest rung" ψ_0 such that

$$\hat{a}_-\psi_0=0.$$

Theorem 2.4.

$$\psi_0(x) = A_0 e^{-m\omega/2\hbar\, x^2}$$

and

$$E_0 = \frac{1}{2}\hbar\omega.$$

Thus we could get

$$\psi_n(x) = A_n (a_+)^n e^{-m\omega/2\hbar\, x^2}, \text{ with } E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

where A_n are used for normalization.

Theorem 2.5. ψ_n and ψ_{n+1} should satisfy:

$$\begin{cases} a_+\psi_n = i\sqrt{(n+1)\hbar\omega} \\ a_-\psi_n = -i\sqrt{n\hbar\omega}\psi_{n-1} \end{cases}.$$

Proof.

$$\int_{-\infty}^{\infty} |a_+\psi_n|^2 \,\mathrm{d}x = (n+1)\hbar\omega$$

and

$$\int_{-\infty}^{\infty} |a_-\psi_n|^2 \,\mathrm{d}x = n\hbar\omega.$$

□

Ultimately,

$$A_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{(-i)^n}{\sqrt{n!(\hbar\omega)^n}}.$$

2.3.2 Analytic method

Things look a little cleaner if we introduce the dimensionless variables

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x \text{ and } K = \frac{2E}{\hbar\omega}.$$

In terms of ξ and K, the Schrodinger equation reads

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = (\xi^2 - K)\psi.$$

To begin with, consider that at very large ξ, ξ^2 completely dominates over the constant K, so in this regime $\mathrm{d}^2\psi/\mathrm{d}\xi^2 = \xi^2\psi$, which means that $\psi \Longrightarrow Ae^{\xi^2/2} + Be^{-\xi^2/2}$. Thus we let $\psi = h(\xi)e^{-\xi^2/2}$. Plugging ψ into Schordinger EQ., we have

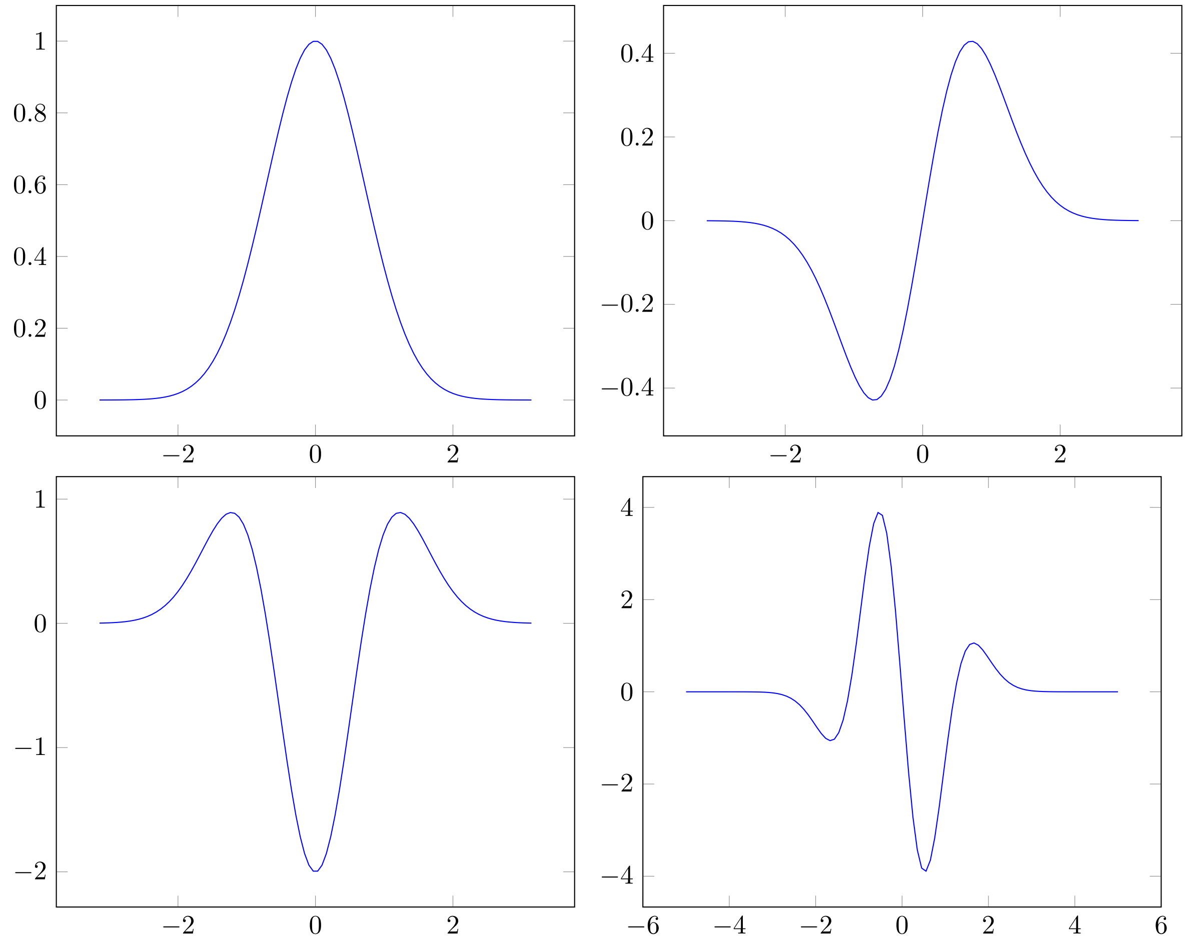
$$h(\xi) = \sum_{n=0}^{\infty} a_n \xi^n \text{ and } a_{n+2} = \frac{2n+1-K}{(n+1)(n+2)}.$$

For physically acceptable solutions (normalizable solutions), then, we must have $K = 2n+1$. Finally,

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

where H_n is the **Hermite polynomials**.

The first four stationary states of the harmonic oscillator are as follows.



2.4 The Free Particle

We turn next to what should have been the simplest case of all: the free particle. The time Schrodinger Eq. reads:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi.$$

Let $k \equiv \sqrt{2mE/\hbar}$, we have

$$\Psi_k(x,t) = Ae^{i(kx - \hbar k^2 t/2m)}.$$

Remark 2.2. The speed of these waves is:

$$v_{\text{quantum}} = \sqrt{E/2m} = 0.5 v_{\text{classical}}$$

And

$$\int_{-\infty}^{\infty} \Psi_k^*(x,t)\Psi_k(x,t)\,\mathrm{d}x = +\infty,$$

which means that a free particle cannot exist in a stationart state.

Theorem 2.6. The general solution to the time-independent Schrodinger EQ. is still a linear combination of separable solutions:

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\hbar k^2t/2m)}\,\mathrm{d}k.$$

Now this wave function can be normalized for appropriated $\phi(k)$. We call it a **wave packet**.

Definition 2.4 (phase velocity and group velocity)**.** For the wave function:

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\omega t)}\,\mathrm{d}k.$$

We define:

$$v_{\text{phase}}=\frac{\omega}{k},\ v_{\text{group}}=\frac{\mathrm{d}\omega}{\mathrm{d}k}.$$

3 Formalism

3.1 Gerneralized Statistical Interpretation

First we assume the spectrum of the wave funtion is discrete, we have

$$\langle Q\rangle=\sum_{n'}\sum_{n}c_{n'}^*c_nq_n\left\langle f_{n'}|f_n\right\rangle=\sum_n|c_n|^2q_n$$

where q_n is the eigenvalue of operator $\hat{Q}$ and $\Psi(x,t)=\sum_n c_n(t)f_n(x)$. What about momentum?

$$\Phi(p,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}e^{-ipx/\hbar}\,\Psi(x,t)\,\mathrm{d}x$$

and

$$\Phi(x,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}e^{-ipx/\hbar}\,\Phi(p,t)\,\mathrm{d}p.$$

3.2 Uncertainty Principle

Theorem 3.1 (generalized uncertainty principle)**.**

$$\sigma_A^2\sigma_B^2\geq\left(\frac{1}{2i}\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right)^2.$$

How to interpret Δt?

Definition 3.1.

$$\Delta t\equiv\frac{\sigma_Q}{|\mathrm{d}\langle Q\rangle/\mathrm{d}t|},$$

where

$$\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t}=\frac{i}{\hbar}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle+\left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle.$$

I recommend you to learn **Hilbert space** and **Dirac notation**.

4 Quantum Mechanics in Three Dimensions

4.1 The schrodinger Equation

The generalization oto three dimensions is straitforward.

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

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

is the **Laplacian**. Also the normalization conditions reads $\int \Psi \mathrm{d}^3\boldsymbol{r} = 1$. If V is independent of time, there will be a complete set of stationary states

$$\Psi_n(\boldsymbol{r}, t) = \psi_n(\boldsymbol{r})e^{-iE_n t/\hbar}.$$

Now we adopt spherical coordinates

Lemma 4.1 (Laplacian in spherical coordinates)**.**

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

If $\Psi = R(r)Y(\theta,\phi)$ and $Y = \Theta(\theta)\Phi(\phi)$, we could separate r, θ and ϕ into three equations with important *separation constants.*

4.1.1 The angular Equation

The ϕ equation is easy

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m^2\Phi \implies \Phi = e^{im\phi}.$$

When ϕ advances by 2π, we return to the same point in space, so it is natural to require that $\Phi(\phi+2\pi) = \Phi(\phi)$. From this it follows that m must be an integer:

$$m = 0, \pm 1, \pm, 2, \cdots.$$

The θ equation reads

$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \Big[l(l+1)\sin^2\theta - m^2\Big]\Theta = 0.$$

Lemma 4.2 (Legendre function)**.** The solution of Θ is

$$\Theta(\theta) = AP_l^m(\cos\theta).$$

where

$$P_l^m(x) \triangleq (-1)^m(1-x^2)^{m/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^m P_l(x)$$

is the **associated Legendre function**, defined by the **Rodrigues formula**

$$P_l(x) \triangleq \frac{1}{2^l l!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^l (x^2-1)^l.$$

Remark 4.1. Notice that l must be a non-negative integer, for Rodrigues formula to make sense; moreover, if $m > l$, we cwill have $P_l^m(x) = 0$. For any given l, then there are $2l+1$ possible values of m:

$$l = 0, 1, 2\cdots \quad \text{and} \quad m = -l,\, -l+1, \cdots, l-1,\, l.$$

By normalization condition

$$\int_0^\pi \int_0^{2\pi} |Y|^2 \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi = 1,$$

we deduce that

$$Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} e^{im\phi} P_l^m(\cos\theta) \tag{4.1}$$

4.1.2 The Radial Equation

Theorem 4.1 (Radial equation)**.**

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

where $u(r) \equiv rR(r)$.

Remark 4.2 (Effective potential)**.**

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

and the latter term is the so-called **centrifugal potential**.

4.2 The Hydrogen Atom

The radical equation says:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu.$$

To tidy up the notation, let

$$\kappa = \frac{\sqrt{-2mE_e}}{\hbar}, \quad \rho = \kappa r \quad \text{and} \quad \rho_0 = \frac{m_e e^2}{2\pi\varepsilon_0\hbar^2\kappa}$$

so that

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

Intuitively, ($\mathrm{d}^2u/\mathrm{d}\rho^2 = u$ when $\rho \to +\infty$ and $\mathrm{d}^2u/\mathrm{d}\rho^2 = ul(l+1)/\rho^2$ when $\rho \to_0$)

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

Now we assume the solution, $v(\rho)$, can be expressed as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{+\infty} c_j \rho^j.$$

Plugin it into the radical equation

$$c_{j+1} = \left\{\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right\}c_j.$$

Theorem 4.2. The series must terminate. I.e., $\exists N \in \mathbb{N}$, $c_N = 0$, which means

$$2(N+l) - \rho_0 = 0.$$

Proof. For large j, the recursion formula says

$$c_{j+1} \approx \frac{2}{j+1} c_j \implies c_{j+1} \approx \frac{2^j}{j!} c_0.$$

Then

$$v(\rho) = c_0 e^{2\rho} \quad \text{and} \quad u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

which could not be **NORMALIZED**. □

Theorem 4.3 (Bohr Formula & Radius).

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right] \quad \text{and} \quad a = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}.$$

Finally, we obtain the spactial wave functions

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

where $R_{nl}(r) = r^{-1}\rho^{l+1}e^{-\rho}v(\rho)$ and $Y_l^m(\theta,\phi)$ is defined by Eq 4.1.

Remark 4.3 (Laguerre Polynomials).

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

where

$$L_q^p(x) \triangleq (-1)^p \left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^p L_{p+q}(x)$$

is an associated Lguerre polynomial, and

$$L_q(x) \triangleq \frac{e^x}{q!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^q (e^{-x}x^q)$$

is the q^{th} Laguerre polynomial. **"Brutally"**,

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/na}\left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na)\right] Y_l^m(\theta,\phi).$$

Definition 4.1 (Quantum Numbers). Intuitively,

- n is the **principal quantum number**; it tells you the energy of electron.
- l is called **azimuthal quantum number** and m the **megnetic quantum number**; they are related to the angular momentum of the electron.

4.3 Angular Momentum