量子力学(I)笔记

吴粮宇

2023 年 1 月 7 日

目录

Introduction

- Professor Yang Sun (Tel.13524506504, E-mail: sunyang@sjtu.edu.cn)
- Office hours: Wednesdays 14:00-15:30, or with special appointment
- Textbook: Introduction to Quantum Mechanics(3^{rd} edition) David J.Griffiths & Darrell F.Schroeter
- 平时作业(25%)+期中考试(35%)+期末考试(40%)
- Richard Feynman:

  "It is safe to say that nobody understands quantum mechanics."
- John Wheeler:

  "If you are not completely confused by quantum mechanics, you do not understand it."
- assuming that you are well prepared with following courses:

  ① Physics: Classical physics + Modern physics

  ② Mathematics: Linear algebra + Calculus + Math methods for physics

1 Chapter 1 The Wave Function

1.1 Introduction

Classical mechanics:

x(t) is obtained by solving:

$$m\frac{d^2x(t)}{dt^2} = F = -\frac{dV}{dx} \tag{1.1.1}$$

with initial conditions: $x = x_0, v = v_0$ at $t = 0$

Quantum mechanics:

A quantum-mechanical particle is described by wavefunction $\Psi(x,t)$.

$\Psi(x,t)$ is obtained by solving the Schroedinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \tag{1.1.2}$$

1.2 The Schroedinger Equation and wave function

- $|\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t)$ is the probability of finding the particle at point x at time t.
- $\int_a^b |\Psi(x,t)|^2\,dx$ = probability of finding the particle between a and b ,at time t.

Question: If your measurement finds the particle at C, where was the particle before you made the measurement?

- Realist (Einstein) : The particle was at C.
- Orthodox (Copenhagen) : The particle was not really anywhere.

1.3 Probability

1.3.1 Definitions

- Probability:

$$P(j) = \frac{N(j)}{N} \tag{1.3.1}$$

- Average value (expectation value):

$$\langle j \rangle = \frac{\sum jN(j)}{N} = \sum_{j=0}^{\infty} jP(j) \tag{1.3.2}$$

- Standard deviation: $\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}$ with $\langle j^2 \rangle \geq \langle j \rangle^2$

  where $\langle j^2 \rangle = \frac{\sum j^2 N(j)}{N} = \sum_{j=0}^{\infty} j^2 P(j)$

  Proof:

$$\begin{aligned} \sigma^2 = \left\langle (\Delta j)^2 \right\rangle &= \sum (j - \langle j \rangle)^2 P(j) \\ &= \sum \left(j^2 - 2j \langle j \rangle + \langle j \rangle^2 \right) P(j) \\ &= \left\langle j^2 \right\rangle - 2 \langle j \rangle \langle j \rangle + \langle j \rangle^2 \\ &= \left\langle j^2 \right\rangle - \langle j \rangle^2 \end{aligned} \tag{1.3.3}$$

1.3.2 Probability in quantum-mechanical wavefunctions

For continuous variables, we define probability density $\rho(x)$:

$$\text{for a given t: } \rho(x) = |\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t)$$

Then define all the quantities:

- $P_{ab} = \int_a^b \rho(x)dx$
- $\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx$
- $\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)\rho(x)dx$
- $\sigma^2 \equiv \left\langle (\Delta x)^2 \right\rangle = \left\langle x^2 \right\rangle - \langle x \rangle^2$

1.3.3 Observables in quantum mechanics

- Expectation value for particle's position:

$$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx = \int_{-\infty}^{\infty} x\Psi^*(x,t)\Psi(x,t)dx = \int_{-\infty}^{\infty} \Psi^*(x,t)x\Psi(x,t)dx \tag{1.3.4}$$

- Expectation value for any physical observable q:

$$\langle q \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\hat{q}\Psi(x,t)dx \tag{1.3.5}$$

1.3.4 Normalization in wavefunction

- For a wavefunction to represent physical states, it must be square-integrable and normalizable.
- Square-integrable:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx < \infty \tag{1.3.6}$$

For a wavefunction to represent physical states, it is sufficient to require:

$$\Psi(x,t) \to 0 \quad as \quad |x| \to \infty \tag{1.3.7}$$

- Normalization:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 1 \tag{1.3.8}$$

- For Schroedinger equation:

If $\Psi(x,t)$ is a solution, then $A\Psi(x,t)$ is also a solution. (A is any complex constant)

To determine A, we can solve the integration:

$$|A|^2 \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 1 \tag{1.3.9}$$

- Normalization is time-independent:

Schroedinger equation automatically preserve the normalization of the wavefunction for any t.

Proof:

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\Psi(x,t)|^2 \, dx \tag{1.3.10}$$

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{\partial}{\partial t} (\Psi^* \Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \tag{1.3.11}$$

Using the Schroedinger equation:

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi \tag{1.3.12}$$

and its comples conjugate form:

$$\frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^* \tag{1.3.13}$$

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right] = \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right] \tag{1.3.14}$$

Ψ must be 0 as x goes to infinity$\Longrightarrow$

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{\infty} = 0 \tag{1.3.15}$$

1.4 Momentum in quantum mechanics

to evaluate $\langle p\rangle = m\dfrac{d\langle x\rangle}{dt}$

$$\frac{d\langle x\rangle}{dt} = \frac{d}{dt}\int x\Psi^*\Psi dx = \int x\left[\frac{\partial}{\partial t}|\Psi|^2\right]dx \tag{1.4.1}$$

where

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\right] \tag{1.4.2}$$

We obtain

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]dx \tag{1.4.3}$$

Apply integration by parts $\int udv = uv - \int vdu$

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\left[-\int_{-\infty}^{\infty}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]dx + x\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]\Bigg|_{-\infty}^{\infty}\right] \tag{1.4.4}$$

We can prove that the second term of the equation must be 0:

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]dx \tag{1.4.5}$$

Apply again integration by parts for the second term above and use the condition: $\Psi(x,t)\to 0$ as $|x|\to\infty$

$$(u = \Psi, du = \frac{\partial\Psi}{\partial x}dx \quad ; \quad v = \Psi^*, dv = \frac{\partial\Psi^*}{\partial x}dx)$$

We obtain:

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{m}\int\Psi^*\frac{\partial\Psi}{\partial x}dx = \langle v\rangle \tag{1.4.6}$$

Analogous to momentum $p = mv$:

$$\langle p\rangle = m\frac{d\langle x\rangle}{dt} = -i\hbar\int\Psi^*\frac{\partial\Psi}{\partial x}dx = \int\Psi^*\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right]\Psi dx \tag{1.4.7}$$

We define quantum-mechanical operators for physical quantities:

position: $\hat{x}\to x$ momentum: $\hat{p}\to\dfrac{\hbar}{i}\dfrac{\partial}{\partial x}$

1.5 Other physical operators

- For kinetic energy $T = \dfrac{1}{2}mv^2 = \dfrac{p^2}{2m}$:

the operator $\hat{T}\to -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$; Expectation value $\langle T\rangle = -\dfrac{\hbar^2}{2m}\int\Psi^*\dfrac{\partial^2}{\partial x^2}\Psi dx$

- Schroedinger equation becomes:

$$i\hbar\frac{\partial\Psi}{\partial t} = (\hat{T} + \hat{V})\Psi \tag{1.5.1}$$

- For angular momentum $\boldsymbol{L} = \boldsymbol{r} \times m\boldsymbol{v} = \boldsymbol{r} \times \boldsymbol{p}$
- In general, for a physical quantity corresponding to the operator $\hat{Q}(\boldsymbol{r}, \boldsymbol{p})$

$$\text{its expectation value } \langle Q(\boldsymbol{r}, \boldsymbol{p})\rangle = \int \Psi^* \left[\hat{Q}(\boldsymbol{r}, \boldsymbol{p})\right] \Psi d\boldsymbol{r}$$

1.6 The uncertainty principle

- the De Broglie formula:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} \tag{1.6.1}$$

- For a particle has definite λ_0, or definite momentum $p_0 = \dfrac{h}{\lambda_0}$:

  The wavefunction is of a plane wave $\psi_{p_0}(x) \sim e^{ip_0x/\hbar}$

  The probability of finding the particle at any x: $|\psi_{p_0}(x)|^2 = 1$

  Then the position is undetermined.

- For a particle has definite x_0:

  The wavefunction is a δ-function: $\psi_{x_0}(x) = \delta(x - x_0)$

  The Fourier transformation:

$$\phi_{x_0}(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} \psi_{x_0}(x)e^{-ipx/\hbar}dx = \frac{1}{\sqrt{2\pi\hbar}}e^{-ipx_0/\hbar} \tag{1.6.2}$$

  The probability of the particle with any p: $|\phi_{x_0}(p)|^2 = \dfrac{1}{2\pi\hbar}$

- Werner Heisenberg suggested **Uncertainty Principle**:

$$\sigma_x\sigma_p \geq \frac{\hbar}{2} \tag{1.6.3}$$

2 Chapter 2 Time-independent Schroedinger equation

2.1 Stationary states

2.1.1 Stationary states

Assume a time-independent potential $V(x, t) \to V(x)$

By the method of separation of variables, we assume $\Psi(x, t) = \psi(x)\varphi(t)$, then

$$\frac{\partial\Psi}{\partial t} = \psi\frac{d\varphi}{dt} \qquad \frac{\partial^2\Psi}{\partial x^2} = \frac{d^2\psi}{dx^2}\varphi \tag{2.1.1}$$

The Schroedinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \Longrightarrow i\hbar\psi\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\varphi + V\varphi\psi \;\rightarrow\; i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) \tag{2.1.2}$$

Letting the above equation equals to E, we obtain two equations

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{2.1.3}$$

The solution of the first one:

$$\varphi(t) = e^{-iEt/\hbar} \tag{2.1.4}$$

The second one depends on x and potential V, it is called time-independent Schroedinger equation (TISE).
We say that the solutions of TISE are stationary states.
The total wavefunction can be written as: $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$.

- The probability density of the total wavefunction is time-independent.

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^* e^{iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2 \tag{2.1.5}$$

- Every expection value is also time-independent.

$$\langle Q(x,p)\rangle = \int \Psi^* Q\left(x, -i\hbar\frac{d}{dx}\right)\Psi dx = \int \psi^* Q\left(x, -i\hbar\frac{d}{dx}\right)\psi dx \tag{2.1.6}$$

2.1.2 States of definite total energy

The total energy is called Hamiltonian

$$H(x,p) = \frac{p^2}{2m} + V(x) \tag{2.1.7}$$

In quantum mechanics, the Hamiltonian operator is:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{2.1.8}$$

The TISE can be simply written as: $\hat{H}\psi = E\psi$

- E is the expectation value of total energy:

$$\langle H\rangle = \int \psi^*\left(\hat{H}\psi\right)dx = E\int|\psi|^2 = E \tag{2.1.9}$$

- $\left\langle H^2\right\rangle = E^2$
- $\sigma_H^2 = \left\langle H^2\right\rangle - \langle H\rangle^2 = E^2 - E^2 = 0$

  This means, for the states of separable solution, every measurement for total energy is certain to get E.

2.1.3 Linear combination

The TISE usually has an infinite set of solutions: $\{\psi_1(x), \psi_2(x), \cdots\}$ and allowed energy $\{E_1, E_2, \cdots\}$
The linear combination of the solution of TISE is itself a solution:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-itE_n/\hbar} \tag{2.1.10}$$

The linear combination of the solution of TISE is the most general solution.
the constants $\{c_1, c_2, \cdots\}$ are determined by the initial conditions and they have important physical meaning:

$$|c_n|^2 \text{ is the probability for a measurement of getting the energy } E_n.$$

The sum of all these probabilities must be 1: $\sum_{n=1}^{\infty} |c_n|^2 = 1$
The expectation value is also a combination, and it is the total engergy:

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n = E \tag{2.1.11}$$

2.2 Infinite square well

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

- Inside the well , V=0:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad \text{or} \qquad \frac{d^2\psi}{dx^2} = -k^2\psi; \quad k \equiv \frac{\sqrt{2mE}}{\hbar}; k^2 \ge 0 \tag{2.2.1}$$

- The most general solution is:

$$\psi(x) = C_1 e^{ikx} + C_2 e^{-ikx} = A sin\, kx + B cos\, kx \tag{2.2.2}$$

- To determine A and B, use the boundary conditions:
  At the boundaries, both ψ and $\frac{d\psi}{dx}$ are continuous:

$$\psi(x=0) = \psi(x=a) = 0 \tag{2.2.3}$$

  At x=0 $\Longrightarrow$

$$\psi(0) = A sin\, 0 + B cos\, 0 = B = 0 \Longrightarrow \psi(x) = A sin\, kx \tag{2.2.4}$$

  At x=a $\Longrightarrow$

$$\psi(a) = A sin\, ka = 0 \Longrightarrow ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \cdots \tag{2.2.5}$$

  k=0 is excluded. Physically, k must be positive integers:

$$k_n = \frac{n\pi}{a}, \text{ with n=1,2,3,}\cdots$$

Using $k \equiv \frac{\sqrt{2mE}}{\hbar}; k^2 \geq 0$, we obtain energies:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{2.2.6}$$

To determine A, we require that ψ be normalized:

$$\int_0^a |\psi|^2 \, dx = 1 \Longrightarrow A = \sqrt{\frac{2}{a}} \tag{2.2.7}$$

Inside the well, the normalized wavefunction:

$$\psi_n(x) = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a}x\right) \tag{2.2.8}$$

- The state with n=1 has the lowest energy, and is called ground state. The other states are called excited states.
- Each successive state has one more node.
- States are mutually orthogonal.

$$\int \psi_m^*(x)\psi_n(x)dx = 0 \quad (m \neq n) \tag{2.2.9}$$

- $\int \psi_m^*(x)\psi_n(x)dx = \delta_{m,n} \qquad \delta_{m,n} = \begin{cases} 0, & (m \neq n) \\ 1, & (m = n) \end{cases}$
- The set of states are complete (i.e. any other function can be expressed as a linear combination of them)

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \qquad c_n = \int \psi_n^*(x) f(x) dx \tag{2.2.10}$$

- The n-th stationary state is:

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar} \tag{2.2.11}$$

For infinite square well:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a}x\right) e^{-iE_n t/\hbar} \tag{2.2.12}$$

The most general solution is the linear combination of stationary states:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a}x\right) e^{-iE_n t/\hbar} \tag{2.2.13}$$

Taking $\Psi(x,0)$ as a special choice for general function $f(x)$, the coefficients can be written as

$$c_n = \sqrt{\frac{2}{a}} \int_0^a sin\left(\frac{n\pi}{a}x\right) \Psi(x,0) dx \tag{2.2.14}$$

2.3 Harmonic oscillator

The potential:

$$V(x) = \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}kx^2 \tag{2.3.1}$$

- It is useful in practice because any potential is approximately parabolic in the neighborhood of a local minimum.
- For any potential V(x), Taylor expansion at $x = x_0$ lets to

$$V(x) = V(x_0) + V'(x_0)\,(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots \tag{2.3.2}$$

- There are reasons to drop the first, the second, as well as the high-order terms:

$$V(x) \simeq \frac{1}{2}V''(x_0)(x - x_0)^2 \tag{2.3.3}$$

- The Schroedinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi \tag{2.3.4}$$

- Two new operators:

$$\hat{a}_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}\left(\mp i\hat{p} + m\omega x\right) \tag{2.3.5}$$

$$[x, \hat{p}] \equiv x\hat{p} - \hat{p}x \tag{2.3.6}$$

apply it onto a "test function" f(x):

$$\begin{aligned}[x, \hat{p}]\, f(x) &= \left[x(-i\hbar)\frac{d}{dx}f - (-i\hbar)\frac{d}{dx}(xf)\right] \\ &= -i\hbar\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right) \\ &= i\hbar f(x)\end{aligned} \tag{2.3.7}$$

$$\Longrightarrow [x, \hat{p}] = i\hbar \tag{2.3.8}$$

- In general, if the commutator of operators A and B, $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is zero, we say the two operators commute to each other, or, is not zero, we say the two operators do not commute to each other.
- Raising and lowering operator:

$$\begin{aligned}\hat{a}_-\hat{a}_+ &= \frac{1}{2\hbar m\omega}\left(i\hat{p} + m\omega x\right)\left(-i\hat{p} + m\omega x\right) \\ &= \frac{1}{2\hbar m\omega}\left[\hat{p}\hat{p} + (m\omega x)^2 - im\omega\left(x\hat{p} - \hat{p}x\right)\right] \\ &= \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2\right] - \frac{i}{2\hbar}\left[x, \hat{p}\right] \\ &= \frac{1}{\hbar\omega}\hat{H} - \frac{i}{2\hbar}i\hbar \\ &= \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2}\end{aligned} \tag{2.3.9}$$

$$\hat{H} = \hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right) \tag{2.3.10}$$

$$\hat{a}_+\hat{a}_- = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2} \tag{2.3.11}$$

$$\hat{H} = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right) \tag{2.3.12}$$

$$[\hat{a}_-, \hat{a}_+] = 1 \tag{2.3.13}$$

The Schroedinger equation for harmonic oscillator can be written:

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi \tag{2.3.14}$$

For the harmonic oscillator Hamiltonian, if ψ is solution of $\hat{H}\psi = E\psi$, then $\hat{a}_+\psi$ is solution of $\hat{H}(\hat{a}_+\psi) = (E + \hbar\omega)(\hat{a}_+\psi)$

Proof:

$$\begin{aligned}
\hat{H}(\hat{a}_+\psi) &= \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)(\hat{a}_+\psi) \\
&= \hbar\omega\left(\hat{a}_+\hat{a}_-\hat{a}_+ + \frac{1}{2}\hat{a}_+\right)\psi \\
&= \hbar\omega\hat{a}_+\left(\hat{a}_-\hat{a}_+ + \frac{1}{2}\right)\psi \\
&= \hat{a}_+\left[\hbar\omega\left(\hat{a}_+\hat{a}_- + 1 + \frac{1}{2}\right)\psi\right] \\
&= \hat{a}_+\left(\hat{H} + \hbar\omega\right)\psi \\
&= \hat{a}_+\left(E + \hbar\omega\right)\psi \\
&= \left(E + \hbar\omega\right)(\hat{a}_+\psi)
\end{aligned} \tag{2.3.15}$$

Similarly, we can have:

$$\hat{H}(\hat{a}_-\psi) = (E - \hbar\omega)(\hat{a}_-\psi) \tag{2.3.16}$$

Raising operator and lowering operator are both ladder operators.

The ground state is the lowest in energy, no other states can be even lower.

$$\hat{a}_-\psi_0 = 0 \tag{2.3.17}$$

$$\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx} + m\omega x\right)\psi_0 = 0 \Longrightarrow \frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0 \tag{2.3.18}$$

We obtain

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2} \tag{2.3.19}$$

Normalization:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-\frac{m\omega}{\hbar}x^2} dx = |A|^2 \sqrt{\frac{\pi\hbar}{m\omega}} \Longrightarrow |A|^2 = \sqrt{\frac{m\omega}{\pi\hbar}} \tag{2.3.20}$$

The ground state wavefunction:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \tag{2.3.21}$$

Using the Schroedinger equation and for the ground state ψ_0:

$$\hbar\omega \left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_0 = E\psi_0 \tag{2.3.22}$$

$$\hat{a}_-\psi_0 = 0 \Longrightarrow \text{ground state energy:} \quad E_0 = \frac{1}{2}\hbar\omega \tag{2.3.23}$$

- Properties of $\hat{a}_\pm$:

  $\hat{a}_\pm$ are mutually hermitian conjugate, which means for any integrable functions f(x) and g(x):

$$\int_{-\infty}^{\infty} f^*(\hat{a}_\pm g)dx = \int_{-\infty}^{\infty} (\hat{a}_\mp f)^* g dx \tag{2.3.24}$$

  Proof:

$$\begin{aligned}\int_{-\infty}^{\infty} f^*(\hat{a}_\pm g)dx &= \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} f^* \left(\mp\hbar\frac{d}{dx} + m\omega x\right) g dx \\ &= \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} \left[\left(\mp\hbar\frac{d}{dx} + m\omega x\right) f\right]^* g dx \\ &= \int_{-\infty}^{\infty} (\hat{a}_\mp f)^* g dx\end{aligned} \tag{2.3.25}$$

  P.S. We have used integration by parts and condition that boundary terms vanish:

$$\int f^* \frac{dg}{dx} dx = -\int \left(\frac{df}{dx}\right)^* g dx \tag{2.3.26}$$

- Solutions for excited states:

  Because $\hat{a}_\pm\psi_n$ is proportional to $\psi_{n\pm1}$, we can write:

$$\hat{a}_+\psi_n = c_n\psi_{n+1}, \quad \hat{a}_-\psi_n = d_n\psi_{n-1} \tag{2.3.27}$$

  From the Schroedinger equation and the energy solution:

$$\hbar\omega \left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E_n\psi, \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{2.3.28}$$

  We have:

$$\hat{a}_+\hat{a}_-\psi_n = n\psi_n, \quad \hat{a}_-\hat{a}_+\psi_n = (n+1)\psi_n \tag{2.3.29}$$

  Using the hermitian conjugate definition:

$$\int_{-\infty}^{\infty} (\hat{a}_+\psi_n)^* (\hat{a}_+\psi_n)\, dx = \int_{-\infty}^{\infty} (\hat{a}_-\hat{a}_+\psi_n)^* \psi_n dx \tag{2.3.30}$$

$$\int_{-\infty}^{\infty}\left(\hat{a}_{+}\psi_n\right)^{*}\left(\hat{a}_{+}\psi_n\right)dx=\left|c_n\right|^2\int_{-\infty}^{\infty}\left|\psi_{n+1}\right|^2dx=\int_{-\infty}^{\infty}\left[(n+1)\psi_n\right]^{*}\psi_n dx=(n+1)\int_{-\infty}^{\infty}\left|\psi_n\right|^2dx \tag{2.3.31}$$

From the second and last terms in the last equation, we get: $|c_n|^2=n+1$.

Therefore:

$$\begin{cases}\hat{a}_{+}\psi_n=\sqrt{n+1}\psi_{n+1}\\ \hat{a}_{-}\psi_n=\sqrt{n}\psi_{n-1}\end{cases} \tag{2.3.32}$$

By stepwise operation, for all excited solutions:

$$\psi_n=\frac{1}{\sqrt{n!}}\left(\hat{a}_{+}\right)^n\psi_0,\quad E_n=\left(n+\frac{1}{2}\right)\hbar\omega \tag{2.3.33}$$

Define $\alpha\equiv\sqrt{\frac{m\omega}{\hbar}}$:

even function: $\psi_0(x)=\frac{\sqrt{\alpha}}{\pi^{\frac{1}{4}}}e^{-\frac{1}{2}\alpha^2x^2}$

odd function: $\psi_1(x)=\frac{\sqrt{2\alpha}}{\pi^{\frac{1}{4}}}\alpha x e^{-\frac{1}{2}\alpha^2x^2}$

even function: $\psi_2(x)=\frac{\sqrt{\frac{\alpha}{2}}}{\pi^{\frac{1}{4}}}\left(2\alpha^2x^2-1\right)e^{-\frac{1}{2}\alpha^2x^2}$

(n=even→ even function; n=odd→ odd function)

- Characteristics of the solution
  - Non-zero ground state energy: $E_0=\frac{1}{2}\hbar\omega\neq 0$

    This is called zero-point energy, required by the uncertainty principle.

    P.S.: Becauese if $E_0=0$, then $T=V=0$.

    $$\text{V(x)=}\frac{1}{2}\omega^2x^2=0\Longrightarrow x=0\rightarrow\Delta x=0\Longrightarrow\text{position exact}$$

    $$\text{T=}0\Longrightarrow p^2=0\rightarrow\Delta p=0\Longrightarrow\text{momentum exact}$$

    $\Delta x\Delta p=0$ is not allowed by the uncertainty principle.
  - Parity is a physical quantity describing space inversion.

    definition:

    $$\psi(-x)=\psi(x)\Longrightarrow\text{even parity (if n is even)}$$

    $$\psi(-x)=-\psi(x)\Longrightarrow\text{odd parity (if n is odd)}$$
  - For the ground state ψ_0, the largest probability to find the particle is at $x=0$. This contradicts the classical physics.

– For ψ_0 at $|\alpha x|^2 = 1$, classical physics says

$$V(x) = \frac{1}{2}m\omega^2 x^2\Big|_{|\alpha x|^2=1} = \frac{1}{2}\omega\hbar\alpha^2 x^2\Big|_{|\alpha x|^2=1} = \frac{1}{2}\omega\hbar = E_0 \tag{2.3.34}$$

Conclusion: No particle can go to $|\alpha x|^2 > 1$. (classical physics)

In quantum mechanics, there is probability to find the particle outside the potential for $|\alpha x|^2 > 1$.

For ψ_0, we can calculate the probability to find the particle outside the potential:

$$\frac{\int_1^\infty e^{-\alpha^2 x^2} d(\alpha x)}{\int_0^\infty e^{-\alpha^2 x^2} d(\alpha x)} \approx 16\% \tag{2.3.35}$$

This is a quantum effect, which is the stongest in the ground state. For highly excited states, the behavior tends to agree with the classical physics.

– For any n-th state, expectation values of T and V are 50% of the total energy E_n.

To calculate, we start from $\hat{a}_\pm$:

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}_+ + \hat{a}_-\right), \quad \hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}\left(\hat{a}_+ - \hat{a}_-\right) \tag{2.3.36}$$

$$x^2 = \frac{\hbar}{2m\omega}\left[(\hat{a}_+)^2 + (\hat{a}_+\hat{a}_-) + (\hat{a}_-\hat{a}_+) + (\hat{a}_-)^2\right] \tag{2.3.37}$$

Expectation value for V:

$$\begin{aligned}
\langle V\rangle &= \left\langle \frac{1}{2}m\omega^2 x^2 \right\rangle \\
&= \frac{1}{2}m\omega^2 \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n dx \\
&= \frac{\hbar\omega}{4}\int_{-\infty}^{\infty} \psi_n^* \left[(\hat{a}_+)^2 + (\hat{a}_+\hat{a}_-) + (\hat{a}_-\hat{a}_+) + (\hat{a}_-)^2\right]\psi_n dx \\
&= \frac{\hbar\omega}{4}(n+n+1) \\
&= \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right)
\end{aligned} \tag{2.3.38}$$

which is half of $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$.

2.4 Free particle

Free particles move in a space with no potential: $V(x) = 0$.

The Schroedinger equation for free particles is simple:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{2.4.1}$$

To solve the Schroedinger equation, we first rewrite it:

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{with} \quad |k| = \frac{\sqrt{2mE}}{\hbar} \tag{2.4.2}$$

The general solution is:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{2.4.3}$$

Add the time-dependent term:

$$e^{-i\frac{E}{\hbar}t} = e^{-i\frac{\hbar^2k^2}{2m\hbar}t} = e^{-ik\frac{\hbar k}{2m}t} \tag{2.4.4}$$

For a k:

$$\Psi(x,t) = Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x+\frac{\hbar k}{2m}t\right)} \tag{2.4.5}$$

- For a given k, $\frac{\hbar k}{2m}$ plays a role of constant velocity $v_k = \frac{\hbar k}{2m}$.
- If we allow k taking both "+" and "-" values, we can combine the two terms to one:

$$\Psi_k(x,t) = Ae^{i\left(kx-\frac{\hbar k^2}{2m}t\right)} \tag{2.4.6}$$

This wavefunction is a propagating wave with fixed wavelength $\lambda = \frac{2\pi}{|k|}$ corresponding to a velocity:

$$v_k = \frac{\hbar\,|k|}{2m} = \sqrt{\frac{E}{2m}} \tag{2.4.7}$$

In classical physics, a particle with kinetic energy:

$$E = \frac{1}{2}mv_{cl}^2 \Longrightarrow v_{cl} = \sqrt{\frac{2E}{m}} = 2v_k \tag{2.4.8}$$

A more serious problem: this wavefunction is not normalizable.

$$\int_{-\infty}^{\infty} \Psi_k^* \Psi_k dx = |A|^2 \int_{-\infty}^{\infty} dx = |A|^2 \cdot \infty \neq 1 \tag{2.4.9}$$

Therefore, the wavefunction with a fixed k can not be a solution of free particle.

However, we can construct a linear combination of different $\Psi_k(x,t)$.

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\Psi_k(x,t)dk = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)e^{i\left(kx-\frac{\hbar k^2}{2m}t\right)}dk \tag{2.4.10}$$

with properly chosen $\phi(k)$, this wavefunction can be normalized.

It is a superposition of different k-waves,corresponding to different energies. We call it wave packet.

There are no doundaries. We use initial conditions to find $\phi(k)$.

Consider the initial state at $t = 0$:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk \tag{2.4.11}$$

Applying the Fourier transformation, we get:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} dx \tag{2.4.12}$$

Put $\phi(k)$ into the wavefunction for wave packet, we get $\Psi(x,t)$.

This is the general solution of the Schroedinger equation for free particles. The normalization is ensured by $\phi(k)$.

- Example: A free particle, which is initially localised in the range $-a < x < a$, is released at time $t = 0$:

$$\Psi(x,0) = \begin{cases} A, \ if \ -a < x < a \\ 0, \ otherwise \end{cases} \tag{2.4.13}$$

where A and a are real positive constants. Find $\Psi(x,t)$.

① First, normalize $\Psi(x,0)$ to find A:

$$\int_{-\infty}^{\infty} |\Psi(x,0)|^2 \, dx = 1 \Longrightarrow A = \frac{1}{\sqrt{2a}} \tag{2.4.14}$$

② Calculate $\phi(k)$:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^{a} e^{-ikx} dx = \frac{1}{\sqrt{a\pi}} \frac{sin(ka)}{k} \tag{2.4.15}$$

③ Finally get (numerical) solution.

$$\Psi(x,t) = \frac{1}{\pi\sqrt{2a}} \int_{-\infty}^{\infty} \frac{sin(ka)}{k} e^{i(kx - \frac{\hbar k^2}{2m} t)} dk \tag{2.4.16}$$

Note:

$\phi(k)$ describes the free particle (at t=0) in terms of $k = \frac{p}{\hbar}$

$\Psi(x,0)$ describes the free particle (at t=0) in terms of position x.

Discussion:

(i) $a \ll 1$: the particle is sharply peaked at the position x=0, the momentum is a constant $\sqrt{\frac{a}{\pi}}$.

(An example of the uncertainty principle.)

(ii) $a \gg 1$: Position of the particle is widely spread in space.

For momentum, $\phi(k) = \sqrt{\frac{a}{\pi}} \frac{sin(ka)}{ka}$ has sharp maximum at $x = 0$.

(Another example of the uncertainty principle.)

- Phase velocity and group velocity.

  The general wavefunction for wave packet:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i\left(kx - \frac{\hbar k^2}{2m} t\right)} dk = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \omega t)} dk \tag{2.4.17}$$

  with $\omega(k) = \dfrac{\hbar k^2}{2m}$.

  Make a Taylor expansion about k_0 up to the second term.

$$\omega(k) \approx \omega(k_0) + \omega'\big|_{k=k_0} (k - k_0) \tag{2.4.18}$$

$$\begin{aligned} \Psi(x,t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i\left[kx - \omega_0 t - \omega_0'(k-k_0)t\right]} dk \\ &= \frac{1}{\sqrt{2\pi}} e^{-i\omega_0 t + ik_0\omega_0' t} \int_{-\infty}^{\infty} \phi(k) e^{ik(x - \omega_0' t) dk} \end{aligned} \tag{2.4.19}$$

  Compare to that at t=0:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk \tag{2.4.20}$$

  As time goes, $x \to x - \omega_0' t = x - v_g t$

  Using dispersion relation:

$$\omega(k) = \frac{\hbar k^2}{2m} \tag{2.4.21}$$

  We obtain:

$$v_g = \omega_0' = \left.\frac{d\omega(k)}{dk}\right|_{k=k_0} = \frac{\hbar k_0}{m} \tag{2.4.22}$$

  v_g is called group velocity.

  $v_k = \left.\dfrac{\hbar k}{2m}\right|_{k=k_0} = \dfrac{\hbar k_0}{2m}$ is called phase velocity.

  Compare them with the classical velocity, we find

$$v_{cl} = v_{group} = 2 v_{phase} \tag{2.4.23}$$

2.5 Delta-function potential

2.5.1 Bound states and scattering state

For TISE, we have seen two different kinds of solutions:

① solutions are normalizable, states are labeled by discrete index n.

These states are called bound states.

② solutions are not normalizable, states are described by continuous variable k.

These states are called scattering states.

quantum tunneling:

Even when $E < V$, particles may leak through finite potential barrier.

$\begin{cases} E < [V(-\infty) \text{ and } V(+\infty)] \Longrightarrow \text{ bound state.} \quad (E < 0) \\ E > [V(-\infty) \text{ or } V(+\infty)] \Longrightarrow \text{ scattering state.} \quad (E > 0) \end{cases}$

2.5.2 The δ-function potential

It's a potential of infinitely high with an infinitesimal narrow spike.

$$\delta(x) = \begin{cases} 0, \text{ if } x \neq 0 \\ \infty, \text{ if } x = 0 \end{cases} \quad \text{with} \quad \int_{-\infty}^{\infty} \delta(x)dx = 1 \tag{2.5.1}$$

for a function f(x):

$$\int_{-\infty}^{\infty} \delta(x-a)f(x)dx = f(a) \tag{2.5.2}$$

① Consider potential $V(x) = -\alpha\delta(x)$ with a positive α and solve the equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi \tag{2.5.3}$$

- E<0 (bound states):

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \equiv \kappa^2\psi, \quad \kappa \equiv \sqrt{\frac{-2mE}{\hbar^2}} \tag{2.5.4}$$

The general solution for region x<0:

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x} \tag{2.5.5}$$

Physically, we must set A=0 (to exclude the first term for $x \to -\infty$)

$$\psi(x) = Be^{\kappa x}, \quad x < 0 \tag{2.5.6}$$

The general solution for region x>0:

$$\psi(x) = Fe^{-\kappa x} + Ge^{\kappa x} \tag{2.5.7}$$

Physically, we must set G=0 (to exclude the second term for $x \to +\infty$)

$$\psi(x) = Fe^{-\kappa x}, \quad x > 0 \tag{2.5.8}$$

Now apply boundary conditions at $x = 0$:

① ψ is always continuous.

② $\dfrac{d\psi}{dx}$ is continuous except at points where the potential is infinite.

$$\psi(x=0) = F = B \Longrightarrow \psi(x) = \begin{cases} Be^{\kappa x}, x \leq 0 \\ Be^{-\kappa x}, x \geq 0 \end{cases} \tag{2.5.9}$$

Using normalization:

$$B = \sqrt{\kappa} \tag{2.5.10}$$

Now apply the continuous condition for $\frac{d\psi}{dx}$ at $x = 0$.

Integrate the Schroedinger equation, for an infinitesimally area $-\varepsilon \to +\varepsilon$ around $x = 0$ and let $\varepsilon \to 0$.

$$\lim_{\epsilon\to 0} -\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{dx^2}dx + \lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon}V(x)\psi(x)dx = \lim_{\epsilon\to 0} E\int_{-\epsilon}^{+\epsilon}\psi(x)dx \tag{2.5.11}$$

The second term

$$\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon}V(x)\psi(x)dx = \lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon}-\alpha\delta(x)\psi(x)dx = -\alpha\psi(0) \tag{2.5.12}$$

The term of right-hand side is 0 when $\epsilon \to 0$.

The first term:

$$\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{dx^2}dx = \lim_{\epsilon\to 0}\left(\left.\frac{d\psi(x)}{dx}\right|_{\epsilon} - \left.\frac{d\psi(x)}{dx}\right|_{-\epsilon}\right) \tag{2.5.13}$$

Using $\psi(x) = \sqrt{\kappa}e^{-\kappa|x|}$

$$\left.\frac{d\psi(x)}{dx}\right|_{\epsilon} = -\sqrt{\kappa}\kappa e^{-\kappa x}(x > 0), \quad \left.\frac{d\psi(x)}{dx}\right|_{-\epsilon} = \sqrt{\kappa}\kappa e^{\kappa x}(x < 0) \tag{2.5.14}$$

We finally get, for the limit $\epsilon \to 0$, $-\frac{\hbar^2}{2m}\left(-2\sqrt{\kappa}\kappa\right) = \alpha\psi(0) = \alpha\sqrt{\kappa}$

$$\kappa = \frac{m\alpha}{\hbar^2} \tag{2.5.15}$$

Using the definition $\kappa \equiv \sqrt{\frac{-2mE}{\hbar^2}}$, we get $E = -\frac{m\alpha^2}{2\hbar^2}$

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar^2}e^{-\frac{m\alpha}{\hbar^2}|x|} \tag{2.5.16}$$

- E>0 (scattering states):

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \equiv -k^2\psi, \quad k \equiv \sqrt{\frac{2mE}{\hbar^2}} \tag{2.5.17}$$

We can write the general solution for the two regions:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (x < 0) \tag{2.5.18}$$

$$\psi(x) = Fe^{ikx} + Ge^{-ikx} \quad (x > 0) \tag{2.5.19}$$

Continuity of $\psi(x)$ at $x = 0$ leads to $F + G = A + B$.

Continuity of $\frac{d\psi}{dx}$ near $x = 0$

$$\frac{d\psi}{dx} = ik\left(Ae^{ikx} - Be^{-ikx}\right), \quad (x < 0), \quad \lim_{\epsilon\to 0}\left.\frac{d\psi}{dx}\right|_{-\epsilon} = ik(A - B) \tag{2.5.20}$$

$$\frac{d\psi}{dx} = ik\left(Fe^{ikx} - Ge^{-ikx}\right), \quad (x > 0), \quad \lim_{\epsilon\to 0}\left.\frac{d\psi}{dx}\right|_{+\epsilon} = ik(F-G) \tag{2.5.21}$$

Consider the difference of these two equations, and $\psi(0) = A + B$, leads to

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B) \tag{2.5.22}$$

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad \beta \equiv \frac{m\alpha}{\hbar^2 k} \tag{2.5.23}$$

Physically, if the initial wave coming from the left, then we have $G = 0$.

A-wave (incident wave)

B-wave (reflected wave)

F-wave (transmitted wave)

We can have B and F expressed by A:

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A \tag{2.5.24}$$

Probability waves:

$$|\psi_A|^2 = A^* e^{-ikx} \cdot Ae^{ikx} = |A|^2 \tag{2.5.25}$$

$$|\psi_B|^2 = |B|^2 = \left|\frac{i\beta}{1 - i\beta}\right|^2 |A|^2 = \left|\frac{i\beta - \beta^2}{1 + \beta^2}\right|^2 |A|^2 \tag{2.5.26}$$

$$|\psi_F|^2 = |F|^2 = \left|\frac{1}{1 - i\beta}\right|^2 |A|^2 = \left|\frac{1 + i\beta}{1 + \beta^2}\right|^2 |A|^2 \tag{2.5.27}$$

Reflection coefficient

$$R = \frac{|\psi_B|^2}{|\psi_A|^2} = \frac{\beta^2}{1 + \beta^2} \tag{2.5.28}$$

Transmission coefficient

$$T = \frac{|\psi_F|^2}{|\psi_A|^2} = \frac{1}{1 + \beta^2} \tag{2.5.29}$$

$$R + T = 1 \tag{2.5.30}$$

Using definitions of β and κ:

$$\beta^2 = \frac{m\alpha^2}{2\hbar^2 E} \tag{2.5.31}$$

for small $E > 0$, $R \to 1$, $T \to 0$;

for large E, T is proportional to E.

② Consider potential $V(x) = \alpha\delta(x)$ with a positive α and solve the equation:

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi \tag{2.5.32}$$

- $\psi(x)$ is normalizable only if $E > V_{min}$

  Argument:

  If $E < V_{min}$, then $\psi(x)$ and its second derivative must have the same sign.

  Then $\psi(x)$ always curves away from the x-axis. In such cases, $\psi(x)$ goes to positive or negative infinity as $x \to \pm\infty$, and therefore, are not normalizable.

- The solution for R and T (depends on α^2) is the same as in the previous example.

  Classically:

  for case of $E < V_{max}$, then $T = 0$ and $R = 1$;

  for case of $E > V_{max}$, then $T = 1$ and $R = 0$;

  Quantum-mechanically:

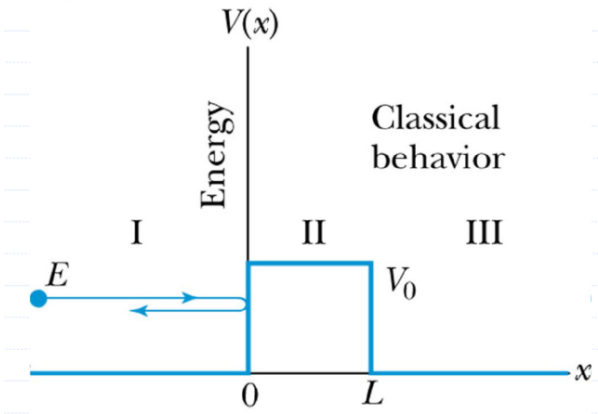
  for case of $E < V_{max}$, T can be nonzero, which is called tunneling.

  for case of $E > V_{max}$, R can be nonzero.

③ Finite square barrier $(0 < E < V)$

Consider a potential:

$$V(x) = \begin{cases} V_0 & (0 \le x \le L) \\ 0 & (x < 0,\ x > L) \end{cases} \tag{2.5.33}$$



- In region I $(x < 0)$ and III $(x > L)$:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi_I}{dx^2} = E\Psi_I \tag{2.5.34}$$

$$\frac{d^2\Psi_I}{dx^2} + k^2\Psi_I = 0 \quad \text{where} \quad k_I = k_{III} = k = \frac{\sqrt{2mE}}{\hbar} \tag{2.5.35}$$

Solution in I contains the incident and reflected wave:

$$\Psi_I = Ae^{ikx} + Be^{-ikx} \tag{2.5.36}$$

Solution in III contains the transmitted wave:

$$\Psi_{III} = Ee^{ikx} + Fe^{-ikx} \to Ee^{ikx} \tag{2.5.37}$$

- In region II ($0 \le x \le L$):

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi_{II}}{dx^2} + V_0\Psi_{II} = E\Psi_{II} \tag{2.5.38}$$

$$\frac{d^2\Psi_{II}}{dx^2} - \kappa_{II}^2\Psi_{II} = 0 \quad \text{where} \quad \kappa_{II} = \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \tag{2.5.39}$$

Solution in II is bound inside the potential

$$\Psi_{II} = Ce^{\kappa x} + De^{-\kappa x} \tag{2.5.40}$$

Use boundary conditions at $x = 0$ and $x = L$ to determine A,B,C,D,E.

At $x = 0$, we have:

$$\begin{cases} \Psi_I(0) = \Psi_{II}(0) \longrightarrow A + B = C + D \\ \left.\dfrac{d\Psi_I(x)}{dx}\right|_{x=0} = \left.\dfrac{d\Psi_{II}(x)}{dx}\right|_{x=0} \longrightarrow ikA - ikB = \kappa C - \kappa D \end{cases} \tag{2.5.41}$$

At $x = L$, we have:

$$\begin{cases} \Psi_{II}(L) = \Psi_{III}(L) \longrightarrow Ce^{\kappa L} + De^{-\kappa L} = Ee^{ikL} \\ \left.\dfrac{d\Psi_{II}(x)}{dx}\right|_{x=L} = \left.\dfrac{d\Psi_{III}(x)}{dx}\right|_{x=L} \longrightarrow \kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikEe^{ikL} \end{cases} \tag{2.5.42}$$

With the above 4 equations, we can express B,C,D,E by A.

Especially, reflection probability $R = \dfrac{|B|^2}{|A|^2}$; transmission probability $T = \dfrac{|E|^2}{|A|^2}$;

$$R + T = 1 \tag{2.5.43}$$

The transmitted wave:

$$E = -e^{ikL}\frac{i4k\kappa}{(ik-\kappa)^2e^{\kappa L} - (ik+\kappa)^2e^{-\kappa L}}A \tag{2.5.44}$$

In practice, $\kappa L \gg 1$:

$$E \approx -e^{ikL}\frac{i4k\kappa}{(ik-\kappa)^2}e^{-\kappa L}A \tag{2.5.45}$$

$$T = \frac{|E|^2}{|A|^2} \approx \frac{16k^2\kappa^2}{(k^2+\kappa^2)^2}e^{-2\kappa L} \tag{2.5.46}$$

With $k \equiv \dfrac{\sqrt{2mE}}{\hbar}$ and $\kappa \equiv \dfrac{\sqrt{2m(V_0 - E)}}{\hbar}$

$$T \approx \frac{16E(V_0 - E)}{V_0^2}e^{-2L\frac{\sqrt{2m(V_0-E)}}{\hbar}} \tag{2.5.47}$$

For given V_0 and E, T decays exponentially with L.

STM (Scanning Tunneling Microscopy):

Using

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2L\frac{\sqrt{2m(V_0-E)}}{\hbar}} \tag{2.5.48}$$

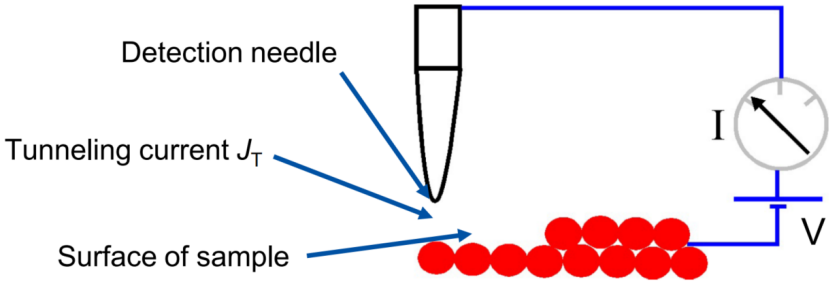
$$J_T \sim V e^{-A\sqrt{\phi}s} \tag{2.5.49}$$

J_T: tunneling current.

s: distance between needle and surface.

ϕ: average height of potential barrier.

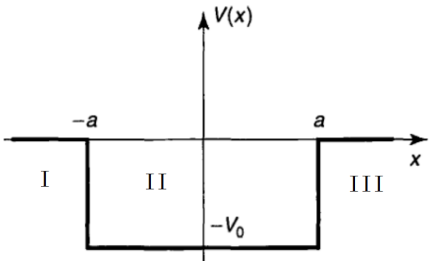
A: constant.



2.6 Finite square well

Consider a potential:

$$V(x) = \begin{cases} -V_0 & (-a \le x \le a) \\ 0 & (x < -a,\ x > a) \end{cases} \tag{2.6.1}$$



- bound state ($E < 0$):

  Region I:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = \kappa^2\psi \quad \left(\kappa = \sqrt{-\frac{2mE}{\hbar^2}}\right) \tag{2.6.2}$$

  The general solution:

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x} \to Be^{\kappa x} \tag{2.6.3}$$

Region II:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -l^2\psi \quad \left(l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}\right) \tag{2.6.4}$$

The general solution (for $-V_0 < E$):

$$\psi(x) = C'e^{ilx} + D'e^{-ilx} = Csin(lx) + Dcos(lx) \tag{2.6.5}$$

Region III:

$$\psi(x) = Fe^{-\kappa x} \tag{2.6.6}$$

Discuss symmetry in the solution:

Since the potential is an even function ($V(x) = V(-x)$), we can prove that the solution $\psi(x)$ can always be taken to be either even or odd.

Assume $\psi(x)$ is an even function:

$$\psi(x) = \begin{cases} Fe^{\kappa x}, & \text{for } x \le -a \\ Dcos(lx), & \text{for } -a < x < +a \\ \psi(-x), & \text{for } x \ge a \end{cases} \tag{2.6.7}$$

Continuity of $\psi(x)$ at $x = a$:

$$Fe^{-\kappa a} = Dcos(la) \tag{2.6.8}$$

Continuity of $\dfrac{d\psi}{dx}$ at $x = a$:

$$-\kappa Fe^{-\kappa a} = -lDsin(la) \tag{2.6.9}$$

We will have:

$$\kappa = ltan(la) \tag{2.6.10}$$

Consider $\kappa = \sqrt{-\dfrac{2mE}{\hbar^2}}$ and $l = \sqrt{\dfrac{2m(E+V_0)}{\hbar^2}}$, and let $z = la$ and $z_0 = \dfrac{a}{\hbar}\sqrt{2mV_0}$.

We obtain:

$$tan\, z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \tag{2.6.11}$$

Then allowed solutions are the intersections.

The allowed energies are:

$$E_n = z_n^2\frac{\hbar^2}{2ma^2} - V_0 \quad (z_n \text{ are the intersections.}) \tag{2.6.12}$$

Discussions:

(a) wide, deep well (z_0 is very large):

The intersection will occur near $z_n \approx \frac{n\pi}{2}$, with n = odd integer.

$$E_n \approx \frac{n^2\pi^2\hbar^2}{2m(2a)^2} - V_0 \tag{2.6.13}$$

(b) shallow, narrow well

As the curve $\sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$ moves down to x-axis, there are fewer and fewer solutions.

Finally, there is only one intersection in $0 < z_0 < \frac{\pi}{2}$ for $z = \epsilon$.

$$E = \frac{\hbar^2\epsilon^2}{2ma^2} - V_0 \tag{2.6.14}$$

- scattering state ($E > 0$):

Region I:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -k^2\psi \quad \left(k = \sqrt{\frac{2mE}{\hbar^2}}\right) \tag{2.6.15}$$

The general solution:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{2.6.16}$$

Region II:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -l^2\psi \quad \left(l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}\right) \tag{2.6.17}$$

The general solution:

$$\psi(x) = Csin(lx) + Dcos(lx) \tag{2.6.18}$$

Region III:

$$\psi(x) = Fe^{ikx} \tag{2.6.19}$$

There are 4 equations from the boundary conditions at $x = -a$ and $x = a$.

$$Ae^{-ika} + Be^{ika} = -Csin(la) + Dcos(la) \tag{2.6.20}$$

$$ik\left(Ae^{-ika} - Be^{ika}\right) = l\left[Ccos(la) - Dsin(la)\right] \tag{2.6.21}$$

$$Fe^{ika} = Csin(la) + Dcos(la) \tag{2.6.22}$$

$$ikFe^{ika} = l\left[Ccos(la) - Dsin(la)\right] \tag{2.6.23}$$

The reflection coefficient:

$$R = \frac{|B|^2}{|A|^2} \tag{2.6.24}$$

The transmission coefficient:

$$T = \frac{|F|^2}{|A|^2} \tag{2.6.25}$$

$$T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)} sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right) \tag{2.6.26}$$

For some energies, the wave becomes transparent.(T=1)

when sine is 0:

$$\frac{2a}{\hbar}\sqrt{2m(E+V_0)} = n\pi \Longrightarrow E_n = n^2\frac{\pi^2\hbar^2}{2m(2a)^2} - V_0 \tag{2.6.27}$$

Ramsauer-Townsend effect

2.7 Some extra examples

2.7.1 Adding a constant term to a potential V

Add a constant V_0 to the potential energy V.

If Ψ is the solution of Schroedinger equation without V_0.

Then the solution with V_0 is:

$$\Psi_0 = \Psi e^{-\frac{iV_0 t}{\hbar}} \tag{2.7.1}$$

Proof:

$$\begin{aligned} i\hbar\frac{\partial\Psi_0}{\partial t} &= i\hbar\frac{\partial\Psi}{\partial t}e^{-\frac{iV_0t}{\hbar}} + i\hbar\Psi\left(-\frac{iV_0}{\hbar}\right)e^{-\frac{iV_0t}{\hbar}} \\ &= \left[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi\right]e^{-\frac{iV_0t}{\hbar}} + V_0\Psi e^{-\frac{iV_0t}{\hbar}} \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi_0}{\partial x^2} + (V+V_0)\Psi_0 \end{aligned} \tag{2.7.2}$$

There is no effect on the expectation value, since

$$|\Psi_0|^2 = |\Psi|^2 \tag{2.7.3}$$

2.7.2 Probability current

If $P_{ab}(t)$ is the probability of finding the particle in the range $(a < x < b)$, at time t, then its time dependence defines probability current.

$$P_{ab}(t) = \int_a^b |\Psi(x,t)|^2\, dx \tag{2.7.4}$$

$$\frac{dP_{ab}}{dt} = \int_a^b \frac{\partial}{\partial t}|\Psi(x,t)|^2\, dx \tag{2.7.5}$$

Using the Schoedinger equation and its complex conjugate form:

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\right] = -\frac{\partial}{\partial x}J(x,t) \tag{2.7.6}$$

$$\frac{dP_{ab}}{dt} = -\int_a^b \frac{\partial}{\partial x} J(x,t)dx = J(a,t) - J(b,t) \tag{2.7.7}$$

where

$$J(x,t) = -\frac{i\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi\right) \tag{2.7.8}$$

Probability is dimensionless, so J has the dimensions 1/time.

2.7.3 Guess the inside of an atomic nucleus

When people observed that an unstable nucleus can emit electrons (β decay), they guessed that a nucleus is made of protons and electrons.

We use the uncertainty principle to show this is not possible:

The α scattering experiment by Rutherford can determine the radius of a nucleus as $r < 10^{-14}m$.

We can roughly take $\sigma_x \sim 10^{-14}m$.

Using uncertainty principle, we then get for the electron momentum

$$\sigma_p \geq \frac{\hbar}{2}\frac{1}{\sigma_x} \sim 10^{-17} gm/s \tag{2.7.9}$$

The estimated electron kinetic energy:

$$T = \frac{p^2}{2m} \sim \frac{(\sigma_p)^2}{2m} \sim 10^3 MeV \tag{2.7.10}$$

which is larger than the fission energy, which is impossible!

Later, people realized that nuclei are made of protons and neutrons.

3 Chapter 3 Formalism

3.1 Hilbert space

In general, expectation values in quantum mechanics consist of two parts: wavefunction and operator.

$$\text{wavefunctions} \longrightarrow \text{(abstract) vectors}$$
$$\text{opertators} \longrightarrow \text{linear transformation between the vectors}$$

3.1.1 Linear transformation

basis transformation

a vector in 3-dimensional space: $\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$ or $\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$

Now we rotate it around the z-axis by an angle θ, to obtain another vector $\vec{r'} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$

In linear algebra, this is done by a linear transformation:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} cos\theta & sin\theta & 0 \\ -sin\theta & cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} xcos\theta + ysin\theta \\ -xsin\theta + ycos\theta \\ z \end{pmatrix} \tag{3.1.1}$$

Vectors are transformed by the rotation: $\vec{r'} = \hat{T}\vec{r}$, with the transformation matrix $\hat{T} = \begin{pmatrix} cos\theta & sin\theta & 0 \\ -sin\theta & cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$

$(\hat{x}, \hat{y}, \hat{z})$ is the basis states of the 3-dimensional space with properties:

$$\text{normalized: } \hat{x} \cdot \hat{x} = \hat{y} \cdot \hat{y} = \hat{z} \cdot \hat{z} = 1$$
$$\text{orthogonal: } \hat{x} \cdot \hat{y} = \hat{y} \cdot \hat{z} = \hat{z} \cdot \hat{x} = 0$$

We can generalize this problem to an abstract N-dimensional space.
For two N-dimensional vectors:

$$|\alpha\rangle \to a = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \qquad |\beta\rangle \to b = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_N \end{pmatrix} \tag{3.1.2}$$

Their inner product is a complex number:

$$\langle\alpha|\beta\rangle = a_1^* b_1 + a_2^* b_2 + \cdots a_N^* b_N \tag{3.1.3}$$

Linear transformation is represented by T, which acts on one vector and transforms it to another vector

$$|\beta\rangle = \boldsymbol{T}|\alpha\rangle \Longrightarrow \boldsymbol{b} = \boldsymbol{T}\boldsymbol{a} = \begin{pmatrix} t_{11} & t_{12} & \cdots & t_{1N} \\ t_{21} & t_{22} & \cdots & t_{2N} \\ \vdots & \vdots & & \vdots \\ t_{N1} & t_{N2} & \cdots & t_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \tag{3.1.4}$$

3.1.2 Notes on vector space

A vector space consists of a set of vectors $(|\alpha\rangle, |\beta\rangle, |\gamma\rangle, \cdots)$, together with a set of scalars $(a, b, c, \cdots)$, which is closed under two operations: vector addition and scalar multiplication.

- **Vector Addition**

  The sum of any two vectors is another vector:

$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle \tag{3.1.5}$$

  Vector addition is commutative and associative:

$$|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle \tag{3.1.6}$$

$$|\alpha\rangle + (|\beta\rangle + |\gamma\rangle) = (|\alpha\rangle + |\beta\rangle) + |\gamma\rangle \tag{3.1.7}$$

There exists a zero (or null) vector, with the property that:

$$|\alpha\rangle + |0\rangle = |\alpha\rangle \tag{3.1.8}$$

For every vector $|\alpha\rangle$ there is an associated inverse vector ($|\alpha\rangle$), such that

$$|\alpha\rangle + |-\alpha\rangle = |0\rangle \tag{3.1.9}$$

- **Scalar Multiplication**

  The product of any scalar with any vector is another vector:

$$a\,|\alpha\rangle = |\gamma\rangle \tag{3.1.10}$$

  Scalar multiplication is distributive with respect to vector addition:

$$a\,(|\alpha\rangle + |\beta\rangle) = a\,|\alpha\rangle + a\,|\beta\rangle \tag{3.1.11}$$

  and with respect to scalar addition:

$$(a+b)\,|\alpha\rangle = a\,|\alpha\rangle + b\,|\alpha\rangle \tag{3.1.12}$$

  It is also associative with respect to the ordinary multiplication of scalars.

$$a\,(b\,|\alpha\rangle) = (ab)\,|\alpha\rangle \tag{3.1.13}$$

  Multiplication by the scalars 0 and 1 has the effect:

$$0\,|\alpha\rangle = |0\rangle\,; \qquad 1\,|\alpha\rangle = |\alpha\rangle \tag{3.1.14}$$

  Evidently,

$$|-\alpha\rangle = -\,|\alpha\rangle \tag{3.1.15}$$

3.1.3 Abstract basis

The linear combination of the solutions of Schroedinger equation is the general solution

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\frac{itE_n}{\hbar}} \tag{3.1.16}$$

When taking out the time-dependent terms:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{3.1.17}$$

$f(x)$ is an abstract vector:

- written in the basis spanned by ψ_n
- basis dimension can be infinity
- coefficient c_n can be complex:

$$c_n = \int \psi_n^*(x) f(x) dx \tag{3.1.18}$$

- $\{\psi_n\}$ are normalized, orthogonal, and completed:

$$\int \psi_m^*(x)\psi_n(x)dx = \delta_{m,n} \qquad \delta_{m,n} = \begin{cases} 0 & (m \neq n) \\ 1 & (m = n) \end{cases} \tag{3.1.19}$$

3.1.4 Hilbert space

Such a vector space is called Hilbert space.
All physical wavefunctions constructed by linear combinations of the basis vectors live in the Hilbert space.
All physical observables are represented by Hermitian operators.

- Schroedinger equation for a Hermitian opertator $\hat{Q}$ is an eigenvalue equation.
- Determinate states of Q are eigenfunctions of $\hat{Q}$.
- Definite "energies" of Q are eigenvalues $\hat{Q}$.

To be a Hilbert space, there are requirements for the functions:

- They are square-integrable:

$$\int |f(x)|^2 \, dx < \infty \tag{3.1.20}$$

Normalization is a stronger condition:

$$\int |f(x)|^2 \, dx = 1 \tag{3.1.21}$$

For two functions $f(x)$ and $g(x)$ in the Hilbert space, their inner product $\langle f|g\rangle = \int_a^b f(x)^* g(x) dx$ is guaranteed to exist by Schwarz inequality.

$$\left| \int_a^b f(x)^* g(x) dx \right| \leq \sqrt{\int_a^b |f(x)|^2 \, dx \int_a^b |g(x)|^2 \, dx} \tag{3.1.22}$$

which can be written in a short notation:

$$|\langle f|g\rangle|^2 \leq \langle f|f\rangle \langle g|g\rangle \tag{3.1.23}$$

- There are several properties:

① $\langle g|f\rangle = \langle f|g\rangle^*$

$$\langle g|f\rangle = \int_a^b g(x)^* f(x) dx = \left(\int_a^b f(x)^* g(x) dx \right)^* = \langle f|g\rangle^* \tag{3.1.24}$$

② $\langle f|f\rangle$ is real and non-negative, and $\langle f|f\rangle = 0$ only when $f(x) = 0$.

③ A function is normalized if the inner product $\langle f|f\rangle = \int_a^b |f(x)|^2\, dx$ is 1.

Two functions are orthogonal if the inner product $\langle f|g\rangle = \int_a^b f(x)^* g(x) dx = 0$

3.2 Observables and Hermitian operator

3.2.1 Hermitian operator

If $Q(x,p)$ is a physical operator, the expectation value of $Q(x,p)$:

$$\langle Q\rangle = \int \Psi^* \hat{Q}\Psi dx = \left\langle \Psi|\hat{Q}\Psi \right\rangle \tag{3.2.1}$$

It corresponds to an observable in experiment, which must be real:

$$\langle Q\rangle = \langle Q\rangle^* \tag{3.2.2}$$

If follows:

$$\left\langle \Psi|\hat{Q}\Psi \right\rangle = \langle Q\rangle = \langle Q\rangle^* = \left\langle \Psi|\hat{Q}\Psi \right\rangle^* = \left\langle \hat{Q}\Psi|\Psi \right\rangle \tag{3.2.3}$$

For the last step:

$$\int \left(\Psi^*\hat{Q}\Psi\right)^* dx = \int \Psi\hat{Q}^*\Psi^* dx = \int \Psi \left(\hat{Q}\Psi\right)^* dx = \int \left(\hat{Q}\Psi\right)^* \Psi dx \tag{3.2.4}$$

More general $\left\langle f|\hat{Q}g \right\rangle = \left\langle \hat{Q}f|g \right\rangle$ for all $f(x), g(x)$.

Such an operator is called **Hermitian operator**.

A hermitian conjugate, or adjoint in short, is defined as:

$$\left\langle f|\hat{Q}g \right\rangle = \left\langle \hat{Q}^\dagger f|g \right\rangle \tag{3.2.5}$$

Therefore, a hermitian operator is its adjoint:

$$\hat{Q}^\dagger = \hat{Q} \tag{3.2.6}$$

Observables in QM are represented by Hermitian operators $\hat{Q}$.

3.2.2 Determinate states

Stationary states are determinate states of the Hamiltonian:

$$\hat{H}\psi_n = E_n\psi_n \tag{3.2.7}$$

In a determinate state, the standard deviation is 0.

$$\sigma^2 = \left\langle \left(\hat{Q} - \langle Q\rangle\right)^2 \right\rangle = \left\langle \Psi| \left(\hat{Q} - q\right)^2 \Psi \right\rangle = \left\langle \left(\hat{Q} - q\right)\Psi| \left(\hat{Q} - q\right)\Psi \right\rangle = 0 \tag{3.2.8}$$

The inner product of $\left(\hat{Q} - q\right)\Psi$ is $0 \Longrightarrow \hat{Q}\Psi = q\Psi$

This is called eigenvalue equation of $\hat{Q}$, with eigenfunction Ψ and eigenvalue q.

Determinate states are eigenfunctions of $\hat{Q}$.

- Every measurement in an eigenstate gives the same eigenvalue:

$$\langle Q \rangle = \left\langle \Psi | \hat{Q} \Psi \right\rangle = q \langle \Psi | \Psi \rangle = q \tag{3.2.9}$$

- Standard deviation is 0.

$$\sigma^2 = \left\langle \left(\hat{Q} - \langle Q \rangle \right)^2 \right\rangle = \left\langle \Psi | \left(\hat{Q} - q \right)^2 \Psi \right\rangle = \left\langle \left(\hat{Q} - q \right) \Psi | \left(\hat{Q} - q \right) \Psi \right\rangle = 0 \tag{3.2.10}$$

- Because $\hat{Q}$ is hermitian, q as the eigenvalue must be real. Eigenvalue corresponds to an observable.

3.2.3 Solutions of hermitian operators

Example 1:

$\hat{H}$ is the Hamiltonian.

Schroedinger equation = eigenvalue equation of $\hat{H}$.

Example 2:

Consider an operator $\hat{Q} \equiv i\frac{d}{d\phi}$, ϕ is the polar coordinate in 2-dimension.

For functions $f(\phi)$ on the finite interval $0 \leq \phi \leq 2\pi$ and stipulate that

$$f(\phi + 2\pi) = f(\phi) \tag{3.2.11}$$

Using integration by parts:

$$\left\langle f | \hat{Q} g \right\rangle = \int_0^{2\pi} f^* \left(i\frac{dg}{d\phi} \right) d\phi = i f^* g |_0^{2\pi} - \int_0^{2\pi} i \left(\frac{df^*}{d\phi} \right) g d\phi = \left\langle \hat{Q} f | g \right\rangle \tag{3.2.12}$$

so $\hat{Q}$ is hermitian.

The eigenvalue equation:

$$i\frac{d}{d\phi} f(\phi) = q f(\phi) \tag{3.2.13}$$

with the general solution:

$$f(\phi) = A e^{-iq\phi} \tag{3.2.14}$$

Equation 3.2.11 restricts the possible values of the q:

$$e^{-iq2\pi} = 1 \Longrightarrow q = 0, \pm 1, \pm 2, \cdots \tag{3.2.15}$$

The spectrum of this operator is the set of all integers, and it is nondegenerate.

Example 3:

Consider an operator $\hat{Q} = \frac{d^2}{d\phi^2}$, ϕ is the polar coordinate in 2-dimension.

$$\begin{aligned} \left\langle f | \hat{Q} g \right\rangle = \int_0^{2\pi} f^* \frac{d^2 g}{d\phi^2} d\phi &= f^* \left. \frac{dg}{d\phi} \right|_0^{2\pi} - \int_0^{2\pi} \frac{df^*}{d\phi} \frac{dg}{d\phi} d\phi \\ &= f^* \left. \frac{dg}{d\phi} \right|_0^{2\pi} - \frac{df^*}{d\phi} \left. g \right|_0^{2\pi} + \int_0^{2\pi} \frac{d^2 f^*}{d\phi^2} g d\phi \\ &= \int_0^{2\pi} \frac{d^2 f^*}{d\phi^2} g d\phi \\ &= \left\langle \hat{Q} f | g \right\rangle \end{aligned} \tag{3.2.16}$$

$\hat{Q}$ is the Hamiltonian.

Solving eigenvalue equation:

$$\hat{Q}f = qf \Longrightarrow f_{\pm}(\phi) = Ae^{\pm\sqrt{q}\phi} \tag{3.2.17}$$

Normalization:

$$A = \frac{1}{\sqrt{2\pi}} \tag{3.2.18}$$

boundary condition: $f(\phi + 2\pi) = f(\phi)$

$$e^{\pm\sqrt{q}\phi} = e^{\pm\sqrt{q}\phi}e^{\pm\sqrt{q}2\pi} \Longrightarrow e^{\pm\sqrt{q}2\pi} = 1 = e^{\pm i2\pi n} \Longrightarrow \sqrt{q}(2\pi) = 2n\pi i \tag{3.2.19}$$

eigenvalues: $q = -n^2, \ \ n = 0, 1, 2, \cdots$

eigenfunctions: $f_{\pm}(\phi) = \frac{1}{\sqrt{2\pi}}e^{\pm in\phi}$

For one eigenvalue q, there exist two eigenfunctions (except n=0), this is called degeneracy.

This solution has two-fold degeneracy.

3.3 Eigenfunctions of a Hermitian operator

Two classes: spectrum is discrete or continuous

3.3.1 Discrete spectra of a hermitian operator

- **Theorem 1:** Eigenvalues are real

  Proof:

  If $\hat{Q}$ is a hermitian operator:

$$\left\langle f|\hat{Q}f\right\rangle = \left\langle \hat{Q}f|f\right\rangle \tag{3.3.1}$$

  Its eigenvalue equation:

$$\hat{Q}f = qf \tag{3.3.2}$$

  For eigenvalue equation:

$$\left\langle f|\hat{Q}f\right\rangle = \langle f|qf\rangle = q\langle f|f\rangle \tag{3.3.3}$$

  and its complex conjugate:

$$\left\langle \hat{Q}f|f\right\rangle = \langle qf|f\rangle = q^*\langle f|f\rangle \tag{3.3.4}$$

$$q\langle f|f\rangle = q^*\langle f|f\rangle \Longrightarrow q = q^* \tag{3.3.5}$$

- **Theorem 2:** Eigenfunctions belonging to different eigenvalues are orthogonal

  Proof:

  Suppose that the two eigenfunctions are f and g, satisfying

$$\hat{Q}f = q_1 f \qquad \hat{Q}g = q_2 g \tag{3.3.6}$$

If $\hat{Q}$ is a Hermitian operator, then $\left\langle f|\hat{Q}g\right\rangle = \left\langle \hat{Q}f|g\right\rangle$

$$q_2 \langle f|g\rangle = q_1^* \langle f|g\rangle = q_1 \langle f|g\rangle \Longrightarrow (q_2 - q_1)\langle f|g\rangle = 0 \tag{3.3.7}$$

If non-degenerate, i.e. q_1 and q_2 are different eigenvalues:

$$\langle f|g\rangle = 0 \Longrightarrow \text{orthogonal} \tag{3.3.8}$$

Axiom:

Eigenfunctions of a Hermitian operator are a complete set, and can express any function as a linear combination.

3.3.2 Continuous spectra of a hermitian operator

Eigenfunctions with continuous eigenvalues are not normalizable.

However, the three properties (reality, orthogonality, completeness) still hold.

Example:

momentum operator $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$

eigenvalue equation: $\hat{p}f_p(x) = pf_p(x)$

general solution: $f_p(x) = Ae^{\frac{ipx}{\hbar}}$

- **orthogonality:**

$$\int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x) dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} dx = |A|^2 2\pi\hbar\delta(p'-p) \tag{3.3.9}$$

To show the last step, use Fourier transformation:

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx \tag{3.3.10}$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k') e^{ik'x} dk' \tag{3.3.11}$$

Put $f(x)$ into the expression of $g(k)$:

$$g(k) = \int_{-\infty}^{\infty} dk' g(k') \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(k'-k)x} dx \tag{3.3.12}$$

consider the property of δ-function:

$$g(k) = \int_{-\infty}^{\infty} g(k')\delta(k'-k) dk' \tag{3.3.13}$$

compare the above two equations:

$$\delta(k'-k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(k'-k)x} dx \tag{3.3.14}$$

put k back to p, we obtain the orthogonality:

$$\int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x) dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} dx = |A|^2 2\pi\hbar\delta(p'-p) \tag{3.3.15}$$

If we choose $A = \frac{1}{\sqrt{2\pi\hbar}} \Longrightarrow f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$

We write the orthogonality in short notation as:

$$\langle f_{p'} | f_p \rangle = \delta(p' - p) \tag{3.3.16}$$

which is called Dirac orthonormality.

- **completeness:**

  Any function can be expressed as

$$f(x) = \int c(p) f_p(x) dp = \frac{1}{\sqrt{2\pi\hbar}} \int c(p) e^{ipx/\hbar} dp \tag{3.3.17}$$

$$\begin{aligned} \langle f_{p'} | f \rangle = \int_{-\infty}^{\infty} f^*_{p'}(x) f(x) dx &= \int_{-\infty}^{\infty} f^*_{p'}(x) \int c(p) f_p(x) dp dx \\ &= \int_{-\infty}^{\infty} c(p) \int_{-\infty}^{\infty} f^*_{p'}(x) f_p(x) dx dp \\ &= \int_{-\infty}^{\infty} c(p) \delta(p' - p) dp \\ &= c(p') \end{aligned} \tag{3.3.18}$$

  Although we cannot normalize $f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$

  We construct the wave packet

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} g(p) e^{ipx/\hbar} dp \tag{3.3.19}$$

  and calculate:

$$\begin{aligned} \langle \psi | \psi \rangle &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dx \left[\int_{-\infty}^{\infty} g(p) e^{ipx/\hbar} dp \right]^* \left[\int_{-\infty}^{\infty} g(p') e^{ip'x/\hbar} dp' \right] \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp g^*(p) \int_{-\infty}^{\infty} dp' g(p') \int_{-\infty}^{\infty} e^{i(p'-p)x/\hbar} dx \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp g^*(p) \int_{-\infty}^{\infty} dp' g(p') \delta(p' - p) \\ &= \frac{1}{2\pi\hbar} \int dp \left| g(p)^2 \right| \end{aligned} \tag{3.3.20}$$

3.4 Generalized statistical Interpretation and more about the Uncertainty Principle

3.4.1 Generalized statistical Interpretation

$$\hat{H} \longrightarrow \text{any observable } Q(x, p)$$

$$\text{Schroedinger equation } \hat{H}\psi_n = E_n \psi_n \longrightarrow \text{eigenvalue equation } \hat{Q} f_n = q_n f_n$$

If we measure Q on a particle in the state $\Psi(x,t)$

The probability of getting a particular eigenvalue q_n with the eigenfunction $f_n(x)$ is $|c_n|^2$, where

$$c_n = \langle f_n|\Psi\rangle \tag{3.4.1}$$

$|c_n|^2$ is the probability that a measurement on Q yields the value q_n.

The total probability:

$$\sum_n |c_n|^2 = 1 \tag{3.4.2}$$

can be obtained by normalization $\langle\Psi|\Psi\rangle = 1$.

The expectation value for Q can be obtained as:

$$\langle Q\rangle = \sum_n q_n |c_n|^2 \tag{3.4.3}$$

Example 1:

Consider the position operator $\hat{x} = x$:

The eigenvalue equation:

$$\hat{x}g_{x'}(x) = x'g_{x'}(x) \tag{3.4.4}$$

We'll have:

$$(x - x')g_{x'}(x) = 0 \Longrightarrow g_{x'}(x) = \delta(x - x') \tag{3.4.5}$$

Then

$$\begin{aligned} c_{x'} &= \langle g_{x'}|\Psi\rangle \\ &= \int g^*_{x'}(x)\Psi(x,t)dx \\ &= \int \delta(x - x')\Psi(x,t)dx \\ &= \Psi(x',t) \end{aligned} \tag{3.4.6}$$

and

$$\left|\Psi(x',t)\right|^2 = |c_{x'}|^2 \tag{3.4.7}$$

Example 2:

Consider the momentum operator $\hat{p} = \dfrac{\hbar}{i}\dfrac{d}{dx}$

The eigenvalue equation:

$$\hat{p}f_p(x) = pf_p(x) \tag{3.4.8}$$

The eigenfunction:

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ipx}{\hbar}} \tag{3.4.9}$$

Momentum space wavefunction (which is c(p)):

$$\Phi(p,t) \equiv \langle f_p|\Psi\rangle \tag{3.4.10}$$

Further

$$\Phi(p,t) = \langle f_p|\Psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} e^{-\frac{ipx}{\hbar}}\Psi(x,t)dx \tag{3.4.11}$$

Inverse:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} e^{\frac{ipx}{\hbar}}\Phi(p,t)dp \tag{3.4.12}$$

A particle of mass m is found in the delta function well. What is the probability that a measurement of its momentum would yield a value greater than p0?

example 2.1:

The delta function well

$$V(x) = -\alpha\delta(x) \tag{3.4.13}$$

and the momentum p_0:

$$p_0 = \frac{m\alpha}{\hbar^2} \tag{3.4.14}$$

The wavefunction is:

$$\Psi(x,t) = \frac{\sqrt{m\alpha}}{\hbar}exp\left(-m\alpha\frac{|x|}{\hbar^2}\right)exp\left(-\frac{iEt}{\hbar}\right); \qquad E = -\frac{m\alpha^2}{2\hbar^2} \tag{3.4.15}$$

The momentum space wavefunction is:

$$\begin{aligned}\Phi(p,t) &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} exp\left(-\frac{ipx}{\hbar}\right)\Psi(x,t)dx \\ &= \frac{\sqrt{m\alpha}}{\hbar}\frac{exp(-\frac{iEt}{\hbar})}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} exp(\frac{-ipx}{\hbar})exp\left(\frac{-m\alpha|x|}{\hbar^2}\right)dx \\ &= \sqrt{\frac{2}{\pi}}\frac{p_0^{\frac{3}{2}}e^{-\frac{iEt}{\hbar}}}{p^2+p_0^2}\end{aligned} \tag{3.4.16}$$

Probability for momentum to be at $p \to p + dp$:

$$|\Phi(p,t)|^2\,dp = \frac{2}{\pi}\frac{p_0^3}{(p^2+p_0^2)^2}dp \tag{3.4.17}$$

Probability for momentum to be at $p > p_0$:

$$\begin{aligned}P_{p>p_0} &= \int_{p_0}^{\infty}|\Phi(p,t)|^2\,dp = \frac{2}{\pi}\int_{p_0}^{\infty}\frac{p_0^3}{(p^2+p_0^2)^2}dp \\ &= \frac{2}{\pi}\left[\frac{pp_0}{p^2+p_0^2} + tan^{-1}\left(\frac{p}{p_0}\right)\right]\Bigg|_{p_0}^{\infty} \\ &= \frac{1}{4} - \frac{1}{2\pi}\end{aligned} \tag{3.4.18}$$

3.4.2 Generalized Uncertainty Principle

The Uncertainty Principle has a general form:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \left[\langle f|g\rangle - \langle g|f\rangle \right] \right)^2 = \left(\frac{1}{2i} \left\langle \left[\hat{A}, \hat{B} \right] \right\rangle \right)^2 \tag{3.4.19}$$

If we write any two observables as A and B, and define:

$$f = \left(\hat{A} - \langle A \rangle \right) \Psi \qquad g = \left(\hat{B} - \langle B \rangle \right) \Psi \tag{3.4.20}$$

Proof:

For any observable A, we have:

$$\sigma_A^2 = \left\langle \left(\hat{A} - \langle A \rangle \right) \Psi | \left(\hat{A} - \langle A \rangle \right) \Psi \right\rangle = \langle f|f\rangle \tag{3.4.21}$$

Likewise, for any observable B:

$$\sigma_B^2 = \left\langle \left(\hat{B} - \langle B \rangle \right) \Psi | \left(\hat{B} - \langle B \rangle \right) \Psi \right\rangle = \langle g|g\rangle \tag{3.4.22}$$

Therefore (invoking the Schwarz inequality):

$$\sigma_A^2 \sigma_B^2 = \langle f|f\rangle \langle g|g\rangle \geq |\langle f|g\rangle|^2 \tag{3.4.23}$$

For any complex number z:

$$|z|^2 = [Re(z)]^2 + [Im(z)]^2 \geq [Im(z)]^2 = \left[\frac{1}{2i}(z - z^*) \right]^2 \tag{3.4.24}$$

Therefore, letting $z = \langle f|g\rangle$,

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \left[\langle f|g\rangle - \langle g|f\rangle \right] \right)^2 \tag{3.4.25}$$

$$\begin{aligned}
\langle f|g\rangle &= \left\langle \left(\hat{A} - \langle A \rangle \right) \Psi | \left(\hat{B} - \langle B \rangle \right) \Psi \right\rangle = \left\langle \Psi | \left(\hat{A} - \langle A \rangle \right) \left(\hat{B} - \langle B \rangle \right) \Psi \right\rangle \\
&= \left\langle \Psi | \left(\hat{A}\hat{B} - \hat{A} \langle B \rangle - \hat{B} \langle A \rangle + \langle A \rangle \langle B \rangle \right) \Psi \right\rangle \\
&= \left\langle \Psi | \hat{A}\hat{B}\Psi \right\rangle - \langle B \rangle \left\langle \Psi | \hat{A}\Psi \right\rangle - \langle A \rangle \left\langle \Psi | \hat{B}\Psi \right\rangle + \langle A \rangle \langle B \rangle \langle \Psi | \Psi \rangle \\
&= \left\langle \hat{A}\hat{B} \right\rangle - \langle B \rangle \langle A \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle \\
&= \left\langle \hat{A}\hat{B} \right\rangle - \langle A \rangle \langle B \rangle
\end{aligned} \tag{3.4.26}$$

Similarly,

$$\langle g|f\rangle = \left\langle \hat{B}\hat{A} \right\rangle - \langle A \rangle \langle B \rangle \tag{3.4.27}$$

So

$$\langle f|g\rangle - \langle g|f\rangle = \left\langle \hat{A}\hat{B} \right\rangle - \left\langle \hat{B}\hat{A} \right\rangle = \left\langle \left[\hat{A}, \hat{B} \right] \right\rangle \tag{3.4.28}$$

Conclusion:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \left\langle \left[\hat{A}, \hat{B} \right] \right\rangle \right)^2 \tag{3.4.29}$$

Example:

If we let $\hat{A} = \hat{x}, \hat{B} = \hat{p} = -i\hbar\dfrac{d}{dx}$ and consider $[\hat{x}, \hat{p}] = i\hbar$

$$\sigma_x^2\sigma_p^2 \geq \left(\frac{1}{2i}i\hbar\right)^2 = \left(\frac{\hbar}{2}\right)^2 \Longrightarrow \sigma_x\sigma_p \geq \frac{\hbar}{2} \tag{3.4.30}$$

3.4.3 Incompatible and compatible observables

Incompatible observables:

For every pair of observables whose operators do not commute.

Incompatible observables do not have shared eigenfunctions.

Compatible observables:

Observables have complete sets of simultaneous eigenfunctions, whose operators commute with each other.

3.4.4 Minimum-uncertainty wave packet

The position-momentum uncertainty limit:

$$\sigma_x\sigma_p = \frac{\hbar}{2} \tag{3.4.31}$$

What is the most general minimum-uncertainty wave packet?

The Schwarz inequality becomes an equality when one function is a multiple of the other:

$$g(x) = cf(x) \quad \text{(c is a complex number)} \tag{3.4.32}$$

Meanwhile, when $Re(z) = Re(\langle f|g\rangle) = Re(c\langle f|f\rangle) = 0$:

$$|z|^2 = [Im(z)]^2 \tag{3.4.33}$$

where $\langle f|f\rangle$ is certainly real, so c must be pure imaginary, let's call it ia.

Solve the equation:

$$\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p\rangle\right)\Psi = ia\left(x - \langle x\rangle\right)\Psi \tag{3.4.34}$$

and obtain the solution:

$$\Psi(x) = Ae^{-\frac{a(x-\langle x\rangle)^2}{2\hbar}}e^{i\langle p\rangle x\hbar} \tag{3.4.35}$$

Conclusion:

The minimum-uncertainty wave packet is a gaussion.

3.4.5 Energy-time uncertainty principle

In special relativity, we have position-time four-vector (x, y, z, t) and momentum-energy four-vector (p_x, p_y, p_z, E).

Position-momentum Uncertainty:

$$\sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}; \quad \sigma_y\sigma_{p_y} \geq \frac{\hbar}{2}; \quad \sigma_z\sigma_{p_z} \geq \frac{\hbar}{2} \tag{3.4.36}$$

Energy-time Uncertainty:

$$\sigma_t \sigma_E \geq \frac{\hbar}{2} \tag{3.4.37}$$

Schroedinger equation is non-relativistic, $x, y, z, p_x, p_y, p_z, E$ are observables.

To obtain energy-time uncertainty principle:

Consider the change of expectation value of an observable $Q(x, p, t)$:

$$\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar}\left\langle [\hat{H}, \hat{Q}] \right\rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle \tag{3.4.38}$$

which is called the generalized Ehrenfest theorem.

Proof:

The Schroedinger equation:

$$\frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar}\hat{H}\Psi \tag{3.4.39}$$

$$\begin{aligned}
\frac{d}{dt}\langle Q \rangle &= \left\langle \frac{\partial \Psi}{\partial t} | \hat{Q}\Psi \right\rangle + \left\langle \Psi | \frac{\partial \hat{Q}}{\partial t}\Psi \right\rangle + \left\langle \Psi | \hat{Q}\frac{\partial \Psi}{\partial t} \right\rangle \\
&= -\frac{1}{i\hbar}\left\langle \hat{H}\Psi | \hat{Q}\Psi \right\rangle + \left\langle \Psi | \frac{\partial \hat{Q}}{\partial t}\Psi \right\rangle + \frac{1}{i\hbar}\left\langle \Psi | \hat{Q}\hat{H}\Psi \right\rangle \\
&= -\frac{1}{i\hbar}\left\langle \Psi | \hat{H}\hat{Q}\Psi \right\rangle + \left\langle \Psi | \frac{\partial \hat{Q}}{\partial t}\Psi \right\rangle + \frac{1}{i\hbar}\left\langle \Psi | \hat{Q}\hat{H}\Psi \right\rangle \\
&= \frac{i}{\hbar}\left\langle [\hat{H}, \hat{Q}] \right\rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle
\end{aligned} \tag{3.4.40}$$

In the typical case where the operator does not depend explicitly on time.

Discussion:

① If $\hat{Q} = 1 \Longrightarrow \frac{d}{dt}\langle \Psi | \Psi \rangle = 0$:

Normalization of Ψ is time-independent.

② If $\hat{Q} = \hat{H} \Longrightarrow \frac{d}{dt}\langle H \rangle = 0$:

Energy conservation.

③ If $\hat{Q}$ and $\hat{H}$ commute and $\left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle = 0$:

Then $\frac{d}{dt}\langle Q \rangle = 0$. Q is a conserved quantity.

For the general uncertainty principle:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i}\left\langle \left[\hat{A}, \hat{B}\right] \right\rangle \right)^2 \tag{3.4.41}$$

Let $A \to H$, $B \to Q$:

$$\sigma_H^2 \sigma_Q^2 \geq \left(\frac{1}{2i}\left\langle \left[\hat{H}, \hat{Q}\right] \right\rangle \right)^2 = \left(\frac{1}{2i}\frac{\hbar}{i}\frac{d}{dt}\langle Q \rangle \right)^2 = \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle Q \rangle}{dt}\right)^2 \tag{3.4.42}$$

i.e.

$$\sigma_H \sigma_Q \geq \frac{\hbar}{2} \left| \frac{d \langle Q \rangle}{dt} \right| \tag{3.4.43}$$

Define $\Delta E \equiv \sigma_H,\ \Delta t \equiv \frac{\sigma_Q}{\left| \frac{d\langle Q \rangle}{dt} \right|}$, then

$$\Delta E \Delta t \geq \frac{\hbar}{2} \tag{3.4.44}$$

P.S.:

Δt : Amount of time that takes for the expectation value of Q to change by one standard devaition.

Example: A particle with a very short lifetime does not have a very well-defined mass.

The Δ-particle can last about 10^{-23} seconds before it decays.

Measurement of its mass shows a bell-shaped curve centered at $1232\text{MeV}/c^2$ with a width of $\sim 120\text{MeV}/c^2$.

If we take Δt to be the lifetime of the particle:

$$\Delta E \Delta t = \left(\frac{120}{2} MeV \right) \left(10^{-23} s \right) = 6 \times 10^{-22} MeV \cdot s > \frac{\hbar}{2} \tag{3.4.45}$$

So the spread in m is about as small as the uncertainty principle allows.

A particle with so short a lifetime just doesn't have a well-defined mass.

3.5 Vectors, operators, and Dirac notation

3.5.1 Bases in Hilbert space

$\Psi(x,t)$ and $\Phi(p,t)$ are considered as vectors in Hilbert space, but are written in different bases.

But not any wavefunction can be written in the position basis. (**electron spin**)

(An electron is a point in mathematics. Therefore, it can not be described by a spatial function.)

For ordinary vector, we can write it in different bases. (**basis transformation**)

Imagine a state vector $|S(t)\rangle$ in Hilbert space. It can be written in different representations:

- position representation: $\Psi(x,t) = \langle x|S(t)\rangle$
- momentum representation: $\Phi(p,t) = \langle p|S(t)\rangle$
- energy representation: $c_n(t) = \langle n|S(t)\rangle$

where $|x\rangle, |p\rangle, |n\rangle$ are corresponding eigenfunctions.

The same wavefunction can be written in different forms:

$$\begin{aligned} |S(t)\rangle &= \int \Phi(p,t) \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ipx}{\hbar}} dp \\ &= \sum_n c_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}} \\ &= \int \Psi(x',t) \delta(x-x') dx' \end{aligned} \tag{3.5.1}$$

Now we use an abstract basis $\{|e_n\rangle\}$ to express vectors.

$$|\alpha\rangle = \sum_n a_n |e_n\rangle, \qquad a_n = \langle e_n|\alpha\rangle \tag{3.5.2}$$

$$|\beta\rangle = \sum_n b_n |e_n\rangle, \qquad b_n = \langle e_n|\beta\rangle \tag{3.5.3}$$

Transformation between the two vectors by operator $\hat{Q}$:

$$|\beta\rangle = \hat{Q}|\alpha\rangle \tag{3.5.4}$$

Matrix elements $Q_{mn} = \left\langle e_m|\hat{Q}|e_n\right\rangle$

$$|\beta\rangle = \hat{Q}|\alpha\rangle \Longrightarrow \sum_n b_n |e_n\rangle = \sum_n a_n \hat{Q}|e_n\rangle \tag{3.5.5}$$

Both sides are multiplied by a vector $|e_m\rangle$ from left:

$$\sum_n b_n \langle e_m|e_n\rangle = \sum_n a_n \left\langle e_m|\hat{Q}|e_n\right\rangle \Longrightarrow b_m = \sum_n Q_{mn} a_n \tag{3.5.6}$$

3.5.2 Daric notation

Dirac proposed the bracket notation for the inner product, **bra** and **ket**.

For every ket, there is a dual space bra.

Ket is expressed as a column matrix; Bra is expressed as a row matrix.

$$\langle\alpha|\alpha\rangle = \begin{pmatrix} a_1^* & a_2^* & \cdots & a_n^* \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} = \sum_n |a_n|^2 \tag{3.5.7}$$

$$\langle\beta|\alpha\rangle = \begin{pmatrix} b_1^* & b_2^* & \cdots & b_n^* \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} = \sum_n b_n^* a_n \tag{3.5.8}$$

Operator is expressed as a square matrix.

① Projection operator:

To obtain the portion of a vector in a particular direction.

$$\hat{P}_\alpha \equiv |\alpha\rangle\langle\alpha|, \qquad \text{where } |\alpha\rangle \text{ are normalized.} \tag{3.5.9}$$

$$\hat{P}_\alpha |\beta\rangle = |\alpha\rangle\langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle|\alpha\rangle \tag{3.5.10}$$

② Identity operator:

A projection onto a complete set of states.

If $\{|e_n\rangle\}$ are orthogonal, $\langle e_m|e_n\rangle = \delta_{m,n}$.

$$|\alpha\rangle = \sum_n a_n |e_n\rangle = \sum_n \langle e_n|\alpha\rangle |e_n\rangle = \sum_n |e_n\rangle \langle e_n|\alpha\rangle \tag{3.5.11}$$

$$\Longrightarrow \sum_n |e_n\rangle \langle e_n| \equiv 1 \Longrightarrow \text{Identity operator} \tag{3.5.12}$$

Similarly, if $\{|e_z\rangle\}$ is a Dirac orthonormalized continuous basis:

$$\langle e_z|e_{z'}\rangle = \delta(z - z') \tag{3.5.13}$$

$$\int |e_z\rangle \langle e_z| \, dz = 1 \tag{3.5.14}$$

Note:

$$\left(\hat{Q} + \hat{R}\right)|\alpha\rangle = \hat{Q}|\alpha\rangle + \hat{R}|\alpha\rangle \tag{3.5.15}$$

$$\hat{Q}\hat{R}|\alpha\rangle = \hat{Q}\left(\hat{R}|\alpha\rangle\right) \tag{3.5.16}$$

$$e^{\hat{Q}} = 1 + \hat{Q} + \frac{1}{2}\hat{Q}^2 + \frac{1}{3!}\hat{Q}^3 + \cdots \tag{3.5.17}$$

Example: Abstract space in 2-dimension.

Imagine a system in which there are just two linearly independent states:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{3.5.18}$$

General vector:

$$|S\rangle = \alpha|1\rangle + \beta|2\rangle \tag{3.5.19}$$

To satisfy the normalization:

$$|\alpha|^2 + |\beta|^2 = 1 \tag{3.5.20}$$

Hamitonian operator is a 2×2 matrix:

$$\hat{H} = \begin{pmatrix} h & g \\ g & h \end{pmatrix} \tag{3.5.21}$$

Schroedinger equation (time-independent):

$$\hat{H}|S\rangle = E|S\rangle \Longrightarrow \begin{pmatrix} h - E & g \\ g & h - E \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0 \tag{3.5.22}$$

$$\begin{vmatrix} h - E & g \\ g & h - E \end{vmatrix} = (h - E)^2 - g^2 = 0 \Longrightarrow h - E = \pm g \tag{3.5.23}$$

Two eigenvalues:

$$E_\pm = h \pm g \tag{3.5.24}$$

To determine the eigenvectors:

$$\begin{pmatrix} h & g \\ g & h \end{pmatrix} = (h \pm g) \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Longrightarrow \beta = \pm\alpha \tag{3.5.25}$$

So the normalized eigenvectors are:

$$|s_\pm\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \tag{3.5.26}$$

Expand the initial state as a linear combination of eigenvectors:

$$|S(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \left(|s_+\rangle + |s_-\rangle\right) \tag{3.5.27}$$

Finally, the standard time-dependent state:

$$\begin{aligned} |S(t)\rangle &= \frac{1}{\sqrt{2}} \left[e^{-\frac{i(h+g)t}{\hbar}} |s_+\rangle + e^{-\frac{i(h-g)t}{\hbar}} |s_-\rangle\right] \\ &= \frac{1}{2} e^{-\frac{iht}{\hbar}} \left[e^{-\frac{igt}{\hbar}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} + e^{\frac{igt}{\hbar}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}\right] \\ &= \frac{1}{2} e^{-\frac{iht}{\hbar}} \begin{pmatrix} e^{-\frac{igt}{\hbar}} + e^{\frac{igt}{\hbar}} \\ e^{-\frac{igt}{\hbar}} - e^{\frac{igt}{\hbar}} \end{pmatrix} = e^{-\frac{iht}{\hbar}} \begin{pmatrix} cos(\frac{gt}{\hbar}) \\ -isin(\frac{gt}{\hbar}) \end{pmatrix} \end{aligned} \tag{3.5.28}$$

3.5.3 Changing bases in Dirac notation

Applying the identity operator:

$$1 = \int dx\, |x\rangle \langle x| \tag{3.5.29}$$

$$1 = \int dp\, |p\rangle \langle p| \tag{3.5.30}$$

$$1 = \sum |n\rangle \langle n| \tag{3.5.31}$$

We can write any state vector $|S(t)\rangle$ and operator $\hat{Q}$ in a particular basis.

Example:

Transform the position-space wavefunction into the momentum-space wavefunction.

$$\begin{aligned} |S(t)\rangle &= \int dx\, |x\rangle \langle x|S(t)\rangle \\ &= \int \Psi(x,t)\, |x\rangle\, dx \end{aligned} \tag{3.5.32}$$

$$\begin{aligned} |S(t)\rangle &= \int dp\, |p\rangle \langle p|S(t)\rangle \\ &= \int \Phi(p,t)\, |p\rangle\, dp \end{aligned} \tag{3.5.33}$$

$$
\begin{aligned}
|S(t)\rangle &= \sum_n |n\rangle \langle n|S(t)\rangle \\
&= \sum_n C_n(t) |n\rangle
\end{aligned}
\tag{3.5.34}
$$

$$
\begin{aligned}
\Phi(p,t) &= \langle p|S(t)\rangle \\
&= \left\langle p| \left(\int dx |x\rangle \langle x| \right) |S(t) \right\rangle \\
&= \int \langle p|x\rangle \langle x|S(t)\rangle dx \\
&= \int \langle p|x\rangle \Psi(x,t) dx
\end{aligned}
\tag{3.5.35}
$$

$\langle x|p\rangle$ is the momentum eigenstate in the position basis $f_p(x)$, So

$$
\langle p|x\rangle = \langle x|p\rangle^* = [f_p(x)]^* = \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{ipx}{\hbar}} \tag{3.5.36}
$$

Therefore,

$$
\Phi(p,t) = \int \langle p|x\rangle \Psi(x,t) dx = \frac{1}{\sqrt{2\pi\hbar}} \int e^{-\frac{ipx}{\hbar}} \Psi(x,t) dx \tag{3.5.37}
$$

which is Fourier transform.

The operator:

in the position basis:

$$
\begin{cases}
\hat{x} \to x \\
\hat{p} \to -i\hbar \dfrac{\partial}{\partial x}
\end{cases}
\tag{3.5.38}
$$

$$
\begin{aligned}
\langle p |\hat{x}| S(t)\rangle &= \left\langle p \left| \hat{x} \int dx \right| x \right\rangle \langle x||S(t)\rangle \\
&= \int \langle p|x|x\rangle \langle x|S(t)\rangle dx \\
&= \int x \langle p|x\rangle \Psi(x,t) dx \\
&= \int x \frac{e^{-\frac{ipx}{\hbar}}}{\sqrt{2\pi\hbar}} \Psi(x,t) dx \\
&= i\hbar \frac{\partial}{\partial p} \int \frac{e^{-\frac{ipx}{\hbar}}}{\sqrt{2\pi\hbar}} \Psi(x,t) dx \\
&= i\hbar \frac{\partial}{\partial p} \Phi(p,t)
\end{aligned}
\tag{3.5.39}
$$

4 Chapter 4 Quantum mechanics in three dimensions

4.1 Schroedinger Equation in spherical coordinates

The 3-D Schroedinger equation is formally the same:

$$
i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{4.1.1}
$$

We assume the potential is time-independent:

$$V = V(\boldsymbol{r}, t) \Longrightarrow V = V(\boldsymbol{r}) \tag{4.1.2}$$

Solving the time-independent Schroedinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{4.1.3}$$

where

$$\boldsymbol{p} = -i\hbar\nabla, \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{4.1.4}$$

We obtain the general solution

$$\Psi(\boldsymbol{r}, t) = \sum c_n \psi_n(\boldsymbol{r}) e^{-\frac{iE_n t}{\hbar}} \tag{4.1.5}$$

Now we assume a central force:

$$V(\boldsymbol{r}) = V(r), \quad x = rsin\theta cos\phi, \quad y = rsin\theta sin\phi, \quad z = rcos\theta \tag{4.1.6}$$

In spherical basis:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{4.1.7}$$

Separate variables by letting: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, and considering:

$$\frac{\partial\psi}{\partial r} = Y\frac{dR}{dr}; \quad \frac{\partial\psi}{\partial\theta} = R\frac{\partial Y}{\partial\theta}; \quad \frac{\partial^2\psi}{\partial\phi^2} = R\frac{\partial^2 Y}{\partial\phi^2} \tag{4.1.8}$$

Then the TISE:

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2 sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right] + V(r)RY = ERY \tag{4.1.9}$$

Dividing by RY and multiplying by $-\frac{2mr^2}{\hbar^2}$:

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right)\right] = -\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right] \tag{4.1.10}$$

Separate the above equation into two equations, by letting them equals to $l(l+1)$.

Radial equation:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right) = l(l+1) \tag{4.1.11}$$

Angular equation:

$$\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right] = -l(l+1) \tag{4.1.12}$$

For the angular equation, Multiply by $Y sin^2\theta$, it becomes:

$$sin\theta \frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial Y}{\partial \theta}\right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1)sin^2\theta Y \tag{4.1.13}$$

Separate variables $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, and divide by $\Theta\Phi$:

$$\frac{1}{\Theta}\left[sin\theta \frac{d}{d\theta}\left(sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \tag{4.1.14}$$

Then we obtain two equations:

ϕ equation:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \tag{4.1.15}$$

θ equation:

$$\frac{1}{\Theta}\left[sin\theta \frac{d}{d\theta}\left(sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)sin^2\theta = m^2 \tag{4.1.16}$$

4.1.1 The ϕ equation

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \tag{4.1.17}$$

consider $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$, the eigenvalue equation for $\hat{L}_z^2$:

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial \phi}\right)^2 \Phi = m^2\hbar^2\Phi \tag{4.1.18}$$

The solution (if we take m as non-negatve values and absorb the constant factor into Θ):

$$\Phi(\phi) = e^{im\phi} \quad \text{and} \quad \Phi(\phi) = e^{-im\phi} \tag{4.1.19}$$

If we allow m as both positive and negative values:

$$\Phi(\phi) = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \cdots \longrightarrow \text{(magnetic quantum number)} \tag{4.1.20}$$

4.1.2 The θ equation

$$\frac{1}{\Theta}\left[sin\theta \frac{d}{d\theta}\left(sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)sin^2\theta = m^2 \tag{4.1.21}$$

The solution for this equation is:

$$\Theta(\theta) = AP_l^m(cos\theta) \tag{4.1.22}$$

associated Legendre function ($l \geq |m| \Rightarrow m = 0, \pm 1, \pm 2, \cdots, \pm l$):

$$P_l^m(x) = (1-x^2)^{\frac{|m|}{2}}\left(\frac{d}{dx}\right)^{|m|} P_l(x), \quad x = cos\theta \tag{4.1.23}$$

with $l-$th Legendre polynomial (l is non-negative$\Rightarrow l = 0, 1, 2, \cdots$):

$$P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l \tag{4.1.24}$$

For each l, there are $2l+1$ m.

4.1.3 Normalized angular wavefunction

Volume element in spherical coordinates:

$$dV = d^3\boldsymbol{r} = r^2 sin\theta dr d\theta d\phi \tag{4.1.25}$$

$$\int_{\text{all space}} |\psi|^2 r^2 sin\theta dr d\theta d\phi = \int_0^\infty R^2 r^2 dr \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} |Y(\theta,\phi)|^2 sin\theta d\theta d\phi = 1 \tag{4.1.26}$$

Normalization of radial function:

$$\int_0^\infty R^2 r^2 dr = 1 \tag{4.1.27}$$

Normalization of angular function:

$$\int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} |Y(\theta,\phi)|^2 sin\theta d\theta d\phi = 1 \tag{4.1.28}$$

Normalized angular wavefunctions are called spherical harmonics:

$$Y_l^m(\theta,\phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(cos\theta);\ \epsilon = \begin{cases} (-1)^m, & \text{for } m \geq 0 \\ 1, & \text{for } m \leq 0 \end{cases} \tag{4.1.29}$$

Normalized angular wavefunctions are called spherical harmonics, which is the eigenfunction of $\hat{L}^2$.

Spherical harmonics are normalized and orthogonal:

$$\int_0^{2\pi} \left\{ \int_0^\pi \left[Y_l^m(\theta,\phi)\right]^* \left[Y_{l'}^{m'}(\theta,\phi)\right] sin\theta d\theta \right\} d\phi = \delta_{ll',mm'} \tag{4.1.30}$$

4.1.4 Radial equation

$$\frac{1}{R}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right) = l(l+1) \tag{4.1.31}$$

Let $u(r) = rR(r) \Longrightarrow R(r) = \dfrac{u(r)}{r}$

$$\frac{dR}{dr} = \frac{r\frac{du}{dr} - u}{r^2} \Longrightarrow r^2 \frac{dR}{dr} = r\frac{du}{dr} - u \tag{4.1.32}$$

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) = r\frac{d^2u}{dr^2} \tag{4.1.33}$$

The radial part becomes:

$$r\frac{d^2u}{dr^2} - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]\frac{u}{r} = l(l+1)\frac{u}{r} \tag{4.1.34}$$

Multiply it by $-\dfrac{\hbar^2}{2mr}$:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu \tag{4.1.35}$$

Consider the effective potential:

$$V_{eff} = V(r) + \frac{\hbar^2}{2mr^2} l(l+1) \tag{4.1.36}$$

If $l = 0$, going back to the normal Schroedinger equation.

If $l > 0$, a large repulsion force near $r = 0$, a quantum "centrifugal force".

Meanwhile, the normalization condition becomes:

$$\int_0^\infty |u|^2 dr = 1 \tag{4.1.37}$$

Example: Infinite spherical well

$$V(r) = \begin{cases} 0, & \text{if } r \leq a \\ \infty, & \text{if } r > a \end{cases} \tag{4.1.38}$$

Inside the well, the radial equation says:

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2\right] u; \quad k \equiv \sqrt{\frac{2mE}{\hbar^2}} \tag{4.1.39}$$

The general solution is a combination of two special functions:

$$u(r) = Arj_l(kr) + Brn_l(kr) \tag{4.1.40}$$

- the l-th order of spherical Bessel function $j_l(x)$

$$j_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{sinx}{x} \tag{4.1.41}$$

$$j_0(x) = \frac{sinx}{x}; \quad j_1(x) = \frac{sinx}{x^2} - \frac{cosx}{x}; \cdots \tag{4.1.42}$$

- the l-th order of spherical Neumann function $n_l(x)$

$$n_l(x) = -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{cosx}{x} \tag{4.1.43}$$

$$n_0(x) = -\frac{cosx}{x}; \cdots \tag{4.1.44}$$

Notice that Bessel functions are finite at the origin, but Neumann functions blow up at the origin.

Therefore, $B_l = 0$ and:

$$R(r) = Aj_l(kr) \tag{4.1.45}$$

Boundary condition:

$$R(r = a) = Aj_l(ka) = 0 \Longrightarrow j_l(ka) = 0 \tag{4.1.46}$$

The solution of $j_l(ka) = 0$ is obtained numerically:

$$k = k_{Nl} = \frac{\beta_{Nl}}{a}, \quad \text{where } N \text{ is an infinite number} \tag{4.1.47}$$

where β_{Nl} is the N-th zero of the l-th spherical Bessel function.

Quantized energies:

$$E_{Nl} = \frac{\hbar^2}{2ma^2}\beta_{Nl}^2 \tag{4.1.48}$$

Wavefunctions:

$$\psi(\boldsymbol{r}) = \psi_{nlm}(r,\theta,\phi) = A_{nl} j_l\left(\frac{r\beta_{Nl}}{a}\right) Y_l^m(\theta,\phi) \tag{4.1.49}$$

n: number of solutions for all l — principal quantum number

4.2 The hydrogen atom

Using the Coulomb law:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{4.2.1}$$

The radial equation for hydrogen atom becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2mr^2}l(l+1)\right]u = Eu \tag{4.2.2}$$

We define:

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \qquad (E<0, \quad \text{a bound state problem}) \tag{4.2.3}$$

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2}\right]u \tag{4.2.4}$$

Define:

$$\rho = \kappa r \qquad \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \tag{4.2.5}$$

The equation becomes:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u \tag{4.2.6}$$

Look for asymptotic solutions:

- for $\rho \to \infty$:

$$\frac{d^2u}{d\rho^2} = u \Longrightarrow u(\rho) = Ae^{-\rho} + Be^{\rho} \longrightarrow B = 0 \text{ (to be physical)} \tag{4.2.7}$$

- for $\rho \to 0$:

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u \Longrightarrow u(\rho) = C\rho^{l+1} + D\rho^{-l} \longrightarrow D = 0 \text{ (to be physical)} \tag{4.2.8}$$

Combine the two asymptotic forms of solution together, we expect:

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho) \tag{4.2.9}$$

with $v(\rho)$ to be determined.

Equation for $v(\rho)$:

$$\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]\,v = 0 \tag{4.2.10}$$

We assume the solution can be expressed as power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \tag{4.2.11}$$

put into the equation and compare the coefficients to get the recursion formula:

$$c_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} c_j \tag{4.2.12}$$

For $j \to \infty$:

$$c_{j+1} \approx \frac{2}{j+1} c_j \Longrightarrow c_j \approx \frac{2^j}{j!} c_0 \tag{4.2.13}$$

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho} \Longrightarrow u(\rho) = c_0 \rho^{l+1} e^{\rho} \to \infty \ (\rho \to \infty) \tag{4.2.14}$$

Therefore, at certain maximal integer j_{max}, $c_j = 0$ for all $j > j_{max}$.

$$2(j_{max} + l + 1) = \rho_0 \tag{4.2.15}$$

$$2n = \rho_0, \qquad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \tag{4.2.16}$$

We define:

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2} \tag{4.2.17}$$

the allowed energies:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, 4, \cdots \tag{4.2.18}$$

with the principal quantum number:

$$n = j_{max} + l + 1, \quad n = 1, 2, 3, 4, \cdots \tag{4.2.19}$$

This is the famous Bohr formula found in 1913, but now as a QM solution.

Conclusions:

- From equation (4.2.16), we find that:

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2}\right)\frac{1}{n} = \frac{1}{an} \tag{4.2.20}$$

  Bohr radius:

$$a = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} m \tag{4.2.21}$$

- ρ can be expressed in terms of Bohr radius:

$$\rho = \rho_n = \frac{r}{an} \tag{4.2.22}$$

- ground-state energy (the lowest allowed energy):

$$E_1 = -13.6eV \tag{4.2.23}$$

  This is also called binding energy of the ground state of hydrogen.

- The wavefunction for hydrogen atom:

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}Y_l^m(\theta,\phi) \tag{4.2.24}$$

with $R_{nl} = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho)$ and $v(\rho)$ is polynomial of degree $j_{max} = n-l-1$, $\rho = \rho_n = \frac{r}{an}$.

The coefficients are given by $c_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$.

4.2.1 Radial functions

In the radial function $R_{nl} = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho)$.
the polynomial $v(\rho)$ is known to be associated Laguerre polynomial.

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \tag{4.2.25}$$

expressed as

$$L_{q-p}^{q}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \tag{4.2.26}$$

where the q-th Laguerre polynomial

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q (e^{-x}x^q) \tag{4.2.27}$$

Normalized total wavefunction for hydrogen atom:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}(\frac{2r}{na})\right] Y_l^m(\theta,\phi) \tag{4.2.28}$$

4.2.2 The quantum numbers

Wavefunction are specified by three quantum numbers:

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}Y_l^m(\theta,\phi) \tag{4.2.29}$$

- Principal quantum number: $n = 1, 2, 3, 4, \cdots$
- Angular momentum quantum number:

$$\text{for each n} \longrightarrow l = 0, 1, 2, \cdots, n-1$$

- Magnetic quantum number:

$$\text{for each } l \longrightarrow |m| \leq l \Longrightarrow m = 0, \pm 1, \pm 2, \cdots, \pm l$$

Energies are specified by one quantum number n:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2},\ n = 1, 2, 3, 4, \cdots \tag{4.2.30}$$

For each n, there are n^2 different states (n^2-fold degeneracy).

4.2.3 The spectrum of hydrogen

Transition energy:

$$E_\gamma = E_i - E_f = -13.63V\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{4.2.31}$$

$$E_\gamma = h\nu = \frac{hc}{\lambda} \Longrightarrow \frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4.2.32}$$

Rydberg constant R:

$$R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 1.097 \times 10^7 m^{-1} \tag{4.2.33}$$

4.2.4 Ground state of hydrogen atom

General wavefunction:

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}Y_l^m(\theta,\phi) \qquad n = 1,2,3,4,\cdots \tag{4.2.34}$$

For ground state, the quantum numbers are $\{n,l,m\} = \{1,0,0\}$.

$$\psi_{100}(r,\theta,\phi) = R_{10}(r)Y_0^0(\theta,\phi) \tag{4.2.35}$$

$$R_{10}(r) = \frac{c_0}{a}e^{-\frac{r}{a}}, \quad Y_0^0 = \frac{1}{\sqrt{4\pi}} \tag{4.2.36}$$

Normalisation:

$$\int_{r=0}^{\infty} R_{10}^2 r^2 dr = 1 \Longrightarrow c_0 = \frac{2}{\sqrt{a}} \Longrightarrow \psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-\frac{r}{a}} \tag{4.2.37}$$

4.3 Angular momentum

In classical physics:

$$\vec{L} = \vec{r} \times \vec{p} \Longrightarrow \begin{cases} L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \\ L_z = xp_y - yp_x \end{cases} \tag{4.3.1}$$

In quantum mechanics, quantities become operators:

$$\begin{array}{l} \vec{r} \longrightarrow (\hat{x},\hat{y},\hat{z}) \\ \vec{p} \longrightarrow (\hat{p}_x,\hat{p}_y,\hat{p}_z) \\ \vec{L} \longrightarrow \left(\hat{L}_x,\hat{L}_y,\hat{L}_z\right) \end{array} \quad \begin{cases} \hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{cases} \tag{4.3.2}$$

Commutation relation for position and momentum:

$$[\hat{x}_i,\hat{p}_j] = i\hbar\delta_{ij}, \quad [\hat{x}_i,\hat{x}_j] = 0, \quad [\hat{p}_i,\hat{p}_j] = 0 \tag{4.3.3}$$

Different components of angular momentum do not commute:

$$\begin{aligned} \left[\hat{L}_x,\hat{L}_y\right] &= i\hbar\hat{L}_z \\ \left[\hat{L}_y,\hat{L}_z\right] &= i\hbar\hat{L}_x \\ \left[\hat{L}_z,\hat{L}_x\right] &= i\hbar\hat{L}_y \end{aligned} \tag{4.3.4}$$

This means the three components are incompatible to each other.

Proof:

$$\begin{aligned}\left[\hat{L}_x, \hat{L}_y\right] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y}\hat{p}_x [\hat{p}_z, \hat{z}] + \hat{x}\hat{p}_y [\hat{z}, \hat{p}_z] \\ &= i\hbar (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) \\ &= i\hbar \hat{L}_z\end{aligned} \tag{4.3.5}$$

Uncertainty Principle applies to any pair of the three components:

$$\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle\right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2 \Longrightarrow \sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle| \tag{4.3.6}$$

Each component of angular momentum commutes with $\boldsymbol{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$.

$$\left[\hat{L}_i, \boldsymbol{L}^2\right] = 0, \quad i = x, y, z \Longrightarrow \left[\hat{L}, \boldsymbol{L}^2\right] = 0 \tag{4.3.7}$$

Proof:

with the following commutator identities:

$$\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B} \tag{4.3.8}$$

$$\begin{aligned}\left[L^2, L_x\right] &= \left[L_x^2, L_x\right] + \left[L_y^2, L_x\right] + \left[L_z^2, L_x\right] \\ &= L_x [L_x, L_x] + [L_x, L_x] L_x + L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_y (-i\hbar L_z) + (-i\hbar L_z) L_y + L_z (i\hbar L_y) + (i\hbar L_y) L_z \\ &= 0\end{aligned} \tag{4.3.9}$$

This means there exist simultaneous eigenstates for $\boldsymbol{L}^2$ and one component of angular momentum.

We usually choose the z-component, L_z, that has simultaneous eigenstates with $\boldsymbol{L}^2$.

Once L_z is chosen, then L_x and L_y cannot be determined in these states.

4.3.1 Ladder operators

Solving eigenvalue equations:

$$L^2 f = \lambda f \qquad L_z f = \mu f \tag{4.3.10}$$

Define ladder operators:

$$L_\pm = L_x \pm i L_y \tag{4.3.11}$$

The commutation relations are:

$$\left[L^2, L_\pm\right] = 0 \qquad [L_z, L_\pm] = \pm\hbar L_\pm \tag{4.3.12}$$

If f is an eigenfunction of L^2 and L_z, so also is $L_\pm f$:

$$L^2\left(L_\pm f\right) = L_\pm\left(L^2 f\right) = L_\pm\left(\lambda f\right) = \lambda\left(L_\pm f\right) \tag{4.3.13}$$

$$L_z\left(L_\pm f\right) = \left(L_z L_\pm - L_\pm L_z\right) f + L_\pm L_z f = \pm\hbar L_\pm f + L_\pm\left(\mu f\right) = \left(\mu \pm \hbar\right)\left(L_\pm f\right) \tag{4.3.14}$$

There exists a top rung, such that:

$$L_+ f_t = 0 \tag{4.3.15}$$

There exists a bottom rung, such that:

$$L_- f_b = 0 \tag{4.3.16}$$

Let $\hbar l$ be the eigencalue of L_z at the top rung, $\hbar l'$ be the eigenvalue of L_z at the bottom rung:

$$L_z f_t = \hbar l f_t; \qquad L_z f_b = \hbar l' f_b \tag{4.3.17}$$

Now,

$$\begin{aligned} L_\pm L_\mp &= \left(L_x \pm i L_y\right)\left(L_x \mp i L_y\right) \\ &= L_x^2 + L_y^2 \mp i\left(L_x L_y - L_y L_x\right) \\ &= L^2 - L_z^2 \mp i(i\hbar L_z) \end{aligned} \tag{4.3.18}$$

$$\Longrightarrow L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z \tag{4.3.19}$$

Apply to f_t:

$$\begin{aligned} L^2 f_t &= \left(L_- L_+ + L_z^2 + \hbar L_z\right) f_t \\ &= \left(0 + \hbar^2 l^2 + \hbar^2 l\right) f_t \\ &= \hbar^2 l(l+1) f_t \\ &= \lambda f_t \end{aligned} \tag{4.3.20}$$

Apply to f_b:

$$\begin{aligned} L^2 f_b &= \left(L_+ L_- + L_z^2 - \hbar L_z\right) f_b \\ &= \left(0 + \hbar^2 l'^2 - \hbar^2 l'\right) f_b \\ &= \hbar^2 l'(l'-1) f_b \\ &= \lambda f_b \end{aligned} \tag{4.3.21}$$

For $l(l+1) = l'(l'-1)$:

One solution: $l' = l + 1$, non-physical.

Another solution: $l' = -l$.

Conclusion:

If l is the largest quantum number of L_z, then $-l$ is the smallest.

How many ladders?

$$l = -l + N \Longrightarrow N = 2l, \quad l \text{ can be integer or half-integer.} \tag{4.3.22}$$

4.3.2 Eigenvalues of angular momentum

The eigenvalues:

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m, \quad L_z f_l^m = \hbar m f_l^m \tag{4.3.23}$$

$$l = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots; \quad m = -l, -l+1, \cdots, l-1, l \tag{4.3.24}$$

L is a vector in 3-dimension:

$$\text{length: } \hbar\sqrt{l(l+1)}$$
$$\text{direction: m (assume z as rotational axis)}$$

Note: the radius is:

$$\sqrt{l(l+1)} > l \tag{4.3.25}$$

This is required by the Uncertainty Principle.

4.3.3 Eigenfunctions of angular momentum

From $\boldsymbol{L} = -i\hbar\left(\boldsymbol{r} \times \nabla\right),\ \nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r sin\theta}\frac{\partial}{\partial \phi}$:

$$\begin{aligned} \boldsymbol{L} &= -i\hbar\left[r\left(\hat{r}\times\hat{r}\right)\frac{\partial}{\partial r} + \left(\hat{r}\times\hat{\theta}\right)\frac{\partial}{\partial\theta} + \left(\hat{r}\times\hat{\phi}\right)\frac{1}{sin\theta}\frac{\partial}{\partial\phi}\right] \\ &= -i\hbar\left(\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{sin\theta}\frac{\partial}{\partial\phi}\right) \end{aligned} \tag{4.3.26}$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components:

$$\begin{aligned} \hat{\theta} &= \left(cos\theta cos\phi\right)\hat{i} + \left(cos\theta sin\phi\right)\hat{j} - sin\theta\hat{k} \\ \hat{\phi} &= -sin\phi\hat{i} + cos\phi\hat{j} \end{aligned} \tag{4.3.27}$$

Thus

$$\boldsymbol{L} = -i\hbar\left[\left(-sin\phi\hat{i} + cos\phi\hat{j}\right)\frac{\partial}{\partial\theta} - \left(\left(cos\theta cos\phi\right)\hat{i} + \left(cos\theta sin\phi\right)\hat{j} - sin\theta\hat{k}\right)\frac{1}{sin\theta}\frac{\partial}{\partial\phi}\right] \tag{4.3.28}$$

So

$$\begin{aligned} L_x &= -i\hbar\left(-sin\phi\frac{\partial}{\partial\theta} - cos\phi cot\theta\frac{\partial}{\partial\phi}\right) \\ L_y &= -i\hbar\left(cos\phi\frac{\partial}{\partial\theta} - sin\phi cot\theta\frac{\partial}{\partial\phi}\right) \\ L_z &= -i\hbar\frac{\partial}{\partial\phi} \end{aligned} \tag{4.3.29}$$

We shall also need the raising and lowering operators:

$$\begin{aligned} L_\pm = L_x \pm iL_y &= -i\hbar\left[\left(-sin\phi \pm icos\phi\right)\frac{\partial}{\partial\theta} - \left(cos\phi \pm isin\phi\right)cot\theta\frac{\partial}{\partial\phi}\right] \\ &= \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} \pm icot\theta\frac{\partial}{\partial\phi}\right) \end{aligned} \tag{4.3.30}$$

In particular:

$$L_+L_- = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + cot\theta\frac{\partial}{\partial\theta} + cot^2\theta\frac{\partial^2}{\partial\phi^2} + i\frac{\partial}{\partial\phi}\right) \tag{4.3.31}$$

and hence:

$$L^2 = -\hbar^2\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right] \tag{4.3.32}$$

Compare with the angular equation and azimuthal equation, the result is the spherical harmonic.
Normalized angular wavefunctions are $Y_l^m(\theta,\phi)$, which are simultaneous eigenfunction of L^2 and L_z.
But $\psi_{n,l,m} = R_{nl}Y_l^m(\theta,\phi)$ is simultaneous eigenfunction of H,L^2 and L_z:

$$\begin{aligned} H\psi &= E\psi \\ L^2\psi &= \hbar^2 l(l+1)\psi \\ L_z\psi &= \hbar m\psi \end{aligned} \tag{4.3.33}$$

4.4 Spin

Spin is not a quantity defined in a space. Therefore, it can not be described by position variables.
Elementary particles carry intrinsic angular momentum S in addition to orbital angular momentum L.

Spin S have the following commutations relations:

$$\begin{aligned} [S_x, S_y] &= i\hbar S_z \\ [S_y, S_z] &= i\hbar S_x \\ [S_z, S_x] &= i\hbar S_y \end{aligned} \tag{4.4.1}$$

$$S^2 = S_x^2 + S_y^2 + S_z^2 \qquad \left[S^2, S_i\right] = 0, \quad i = x, y, z \tag{4.4.2}$$

4.4.1 Eigenvalues of spin

S^2 and S_z commute and have simultaneous eigenfunctions $|sm\rangle$.

$$S^2\,|sm\rangle = \hbar^2 s(s+1)\,|sm\rangle \tag{4.4.3}$$

$$S_z\,|sm\rangle = \hbar m\,|sm\rangle \tag{4.4.4}$$

$$s = 0, \frac{1}{2}, \frac{3}{2}, \cdots; \qquad m = -s, -s+1, \cdots, s-1, s \tag{4.4.5}$$

In addition, there are raising and lowering operators, with the following properties:

$$S_\pm = S_x \pm iS_y \tag{4.4.6}$$

$$S_\pm\,|sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm1)}\,|s(m\pm1)\rangle \tag{4.4.7}$$

4.4.2 Spin 1/2

Electrons, protons, neutrons, all quarks, all leptons,$\cdots$
When $s = \frac{1}{2} \Longrightarrow m = \frac{1}{2}$ or $-\frac{1}{2}$.
Then spin 1/2 has only two eigenstates:

$$\text{sign-up state: } \left|\frac{1}{2}\frac{1}{2}\right\rangle \qquad \text{or spin-down state: } \left|\frac{1}{2}\left(-\frac{1}{2}\right)\right\rangle \tag{4.4.8}$$

They can express general vectors in 2-dimensional spin space:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \tag{4.4.9}$$

with spin-up $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, spin-down $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$
with normalization:

$$\chi^+\chi = (a^* b^*) \begin{pmatrix} a \\ b \end{pmatrix} = |a|^2 + |b|^2 = 1 \tag{4.4.10}$$

4.4.3 Matrices in the spin basis

Since S^2 and S_z commute, they have simultaneous eigenstates.

In this space, all operators have matrix form.

Equation (4.4.3) says:

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+; \qquad S^2\chi_- = \frac{3}{4}\hbar^2\chi_- \tag{4.4.11}$$

Equation (4.4.4) says:

$$S_z\chi_+ = \frac{\hbar}{2}\chi_+; \qquad S_z\chi_- = -\frac{\hbar}{2}\chi_- \tag{4.4.12}$$

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.4.13}$$

Proof:

If we write S^2 as a matrix with undetermined elements:

$$S^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix} \tag{4.4.14}$$

The first equation says:

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \Longrightarrow \begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4}\hbar^2 \\ 0 \end{pmatrix} \tag{4.4.15}$$

The second equation says:

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \Longrightarrow \begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4}\hbar^2 \end{pmatrix} \tag{4.4.16}$$

Conclusion:

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4.4.17}$$

For the other two components:

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{4.4.18}$$

For the raising and lowering operators:

$$S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}; \qquad S_- = S_+^+ \tag{4.4.19}$$

From equation (4.4.7):

$$S_+\chi_- = \hbar\chi_+, \quad S_-\chi_+ = \hbar\chi_- \tag{4.4.20}$$

$$S_+\chi_+ = S_-\chi_- = 0 \tag{4.4.21}$$

Note:

S_x, S_y, S_z and S^2 are all hermitian matrices (as they should be, since they represent observables).

On the other hand, S_+ and S_- are not hermitian (evidently they are not observable).

4.4.4 Pauli matrices

The Pauli matrices are related to the S matrices by:

$$S = \frac{\hbar}{2}\vec{\sigma} \tag{4.4.22}$$

The Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.4.23}$$

together with the unit matrix:

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4.4.24}$$

They form a complete basis in which arbitrary operator of dimension 2 can be expanded.

Measurements:

For $\chi = a\chi_+ + b\chi_-$:

① Measure S_z in χ:

$$\left.\begin{array}{l} \text{get } +\dfrac{\hbar}{2} \text{ with probability } |a|^2 \\ \text{get } -\dfrac{\hbar}{2} \text{ with probability } |b|^2 \end{array}\right\} |a|^2 + |b|^2 = 1$$

② Measure S_y in χ:

must solve an equation:

$$S_y \begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \gamma \begin{pmatrix} a \\ b \end{pmatrix}, \quad \gamma = \frac{2\lambda}{\hbar} \tag{4.4.25}$$

$$\begin{pmatrix} -\gamma & -i \\ i & -\gamma \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0 \Longrightarrow \begin{vmatrix} -\gamma & -i \\ i & -\gamma \end{vmatrix} = 0 \Longrightarrow \gamma^2 - 1 = 0 \Longrightarrow \lambda = \pm\frac{\hbar}{2} \tag{4.4.26}$$

- $\lambda = \frac{\hbar}{2}$ $(\gamma = 1)$:

$$\begin{pmatrix} -1 & -i \\ i & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0 \Longrightarrow b = ia \Longrightarrow a = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \tag{4.4.27}$$

$$\left| S = \frac{1}{2}, S_y = \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} = \chi_+^{(y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{i}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4.4.28}$$

- $\lambda = -\frac{\hbar}{2}$ $(\gamma = -1)$:

$$\left| S = \frac{1}{2}, S_y = -\frac{1}{2} \right\rangle = \chi_-^{(y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} - \frac{i}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4.4.29}$$

orthogonality:

$$\left| S = \frac{1}{2}, S_y = \frac{1}{2} | S = \frac{1}{2}, S_y = -\frac{1}{2} \right\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} = 0 \tag{4.4.30}$$

$$\begin{aligned} \chi &= a\chi_+^{(z)} + b\chi_-^{(z)} \\ &= \left(\frac{a+b}{\sqrt{2}} \right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}} \right) \chi_-^{(x)} \\ &= \left(\frac{a+ib}{\sqrt{2}} \right) \chi_+^{(y)} + \left(\frac{a-ib}{\sqrt{2}} \right) \chi_-^{(y)} \end{aligned} \tag{4.4.31}$$

4.5 Electron in a magnetic field

A spinning charged particle constitutes a magnetic dipole.

From an orbital motion, one can derive for an electron:

$$\vec{\mu} = -\gamma \vec{L} \tag{4.5.1}$$

$\vec{\mu}$: magnetic dipole moment

γ: gyromagnetic ratio (or g-factor)

More general, for any angular momentum (orbital angular momentum, spin, or coupled angular momenta):

$$\vec{\mu} = \gamma \vec{J} \tag{4.5.2}$$

Classical derivation for an orbital electron $\vec{\mu} = -\gamma\vec{L}$:

$$\vec{\mu} = IA\hat{z} \tag{4.5.3}$$

$$|\mu| = \frac{-e}{T}\pi r^2 = \frac{-e}{\frac{2\pi r}{v}}\pi r^2 = \frac{-evr}{2} = \frac{-e}{2m}mvr \tag{4.5.4}$$

$$\vec{\mu} = -\frac{e}{2m}\vec{r}\times\vec{p} = -\frac{e}{2m}\vec{L} = -\gamma\vec{L} \tag{4.5.5}$$

For $\vec{\mu} = \gamma\vec{S}$ in a magnetic field, there is a magnetic interaction between the dipole and the field.
The particle feels a potential, which can be written as:

$$H = -\vec{\mu}\cdot\vec{B} \tag{4.5.6}$$

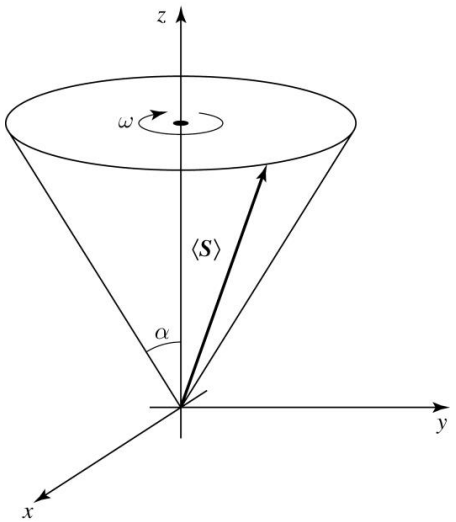
$\vec{\mu}$ feels a torque from the field, to force $\vec{\mu}$ to align with the direction of $\vec{B}$:

$$\vec{\tau} = \vec{\mu}\times\vec{B} \tag{4.5.7}$$

4.5.1 Larmor precession

Larmor precession of magnetic moments of spin $\frac{1}{2}$ particles leads to:

for electrons: Electron Paramagnetic Resonance (EPR)
for nuclei: Nuclear Magnetic Resonance (NMR)



Consider a spin $\frac{1}{2}$ at rest in a uniform magnetic field pointing to the z-direction:
the magnetic field:

$$\vec{B} = B_0\hat{z} \tag{4.5.8}$$

The Hamiltonian is:

$$H = -\gamma B_0 \hat{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.5.9}$$

Recall the eigenstates of $\hat{S}_z$:

- $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, with energy $E_+ = -\frac{\gamma B_0 \hbar}{2}$;
- $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, with energy $E_- = +\frac{\gamma B_0 \hbar}{2}$;

The general solution to the time-dependent Schrodinger equation:

$$i\hbar \frac{\partial \chi}{\partial t} = H\chi \tag{4.5.10}$$

can be expressed in terms of the stationary states:

$$\chi(t) = a\chi_+ e^{-\frac{iE_+ t}{\hbar}} + b\chi_- e^{-\frac{iE_- t}{\hbar}} = \begin{pmatrix} ae^{\frac{i\gamma B_0 t}{2}} \\ be^{-\frac{i\gamma B_0 t}{2}} \end{pmatrix} \tag{4.5.11}$$

The constants a and b are determined by the initial conditions:

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix}; \qquad \left(|a|^2 + |b|^2 = 1\right) \tag{4.5.12}$$

With no essential loss of generality, rewrite:

$$a = cos\left(\frac{\alpha}{2}\right), \quad b = sin\left(\frac{\alpha}{2}\right) \tag{4.5.13}$$

Thus,

$$\chi(t) = \begin{pmatrix} cos\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \\ sin\left(\frac{\alpha}{2}\right) e^{-\frac{i\gamma B_0 t}{2}} \end{pmatrix} \tag{4.5.14}$$

Calculate the expectation value of $\boldsymbol{S}$:

$$\begin{aligned} \langle S_x \rangle &= \chi(t)^\dagger S_x \chi(t) \\ &= \begin{pmatrix} cos\left(\frac{\alpha}{2}\right) e^{-\frac{i\gamma B_0 t}{2}} & sin\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} cos\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \\ sin\left(\frac{\alpha}{2}\right) e^{-\frac{i\gamma B_0 t}{2}} \end{pmatrix} \\ &= \frac{\hbar}{2} sin\alpha cos\left(\gamma B_0 t\right) \end{aligned} \tag{4.5.15}$$

Similarly,

$$\langle S_y \rangle = \chi(t)^\dagger S_y \chi(t) = -\frac{\hbar}{2} sin\alpha sin\left(\gamma B_0 t\right) \tag{4.5.16}$$

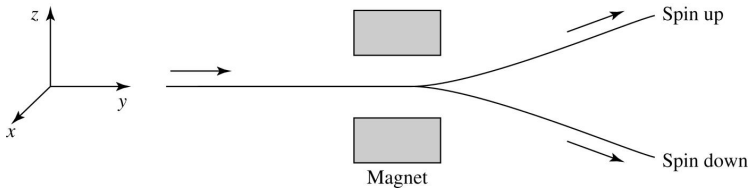
$$\langle S_z \rangle = \chi(t)^\dagger S_z \chi(t) = -\frac{\hbar}{2} cos\alpha \tag{4.5.17}$$

Thus $\langle \boldsymbol{S} \rangle$ is tilted at a constant angle α to the z axis, and precesses about the field at the Larmor frequency:

$$\omega = \gamma B_0 \tag{4.5.18}$$

4.5.2 The Stern-Gerlach experiment

Performed by Otto Stern and Walther Gerlach in 1922, which proves quantalization of angular momentum.



No Lorentz force, Only magnetic force:

$$\vec{F} = -\nabla V = \nabla\left(\vec{\mu}\cdot\vec{B}\right) \qquad \vec{\mu} = \gamma\vec{S} \tag{4.5.19}$$

This force can be used to separate out particles with a particular spin orientation.
The inhomogeneous magnetic field:

$$\boldsymbol{B}(x,y,z) = -\alpha x\hat{i} + (B_0 + \alpha z)\,\hat{k} \tag{4.5.20}$$

where B_0 is a strong uniform field and the constant α describes a small deviation from homogeneity.
(The x component is neccessary because the electromagnetic law $\nabla\cdot\vec{B} = 0$ can not be violated.)
The force on the atoms:

$$\boldsymbol{F} = \gamma\alpha\left(-S_x\hat{i} + S_z\hat{k}\right) \tag{4.5.21}$$

Because of the Larmor precession about B_0, S_x oscillates rapidly, and averages to zero.
The net force is in the z direction:

$$F_z = \gamma\alpha S_z \tag{4.5.22}$$

So the beam is in proportion to the z component of the spin angular momentum.
Fact:
The beam splits into $2s+1$ separate streams, demonstrating the quantization of angular momentum.

4.5.3 Addition of angular momenta

Suppose that we have two particles, with spin operators $\boldsymbol{S}^{(1)}$ and $\boldsymbol{S}^{(2)}$ with their eigenvalue equations ($i = 1, 2$):

$$S^{(i)^2}\,|s_i m_i\rangle = \hbar^2 s_i(s_i+1)\,|s_i m_i\rangle \tag{4.5.23}$$

$$S_z^{(i)}\,|s_i m_i\rangle = \hbar m_i\,|s_i m_i\rangle \tag{4.5.24}$$

We denote the composite state by $|s_1 s_2 m_1 m_2\rangle$:

$$\begin{aligned}
S^{(1)^2}\,|s_1 s_2 m_1 m_2\rangle &= s_1(s_1+1)\hbar^2\,|s_1 s_2 m_1 m_2\rangle \\
S^{(2)^2}\,|s_1 s_2 m_1 m_2\rangle &= s_2(s_2+1)\hbar^2\,|s_1 s_2 m_1 m_2\rangle \\
S_z^{(1)}\,|s_1 s_2 m_1 m_2\rangle &= m_1\hbar\,|s_1 s_2 m_1 m_2\rangle \\
S_z^{(2)}\,|s_1 s_2 m_1 m_2\rangle &= m_2\hbar\,|s_1 s_2 m_1 m_2\rangle
\end{aligned} \tag{4.5.25}$$

For the z component:

$$\begin{aligned} S_z \left|s_1 s_2 m_1 m_2\right\rangle &= S_z^{(1)} \left|s_1 s_2 m_1 m_2\right\rangle + S_z^{(2)} \left|s_1 s_2 m_1 m_2\right\rangle \\ &= \hbar(m_1 + m_2) \left|s_1 s_2 m_1 m_2\right\rangle \\ &= \hbar m \left|s_1 s_2 m_1 m_2\right\rangle \end{aligned} \tag{4.5.26}$$

so

$$m = m_1 + m_2 \tag{4.5.27}$$

Consider the case of two spin-$\frac{1}{2}$ particles:
There are four possibilities in all:

$$\begin{aligned} |\uparrow\uparrow\rangle &= \left|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\rangle, \qquad m = 1 \\ |\uparrow\downarrow\rangle &= \left|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{-1}{2}\right\rangle, \qquad m = 0 \\ |\downarrow\uparrow\rangle &= \left|\frac{1}{2}\frac{1}{2}\frac{-1}{2}\frac{1}{2}\right\rangle, \qquad m = 0 \\ |\downarrow\downarrow\rangle &= \left|\frac{1}{2}\frac{1}{2}\frac{-1}{2}\frac{-1}{2}\right\rangle, \qquad m = -1 \end{aligned} \tag{4.5.28}$$

Apply the lowering operator, $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $|\uparrow\uparrow\rangle$:

$$\begin{aligned} S_- \left|\uparrow\uparrow\right\rangle &= \left(S_-^{(1)} \left|\uparrow\right\rangle\right) \left|\uparrow\right\rangle + \left|\uparrow\right\rangle \left(S_-^{(2)} \left|\uparrow\right\rangle\right) \\ &= \left(\hbar \left|\downarrow\right\rangle\right) \left|\uparrow\right\rangle + \left|\uparrow\right\rangle \left(\hbar \left|\downarrow\right\rangle\right) \\ &= \hbar \left(\left|\downarrow\uparrow\right\rangle + \left|\uparrow\downarrow\right\rangle\right) \end{aligned} \tag{4.5.29}$$

Evidently the three states with $s = 1$ are:

$$\left.\begin{aligned} |1\,1\rangle &= |\uparrow\uparrow\rangle \\ |1\,0\rangle &= \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\ |1\,-1\rangle &= |\downarrow\downarrow\rangle \end{aligned}\right\} s = 1 \text{ (triplet)} \tag{4.5.30}$$

The orthogonal state with $m = 0$ carries $s = 0$:

$$\left.|0\,0\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)\right\} s = 0 \text{ (singlet)} \tag{4.5.31}$$

Then, the combination of two spin-$\frac{1}{2}$ particles can carry a total spin of 1 or 0.
It depends on whether they occupy the triplet or the singlet configuration.

Now determine the eigenvalue of S^2 for the triplet and the singlet:

$$\begin{aligned} S^2 &= \left(\boldsymbol{S}^{(1)} + \boldsymbol{S}^{(2)}\right) \cdot \left(\boldsymbol{S}^{(1)} + \boldsymbol{S}^{(2)}\right) \\ &= \left(\boldsymbol{S}^{(1)}\right)^2 + \left(\boldsymbol{S}^{(2)}\right)^2 + 2\boldsymbol{S}^{(1)} \cdot \boldsymbol{S}^{(2)} \end{aligned} \tag{4.5.32}$$

We have:

$$\begin{aligned}\boldsymbol{S}^{(1)}\cdot\boldsymbol{S}^{(2)}\left|\uparrow\downarrow\right\rangle &= \left(S_x^{(1)}\left|\uparrow\right\rangle\right)\left(S_x^{(2)}\left|\downarrow\right\rangle\right)+\left(S_y^{(1)}\left|\uparrow\right\rangle\right)\left(S_y^{(2)}\left|\downarrow\right\rangle\right)+\left(S_z^{(1)}\left|\uparrow\right\rangle\right)\left(S_z^{(2)}\left|\downarrow\right\rangle\right)\\ &= \left(\frac{\hbar}{2}\left|\downarrow\right\rangle\right)\left(\frac{\hbar}{2}\left|\uparrow\right\rangle\right)+\left(\frac{i\hbar}{2}\left|\downarrow\right\rangle\right)\left(\frac{-i\hbar}{2}\left|\uparrow\right\rangle\right)+\left(\frac{\hbar}{2}\left|\uparrow\right\rangle\right)\left(\frac{-\hbar}{2}\left|\downarrow\right\rangle\right)\\ &= \frac{\hbar^2}{4}\left(2\left|\downarrow\uparrow\right\rangle-\left|\uparrow\downarrow\right\rangle\right)\end{aligned} \tag{4.5.33}$$

Similarly,

$$\boldsymbol{S}^{(1)}\cdot\boldsymbol{S}^{(2)}\left(\left|\downarrow\uparrow\right\rangle\right)=\frac{\hbar^2}{4}\left(2\left|\uparrow\downarrow\right\rangle-\left|\downarrow\uparrow\right\rangle\right) \tag{4.5.34}$$

It follows that:

$$\begin{aligned}\boldsymbol{S}^{(1)}\cdot\boldsymbol{S}^{(2)}\left|1\,0\right\rangle &= \frac{\hbar^2}{4}\frac{1}{\sqrt{2}}\left(2\left|\downarrow\uparrow\right\rangle-\left|\uparrow\downarrow\right\rangle+2\left|\uparrow\downarrow\right\rangle-\left|\downarrow\uparrow\right\rangle\right)=\frac{\hbar^2}{4}\left|1\,0\right\rangle\\ \boldsymbol{S}^{(1)}\cdot\boldsymbol{S}^{(2)}\left|0\,0\right\rangle &= \frac{\hbar^2}{4}\frac{1}{\sqrt{2}}\left(2\left|\downarrow\uparrow\right\rangle-\left|\uparrow\downarrow\right\rangle-2\left|\uparrow\downarrow\right\rangle+\left|\downarrow\uparrow\right\rangle\right)=-\frac{3\hbar^2}{4}\left|0\,0\right\rangle\end{aligned} \tag{4.5.35}$$

Then we conclude that:

$$S^2\left|1\,0\right\rangle=\left(\frac{3\hbar^2}{4}+\frac{3\hbar^2}{4}+2\frac{\hbar^2}{4}\right)\left|1\,0\right\rangle=2\hbar^2\left|1\,0\right\rangle \tag{4.5.36}$$

so $\left|1\,0\right\rangle$ is indeed an eigenstate of S^2 with eigenvalue $2\hbar^2$.

and

$$S^2\left|0\,0\right\rangle=\left(\frac{3\hbar^2}{4}+\frac{3\hbar^2}{4}-2\frac{3\hbar^2}{4}\right)\left|0\,0\right\rangle=0 \tag{4.5.37}$$

so $\left|0\,0\right\rangle$ is an eigenstate of S^2 with eigenvalue 0.

General results for coupling of spin s_1 with spin s_2:

$$s=(s_1+s_2),\,(s_1+s_2-1),\,(s_1+s_2-2),\,\cdots,\,|s_1-s_2| \tag{4.5.38}$$

$$m=-s,-s+1,\cdots,s-1,s \tag{4.5.39}$$

The combined state $|sm\rangle$ with total spin s and z-component m will be some linear combination of the composite states $|s_1s_2m_1m_2\rangle$:

$$|sm\rangle=\sum_{m_1+m_2=m}C_{m_1m_2m}^{s_1\,s_2\,s}\,|s_1s_2m_1m_2\rangle \tag{4.5.40}$$

The constants $C_{m_1m_2m}^{s_1\,s_2\,s}$ are called Clebsch–Gordan coefficients(C-G coefficients).

5 Chapter 5 Identical Particles

5.1 Two-particle systems

Discuss two-particle systems with wavefunction $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,t)$.

The Hamiltonian for two-particle systems:

$$H=-\frac{\hbar^2}{2m_1}\nabla_1^2-\frac{\hbar^2}{2m_2}\nabla_2^2+V(\boldsymbol{r}_1,\boldsymbol{r}_2,t) \tag{5.1.1}$$

and the Schroedinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{5.1.2}$$

The probability of finding particle 1 in the volume $d^3\boldsymbol{r}_1$ and particle 2 in the volume $d^3\boldsymbol{r}_2$:

$$|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)|^2 \, d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \tag{5.1.3}$$

As always, Ψ must be normalized:

$$\int |\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)|^2 \, d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 = 1 \tag{5.1.4}$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2)e^{-\frac{iEt}{\hbar}} \tag{5.1.5}$$

Time-independent Schroedinger equation:

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi \tag{5.1.6}$$

where E is the total energy of the system.

Two special cases can be reduced to one-particle problems:

- **Non-interacting particles:**

  Suppose the particles do not interact with one another, but each is subject to some external force.

  $$V(\boldsymbol{r}_1, \boldsymbol{r}_2) = V_1(\boldsymbol{r}_1) + V_2(\boldsymbol{r}_2), \qquad m = m_1 = m_2 \tag{5.1.7}$$

  so that we can separate variables:

  $$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \tag{5.1.8}$$

  and:

  $$-\frac{\hbar^2}{2m}\nabla_1^2\psi_a(\boldsymbol{r}_1) + V_1(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_1) = E_a\psi_a(\boldsymbol{r}_1) \tag{5.1.9}$$

  $$-\frac{\hbar^2}{2m}\nabla_2^2\psi_b(\boldsymbol{r}_2) + V_2(\boldsymbol{r}_2)\psi_b(\boldsymbol{r}_2) = E_b\psi_b(\boldsymbol{r}_2) \tag{5.1.10}$$

  and $E = E_a + E_b$.

  The two-particle wave function is a product of one-particle wavefunctions:

  $$\begin{aligned}\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) &= \psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)e^{-\frac{i(E_a+E_b)t}{\hbar}} \\ &= \left(\psi_a(\boldsymbol{r}_1)e^{-\frac{iE_at}{\hbar}}\right)\left(\psi_b(\boldsymbol{r}_2)e^{-\frac{iE_bt}{\hbar}}\right) \\ &= \Psi_a(\boldsymbol{r}_1, t)\,\Psi_b(\boldsymbol{r}_2, t)\end{aligned} \tag{5.1.11}$$

- **Central potentials:**

  Suppose the particles interact only with one another, via a potential that depends on their separation:

  $$V(\boldsymbol{r}_1, \boldsymbol{r}_2) \longrightarrow V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \tag{5.1.12}$$

  For the hydrogen atom, if we include the motion of the proton.

  The two-body problem reduces to an equivalent one-body problem.

5.1.1 Generalized Symmetrization Principle

We define exchange operator P:

$$Pf(\boldsymbol{r}_1, \boldsymbol{r}_2) = f(\boldsymbol{r}_2, \boldsymbol{r}_1) \tag{5.1.13}$$

$$P^2 = 1, \quad [P, H] = 0 \tag{5.1.14}$$

and hence

$$\frac{d\langle P \rangle}{dt} = 0 \tag{5.1.15}$$

P and H have simultaneous eigenstates:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \pm\psi(\boldsymbol{r}_2, \boldsymbol{r}_1) \quad (+ \text{ for bosons, } - \text{ for fermions}) \tag{5.1.16}$$

Two ways to write wavefunctions with exchange property:

$$\psi_\pm(\boldsymbol{r}_1, \boldsymbol{r}_2) = A\left[\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \pm \psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)\right] \tag{5.1.17}$$

5.1.2 Bosons and Fermions

Suppose we have two noninteracting particles, $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the product:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \tag{5.1.18}$$

Construct a wave function that is noncommittal as to which particle is in which state:

$$\psi_\pm(\boldsymbol{r}_1, \boldsymbol{r}_2) = A\left[\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \pm \psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)\right] \tag{5.1.19}$$

The theory admits two kinds of identical particles: bosons (the plus sign), and fermions (the minus sign).
Boson states are symmetric under interchange:

$$\psi_+(\boldsymbol{r}_2, \boldsymbol{r}_1) = \psi_+(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{5.1.20}$$

Fermion states are antisymmetric under interchange:

$$\psi_-(\boldsymbol{r}_2, \boldsymbol{r}_1) = -\psi_-(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{5.1.21}$$

It so happens that:

all particles with integer spin are bosons.
all particles with half integer spin are fermions.

Two identical fermions cannot occupy the same state.
For if $\psi_a = \psi_b$, then:

$$\psi_-(\boldsymbol{r}_1, \boldsymbol{r}_2) = A\left[\psi_a(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2) - \psi_a(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)\right] = 0 \tag{5.1.22}$$

There are left with no wave function at all. This is the famous Pauli exclusion principle.

For two noninteracting particles, with same mass, in the infinite square well.
One particle states are:

$$\psi_n(x) = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a}x\right), \qquad E_n = n^2 K \tag{5.1.23}$$

- **Case 1: They are distinguishable.**

  Ground state:

$$\psi_{11} = \frac{2}{a} sin\left(\frac{\pi x_1}{a}\right) sin\left(\frac{\pi x_2}{a}\right), \qquad E_{11} = 2K \tag{5.1.24}$$

  First excited state is doubly degenerate:

$$\psi_{12} = \frac{2}{a} sin\left(\frac{\pi x_1}{a}\right) sin\left(\frac{2\pi x_2}{a}\right), \qquad E_{12} = 5K \tag{5.1.25}$$

$$\psi_{21} = \frac{2}{a} sin\left(\frac{2\pi x_1}{a}\right) sin\left(\frac{\pi x_2}{a}\right), \qquad E_{21} = 5K \tag{5.1.26}$$

- **Case 2: They are identical bosons.**

  Ground state:

$$\psi_{11} = \frac{2}{a} sin\left(\frac{\pi x_1}{a}\right) sin\left(\frac{\pi x_2}{a}\right), \qquad E_{11} = 2K \tag{5.1.27}$$

  First excited state is nondegenerate:

$$\frac{\sqrt{2}}{a}\left[sin\left(\frac{\pi x_1}{a}\right) sin\left(\frac{2\pi x_2}{a}\right) + sin\left(\frac{2\pi x_1}{a}\right) sin\left(\frac{\pi x_2}{a}\right)\right], \qquad E = 5K \tag{5.1.28}$$

- **Case 3: They are identical fermions.**

  Ground state: $E = 2K$ state is not allowed.

  The lowest state can only be of $E = 5K$:

$$\frac{\sqrt{2}}{a}\left[sin\left(\frac{\pi x_1}{a}\right) sin\left(\frac{2\pi x_2}{a}\right) - sin\left(\frac{2\pi x_1}{a}\right) sin\left(\frac{\pi x_2}{a}\right)\right] \tag{5.1.29}$$

5.1.3 Exchange Forces

Suppose one particle is in state $\psi_a(x)$, the other is in state $\psi_b(x)$, and they are orthogonal and normalized.
If the two particles are distinguishable:

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) \tag{5.1.30}$$

If they are identical bosons:

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right] \tag{5.1.31}$$

If they are identical fermions:

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)\right] \tag{5.1.32}$$

Calculate the expectation value of the square of the separation distance between the two particles:

$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x_1^2 \right\rangle + \left\langle x_2^2 \right\rangle - 2\left\langle x_1 x_2 \right\rangle \tag{5.1.33}$$

- Distinguishable particles:

$$\left\langle x_1^2 \right\rangle = \int x_1^2 \left|\psi_a(x_1)\right|^2 dx_1 \int \left|\psi_b(x_2)\right|^2 dx_2 = \left\langle x^2 \right\rangle_a \tag{5.1.34}$$

$$\left\langle x_2^2 \right\rangle = \int \left|\psi_a(x_1)\right|^2 dx_1 \int x_2^2 \left|\psi_b(x_2)\right|^2 dx_2 = \left\langle x^2 \right\rangle_b \tag{5.1.35}$$

$$\left\langle x_1 x_2 \right\rangle = \int x_1 \left|\psi_a(x_1)\right|^2 dx_1 \int x_2 \left|\psi_b(x_2)\right|^2 dx_2 = \left\langle x \right\rangle_a \left\langle x \right\rangle_b \tag{5.1.36}$$

Then,

$$\left\langle (x_1 - x_2)^2 \right\rangle_d = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2 \left\langle x \right\rangle_a \left\langle x \right\rangle_b \tag{5.1.37}$$

- Identical particles:

$$\begin{aligned}
\left\langle x_1^2 \right\rangle &= \frac{1}{2}\left[\int x_1^2 \left|\psi_a(x_1)\right|^2 dx_1 \int \left|\psi_b(x_2)\right|^2 dx_2 + \int x_1^2 \left|\psi_b(x_1)\right|^2 dx_1 \int \left|\psi_a(x_2)\right|^2 dx_2 \right. \\
&\left. \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\
&= \frac{1}{2}\left[\left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b \pm 0 \pm 0\right] \\
&= \frac{1}{2}\left(\left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b\right)
\end{aligned} \tag{5.1.38}$$

Similarly,

$$\left\langle x_2^2 \right\rangle = \frac{1}{2}\left(\left\langle x^2 \right\rangle_b + \left\langle x^2 \right\rangle_a\right) \tag{5.1.39}$$

$$\begin{aligned}
\left\langle x_1 x_2 \right\rangle &= \frac{1}{2}\left[\int x_1 \left|\psi_a(x_1)\right|^2 dx_1 \int x_2 \left|\psi_b(x_2)\right|^2 dx_2 + \int x_1 \left|\psi_b(x_1)\right|^2 dx_1 \int x_2 \left|\psi_a(x_2)\right|^2 dx_2 \right. \\
&\left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\
&= \frac{1}{2}\left[\left\langle x \right\rangle_a \left\langle x \right\rangle_b + \left\langle x \right\rangle_b \left\langle x \right\rangle_a \pm \left\langle x \right\rangle_{ab} \left\langle x \right\rangle_{ba} \pm \left\langle x \right\rangle_{ba} \left\langle x \right\rangle_{ab}\right] \\
&= \left\langle x \right\rangle_a \left\langle x \right\rangle_b \pm \left|\left\langle x \right\rangle_{ab}\right|^2
\end{aligned} \tag{5.1.40}$$

where

$$\left\langle x \right\rangle_{ab} = \int x \psi_a(x)^* \psi_b(x) dx \tag{5.1.41}$$

Thus,

$$\left\langle (x_1 - x_2)^2 \right\rangle_\pm = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2 \left\langle x \right\rangle_a \left\langle x \right\rangle_b \mp 2 \left|\left\langle x \right\rangle_{ab}\right|^2 \tag{5.1.42}$$

which is:

$$\left\langle (\Delta x)^2 \right\rangle_\pm = \left\langle (\Delta x)^2 \right\rangle_d \mp 2 \left|\left\langle x \right\rangle_{ab}\right|^2 \tag{5.1.43}$$

Identical bosons tend to be closer together, and identical fermions farther apart, than distinguishable particles in the same two states.

We call it an exchange force, although it' s not really a force at all.

5.1.4 Spin

The complete state of an electron also includes a spinor, describing the orientation of its spin:

$$\psi(\boldsymbol{r})\chi(s) \tag{5.1.44}$$

Put together the two-particle state:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi(1,2) \tag{5.1.45}$$

For two electrons:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi(1,2) = -\psi(\boldsymbol{r}_2, \boldsymbol{r}_1)\chi(2,1) \tag{5.1.46}$$

For n identical particles (bosons or fermions), the allowed states must be symmetric or antisymmetric under interchange of any two:

$$|(1, 2, \cdots, i, \cdots, j, \cdots, n)\rangle = \pm\,|(1, 2, \cdots, j, \cdots, i, \cdots, n)\rangle \tag{5.1.47}$$

5.2 Atoms

For a neutral atom of atomic number Z, with electric charge Ze, surrounded by Z electrons, the Hamiltonian for this system:

$$\hat{H} = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\sum_{j\neq k}^{Z} \frac{e^2}{|\boldsymbol{r}_j - \boldsymbol{r}_k|} \tag{5.2.1}$$

- The first term represents the kinetic plus potential energy of the jth electron, in the electric field of the nucleus.
- The second sum is the potential energy associated with the mutual repulsion of the electrons. (The factor of $1/2$ in front corrects for the fact that the summation counts each pair twice.)

The problem is to solve Schroedinger's equation for $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_Z)$:

$$\hat{H}\psi = E\psi \tag{5.2.2}$$

which cannot be solved exactly, except for the very simplest case, $Z = 1$.

5.2.1 Helium

For helium ($Z = 2$), the Hamiltonian,

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{5.2.3}$$

The last term describes the repulsion of the two electrons. If we simply ignore it, the Schroedinger's equation separates, and the solutions can be written as products of hydrogen wave functions:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{nlm}(\boldsymbol{r}_1)\psi_{n'l'm'}(\boldsymbol{r}_2) \tag{5.2.4}$$

only with half the Bohr radius, and four times the Bohr energies.

The total energy would be:

$$E = 4\,(E_n + E_{n'}) \tag{5.2.5}$$

where $E_n = -\dfrac{13.6}{n^2}$ eV.
The ground state would be:

$$\psi_0(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2) = \frac{8}{\pi a^3} e^{-\frac{2(r_1+r_2)}{a}} \tag{5.2.6}$$

and its energy would be:

$$E_0 = 8 \times (-13.6eV) = 108.8eV \tag{5.2.7}$$

Because ψ_0 is a symmetric function, the spin state has to be antisymmetric:

$$|0\,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad s = 0 \quad \text{(spin singlet state)} \tag{5.2.8}$$

The actual ground state of helium is indeed a singlet, but the experimentally determined energy is -78.975eV, so the agreement is not very good. (We ignored electron–electron repulsion.)

The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state:

$$\psi_{nlm}\psi_{100} \tag{5.2.9}$$

We can construct both symmetric and antisymmetric combinations:

- antisymmetric spin configuration : parahelium
- symmetric spin configuration : orthohelium

5.2.2 The Periodic Table

- K-shell (n=1) has 2 different states, allowed maximal 2 electrons.
- L-shell (n=2) has 8 different states, allowed maximal 8 electrons.
- nth-shell allowed maximal $2n^2$ electrons.

Assumption for effective potential:
The net potential energy produced by the nucleus and other $(Z-1)$ electrons is assumed as $V_{eff}(r)$:

$$V_{eff}(r) = -\frac{Z(r)e^2}{4\pi\varepsilon_0 r} \tag{5.2.10}$$

$Z(r)$ is the screening function.

- $Z(r) \to Z$, when $r \to 0$ (no screening);
- $Z(r) \to 1$, when $r \to \infty$ (full screening).

Calculation procedure:

① Initial guess for $V_{eff}(r) = -\dfrac{Z(r)e^2}{4\pi\varepsilon_0 r}$

② Solve the one-particle Schroedinger equation numerically,

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n = E_n\psi_n \tag{5.2.11}$$

get energy and wavefunction.

③ Fill the states with one electron each in the order of increasing energy.

$\Longrightarrow$ get total wavefunction for Z electrons.

The total wavefunction must be antisymmetric under exchange property.

④ Use the new wavefunction to calculate $Z(r)$, put it into $V_{eff}(r)$.

⑤ Go to ②, repeat the calculation until the result converges.

Properties of the multi-electron states:

- Radii of all atoms are similar.
- Outer electron energy (first ionization potential) are similar.
- In a given n, energy levels depend on l.
- Two electrons are allowed in one orbital, in spin-singlet state.
- For a subshell (n, l), total of $2(2l + 1)$ electrons are allowed.

Notation:

- $l = 0, 1, 2, 3, \cdots \Longrightarrow$symbol $s, p, d, f, \cdots$
- ${}^{2S+1}L_J$:
  - S: total spin.
  - J: total angular momentum.
  - L: total orbital angular momentum.

5.3 Solids

Solid states consist of many valence electrons of all atoms.

Valence electrons are loosely-bound outermost electrons, belong to a combined potential of entire crystal lattice.

The number of such electrons is of the order of Avogadro's number.

Two extreme models can simplify the problem:

(1) The free electron gas model;

(2) The Bloch theory.

5.3.1 The free electron gas model

This model is essentially a 3-dimensional infinite-square well.

$$V(x,y,z) = \begin{cases} 0, & \text{if } (0 < x < l_x, 0 < y < l_y, 0 < z < l_z) \\ \infty, & \text{otherwise} \end{cases} \tag{5.3.1}$$

If we write $\psi(x,y,z) = X(x)Y(y)Z(z)$, the Schroedinger equation can be separated into three equations:

$$\left.\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} &= E_x X \\ -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} &= E_y Y \\ -\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} &= E_z Z \end{aligned}\right\} E = E_x + E_y + E_z \tag{5.3.2}$$

Let

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar} \tag{5.3.3}$$

By applying the boundary conditions, we get normalized wavefunctions and energies:

$$\begin{aligned} \psi_{n_x n_y n_z} &= \sqrt{\frac{8}{l_x l_y l_z}} sin\left(\frac{n_x\pi}{l_x}x\right) sin\left(\frac{n_y\pi}{l_y}y\right) sin\left(\frac{n_z\pi}{l_z}z\right) \\ E_{n_x n_y n_z} &= \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) = \frac{\hbar^2 k^2}{2m} \\ n_x &= 1,2,3,\cdots; \quad n_y = 1,2,3,\cdots; \quad n_z = 1,2,3,\cdots; \end{aligned} \tag{5.3.4}$$

We introduced wave vector:

$$\boldsymbol{k} = (k_x, k_y, k_z) \tag{5.3.5}$$

$\boldsymbol{k}$ opens a 3-dimensional space:

$$n_x = 1,2,3,\cdots; \quad n_y = 1,2,3,\cdots; \quad n_z = 1,2,3,\cdots \tag{5.3.6}$$

$$k_x = \frac{\pi}{l_x}n_x, \quad ; k_y = \frac{\pi}{l_y}n_y, \quad ; k_z = \frac{\pi}{l_z}n_z \tag{5.3.7}$$

In this 3-dimensional space, each unit volume corresponds to one state, occupied by two electrons.

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \tag{5.3.8}$$

V is the volume in $\boldsymbol{r}$ space, $\dfrac{\pi^3}{V}$ is the volume in $\boldsymbol{K}$ space.
In the $\boldsymbol{K}$ space, we calculate total energy of N atoms in the ground state ($T = 0$).
If each atom has q valence electrons, there are total of Nq identical electrons:

$$\frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{Nq}{2}\left(\frac{\pi^3}{V}\right) \tag{5.3.9}$$

Thus the Fermi surface:

$$k_F = \left(3\rho\pi^2\right)^{\frac{1}{3}} \tag{5.3.10}$$

The boundary between occupied and unoccupied states, in $k-$space is called the Fermi surface.

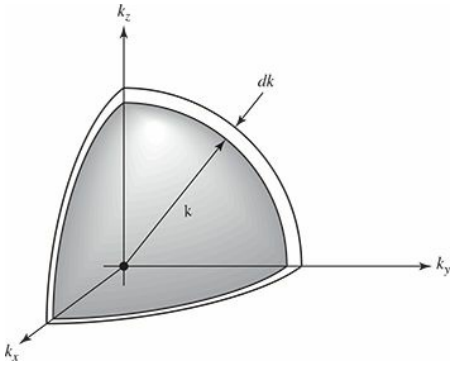
with free electron density:

$$\rho = \frac{Nq}{V} \tag{5.3.11}$$

Fermi energy:

$$E_F = \frac{\hbar^2}{2m}\left(3\rho\pi^2\right)^{\frac{2}{3}} \tag{5.3.12}$$

Calculation of the total energy of the electron gas:



A shell of thickness dk contains a volume:

$$\frac{1}{8}\left(4\pi k^2\right)dk \tag{5.3.13}$$

The number of electron states in the shell:

$$\frac{2\times\frac{1}{8}\left(4\pi k^2\right)dk}{\frac{\pi^3}{V}} = \frac{V}{\pi^2}k^2dk \tag{5.3.14}$$

Each of these states carries an energy $\dfrac{\hbar^2k^2}{2m}$, so the energy of the electrons in the shell:

$$dE = \frac{\hbar^2k^2}{2m}\frac{V}{\pi^2}k^2dk \tag{5.3.15}$$

Hence the total energy of all the filled states:

$$E_{tot} = \frac{\hbar^2V}{2\pi^2m}\int_0^{k_F}k^4dk = \frac{\hbar^2k_F^5V}{10\pi^2m} = \frac{\hbar^2\left(3\pi^2Nd\right)^{\frac{5}{3}}}{10\pi^2m}V^{-\frac{2}{3}} \tag{5.3.16}$$

The energy exerts a pressure on the walls, for if the box expands by dV, the total energy decreases:

$$dE_{tot} = -\frac{2}{3}\frac{\hbar^2\left(3\pi^2Nd\right)^{\frac{5}{3}}}{10\pi^2m}V^{-\frac{5}{3}}dV = -\frac{2}{3}E_{tot}\frac{dV}{V} \tag{5.3.17}$$

This shows up as work done on the outside by the quantum pressure P:

$$P = \frac{dW}{dV} = \frac{2}{3}\frac{E_{tot}}{V} = \frac{2}{3}\frac{\hbar^2k_F^5}{10\pi^2m} = \frac{\left(3\pi^2\right)^{\frac{2}{3}}\hbar^2}{5m}\rho^{\frac{5}{3}} \tag{5.3.18}$$

P is quantum-mechanical pressure because of Pauli Principle, and it is called degeneracy pressure (or exclusion pressure).

NOTE:

- P is not an internal pressure by electron-electron repulsion.
- P is not a pressure because of thermal motion.

5.3.2 Band Structure

Bloch's theorem:

For a periodic potential:

$$V(x+a) = V(x) \tag{5.3.19}$$

For such a potential the solutions to the Schroedinger equation:

$$-\frac{\hbar^2}{2m}\frac{d\psi^2}{dx^2} + V(x)\psi = E\psi \tag{5.3.20}$$

can be taken to satisfy the condition:

$$\psi(x+a) = e^{iqa}\psi(x) \tag{5.3.21}$$

So the $|\psi(x)|^2$ is periodic:

$$|\psi(x+a)|^2 = |\psi(x)|^2 \tag{5.3.22}$$

Proof:

Define an operator D:

$$Df(x) = f(x+a) \tag{5.3.23}$$

For a periodic potential, D commutes with H. Therefore,

$$D\psi(x) = \psi(x+a) = e^{ip(x+a)}u(x+a) = e^{ipx}e^{ipa}u(x) = e^{ipa}\psi(x) \tag{5.3.24}$$

No real solid goes on forever, we wrap the x axis around in a circle.

Formally, we impose the boundary condition:

$$\psi(x+Na) = \psi(x) \tag{5.3.25}$$

It follows that:

$$e^{iNqa}\psi(x) = \psi(x) \Longrightarrow e^{iNqa} = 1 \tag{5.3.26}$$

Hence,

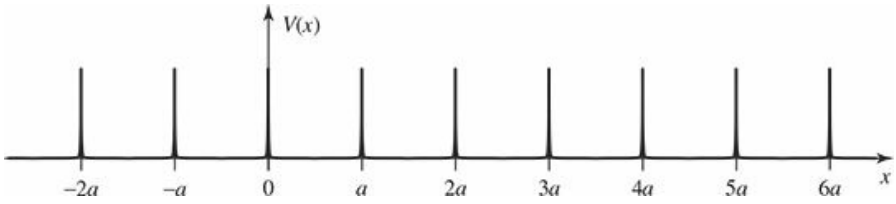
$$q = \frac{2\pi n}{Na}, \quad (n = 0, \pm 1, \pm 2, \cdots) \tag{5.3.27}$$

which tells that q is necessarily real.

We need only solve the Schroedinger equation within a single cell, and recursive application generates the solution everywhere else.

Suppose the potential consists of a long string of delta-function spikes:

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja) \tag{5.3.28}$$



In the region $0 < x < a$ the potential is zero:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \Longrightarrow \frac{d^2\psi}{dx^2} = -k^2\psi, \qquad k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{5.3.29}$$

The general solution:

$$\psi(x) = Asin(kx) + Bcos(kx), \qquad 0 < x < a \tag{5.3.30}$$

According to Bloch's theorem, the wave function in the cell to the left of the origin:

$$\psi(x) = e^{-iqa}\left\{Asin\left[k(x+a)\right] + Bcos\left[k(x+a)\right]\right\}, \quad -a < x < 0 \tag{5.3.31}$$

At $x = 0$, ψ must be continuous, so:

$$B = e^{-iqa}\left[Asin(ka) + Bcos(ka)\right] \tag{5.3.32}$$

Its derivative suffers a discontinuity proportional to the strength of the delta function:

$$kA - e^{-iqa}k\left[Acos(ka) - Bsin(ka)\right] = \frac{2m\alpha}{\hbar^2}B \tag{5.3.33}$$

Solving Equation (5.3.32) for $Asin(ka)$ yields:

$$Asin(ka) = \left[e^{iqa} - cos(ka)\right]B \tag{5.3.34}$$

Substituting this into Equation (5.3.33), and cancelling kB, we find:

$$\left[e^{iqa} - cos(ka)\right]\left[1 - e^{-iqa}cos(ka)\right] + e^{-iqa}sin^2(ka) = \frac{2m\alpha}{\hbar^2 k}sin(ka) \tag{5.3.35}$$

which simplifies to:

$$cos(qa) = cos(ka) + \frac{m\alpha}{\hbar^2 k}sin(ka) \tag{5.3.36}$$

This is the fundamental result, from which all else follows.

Equation (5.3.36) determines the possible values of k, and hence the allowed energies.

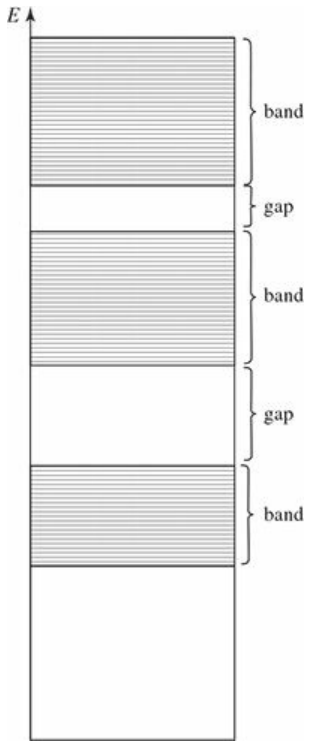
Let

$$z \equiv ka, \qquad \beta \equiv \frac{m\alpha a}{\hbar^2} \tag{5.3.37}$$

So the right side of Equation (5.3.36) can be written as:

$$f(z) = cos(z) + \beta\frac{sin(z)}{z} \tag{5.3.38}$$

The constant β is a dimensionless measure of the strength of the delta function.



For Nd electrons:

if $d = 1$, they will half fill the first band;

if $d = 2$, they will completely fill the first band;

if $d = 3$, they will half fill the second band, and so on.

6 Chapter 6 Symmetries & Conservation Laws

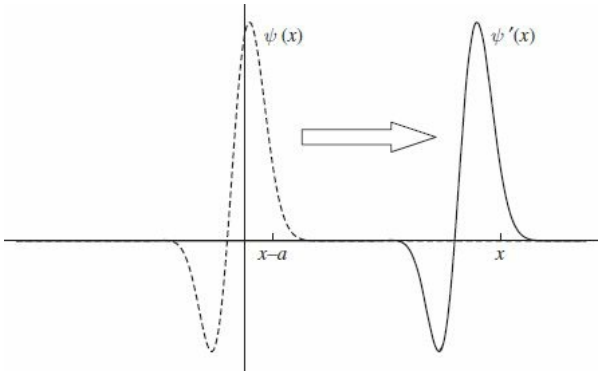
6.1 Introduction

If a system has a symmetry$\longrightarrow$ the Hamiltonian is unchanged by some transformation.

6.1.1 Transformations in Space

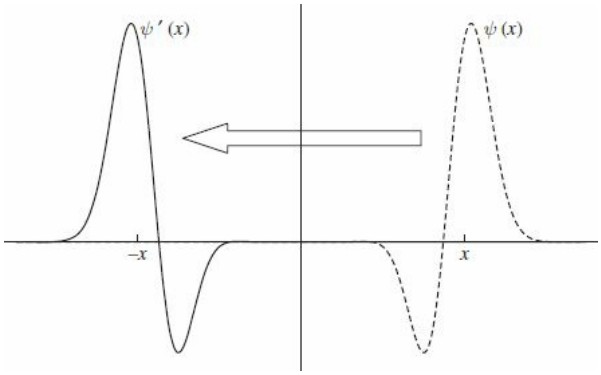
The translation operator:

$$\hat{T}(a)\psi(x) = \psi'(x) = \psi(x-a) \tag{6.1.1}$$



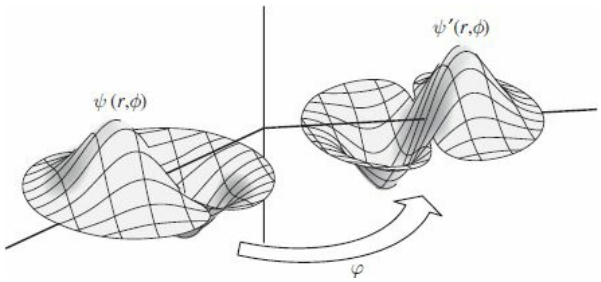
The parity operator:

$$\hat{\Pi}\psi(x) = \psi'(x) = \psi(-x) \tag{6.1.2}$$



The rotation operator:

$$\hat{R}_z(\varphi)\psi(r,\theta,\phi) = \psi'(r,\theta,\phi) = \psi(r,\theta,\phi-\varphi) \tag{6.1.3}$$



6.2 The Translation Operator

Express $\hat{T}(a)$ in terms of the momentum operator:

$$\begin{aligned}\hat{T}(a)\psi(x) = \psi(x-a) &= \sum_{n=0}^{\infty}\frac{1}{n!}(-a)^n\frac{d^n}{dx^n}\psi(x)\\ &= \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{-ia}{\hbar}\hat{p}\right)^n\psi(x)\\ &= exp\left[\frac{-ia}{\hbar}\hat{p}\right]\psi(x)\end{aligned} \tag{6.2.1}$$

So

$$\hat{T}(a) = exp\left[\frac{-ia}{\hbar}\hat{p}\right] \tag{6.2.2}$$

We say that momentum is the generator of translations.

Note that the translation operator is unitary:

$$\hat{T}(a)^{-1} = \hat{T}(-a) = \hat{T}(a)^{\dagger} \tag{6.2.3}$$

6.2.1 How Operators Transform

$\hat{Q}'$ is defined to be the operator that gives the same expectation value in the untranslated state ψ as does the operator $\hat{Q}$ in the translated state ψ':

$$\left\langle \psi' | \hat{Q} | \psi' \right\rangle = \left\langle \psi | \hat{Q}' | \psi \right\rangle \tag{6.2.4}$$

understand the transformation in two ways:

- active transformation: shift the wavefunction over some distance.
- passive transformation: shift the origin of our coordinate system by the same amount in the opposite direction.

$$\left\langle \psi' | \hat{Q} | \psi' \right\rangle = \left\langle \psi | \hat{T}^\dagger \hat{Q} \hat{T} | \psi \right\rangle = \left\langle \psi | \hat{Q}' | \psi \right\rangle \tag{6.2.5}$$

It follows that:

$$\hat{Q}' = \hat{T}^\dagger \hat{Q} \hat{T} \tag{6.2.6}$$

Find the operator $\hat{x}'$ obtained by applying a translation through a distance a to the operator $\hat{x}$.

$$\begin{aligned} \hat{x}' f(x) &= \hat{T}^\dagger(a) \hat{x} \hat{T}(a) f(x) \\ &= \hat{T}(-a) \hat{x} \hat{T}(a) f(x) \\ &= \hat{T}(-a) \left[x f(x-a) \right] \\ &= (x+a) f(x) \end{aligned} \tag{6.2.7}$$

Finally we may read off the operator:

$$\hat{x}' = \hat{x} + a \tag{6.2.8}$$

Besides,

$$\hat{p}' = \hat{p} \tag{6.2.9}$$

Proof:

$$\begin{aligned} \hat{p}' f(x) &= \hat{T}^\dagger(a) \frac{\hbar}{i} \frac{d}{dx} \hat{T}(a) f(x) \\ &= \hat{T}(-a) \frac{\hbar}{i} \frac{d}{dx} f(x-a) \\ &= \hat{T}(-a) \frac{\hbar}{i} f'(x-a) \\ &= \frac{\hbar}{i} \frac{d}{dx} f(x) \end{aligned} \tag{6.2.10}$$

For any operator:

$$\hat{Q}'(\hat{x}, \hat{p}) = \hat{T}^\dagger \hat{Q}(\hat{x}, \hat{p}) \hat{T} = \hat{Q}(\hat{x}', \hat{p}') = \hat{Q}(\hat{x} + a, \hat{p}) \tag{6.2.11}$$

6.2.2 Translational Symmetry

A system is translationally invariant (equivalent to saying it has translational symmetry) if:

$$\hat{H}' = \hat{T}^\dagger \hat{H} \hat{T} = \hat{H} \tag{6.2.12}$$

Because $\hat{T}$ is unitary, so:

$$\hat{H}\hat{T} = \hat{T}\hat{H} \tag{6.2.13}$$

Therefore, a system has translational symmetry if:

$$\left[\hat{H}, \hat{T}\right] = 0 \tag{6.2.14}$$

For a particle of mass m moving in a one-dimensional potential, the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{6.2.15}$$

the transformed Hamiltonian:

$$\hat{H}' = \frac{\hat{p}^2}{2m} + V(x+a) \tag{6.2.16}$$

So translational symmetry implies that:

$$V(x+a) = V(x) \tag{6.2.17}$$

Two different physical settings:

- a constant potential: euqation holds for every value of a.
- a periodic potential: euqation holds for a discrete set of a.

Discrete Translational Symmetry and Bloch's Theorem

If the Hamiltonian is translationally invariant:

$$\hat{H}\psi(x) = E\psi(x) \qquad \hat{T}(a)\psi(x) = \lambda\psi(x) \tag{6.2.18}$$

Since $\hat{T}$ is unitary, its eigenvalues have magnitude 1:

$$\lambda = e^{i\phi}, \quad \phi = -qa \quad \text{(where } \phi \text{ is real number)} \tag{6.2.19}$$

$\hbar q$ is called crystal momentum.

Therefore, the stationary states of a particle of mass m moving in a periodic potential have:

$$\psi(x-a) = e^{-iqa}\psi(x) \tag{6.2.20}$$

A more illuminating way to write equation(6.2.20):

$$\psi(x) = e^{iqx}u(x) \tag{6.2.21}$$

where $u(x)$ is a periodic function: $u(x+a) = u(x)$, e^{iqx} is a traveling wave.

Equation(6.2.21) is Bloch's theorem:

The stationary states of a particle in a periodic potential are periodic functions multiplying traveling waves.

Continuous Translational Symmetry and Momentum Conservation

Consider an infinitesimal translation:

$$\hat{T}(\delta) = e^{-\frac{i\delta\hat{p}}{\hbar}} \approx 1 - i\frac{\delta}{\hbar}\hat{p} \tag{6.2.22}$$

where δ is an infinitesimal length.

If the Hamiltonian has continuous translational symmetry:

$$\left[\hat{H}, \hat{T}(\delta)\right] = \left[\hat{H}, 1 - i\frac{\delta}{\hbar}\hat{p}\right] = 0 \Longrightarrow \left[\hat{H}, \hat{p}\right] = 0 \tag{6.2.23}$$

According to the "generalized Ehrenfest's theorem":

$$\frac{d}{dt}\langle p\rangle = \frac{i}{\hbar}\left\langle\left[\hat{H}, \hat{p}\right]\right\rangle = 0 \tag{6.2.24}$$

which shows that continuous translational symmetry implies that momentum is conserved.

6.3 Conservation Laws

Two possibilities for the observable Q is conserved:

- First definition: The expectation value $\langle Q\rangle$ is independent of time.
- Second definition: The probability of getting any particular value is independent of time.

Assume the observable in question does not depend explicitly on time:

$$\frac{\partial Q}{\partial t} = 0 \tag{6.3.1}$$

The generalized Ehrenfest theorem tells us that the expectation value of Q is independent of time if:

$$\left[\hat{Q}, \hat{H}\right] = 0 \tag{6.3.2}$$

The same criterion guaranatees conservation by the second definition.

Proof:

The probability of getting the result q_n in a measurement of Q at time t:

$$P(q_n) = |\langle f_n|\Psi(t)\rangle|^2 \tag{6.3.3}$$

where f_n is the corresponding eigenvector:

$$\hat{Q}\,|f_n\rangle = q_n\,|f_n\rangle \tag{6.3.4}$$

The time evolution of the wave function:

$$|\Psi(t)\rangle = \sum_m e^{-\frac{iE_m t}{\hbar}} c_m\,|\psi_m\rangle \tag{6.3.5}$$

where the $|\psi_n\rangle$ are the eigenstates of $\hat{H}$, and therefore

$$P(q_n) = \left| \sum_m e^{-\frac{iE_m t}{\hbar}} c_m \langle f_n | \psi_m \rangle \right|^2 \tag{6.3.6}$$

Since $\hat{Q}$ and $\hat{H}$ commute, we can find a complete set of simultaneous eigenstates for them.
Without loss of generality then $|f_n\rangle = |\psi_n\rangle$.
Using the orthonormality of the $|\psi_n\rangle$,

$$P(q_n) = \left| \sum_m e^{-\frac{iE_m t}{\hbar}} c_m \langle \psi_n | \psi_m \rangle \right|^2 = |c_n|^2 \tag{6.3.7}$$

which is independent of time.

6.4 Parity

6.4.1 Parity in One Dimension

In one dimension:

$$\hat{\Pi}\psi(x) = \psi'(x) = \psi(-x) \tag{6.4.1}$$

The parity operator is unitary:

$$\hat{\Pi}^{-1} = \hat{\Pi} = \hat{\Pi}^\dagger \tag{6.4.2}$$

Operators transform under a spatial inversion:

$$\hat{Q}' = \hat{\Pi}^\dagger \hat{Q} \hat{\Pi} \tag{6.4.3}$$

The position and momentum operators are odd under parity:

$$\begin{aligned} \hat{x}' &= \hat{\Pi}^\dagger \hat{x} \hat{\Pi} = -\hat{x} \\ \hat{p}' &= \hat{\Pi}^\dagger \hat{p} \hat{\Pi} = -\hat{p} \end{aligned} \tag{6.4.4}$$

Therefore, any operator transforms:

$$\hat{Q}'(\hat{x}, \hat{p}) = \hat{\Pi}^\dagger \hat{Q}(\hat{x}, \hat{p}) \hat{\Pi} = \hat{Q}(-\hat{x}, -\hat{p}) \tag{6.4.5}$$

A system has inversion symmetry if the Hamiltonian is unchanged by a parity transformation:

$$\hat{H}' = \hat{\Pi}^\dagger \hat{H} \hat{\Pi} = \hat{H} \tag{6.4.6}$$

or, using the unitarity of the parity operator,

$$\left[\hat{H}, \hat{\Pi}\right] = 0 \tag{6.4.7}$$

Inversion symmetry means that the potential is an even function of position:

$$V(x) = V(-x) \tag{6.4.8}$$

The implications of inversion symmetry:

- we can find a complete set of simultaneous eigenstates of $\hat{\Pi}$ and $\hat{H}$.

  Let such an eigenstate be written ψ_n, it satisfies:

$$\hat{\Pi}\psi_n(x) = \psi_n(-x) = \pm\psi_n(x) \tag{6.4.9}$$

  since the eigenvalues of the parity operator are restricted to ± 1.

  So the stationary states of a potential that is an even function of position are themselves even or odd functions.

- According to Ehrenfest' s theorem, if the Hamiltonian has an inversion symmetry then:

$$\frac{d}{dt}\langle \Pi \rangle = \frac{i}{\hbar}\left\langle \left[\hat{H}, \hat{\Pi}\right] \right\rangle = 0 \tag{6.4.10}$$

  So parity is conserved for a particle moving in a symmetric potential.

  Not just the expectation value, but the probability of any particular outcome in a measurement.

6.4.2 Parity in Three Dimensions

The spatial inversion generated by the parity operator in three dimensions:

$$\hat{\Pi}\psi(\boldsymbol{r}) = \psi'(\boldsymbol{r}) = \psi(-\boldsymbol{r}) \tag{6.4.11}$$

The operators $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ transform as:

$$\hat{\boldsymbol{r}}' = \hat{\Pi}^\dagger \hat{\boldsymbol{r}} \hat{\Pi} = -\hat{\boldsymbol{r}} \tag{6.4.12}$$

$$\hat{\boldsymbol{p}}' = \hat{\Pi}^\dagger \hat{\boldsymbol{p}} \hat{\Pi} = -\hat{\boldsymbol{p}} \tag{6.4.13}$$

Any other operator transforms as:

$$\hat{Q}'\left(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}\right) = \hat{\Pi}^\dagger \hat{Q}\left(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}\right) \hat{\Pi} = \hat{Q}\left(-\hat{\boldsymbol{r}}, -\hat{\boldsymbol{p}}\right) \tag{6.4.14}$$

Example: Find the parity-transformed angular momentum operator $\hat{L}' = \hat{\Pi}^\dagger \hat{L} \hat{\Pi}$, in terms of $\hat{L}$.
Since $\mathrm{L} = \boldsymbol{r} \times \boldsymbol{p}$:

$$\hat{L}' = \hat{\Pi}^\dagger \hat{L} \hat{\Pi} = \hat{\boldsymbol{r}}' \times \hat{\boldsymbol{p}}' = (-\hat{\boldsymbol{r}}) \times (-\hat{\boldsymbol{p}}) = \hat{L} \tag{6.4.15}$$

The Hamiltonian for a particle will have inversion symmetry if $V(-\boldsymbol{r}) = V(\boldsymbol{r})$, and parity is conserved.
(any central potential satisfies this condition)
The eigenstates of a particle in a central potential are eigenstates of parity:

$$\hat{\Pi}\psi_{nlm}(r, \theta, \phi) = (-1)^l \psi_{nlm}(r, \theta, \phi) \tag{6.4.16}$$

6.4.3 Parity Selection Rules

A matrix element is any object of the form $\left\langle b|\hat{Q}|a\right\rangle$.

An expectation value is a special case of a matrix element with $a = b = \psi$.

The electric dipole moment operator:

$$\hat{\boldsymbol{p}}_e = q\hat{\boldsymbol{r}} \tag{6.4.17}$$

It's odd under parity since $\hat{\boldsymbol{r}}$ is odd:

$$\hat{\Pi}^\dagger \hat{\boldsymbol{p}}_e \hat{\Pi} = -\hat{\boldsymbol{p}}_e \tag{6.4.18}$$

Consider the matrix elements of the electric dipole operator between two states ψ_{nlm} and $\psi_{n'l'm'}$:

$$\begin{aligned} \left\langle n'l'm'\left|\hat{\boldsymbol{p}}_e\right|nlm\right\rangle &= -\left\langle n'l'm'\left|\hat{\Pi}^\dagger\hat{\boldsymbol{p}}_e\hat{\Pi}\right|nlm\right\rangle \\ &= -\left\langle n'l'm'\left|(-1)^{l'}\hat{\boldsymbol{p}}_e(-1)^{l}\right|nlm\right\rangle \\ &= (-1)^{l+l'+1}\left\langle n'l'm'\left|\hat{\boldsymbol{p}}_e\right|nlm\right\rangle \end{aligned} \tag{6.4.19}$$

From this we see immediately that:

$$\left\langle n'l'm'\left|\hat{\boldsymbol{p}}_e\right|nlm\right\rangle = 0 \quad \text{if } l + l' \text{ is even} \tag{6.4.20}$$

This is called Laporte's rule:

Matrix elements of the dipole moment operator vanish between states with the same parity.拉波特

In particular, Laporte's rule applies to any operator that is odd under parity.

6.5 Rotational Symmetry

6.5.1 Rotations About the z Axis

The operator that rotates a function about the z axis by an angle φ:

$$\hat{R}_z(\varphi)\psi(r,\theta,\phi) = \psi'(r,\theta,\phi) = \psi(r,\theta,\phi-\varphi) \tag{6.5.1}$$

We can derive:

$$\hat{R}_z(\varphi) = exp\left[-\frac{i\varphi}{\hbar}\hat{L}_z\right] \tag{6.5.2}$$

$\hat{L}_z$ is the generator of rotations about the z axis.

Use the infinitesimal form of the operator:

$$\hat{R}_z(\delta) \approx 1 - \frac{i\delta}{\hbar}\hat{L}_z \tag{6.5.3}$$

Then the operator $\hat{x}$ transforms as:

$$\begin{aligned} \hat{x}' = \hat{R}^\dagger\hat{x}\hat{R} &\approx \left(1+\frac{i\delta}{\hbar}\hat{L}_z\right)\hat{x}\left(1-\frac{i\delta}{\hbar}\hat{L}_z\right) \\ &= \hat{x} + \frac{i\delta}{\hbar}\left[\hat{L}_z,\hat{x}\right] \approx \hat{x} - \delta\hat{y} \end{aligned} \tag{6.5.4}$$

Similar calculations show that:

$$\hat{y}' = \hat{y} + \delta\hat{x}, \qquad \hat{z}' = \hat{z} \tag{6.5.5}$$

Combine these results into a matrix equation:

$$\begin{pmatrix} \hat{x}' \\ \hat{y}' \\ \hat{z}' \end{pmatrix} = \begin{pmatrix} 1 & -\delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} \tag{6.5.6}$$

Change δ back to φ:

$$\begin{pmatrix} \hat{x}' \\ \hat{y}' \\ \hat{z}' \end{pmatrix} = \begin{pmatrix} cos\varphi & -sin\varphi & 0 \\ sin\varphi & cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} \tag{6.5.7}$$

6.5.2 Rotations in Three Dimensions

Equation(6.5.2) can be generalized to a rotation about an axis along the unit vector $\boldsymbol{n}$:

$$\hat{R}_{\boldsymbol{n}}(\varphi) = exp\left[-\frac{i\varphi}{\hbar}\boldsymbol{n}\cdot\hat{L}\right] \tag{6.5.8}$$

Angular momentum is the generator of rotations.

For a rotation about the z axis, we would have:

$$\begin{pmatrix} \hat{V}_x' \\ \hat{V}_y' \\ \hat{V}_z' \end{pmatrix} = \begin{pmatrix} cos\varphi & -sin\varphi & 0 \\ sin\varphi & cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{V}_x \\ \hat{V}_y \\ \hat{V}_z \end{pmatrix} \tag{6.5.9}$$

This transformation rule follows from the commutation relations:

$$\left[\hat{L}_i, \hat{V}_j\right] = i\hbar\varepsilon_{ijk}\hat{V}_k \tag{6.5.10}$$

We take equation(6.5.10) as the definition of a vector operator.

For three such operators we have encountered ($\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}, \hat{\boldsymbol{L}}$):

$$\left[\hat{L}_i, \hat{r}_j\right] = i\hbar\varepsilon_{ijk}\hat{r}_k, \quad \left[\hat{L}_i, \hat{p}_j\right] = i\hbar\varepsilon_{ijk}\hat{p}_k, \quad \left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \tag{6.5.11}$$

A scalar operator is a single quantity that is unchanged by rotations.

This is equivalent to saying that the operator commutes with $\hat{L}$:

$$\left[\hat{L}_i, \hat{f}\right] = 0 \tag{6.5.12}$$

We can now classify operators as either scalars or vectors, based on their commutation relations with $\hat{\boldsymbol{L}}$.

- Pseudovector: vectors are even under parity.
- True vector: vectors are odd under parity.

- Pseudoscalars: scalars are odd under parity.
- True scalars: scalars are even under parity.

	parity	rotations	examples
true vector $\hat{\mathbf{V}}$	$\left\{\hat{\Pi}, \hat{V}_i\right\} = 0$	$\left[\hat{L}_i, \hat{V}_j\right] = i\,\hbar\epsilon_{ijk}\,\hat{V}_k$	$\hat{\mathbf{r}}, \hat{\mathbf{p}}$
pseudovector $\hat{\mathbf{V}}$	$\left[\hat{\Pi}, \hat{V}_i\right] = 0$	$\left[\hat{L}_i, \hat{V}_j\right] = i\,\hbar\epsilon_{ijk}\,\hat{V}_k$	$\hat{\mathbf{L}}$
true scalar $\hat{f}$	$\left[\hat{\Pi}, \hat{f}\right] = 0$	$\left[\hat{L}_i, \hat{f}\right] = 0$	$\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}$
pseudoscalar $\hat{f}$	$\left\{\hat{\Pi}, \hat{f}\right\} = 0$	$\left[\hat{L}_i, \hat{f}\right] = 0$	

Continuous rotational symmetry:

For a particle of mass m moving in a potential $V(\boldsymbol{r})$, the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\boldsymbol{r}) \tag{6.5.13}$$

is rotationally invariant if $V(\boldsymbol{r}) = V(r)$.

In this case the Hamiltonian commutes with a rotation by any angle about an arbitrary axis:

$$\left[\hat{H}, \hat{R}_{\boldsymbol{n}}(\varphi)\right] = 0 \tag{6.5.14}$$

In particular, Equation(6.5.14) must hold for an infinitesimal rotation:

$$\hat{R}_{\boldsymbol{n}}(\delta) \approx 1 - i\frac{\delta}{\hbar}\boldsymbol{n} \cdot \hat{\boldsymbol{L}} \tag{6.5.15}$$

which means that the Hamiltonian commutes with the three components of $\boldsymbol{L}$:

$$\left[\hat{H}, \hat{\boldsymbol{L}}\right] = 0 \tag{6.5.16}$$

From equation(6.5.16) and Ehrenfest' s theorem, for a central potential:

$$\frac{d}{dt}\langle \boldsymbol{L} \rangle = \frac{i}{\hbar}\left\langle \left[\hat{H}, \hat{\boldsymbol{L}}\right] \right\rangle = 0 \tag{6.5.17}$$

Thus, angular momentum conservation is a consequence of rotational invariance.

Since the Hamiltonian for a central potential commutes with all three components of angular momentum, it also commutes with $\hat{L}^2$.

The operators $\hat{H}, \hat{L}_z, \hat{L}^2$ form a complete set of compatible observables for the bound states of a central potential.

Compatible means that they commute pairwise:

$$\left[\hat{H}, \hat{L}^2\right] = 0 \tag{6.5.18}$$

$$\left[\hat{H}, \hat{L}_z\right] = 0 \tag{6.5.19}$$

$$\left[\hat{L}_z, \hat{L}^2\right] = 0 \tag{6.5.20}$$

so that the eigenstates of $\hat{H}$ can be chosen to be simultaneous eigenstates of $\hat{L}^2$ and $\hat{L}_z$.

$$\hat{H}\psi_{nlm} = E_n\psi_{nlm} \tag{6.5.21}$$

$$\hat{L}_z\psi_{nlm} = m\hbar\psi_{nlm} \tag{6.5.22}$$

$$\hat{L}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm} \tag{6.5.23}$$

Saying they are complete means that the quantum numbers n, l, m uniquely specify a bound state of the Hamiltonian.

6.6 Degeneracy

Symmetry is the source of most degeneracy in quantum mechanics.

A symmetry implies the existence of an operator $\hat{Q}$ that commutes with the Hamiltonian : $[\hat{H}, \hat{Q}] = 0$

If we have a stationary state $|\psi_n\rangle$, then $|\psi'_n\rangle = \hat{Q}|\psi_n\rangle$ is a stationary state with the same energy.

$$\hat{H}\left|\psi'_n\right\rangle = \hat{H}\left(\hat{Q}|\psi_n\rangle\right) = \hat{Q}\hat{H}|\psi_n\rangle = \hat{Q}E_n|\psi_n\rangle = E_n\left(\hat{Q}|\psi_n\rangle\right) = E_n\left|\psi'_n\right\rangle \tag{6.6.1}$$

If two operators that commute with the Hamiltonian, but do not commute with each other. Then degeneracy in the energy spectrum is inevitable.

Example

Consider an eigenstate of a central potential ψ_{nlm} with energy E_n, show that $\psi_{nlm\pm1}$ are necessarily also eigenstates with the same energy as ψ_{nlm}.

Solution:

Since the Hamiltonian commutes with $\hat{L}_\pm$, we have:

$$\left(\hat{H}\hat{L}_\pm - \hat{L}_\pm\hat{H}\right)\psi_{nlm} = 0 \tag{6.6.2}$$

so

$$\hat{H}\hat{L}_\pm\psi_{nlm} = \hat{L}_\pm\hat{H}\psi_{nlm} = E_n\hat{L}_\pm\psi_{nlm} \Longleftrightarrow \hat{H}\psi_{nlm\pm1} = E_n\psi_{nlm\pm1} \tag{6.6.3}$$

Rotational invariance explains why states which differ only in the quantum number m have the same energy.

6.7 Rotational Selection Rules

6.7.1 Selection Rules for Scalar Operators

The commutation relations for a scalar operator $\hat{f}$ with the three components of angular momentum:

$$\left[\hat{L}_z, \hat{f}\right] = 0, \quad \left[\hat{L}_\pm, \hat{f}\right] = 0, \quad \left[\hat{L}^2, \hat{f}\right] = 0 \tag{6.7.1}$$

$|nlm\rangle$ is an eigenstate of $\hat{L}^2$ and $\hat{L}_z$, sandwiching equation between two such states:

$$\left\langle n'l'm'\right|\left[\hat{L}_z, \hat{f}\right]|nlm\rangle = 0 \Longleftrightarrow \left\langle n'l'm'|\hat{L}_z\hat{f}|nlm\right\rangle - \left\langle n'l'm'|\hat{f}\hat{L}_z|nlm\right\rangle = 0 \tag{6.7.2}$$

and therefore,

$$\left(m' - m\right)\left\langle n'l'm'|\hat{f}|nlm\right\rangle = 0 \tag{6.7.3}$$

which means that the matrix elements of a scalar operator vanish unless $m' - m \equiv \Delta m = 0$.

Repeating this procedure:

$$\left\langle n'l'm'|\left[\hat{L}^2, \hat{f}\right]|nlm\right\rangle = 0 \Longleftrightarrow \left\langle n'l'm'|\hat{L}^2\hat{f}|nlm\right\rangle - \left\langle n'l'm'|\hat{f}\hat{L}^2|nlm\right\rangle = 0 \tag{6.7.4}$$

and therefore,

$$\left[l'(l'+1) - l(l+1)\right]\left\langle n'l'm'|\hat{f}|nlm\right\rangle = 0 \tag{6.7.5}$$

which means that the matrix elements of a scalar operator vanish unless $l' - l \equiv \Delta l = 0$.

Then, are the selection rules for a scalar operator: $\Delta l = 0, \Delta m = 0$.

From the remaining commutators:

$$\left\langle n'l'm'|\left[\hat{L}_+, \hat{f}\right]|nlm\right\rangle = 0 \Longleftrightarrow \left\langle n'l'm'|\hat{L}_+\hat{f}|nlm\right\rangle - \left\langle n'l'm'|\hat{f}\hat{L}_+|nlm\right\rangle = 0 \tag{6.7.6}$$

and therefore,

$$B^{m'}_{l'}\left\langle n'l'(m'-1)|\hat{f}|nlm\right\rangle - A^m_l\left\langle n'l'm'|\hat{f}|nl(m+1)\right\rangle = 0 \tag{6.7.7}$$

where:

$$A^l_m = \hbar\sqrt{l(l+1) - m(m+1)}, \quad B^l_m = \hbar\sqrt{l(l+1) - m(m-1)} \tag{6.7.8}$$

Equation(6.7.6) are zero unless $m' = m + 1$ and $l' = l$.

When these conditions are satisfied, the two coefficients are equal and Equation(6.7.6) reduces to:

$$\left\langle n'lm|\hat{f}|nlm\right\rangle = \left\langle n'l(m+1)|\hat{f}|nl(m+1)\right\rangle \tag{6.7.9}$$

Evidently the matrix elements of a scalar operator are independent of m.

The results of this section can be summarized as follows:

$$\left\langle n'l'm'|\hat{f}|nlm\right\rangle = \delta_{ll'}\delta_{mm'}\left\langle n'l||f||nl\right\rangle \tag{6.7.10}$$

The matrix element on the right with two bars is called a reduced matrix element, which is shorthand for "a constant that depends on n,l, and n', but not m."

Example

(a) Find $\langle r^2\rangle$ for all four of the degenerate $n = 2$ states of a hydrogen atom.

Solution: For the states with $l = 1$:

$$\langle 211|r^2|211\rangle = \langle 210|r^2|210\rangle = \langle 21-1|r^2|21-1\rangle \equiv \langle 21||r^2||21\rangle \tag{6.7.11}$$

To calculate the reduced matrix element, we simply pick any one of these expectation values:

$$\begin{aligned}\langle 21||r^2||21\rangle &= \langle 210|r^2|210\rangle \\ &= \int r^2|\psi_{210}(r)|^2 d^3\boldsymbol{r} \\ &= \int_0^\infty r^4|R_{21}(r)|^2 dr \int |Y^0_1(\theta,\phi)|^2 d\Omega \\ &= \int_0^\infty r^4 \frac{1}{24a^3}\frac{r^2}{a^2}e^{-\frac{r}{a}}dr = 30a^2\end{aligned} \tag{6.7.12}$$

$$\begin{aligned}\langle 20||r^2||20\rangle &= \langle 200|r^2|200\rangle \\ &= \int r^2|\psi_{200}(r)|^2 d^3\boldsymbol{r} \\ &= \int_0^\infty r^4|R_{20}(r)|^2 dr \int |Y_0^0(\theta,\phi)|^2 d\Omega \\ &= \int_0^\infty r^4 \frac{1}{2a^3}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{a}}dr = 42a^2\end{aligned} \tag{6.7.13}$$

(b) Find the expectation value of r^2 for an electron in the superposition state $|\psi\rangle = \frac{1}{\sqrt{2}}(|200\rangle - i\,|211\rangle)$

$$\begin{aligned}\langle\psi|r^2|\psi\rangle &= \frac{1}{2}\left(\langle 200| + i\,\langle 211|\right) r^2 \left(|200\rangle - i\,|211\rangle\right) \\ &= \frac{1}{2}\left(\langle 200|r^2|200\rangle + i\,\langle 211|r^2|200\rangle - i\,\langle 200|r^2|211\rangle + \langle 211|r^2|211\rangle\right) \\ &= \frac{1}{2}\left(\langle 20||r^2||20\rangle + \langle 21||r^2||21\rangle\right) = 36a^2\end{aligned} \tag{6.7.14}$$

6.7.2 Selection Rules for Vector Operators

Define operators: $\hat{V}_\pm \equiv \hat{V}_x \pm i\hat{V}_y$

Written in terms of these operators:

$$\left[\hat{L}_z, \hat{V}_z\right] = 0, \quad \left[\hat{L}_z, \hat{V}_\pm\right] = \pm\hbar\hat{V}_\pm, \quad \left[\hat{L}_\pm, \hat{V}_\pm\right] = 0, \quad \left[\hat{L}_\pm, \hat{V}_z\right] = \mp\hbar\hat{V}_\pm, \quad \left[\hat{L}_\pm, \hat{V}_\mp\right] = \pm 2\hbar\hat{V}_z \tag{6.7.15}$$

Sandwich each of these commutators between two states of definite angular momentum:

$$\left\langle n'l'm'|\hat{L}_z\hat{V}_\pm|nlm\right\rangle - \left\langle n'l'm'|\hat{V}_\pm\hat{L}_z|nlm\right\rangle = \pm\hbar\left\langle n'l'm'|\hat{V}_\pm|nlm\right\rangle \tag{6.7.16}$$

and since our states are eigenstates of $\hat{L}_z$, this simplifies to:

$$\left[m' - (m \pm 1)\right]\left\langle n'l'm'|\hat{V}_\pm|nlm\right\rangle = 0 \tag{6.7.17}$$

which means that either $m' = m + 1$, or else the matrix element of $\hat{V}_\pm$ must vanish.

Similarly.

$$\left\langle n'l'm'|\hat{V}_+|nlm\right\rangle = 0 \qquad \text{unless } m' = m+1 \tag{6.7.18}$$

$$\left\langle n'l'm'|\hat{V}_z|nlm\right\rangle = 0 \qquad \text{unless } m' = m \tag{6.7.19}$$

$$\left\langle n'l'm'|\hat{V}_-|nlm\right\rangle = 0 \qquad \text{unless } m' = m-1 \tag{6.7.20}$$

These expressions can be turned back into selection rules for the $x-$ and $y-$ components of our operator:

$$\left\langle n'l'm'|\hat{V}_x|nlm\right\rangle = \frac{1}{2}\left[\left\langle n'l'm'|\hat{V}_-|nlm\right\rangle + \left\langle n'l'm'|\hat{V}_+|nlm\right\rangle\right] \tag{6.7.21}$$

$$\left\langle n'l'm'|\hat{V}_y|nlm\right\rangle = \frac{i}{2}\left[\left\langle n'l'm'|\hat{V}_-|nlm\right\rangle - \left\langle n'l'm'|\hat{V}_+|nlm\right\rangle\right] \tag{6.7.22}$$

The remaining commutators yield a selection rule on l and relations among the nonzero matrix elements.

$$\left\langle n'l'm'|\hat{V}_+|nlm\right\rangle = -\sqrt{2}C^{ll'}_{m1m'}\left\langle nl'||V||nl\right\rangle \tag{6.7.23}$$

$$\left\langle n'l'm'|\hat{V}_-|nlm\right\rangle = \sqrt{2}C^{l1l'}_{m-1m'}\left\langle nl'||V||nl\right\rangle \tag{6.7.24}$$

$$\left\langle n'l'm'|\hat{V}_z|nlm\right\rangle = C^{l1l'}_{m0m'}\left\langle nl'||V||nl\right\rangle \tag{6.7.25}$$

The constants $C^{j_1j_2J}_{m_1m_2M}$ are precisely the Clebsch–Gordan coefficients.

The Clebsch–Gordan coefficients vanishes unless $M = m_1 + m_2$ and unless $J = j_1 + j_2, j_1 + j_2 - 1, \cdots, |j_1 - j_2|$.

The matrix elements of any component of a vector operator $\left\langle n'l'm'|\hat{V}_i|nlm\right\rangle$ are nonzero only if:

$$\Delta l = 0, \pm 1, \quad \text{and} \quad \Delta m = 0, \pm 1 \tag{6.7.26}$$

6.8 Translations in Time

Consider a solution $\Psi(x,t)$ to the time-dependent Schroedinger equation:

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t) \tag{6.8.1}$$

Define the operator that propagates the wave function forward in time, $\hat{U}(t)$:

$$\hat{U}(t)\Psi(x,0) = \Psi(x,t) \tag{6.8.2}$$

Expanding the right-hand side of the above equation:

$$\hat{U}(t)\Psi(x,0) = \Psi(x,t) = \sum_{n=0}^{\infty}\frac{1}{n!}\left.\frac{\partial^n}{\partial t^n}\Psi(x,t)\right|_{t=0} t^n = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\hat{H}t\right)^n\Psi(x,0) \tag{6.8.3}$$

Therefore, in the case of a time-independent Hamiltonian, the time-evolution operator is:

$$\hat{U}(t) = exp\left(-\frac{it}{\hbar}\hat{H}\right) \tag{6.8.4}$$

The Hamiltonian is the generator of translations in time.

$\hat{U}(t)$ is a unitary operator.

Write out the wave function at time $t = 0$ as a superposition of stationary states ($\hat{H}\psi_n = E_n\psi_n$):

$$\Psi(x,0) = \sum_n c_n\psi_n(x) \tag{6.8.5}$$

Then

$$\begin{aligned}\Psi(x,t) = \hat{U}(t)\Psi(x,0) &= \sum_n c_n\hat{U}(t)\psi_n(x) \\ &= \sum_n c_n e^{-\frac{i\hat{H}t}{\hbar}}\psi_n(x) = \sum_n c_n e^{-\frac{iE_nt}{\hbar}}\psi_n(x)\end{aligned} \tag{6.8.6}$$

In this sense Equation(6.8.4) is shorthand for the process of expanding the initial wave function in terms of stationary states and then tacking on the "wiggle factors" to obtain the wave function at a later time.

6.8.1 The Heisenberg Picture

Apply time translation to operators, the transformed operators are called Heisenberg-picture operators. Follow the convention of giving them a subscript H rather than a prime:

$$\hat{Q}_H(t) = \hat{U}^\dagger(t)\hat{Q}\hat{U}(t) \tag{6.8.7}$$

Example

A particle of mass m moves in one dimension in a potential $V(x)$:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{6.8.8}$$

Find the position operator in the Heisenberg picture for an infinitesimal time translation δ.

Solution:

From Equation(6.8.4): $\hat{U}(\delta) \approx 1 - i\frac{\delta}{\hbar}\hat{H}$

Applying Equation(6.8.7):

$$\hat{x}_H(\delta) \approx \left(1 + i\frac{\delta}{\hbar}\hat{H}^\dagger\right)\hat{x}\left(1 - i\frac{\delta}{\hbar}\hat{H}\right) \approx \hat{x} - i\frac{\delta}{\hbar}\left[\hat{x}, \hat{H}\right] \approx \hat{x} - i\frac{\delta}{\hbar}i\hbar\frac{\hat{p}}{m} \tag{6.8.9}$$

so

$$\hat{x}_H(\delta) \approx \hat{x}_H(0) + \frac{1}{m}\hat{p}_H(0)\delta \tag{6.8.10}$$

This looks exactly like classical mechanics: $x(\delta) \approx x(0) + v(0)\delta$.

Example

A particle of mass m moves in one dimension in a harmonic-oscillator potential:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{6.8.11}$$

Find the position operator in the Heisenberg picture at time t.

Solution:

Consider the action of $\hat{x}_H$ on a stationary ψ_n.

Writing $\hat{x}$ in terms of raising and lowering operators we have:

$$\begin{aligned}
\hat{x}_H(t)\psi_n(x) &= \hat{U}^\dagger(t)\hat{x}\hat{U}(t)\psi_n(x) \\
&= e^{\frac{i\hat{H}t}{\hbar}}\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-)e^{-\frac{i\hat{H}t}{\hbar}}\psi_n(x) \\
&= \sqrt{\frac{\hbar}{2m\omega}}e^{-\frac{iE_nt}{\hbar}}e^{\frac{i\hat{H}t}{\hbar}}(\hat{a}_+ + \hat{a}_-)\psi_n(x) \\
&= \sqrt{\frac{\hbar}{2m\omega}}e^{-\frac{iE_nt}{\hbar}}e^{\frac{i\hat{H}t}{\hbar}}\left[\sqrt{n+1}\psi_{n+1}(x) + \sqrt{n}\psi_{n-1}(x)\right] \\
&= \sqrt{\frac{\hbar}{2m\omega}}e^{-\frac{iE_nt}{\hbar}}\left[\sqrt{n+1}e^{\frac{iE_{n+1}t}{\hbar}}\psi_{n+1}(x) + \sqrt{n}e^{\frac{iE_{n-1}t}{\hbar}}\psi_{n-1}(x)\right] \\
&= \sqrt{\frac{\hbar}{2m\omega}}\left[\sqrt{n+1}e^{i\omega t}\psi_{n+1}(x) + \sqrt{n}e^{-i\omega t}\psi_{n-1}(x)\right]
\end{aligned} \tag{6.8.12}$$

Thus

$$\hat{x}_H(t) = \sqrt{\frac{\hbar}{2m\omega}}\left[e^{i\omega t}\hat{a}_+ + e^{-i\omega t}\hat{a}_-\right] \tag{6.8.13}$$

Express $\hat{a}_\pm$ in terms of $\hat{x}$ and $\hat{p}$,

$$\hat{x}_H(t) = \hat{x}_H(0)cos(\omega t) + \frac{1}{m\omega}\hat{p}_H(0)sin(\omega t) \tag{6.8.14}$$

The Heisenberg-picture operator satisfies the classical equation of motion for a mass on a spring.

In the Schroedinger picture, the wave function evolves in time according to the Schroedinger equation:

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t) \tag{6.8.15}$$

The operators $\hat{x} = x$ and $\hat{p} = -i\hbar\partial_x$ have no time dependence of their own, and the time dependence of expectation values comes from the time dependence of the wave function:

$$\left\langle \hat{Q} \right\rangle = \left\langle \Psi(t)|\hat{Q}|\Psi(t) \right\rangle \tag{6.8.16}$$

In the Heisenberg picture, the wave function is constant in time, $\Psi_H(x) = \Psi(x,0)$, and the operators evolve in time according to Equation(6.8.7).

In the Heisenberg picture, the time dependence of expectation values is carried by the operators.

$$\left\langle \hat{Q} \right\rangle = \left\langle \Psi_H|\hat{Q}_H(t)|\Psi_H \right\rangle \tag{6.8.17}$$

The two pictures are entirely equivalent since

$$\left\langle \Psi(t)|\hat{Q}|\Psi(t) \right\rangle = \left\langle \Psi(0)|\hat{U}^\dagger\hat{Q}\hat{U}|\Psi(0) \right\rangle = \left\langle \Psi_H|\hat{Q}_H(t)|\Psi_H \right\rangle \tag{6.8.18}$$

6.8.2 Time-Translation Invariance

If the Hamiltonian is time-dependent one can still write the formal solution to the Schroedinger equation in terms of the time-translation operator,$\hat{U}$:

$$\Psi(x,t) = \hat{U}(t,t_0)\Psi(x,t_0) \tag{6.8.19}$$

For an infinitesimal time interval δ:

$$\hat{U}(t_0+\delta,t_0) \approx 1 - \frac{i}{\hbar}\hat{H}(t_0)\delta \tag{6.8.20}$$

Time-translation invariance means that:

For any choice of t_1 and t_2, the time evolution is independent of which time interval we are considering.

$$\hat{U}(t_1+\delta,t_1) = \hat{U}(t_2+\delta,t_2) \tag{6.8.21}$$

Plugging Equation(6.8.20) into Equation(6.8.21), we see that the requirement is $\hat{H}(t_1) = \hat{H}(t_2)$.

since this must hold true for all t_1 and t_2, Hamiltonian is in fact time-independent: $\dfrac{\partial\hat{H}}{\partial t} = 0$.

In that case the generalized Ehrenfest theorem says:

$$\frac{d}{dt}\left\langle \hat{H} \right\rangle = \frac{i}{\hbar}\left\langle \left[\hat{H},\hat{H}\right] \right\rangle + \left\langle \frac{\partial\hat{H}}{\partial t} \right\rangle = 0 \tag{6.8.22}$$

Therefore, energy conservation is a consequence of time-translation invariance.