

Personal Notes on

# Quantum Mechanics

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# 1 Quantum Mechanics

## 1.1 Schrodinger equation

Schrodinger Equation:

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

**Definition:** The average value of  $j$  or the expectation value:

$$\langle j \rangle = \frac{\sum j N(j)}{N} = \sum j j P(j)$$

for a continuous distribution we use probability density  $\rho(x)$  so the probability of a particle between  $a$  and  $b$  is:

$$\int_b^a \rho(x) dx$$

here are a few equations to take note of:

- Expected Position:

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\psi(x, t)|^2 dx$$

- Expected momentum:

$$\langle p \rangle = \int_{-\infty}^{+\infty} -i\hbar (\psi^* \frac{\partial \psi}{\partial x}) dx$$

a few important things i learned:

- if LHS is dependent on  $t$  and RHS dependent on  $x$ , the only possibility is that both sides are constant.
- if we want an operator just sub in the form of the  $p$  - momentum
- $c_n$  is the probability of measurement of the energy would return the value  $E_n$

The Schrodinger equation can be solved by **seperation of variables**

$$\Psi(x, t) = \psi(x)\phi(t)$$

and by separating variables we got :

$$E = i\hbar \frac{\partial \phi}{\partial t}$$

in other words:

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

There are 3 reasons to use separable solutions:

- Stationary States:

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

where the wavefunction does not depend on time:

$$|\Psi(x, t)|^2 = |\psi(x)|^2$$

- States of Defined energy: Where the total Hamiltonian of the system is a constant:

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

where the hamiltonian operator is:

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

The time independent Schrodinger equation is:

$$\hat{H}\psi(x) = E\psi(x)$$

where the variance of H is 0 aka all the measurements should return the same energy E.

- General Solution is linear combination of separable solutions: A collection of solutions( $\psi_1(x), \psi_2(x), \psi_3(x)$ ) can be combined to form a general solution: each with a defined separation constant( $E_1, E_2, E_3$ ) thus there is a different wave function for each allowed energy.

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$$

and every time dependent solution can be written in this form.

To solve schrodinger equation, with a given potential V and  $\Psi(x, 0)$  we can always fit the  $t = 0$  state by:

$$\Psi(x, 0) = \sum_n c_n \psi_n(x)$$

with an appropriate choice of  $c_n$  we can always fit the initial state.

and  $|c_n|^2$  is the probability of measurement of the energy would return the value  $E_n$  and the sum should be equivalent to 1. With the expectation hamiltonian being:

$$\langle H \rangle = \sum_n |c_n|^2 E_n$$

### 1.1.1 Infinite Square Well

suppose we need a boundary condition for the wave function to be 0 at the boundaries of the well.

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

and the equation of time-independent schrodinger equation is:

$$-\frac{h^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

which is a simple harmonic oscillator equation. and the solution is:

$$\psi(x) = A \sin(kx)$$

where k is the wave number:  $k = \frac{\sqrt{2mE}}{\hbar}$  since the boundary condition requires the wave function to be 0 at the boundaries. So ka must be a multiple of  $\pi$ : By subbing the new equation into the original time-independent schrodinger equation, the possible values of E in each mode is:

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

and the solutions is:

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

$\psi_1$  is called ground state and states with energies increase in proportion to  $n^2$  is called excited States.

and here are a few interesting properties:

- They are alternately even and odd.

- each successive state has one more node.
- They are mutually orthogonal such that:

$$\int \psi_m(x)^* \psi_n(x) dx = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases}$$

- They are complete, such that any other function  $f(x)$  can be expressed as a linear combination of them.

To find  $c_n$  we can use fourier trick: let

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

to find the probability factor for one state -m - is:

$$c_m = \int \psi_m^*(x) \psi(x) dx$$

in addition, the stationary states are:

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

Therefore, the coefficient is:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0) dx$$

### 1.1.2 Harmonic Oscillator

Any simple harmonic oscillator can be approximated as:

$$V(x) = \frac{1}{2} V''(x_0)(x - x_0)^2$$

and for quantum problem we can further simplify it into:

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

and sub it into the time independent schrodinger equation:

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

and there are two solutions

- power series method
- Ladder operators method

Algebraic Method: Ladder Method we can rewrite time independent schrodinger equation into this form:

$$\frac{1}{2m} (\hat{p}^2 + m^2 \omega^2 \hat{x}^2) \psi = E \psi$$

and the basic idea is to factor the hamiltonian. here we have the famous **ladder operator**

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

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

and the relationship between hamiltonian is:

$$\hat{a}_- \hat{a}_+ = \frac{1}{\hbar\omega} \hat{H} + \frac{1}{2}$$

if we reverse the order of multiplication in the left hand side, the sign of that one have reverses. aka the **commutator** of the two operators is:

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

by subbing the new hamiltonian equation into the solution we obtain:

$$h\omega(\hat{a}_+\hat{a}_- + \frac{1}{2})\psi = E\psi$$

**Definition:** If  $\psi$  satisfies the schrodinger equation with energy  $E$ , then  $\hat{a}_+\psi$  also satisfies the schrodinger equation with energy  $E + h\omega$

$$\hat{H}(\hat{a}_+\psi) = (E + h\omega)(\hat{a}_+\psi)$$

**Idea:** HOWEVER, it is not guaranteed that the new solution is normalize.

In practice, there is a lowest rung such that

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

so

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$$

Therefore a generalized expression for the solutions of the Harmonic Oscillator is:

$$\psi_n(x) = A_n(\hat{a}_+)^n \psi_0(x) \quad \text{with} \quad E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (1)$$

The relationship between  $n$  and  $n+1$  stage is

$$\hat{a}_+ \psi_n = \sqrt{n+1} \psi_{n+1} \quad , \quad \hat{a}_- \psi_n = \sqrt{n} \psi_{n-1} \quad (2)$$

Therefore, we can conclude that the expression for arbitrary mode is

$$\psi_n = \frac{1}{\sqrt{n!}} (\hat{a}_+)^n \psi_0 \quad (3)$$

Yet in this harmonic oscillator the stationary states are still Orthogonal.

### 1.1.3 Hermite Polynomials

The time independent solution for Schrodinger Equation can be expressed as

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}, \quad (4)$$

where as the  $h(\xi)$  can be seek in the form of power series

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j\xi^j.$$

and

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)} a_j.$$

For the equation to be normalizable, the power series must terminate somewhere, this indicate that  $a_{n+2} = 0$  which indicates that either the even or the odd terms must be zero from the start. This also indicates that  $K = 2n + 1$ , and the solution for the harmonic oscillator are

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

### 1.1.4 The Free Particle

The free particle should have been the simplest case ( $V(x) = 0$  everywhere). It is just a motion at constant velocity. However it is kinda subtle. For the simplified Schrodinger Equation:

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

The solution is simply a general solution for a second order ODE:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}$$

Taking on the standard time dependent exponential term, the general solution for the time dependent free partial equation becomes:

$$\Psi(x, t) = Ae^{ik(x - \frac{\hbar k}{2m}t)} + Be^{-ik(x + \frac{\hbar k}{2m}t)}$$

Where the first term is a wave packet traveling to the right, and the second term is to the left. Since they are only differ by the the sign of  $k$ , we might as well write the equation in

$$\Psi_k(x, t) = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}, \quad (5)$$

essentially if  $k$  is larger than 0 it is traveling to the right and vice versa. Therefore, the stationary states of these are simply free particles of propagating waves, they carry momentum

$$p = \hbar k$$

with a velocity of

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

Yet as soon as we realized, this equation is not normalizable. In fact, *There is no such thing as a free particle with a definite energy.* Yet, it is still separable, but this time it is a continuous equation.

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} dk. \quad (6)$$

the  $\frac{1}{\sqrt{2\pi}}\phi(k)$  is essentially  $c_n$  and now this equation is normalizable with a appropriate  $\phi(k)$ . Now everything that is left is how to determine  $\phi(k)$ , which is something fourier transform can handle.

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} dk \iff F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx. \quad (7)$$

Therefore,

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x, 0) e^{-ikx} dx. \quad (8)$$

Note that for small  $a$   $\Psi(x, 0)$  is narrow while  $\phi(k)$  is broad and vice versa for large  $a$ . Physically, this is because forming a narrower wave requires more waves to superimpose, and mathematically we can explain by the uncertainty principles since  $k$  is directly related to momentum.

Now we shift our focus to deducing why the group velocity of the wave packet (quantum velocity) is twice of the phase velocity (particle velocity). By taking a fourier transform and taylor expand the function  $\omega(k)$  we can obtain the relationships

$$v_{phase} = \frac{\omega}{k}$$

and the group velocity is

$$v_{group} = \frac{d\omega}{dk}$$

### 1.1.5 Bound States and Scattering States

The free particle and infinite squared well solutions perfectly correspond to the scattering and bound state of a particle. Defined as below.

$$\begin{cases} E < V(-\infty) \text{ and } V(+\infty) \implies \text{bound state,} \\ E > V(-\infty) \text{ or } V(+\infty) \implies \text{scattering state.} \end{cases} \quad (9)$$

Physically, bound state is defined as when  $E$  is smaller than the potential and it cannot escape, whereas the scattering state can be imagined as how an electron getting slowed in a potential field. However, since tunneling exists, so the particle can leak through any finite potential barrier so only thing that matters is the potential at infinity. In real life, most potentials go to zero at infinity.

### 1.1.6 The Delta-Function Well

The essence of this case is to use **Dirac Delta Function** to construct the potential of the system.

$$\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}, \quad \text{with } \int_{-\infty}^{+\infty} \delta(x) dx = 1.$$

Consider a potential of the form

$$V(x) = -\alpha\delta(x)$$

the solution yields 2 possibilities (bound states and scattering states) considering the bound states. In the region  $x < 0$ ,  $V(x) = 0$  so

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi,$$

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}.$$

the solution to this 2nd ODE is what we have learned before

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}$$

since the first term blows up as  $x$  goes to negative infinity, what is left is

$$\psi(x) = Be^{\kappa x}$$

Similar results can be obtained for  $x$  larger than 0

$$\psi(x) = Fe^{-\kappa x}$$

Yet, two important ideas for the wave function is that:

1.  $\psi$  is always continuous;
2.  $\frac{d\psi}{dx}$  is continuous except at points where the potential is infinite.

The trick to find the solution is to integrate the schrodinger equation from  $-\epsilon$  to  $+\epsilon$  and take the limit as  $\epsilon$  goes to 0.

$$\Delta\left(\frac{d\psi}{dx}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0)$$

from the case at hand, we can tell that the first term is  $-2B\kappa$  by taking direct derivative to the solutions we obtained before. Therefore, we can obtain that

$$\kappa = \frac{m\alpha}{\hbar^2}$$

making the allowed energy as

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

We then normalize  $\psi$  yielding one bound state

$$\psi(x) = \sqrt{\frac{m\alpha}{\hbar}} e^{-m\alpha|x|/\hbar^2}, \quad E = -\frac{m\alpha^2}{2\hbar^2}.$$

Now we can discuss about **Scattering States** where  $E > 0$  at  $\infty$  where

$$k = \frac{\sqrt{2mE}}{\hbar}$$

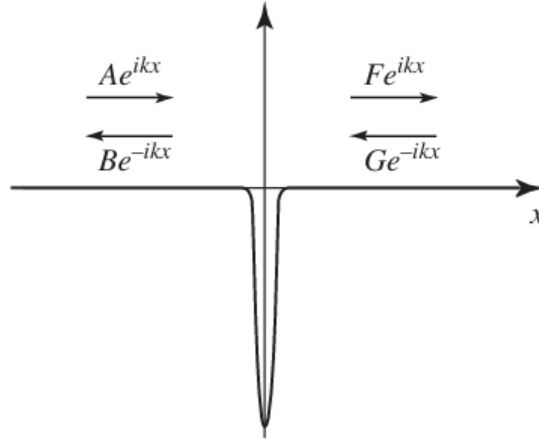
is real and positive, so the general solution is

$$\psi(x) = Fe^{ikx} + Ge^{-ikx} \quad x > 0$$

and

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad x < 0$$

by the continuity equations, we obtain In reality particles are fired from one direction, so  $G = 0$  (since it is coming



from the right)

A is the amplitude of the **incident wave** and B is the amplitude of the **reflected wave**, and F is the amplitude of the transmitted wave. Using similar method as the Bound state, we can obtain

$$B = \frac{i\beta}{1 - i\beta} A, \quad F = \frac{1}{1 - i\beta} A. \quad (10)$$

where  $\beta = \frac{m\alpha}{\hbar^2 k}$  Speaking in the language of probability, the relative probability that an incident particle would reflect is

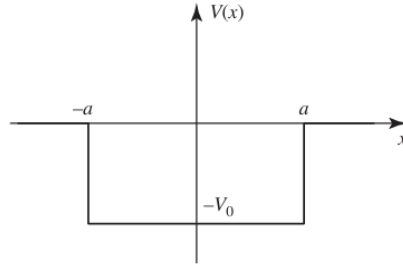
$$R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2} \quad T = \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}$$

so

$$R = \frac{1}{1 + \left(\frac{2\hbar^2 E}{m\alpha^2}\right)}, \quad T = \frac{1}{1 + \left(\frac{m\alpha^2}{2\hbar^2 E}\right)}. \quad (11)$$

- The higher the energy, the greater the probability of transmission
- The only way to obtain a normalizable solution is similar to the free particle solution





## 1.2 Finite Square Well

For a finite square well as shown above we can find three expressions for the solutions. Since the potential is even, so the old theorem says that the bound state solution should be either even or odd. First, the Schrodinger equation looks as below within the well

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi = E\psi \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -l^2\psi \quad (12)$$

where  $l = \frac{\sqrt{2m(E + V_0)}}{\hbar}$  the solutions are

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & x > a, \\ D \cos(lx), & 0 < x < a, \\ \psi(-x), & x < 0. \end{cases}$$

lets first consider the even function. By the continuity of the wave function and the derivative, we find that

$$k = l \tan(la)$$

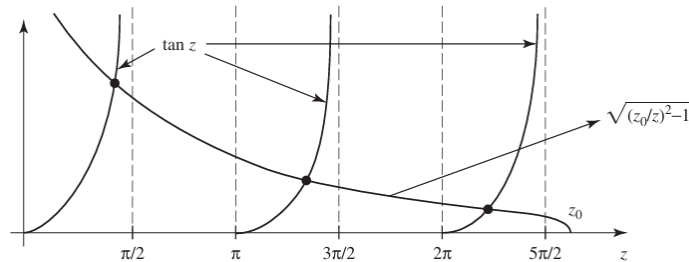
Since k and l are both functions of E, to find E we need some simplification and analytical solutions

$$z = la \quad \text{and} \quad z_0 = \frac{a}{\hbar} \sqrt{2mV_0}$$

and the equation becomes

$$\tan(z) = \sqrt{(z_0/z)^2 - 1}$$

plotting them together we have the following diagram.



There are two major solutions we can draw from this diagram

- **Wide Deep wall:** For large  $z_0$  the intersection goes very close to  $z_n = n\pi/2$  with n odd; which follows that

$$E_n + V_0 = \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} \quad n = 1, 3, 5 \dots$$

- **Shallow Narrow Wall:** as  $z_0$  decreases, there are fewer and fewer bound states, until for  $z_0 < \pi/2$  only one remains. There is always at least one bound state no matter how "weak" the well becomes.

## 2 Quantum Mechanics in Three Dimensions

### 2.1 3D Schrodinger Equation

Schrodinger Equation can be generalized as

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

and the Hamiltonian is obtained by

$$\hat{H} = \frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

In terms of operator languages, the equation then simplifies to

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi} \quad (13)$$

The normalization factor is by volume

$$\int |\Psi|^2 d^3r = 1$$

and if V is independent of time, the time dependent solution is

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

so the time independent Schrodinger Equation is

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi} \quad (14)$$

### 2.2 Two Dimensional Square Box

A simpler case is a two dimensional system such that

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{2M}{\hbar^2} [U - E] \psi$$

considering the potential as a infinite square wall of width x. by separation of variables in X and Y coordinates, we see the solution

$$\begin{aligned} X(x) &= B \sin\left(\frac{n_x \pi x}{a}\right) \\ Y(y) &= C \sin\left(\frac{n_y \pi y}{a}\right) \end{aligned}$$

The complete wave function becomes

$$\psi(x, y) = BC \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right)$$

The allowed energies of the states can be derived by subbing in the derived equations back into the original expression

$$E = E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2Ma^2} (n_x^2 + n_y^2)$$

### Degeneracy

One properties to mention is that there can be several different wave functions for which the particle has the same energy. In general, if there are N independent wave functions all with the same energy E, we say that the energy level E is degenerate and has degeneracy N.

### 2.3 Two-Dimensional Central-Force

In terms of polar Coordinate, the LHS of Schrodinger Equation can be expressed as:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} = \frac{2m}{\hbar^2} (U - E) \psi$$

By separation of variables we can assume a constant  $M$  such that

$$\Phi''(\phi) = -M^2 \Phi(\phi)$$

and

$$R'' + \frac{R'}{r} - \left[ \frac{M^2}{r^2} + \frac{2m}{\hbar^2} (U - E) \right] R = 0$$

Which we can derive that

$$\Phi(\phi) = e^{iM\phi}$$

However, for this function to be periodic we realized that  $m$  must be an integer.

### Angular Momentum

Using the expression we had above, we can draw an analogy by changing the form of the equation above

$$\psi(r, \phi) = R(r) e^{i(M/r)s}$$

where  $k = M/r$  and this gives us the expression for the tangential momentum as

$$p_{tang} = \hbar \frac{M}{r}$$

and the angular momentum is

$$L_z = M\hbar$$

just remember that  $M$  is essentially the wave number/ quantum number of the wave function.

The allowed energy for each  $M$  has multiple energy levels labeled by  $n = 1, 2, 3, 4, \dots$ . Yet, since  $M$  is related to the energy by  $\frac{m^2}{r^2}$  so there is degeneracy except when  $m = 0$

$$E_{n,m} = E_{n,-m}$$

### 2.4 The Three-Dimensional Central-Force Problem

recalled that we need to express Schrodinger's Equation in spherical polar coordinate.

$$x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta$$

which we obtained that

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} = \frac{2m}{\hbar^2} [U(r) - E] \psi \quad (15)$$

By the separation of variable, we can once again obtain the following equations

$$\begin{aligned} \Phi''(\phi) &= -m^2 \Phi(\phi) \\ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( k - \frac{M^2}{\sin^2 \theta} \right) \Theta &= 0 \end{aligned} \quad (16)$$

and

$$\frac{d^2}{dr^2} (rR) = \frac{2m}{\hbar^2} \left[ U(r) + \frac{k\hbar^2}{2Mr^2} - E \right] (rR) \quad (17)$$

where  $k$  is the constant that  $\frac{\Theta''}{\Theta}$  and the other function are equal to.

Note that  $\phi$  and  $\theta$  are not related to the potential energy function, this means that the solutions for these two won't apply to any central-force problem.

Quantum number, $l$ :	0	1	2	3	4	...
Magnitude:	0	$\sqrt{2}\hbar$	$\sqrt{6}\hbar$	$\sqrt{12}\hbar$	$\sqrt{20}\hbar$	...

## 2.5 Quantization of Angular Momentum

the  $k$  term followed the Legendre's Polynomials. Yet we can discuss one of the acceptable solution

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

where  $l$  is a positive integer greater than or equal in magnitude to  $m$ .  $l \geq |m|$  such that the wavefunction is

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)e^{im\phi}$$

In reality, the angular momentum is

$$L = \sqrt{l(l+1)}\hbar$$

for large  $l$  we can approximate that  $L \approx l\hbar$

## 2.6 Hydrogen Atom

- In any central-force problem, a level with  $L = \sqrt{l(l+1)}\hbar$  will always be at least  $(2l+1)$  fold degenerate.

Consider a hydrogen atom having

$$U(r) = \frac{-ke^2}{r}$$

where we can find the equation to the corresponding Schrodinger's Equation must have the allowed energy of the form

$$E = -\frac{m_e(ke^2)^2}{2\hbar^2} \frac{1}{n^2}$$

where  $n$  is any integer greater than 1. The first energy level is the Rydberg Energy 13.6 eV. This yields the Bohr model of energy levels.

## Hydrogenic Wave Functions

Based on the spherical coordinate representation of Schrodinger's Equation, we can find that the ground state with  $n = 1, l = 0, m = 0$  of a hydrogen atom is

$$\psi_{1s}(r, \theta, \phi) = R_{1s}(r)$$

substituting the energy and the potential we have

$$R_{1s}(r) = Ae^{-r/a_B}$$

This represents the probability density of the electron around hydrogen.

- For any state with  $l \neq 0$   $|\psi|^2$  is zero at the origin.

If we find the probability density of finding electron within a finite radial volume around the atom we have

$$P(r) = 4\pi r^2 |R(r)|^2$$

For non-Ground state (2s State) we have  $n = 2$  with  $E = -E_R/4$ , which yields 4 independent wave functions to consider. Speaking of 2s state, it is only  $r$  dependent

$$R_{2s} = A\left(2 - \frac{r}{a_B}\right)e^{-r/2a_B}$$

2p state has three directions to consider in  $x, y$ , and  $z$  directions. The  $z$  direction ( $l = 1$ ) can be written as

$$\psi(r, \theta, \phi) = Aze^{-r/2a_B} \cos(\theta) = Aze^{-r/2a_B}$$

therefore wave functions in other directions are

$$\psi_x = Axe^{-r/2a_B}$$

$$\psi_y = Aye^{-r/2a_B}$$

## Electron Spin

The angular momentum of an electron spin is obtained by

$$S = \sqrt{s(s+1)}\hbar$$

where  $s$  always has a fixed value  $s = \frac{1}{2}$ , and similarly, the possible value of  $S_z$  is

$$S_z = m_s \hbar$$

where  $m_s$  can be either  $\frac{1}{2}$  or  $-\frac{1}{2}$ .

- The energy is independent of electron spin, so a ground state can have 2 degeneracy, and therefore, the degeneracy of  $n$ th level is  $2n^2$

## Magnetic Moments

A few equations to remember are

- Potential Energy:  $U = -\mu \cdot B$
- Gyromagnetic Ratio:  $\mu = -\frac{e}{2m_e}L$
- Zeeman Effect:  $\Delta E = -\mu \cdot B = (\frac{e}{2m_e})L_z B = m\mu_B B$
- Spin Magnetic Moment:  $\mu_{spin} = -\frac{e}{m_e}S = \gamma S$

The total Magnetic Moment is the sum of the orbital magnetic moment and the spin magnetic moment

$$\mu_{tot} = -\frac{e}{2m_e}(L + 2S)$$

## 2.7 Multielectron Atoms

One method is to use IPA(independent-particle approximation) or Central-Field Approximation disregarding the forces from other electrons. Essentially using the potential energy function to solve the Schrodinger Equation and obtain a new set of potential function so called the **Hartree-Fock method** such that as the electron goes outside of other electrons

$$U(r) = -\frac{ke^2}{r}$$

and when the electron is close to nucleus

$$U(r) = -\frac{Zke^2}{r}$$

## 3 Quantum Formalism

### 3.1 Hilbert Space

#### Definition: Hilbert Space

a set of all square integrable functions on a specified interval  $f(x)$  such that

$$\int_a^b |f(x)|^2 dx < \infty \quad (18)$$

constitutes a vector space of  $L^2(a, b)$  namely **Hilbert Space**.

And for two functions that live in Hilbert Space, the inner product is defined as:

$$\langle f|g \rangle = \int_a^b f^*(x)g(x)dx \quad (19)$$

which follows the integral **Schwarz Inequality**:

$$|\langle f|g\rangle| \leq \sqrt{\langle f|f\rangle} \sqrt{\langle g|g\rangle} \quad (20)$$

a bit more definition for a terms:

- **Normalized**: if the inner product with itself is 1
- **Orthogonal**: if the inner product with another function is 0
- **Orthonormal**: if the inner product with itself is 1 and with another function is 0
- **Complete**: if any other function can be expressed as a linear combination of the existing functions
- **Hermitian Conjugate**: The Hermitian(adjoint) conjugate of an operator  $\hat{Q}$  is  $\hat{Q}^\dagger$

$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}^\dagger f|g\rangle$$

an **Hermitian Operator** is equal to its adjoint  $\hat{Q} = \hat{Q}^\dagger$

- **Determinate States**:

The state observed is always  $\langle Q|Q\rangle = q$  by computing the standard deviation of a determinate states  $\sigma^2 = \langle (\hat{Q} - q)\Psi | (\hat{Q} - q)\Psi \rangle$ , the only available solution is

$$\hat{Q}\Psi = q\Psi$$

Therefore, Determinate states of  $Q$  are eigenfunctions of  $\hat{Q}$

- **Spectrum**: It is the list of eigenvalues that follow the eigenvalue problem in the determinate states of a system.
- **Discrete Spectra**: It is when the eigenvalues are
  1. Real
  2. Orthogonal for each corresponding eigenfunctions: However, degeneracy tells us that any linear combination of them is itself an eigenfunction with the same eigenvalue. Therefore we need to use **Gram-Schmidt Orthogonalization procedure** to construct orthogonal eigenfunctions within the degenerate subspace(Problem 3.7 Griffiths).
- **Continuous Spectra**: Momentum doesn't have a continuous spectra, and

$$-i\hbar \frac{d}{dx} f_p(x) = p f_p(x) \rightarrow f_p(x) = A e^{ipx/\hbar}$$

Yet, we find the **Dirac Orthonormality**

$$\langle f_{p'} | f_p \rangle = \delta(p - p')$$

Any complete function associated to momentum can be written as

$$f(x) = \int_{-\infty}^{\infty} c(p) f_p(x) dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{ipx/\hbar} dp$$

and the coefficients can be found by Fourier's Trick:

$$\langle f_{p'} | f \rangle = \int_{-\infty}^{\infty} c(p) \langle f_{p'} | f_p \rangle dp = \int_{-\infty}^{\infty} c(p) \delta(p - p') dp = c(p')$$

### 3.2 Statistical Interpretation

A general interpretation of is that

If you measure an observable  $Q$  on a particle in the state  $\Psi$ , you are certain to get one of the eigenvalues of the hermitian operator  $\hat{Q}$ , if the spectrum is

- **Discrete:** the probability of getting the particular eigenvalue is

$$|c_n|^2, \quad \text{where } c_n = \langle f_n | \Psi \rangle$$

- **Continuous:** for eigenfunctions  $f_z(x)$ , the probability of getting a result in range  $dz$  is

$$|c(z)|^2 dz \quad \text{where } c(z) = \langle f_z | \Psi \rangle$$

Another finding is related to the Uncertainty theorem: through sets of inequalities, you can obtain the relation that

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

The generalized Ehrenfest Theorem also reads

$$\frac{d}{dt} \langle \hat{Q} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle \quad (21)$$

by directly taking derivative to the  $\langle Q | Q \rangle = \langle \Psi | \hat{Q} \Psi \rangle$

### 3.3 Bases and Operations

**Griffiths P3.13**