# Quantum Mechanics

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**Abstract**

This note is based on Quantum Mechanics B, taught by Hepeng Yao in Fall 2025 at Peking University, and also refers to the Lecture Notes of Quantum Mechanics by Linhui Ye, Peking University.

## Contents

# 1 Dynamical Picture of Quantum Mechanics

## 1.1 Wave-Particle Duality

There are three experiments that shows the wave-particle duality:

- Double-slit experiment with electrons
- Photoelectric effect
- Planck's law of blackbody radiation

**Example 1.1.** Planck's law of blackbody radiation is given by

$$\mathscr{I}(\nu, T) = \frac{2h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \tag{1.1}$$

We can rewrite it as

$$\mathscr{I}(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

*Proof.* Notice that

$$|f_2(\lambda)\mathrm{d}\lambda| = |f_1(\nu)\mathrm{d}\nu|$$

and $\nu = \frac{c}{\lambda}$, we have $\mathrm{d}\nu = -\frac{c}{\lambda^2}\mathrm{d}\lambda$. Hence, we have

$$\mathscr{I}(\lambda, T) = \mathscr{I}(\nu, T)\left|\frac{\mathrm{d}\nu}{\mathrm{d}\lambda}\right| = \frac{2h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \frac{c}{\lambda^2} = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

□

The corresponding relations are:

$$E = h\nu = h\frac{\omega}{2\pi} \equiv \hbar\omega \tag{1.2}$$

$$p = \frac{h}{\lambda} = \hbar k \tag{1.3}$$

## 1.2 Quantum Mechanical Description of Motion

The first postulate of quantum mechanics states that the state of a quantum mechanical system is completely specified by a wave function $\psi(x, t)$ in Hilbert space.

**Proposition 1.2** (Born)**.** *The probability density of finding a particle at position $x$ and time $t$ is given by*

$$\rho(\boldsymbol{r}, t) = |\psi(\boldsymbol{r}, t)|^2 \tag{1.4}$$

*Hence, we have*

$$\int_{-\infty}^{+\infty} |\psi(\boldsymbol{r}, t)|^2 \mathrm{d}^3\boldsymbol{r} = 1 \tag{1.5}$$

We give the double-slit experiment as an example to illustrate the probability wave function. Assume the original wave function is $\psi(x) = R(\boldsymbol{r})e^{i\phi(\boldsymbol{r})}$, then the wave function after passing through the double-slit is $\psi(x) = \psi_1(x)+\psi_2(x) = R_1(\boldsymbol{r})e^{i\phi_1(\boldsymbol{r})}+R_2(\boldsymbol{r})e^{i\phi_2(\boldsymbol{r})}$. Then the brightness on the screen is proportional to the probability density:

$$I(\boldsymbol{r})\propto|\psi(x)|^2 = R_1^2(\boldsymbol{r}) + R_2^2(\boldsymbol{r}) + 2R_1(\boldsymbol{r})R_2(\boldsymbol{r})\cos(\phi_1(\boldsymbol{r}) - \phi_2(\boldsymbol{r}))$$

The last term is the interference term.

**Proposition 1.3.** *Assume that $\psi(\boldsymbol{r})$ is normalized, then we have*

$$\overline{\boldsymbol{r}} = \int_{-\infty}^{+\infty} \boldsymbol{r}|\psi(\boldsymbol{r})|^2 \mathrm{d}^3\boldsymbol{r} \tag{1.6}$$

$$(\Delta\boldsymbol{r})^2 = \int_{-\infty}^{+\infty} (\boldsymbol{r} - \overline{\boldsymbol{r}})^2|\psi(\boldsymbol{r})|^2 \mathrm{d}^3\boldsymbol{r} \tag{1.7}$$

The second postulate of quantum mechanics states that the time evolution of the wave function is governed by the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = \hat{H}\psi(\boldsymbol{r},t) \tag{1.8}$$

**Example 1.4.** Verify that the plane wave function $\psi(x,t) = Ae^{i(k\cdot x-\omega t)}$ satisfies the Schrödinger equation.

*Proof.* By the wave-particle duality, we have $\psi(x,t) = Ae^{i(\frac{p}{\hbar}\cdot x-\frac{E}{\hbar}t)}$. Then we have

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = E\psi(x,t) = \hat{H}\psi(x,t) \tag{1.9}$$

□

**Proposition 1.5.** *Every wave function can be expressed as a superposition of plane waves:*

$$\psi(\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}}\int_{-\infty}^{+\infty} \phi(\boldsymbol{k})e^{i(\boldsymbol{k}\cdot\boldsymbol{r})}\mathrm{d}^3\boldsymbol{k} \tag{1.10}$$

*where $\phi(\boldsymbol{k})$ is the Fourier transform of $\psi(\boldsymbol{r})$:*

$$\phi(\boldsymbol{k}) = \frac{1}{(2\pi)^{3/2}}\int_{-\infty}^{+\infty} \psi(\boldsymbol{r})e^{-i(\boldsymbol{k}\cdot\boldsymbol{r})}\mathrm{d}^3\boldsymbol{r} \tag{1.11}$$

**Proposition 1.6.** *The Fourier transformation between $\boldsymbol{r}$ and $\boldsymbol{p}$ is given by*

$$\varphi(\boldsymbol{p}) = \frac{1}{\hbar^{\frac{3}{2}}}\phi(\boldsymbol{k}) = \frac{1}{(2\pi\hbar)^{3/2}}\int_{-\infty}^{+\infty} \psi(\boldsymbol{r})e^{-i(\frac{\boldsymbol{p}}{\hbar}\cdot\boldsymbol{r})}\mathrm{d}^3\boldsymbol{r}$$

$$\psi(\boldsymbol{r}) = \frac{1}{(2\pi\hbar)^{3/2}}\int_{-\infty}^{+\infty} \varphi(\boldsymbol{p})e^{i(\frac{\boldsymbol{p}}{\hbar}\cdot\boldsymbol{r})}\mathrm{d}^3\boldsymbol{p}$$

**Definition 1.7.** A set of functions $\{\phi_n(x)\}$ is called a set of **basis functions** in a Hilbert space $\mathcal{H}$ if any function $\psi(x) \in \mathcal{H}$ can be expressed as a linear combination of these functions. If the basis functions are orthonormal, they satisfy

$$\int \phi_n^*(x)\phi_m(x)\,dx = \delta_{nm} \tag{1.12}$$

Another fewer used definition of orthonormality is

$$\int \phi_\alpha^*(x)\phi_\beta(x)\,dx = \delta(\alpha - \beta) \tag{1.13}$$

For example, the set of the plane waves $\{e^{ikx}\}$, $\delta$ functions $\{\delta(x-a)\}$, and spherical harmonics $\{Y_{lm}(\theta,\phi)\}$ are all basis functions in their respective Hilbert spaces.

**Definition 1.8.** If the superposition is expressed as an integral, the basis functions are called a **continuous basis**. If the superposition is expressed as a sum, the basis functions are called a **discrete basis**.

**Definition 1.9.** The **inner product** of two functions $f(\boldsymbol{r})$ and $g(\boldsymbol{r})$ in a Hilbert space $\mathcal{H}$ is defined as

$$(f(\boldsymbol{r}), g(\boldsymbol{r})) = \int f^*(\boldsymbol{r})g(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r} \tag{1.14}$$

We have some orthonormal basis functions, like the plane waves, the spherical harmonics, $\delta$ functions, Legendre polynomials $P_l(x) = \frac{1}{2^l l!}\frac{\mathrm{d}^l}{\mathrm{d}x^l}(x^2-1)^l$ and Chebyshev polynomials $T_n(x) = \cos(n \arccos x)$. When we normalize the wave functions, there always exists an uncertainty of constant phase factor.

## 1.3 Mechanical Quantities

**Definition 1.10.** Repeat a mechanical quantity $A$ for $N$ times and the average value is $\bar{A}$. The results of measurement of $A$ are $A_1, A_2, \cdots, A_N$. The **statistical fluctuation** of $A$ is defined as

$$(\Delta A)^2 = \frac{1}{N}\sum_{i=1}^{N}(A_i - \bar{A})^2 \tag{1.15}$$

**Definition 1.11.** Given a wave function $\psi(\boldsymbol{r})$, $\hat{A}$ is called an **operator** of mechanical quantity $A$ if the expectation value of $A$ is given by

$$\overline{A} = \int \psi^*(\boldsymbol{r})\hat{A}\psi(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r} = \left(\psi, \hat{A}\psi\right) \tag{1.16}$$

**Example 1.12.** The operators of momentum $\boldsymbol{p}$ is given by

$$\hat{\boldsymbol{p}} = \frac{\hbar}{i}\nabla. \tag{1.17}$$

The operator of kinetic energy $T$ is given by

$$\hat{T} = \frac{\hat{\boldsymbol{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2. \tag{1.18}$$

The operator of angular momentum $\boldsymbol{l}$ is given by

$$\hat{\boldsymbol{l}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = \begin{vmatrix} \boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z \\ x & y & z \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} = \boldsymbol{e}_x\left(y\hat{p}_z - z\hat{p}_y\right) + \boldsymbol{e}_y\left(z\hat{p}_x - x\hat{p}_z\right) + \boldsymbol{e}_z\left(x\hat{p}_y - y\hat{p}_x\right) \tag{1.19}$$

*Proof.*

$$
\begin{aligned}
\overline{p} &= \int_{-\infty}^{+\infty} \varphi^*(p) p \varphi(p) \mathrm{d}p = \int_{-\infty}^{+\infty} \left( \int_{-\infty}^{\infty} \psi(x) \frac{1}{\sqrt{2\pi\hbar}} e^{-i\frac{px}{\hbar}} \mathrm{d}x \right)^* p\varphi(p) \mathrm{d}p \\
&= \int_{-\infty}^{+\infty} \psi^*(x) \left( \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \varphi(p) \left( \frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}x} e^{i\frac{px}{\hbar}} \right) \mathrm{d}p \right) \mathrm{d}x \\
&= \int_{-\infty}^{+\infty} \psi^*(x) \frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}x} \left( \int_{-\infty}^{+\infty} \varphi(p) \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{px}{\hbar}} \mathrm{d}p \right) \mathrm{d}x = \int_{-\infty}^{+\infty} \psi^*(x) \frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}x} \psi(x) \mathrm{d}x
\end{aligned}
$$

□

**Definition 1.13.** $\alpha$ is called an **eigenvalue** of operator $\hat{A}$ if there exists a non-zero function $\psi(\boldsymbol{r})$ such that

$$\hat{A}\psi(\boldsymbol{r}) = \alpha\psi(\boldsymbol{r}) \tag{1.20}$$

In this case, $\psi(\boldsymbol{r})$ is called an **eigenfunction** of $\hat{A}$ corresponding to eigenvalue $\alpha$.

Any non-eigenfunction can be expressed as a superposition of eigenfunctions.

**Example 1.14.** The eigenfunctions of the momentum operator are the plane waves and the eigenfunctions of the position operator are the $\delta$ functions.

*Proof.* For the momentum operator, we have

$$\frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}x} \psi(x) = p\psi(x)$$

The solution is $\psi(x) = Ae^{i\frac{p}{\hbar}x}$, which is a plane wave. For the position operator, we have

$$\hat{x}\psi(x) = x\psi(x) = x_0\psi(x)$$

The solution is $\psi(x) = \delta(x - x_0)$. □

The measurement of a mechanical quantity $A$ under an eigenfunction is unique and equals to the corresponding eigenvalue.

The third postulate of quantum mechanics states that the only possible result of the measurement of a mechanical quantity $A$ is one of the eigenvalues of the corresponding operator $\hat{A}$.

**Proposition 1.15** (Heisenberg's Uncertainty Principle)**.** *For the standard deviations of position and momentum, we have*

$$\Delta x \Delta p \geqslant \frac{\hbar}{2} \tag{1.21}$$

## 1.4 Schrödinger Equation

If the Hamiltonian $\hat{H}$ does not depend on time, we can solve the Schrödinger equation by separation of variables. Assume $\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r}) f(t)$, then we have

$$i\hbar \frac{1}{f(t)} \frac{\mathrm{d}f(t)}{\mathrm{d}t} = \frac{1}{\psi(\boldsymbol{r})} \hat{H}\psi(\boldsymbol{r}) = E.$$

Then we have

$$
\begin{gathered}
f(t) = f(0)e^{-\frac{i}{\hbar}Et}, \\
\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})e^{-\frac{i}{\hbar}Et}.
\end{gathered}
$$

**Definition 1.16.** The **probability density** $\rho(\boldsymbol{r}, t)$ is defined as

$$\rho(\boldsymbol{r}, t) = |\Psi(\boldsymbol{r}, t)|^2.$$

The **probability current density** $\boldsymbol{j}(\boldsymbol{r}, t)$ is defined as

$$\boldsymbol{j}(\boldsymbol{r}, t) = \frac{\hbar}{2mi}\left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^*\right).$$

**Proposition 1.17.** *The law of conservation of probability states that*

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{-\infty}^{+\infty} |\Psi(\boldsymbol{r}, t)|^2 \, \mathrm{d}r = 0. \tag{1.22}$$

*Proof.*

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} \int_{-\infty}^{+\infty} |\Psi(\boldsymbol{r}, t)|^2 \, \mathrm{d}r &= \int_{-\infty}^{+\infty} \left(\Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi\right) \mathrm{d}r \\
&= \frac{1}{i\hbar} \int_{-\infty}^{+\infty} \left(\Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\boldsymbol{r})\right) \Psi - \Psi \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\boldsymbol{r})\right) \Psi^*\right) \mathrm{d}r \\
&= \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \nabla \cdot \left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^*\right) \mathrm{d}r = \frac{i\hbar}{2m} \oint_{S \to \infty} \left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^*\right) \cdot \mathrm{d}\boldsymbol{S} = 0
\end{aligned}$$

The last step is because $\int |\Psi|^2 \mathrm{d}r$ is finite, so $\Psi \to r^{-\frac{3}{2}+s}$, $s > 0$ as $r \to \infty$. $\square$

**Proposition 1.18.** *In the proof of Proposition 1.17, we notice that*

$$\frac{\partial \rho(\boldsymbol{r}, t)}{\partial t} + \nabla \cdot \boldsymbol{j}(\boldsymbol{r}, t) = 0 \tag{1.23}$$

*which is called the* ***continuity equation****.*

# 2 Particle in One-Dimensional Potential Field

## 2.1 Basic Properties of Particle Energy States

**Definition 2.1.** $\psi_1, \psi_2$ are **degenerate eigenstates**, or **degenerate states** of operator $\hat{O}$ if they correspond to the same eigenvalue $o$.

**Proposition 2.2.** *If $\psi_1, \psi_2$ are two degenerate eigenstates of operator $\hat{O}$, then any linear combination of them is also an eigenstate of $\hat{O}$ corresponding to the same eigenvalue $o$.*

**Definition 2.3. Spatial Reflection Operator** $\hat{P}$ is defined as $\hat{P}f(\boldsymbol{r}) = f(-\boldsymbol{r})$.

**Definition 2.4.** $f(\boldsymbol{r})$ has **even parity** if $f(-\boldsymbol{r}) = f(\boldsymbol{r})$, and has **odd parity** if $f(-\boldsymbol{r}) = -f(\boldsymbol{r})$.

**Theorem 2.5.** *If $\psi(x)$ is an eigenstate of $\hat{H}$, then $\psi^*(-x)$ is also an eigenstate of $\hat{H}$ corresponding to the same eigenvalue. Hence, we can always choose the eigenstates of $\hat{H}$ to be real functions.*

**Theorem 2.6.** *If the potential $V(x)$ satisfies $V(-x) = V(x)$, then for every eigenstates $\psi(x)$ of $\hat{H}$, $\psi(-x)$ is also an eigenstate of $\hat{H}$ corresponding to the same eigenvalue. Hence, we can always choose the eigenstates of $\hat{H}$ to have definite parity.*

**Theorem 2.7.** *If the potential $V(x)$ is finite for any $x \in (-\infty, +\infty)$, then $\psi'(x)$ is continuous whether $V(x)$ is continuous or not.*

*Proof.* By the Schrödinger equation, we have

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}(V(x) - E)\psi(x) \Leftrightarrow \psi'(x + \mathrm{d}x) - \psi'(x) = \frac{2m}{\hbar^2}(V(x) - E)\psi(x)\mathrm{d}x \sim 0.$$

□

**Theorem 2.8.** *If eigenstates $\psi_1(x), \psi_2(x)$ are degenerate eigenstates, then we have*

$$\psi_1\psi_2' - \psi_2\psi_1' = \textit{Constant} \tag{2.1}$$

*Proof.* By $\psi'' = \frac{2m}{\hbar^2}(V - E)\psi$, we have $\psi_1''\psi_2 - \psi_2''\psi_1 = 0 \Rightarrow \frac{\mathrm{d}}{\mathrm{d}x}(\psi_1'\psi_2 - \psi_2'\psi_1) = 0$. □

**Definition 2.9.** A **bound state** is the state of a particle, which is confined to a finite region of space by the potential $V(x)$, i.e. whose wave function tends to zero as $x \to \pm\infty$. The opposite of bound state is scattering state.

For bound states, we have $\psi_1\psi_2' - \psi_2\psi_1' = 0$.

**Theorem 2.10.** *The eigenvalues of bound states are non-degenerate in the one dimensional typical case.*

*Proof.* If $\psi_1, \psi_2$ are two degenerate eigenstates of bound states, then we have $\psi_1\psi_2' - \psi_2\psi_1' = 0$. Hence, $\frac{\psi_1'}{\psi_1} = \frac{\psi_2'}{\psi_2} \Rightarrow \ln|\psi_1| = \ln|\psi_2| + C \Rightarrow \psi_1 = e^C\psi_2$. □

However, if there exists a singular point in the potential, the eigenvalues can be degenerate.

## 2.2 Solutions to Bound States in Square Potential Wells

The one-dimensional infinite potential well is defined as

$$V(x)=\begin{cases}0, & 0<x<a\\ \infty, & x\leqslant 0 \text{ or } x\geqslant a\end{cases}$$

For $x\leqslant 0$ or $x\geqslant a$, we have $\psi(x)=0$. For $0<x<a$, we have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}=E\psi(x)\Rightarrow\psi(x)=Ce^{ikx}+De^{-ikx},k=\frac{\sqrt{2mE}}{\hbar}.$$

By the boundary condition $\psi(0)=\psi(a)=0$, we have $C+D=0$ and $C\left(e^{ika}-e^{-ika}\right)=0$. Hence, we have $e^{ika}=e^{-ika}\Rightarrow k=\frac{n\pi}{a},n=1,2,3,\cdots$. The solutions are

$$E_n=\frac{n^2\pi^2\hbar^2}{2ma^2},\quad \psi_n(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right),n=1,2,3,\cdots. \tag{2.2}$$

$x=0$ and $x=a$ are fixed, so this is a standing wave and the wave function has more nodes as $n$ increases.

The finite symmetric potential well is defined as

$$V(x)=\begin{cases}0, & |x|<\frac{a}{2}\\ V_0, & |x|\geqslant\frac{a}{2}\end{cases}$$

By Theorem 2.6, it suffices to consider the even and odd parity solutions separately. We only consider the bound states with $0<E<V_0$. For $|x|\geqslant\frac{a}{2}$, we have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V_0\psi(x)=E\psi(x)\Rightarrow\psi(x)=Ae^{\beta x}+Be^{-\beta x},\beta=\frac{\sqrt{2m(V_0-E)}}{\hbar}.$$

Since $\psi(x)$ must be finite as $x\to\pm\infty$, we have

$$\psi(x)=\begin{cases}Ce^{\beta x}, & x\leqslant-\frac{a}{2}\\ Ae^{ikx}+Be^{-ikx}, & |x|<\frac{a}{2}\\ De^{-\beta x}, & x\geqslant\frac{a}{2}\end{cases},\quad\left(k=\frac{\sqrt{2mE}}{\hbar},\beta=\frac{\sqrt{2m(V_0-E)}}{\hbar}\right).$$

For even parity, we have $A=B$ and $C=D$. By the continuity of $\psi(x)$ and $\psi'(x)$ at $x=\frac{a}{2}$, we have $A\left(e^{i\frac{ka}{2}}+e^{-i\frac{ka}{2}}\right)=De^{-\beta\frac{a}{2}},ikA\left(e^{i\frac{ka}{2}}-e^{-i\frac{ka}{2}}\right)=-\beta De^{-\beta\frac{a}{2}}$. Hence, we have $\beta=k\tan\left(\frac{ka}{2}\right)$ and $\beta^2+k^2=\frac{2mV_0}{\hbar^2}$. Let $\xi=\frac{ka}{2},\eta=\frac{\beta a}{2}$. Then we have $\xi^2+\eta^2=\frac{mV_0a^2}{\hbar^2}$ and $\eta=\xi\tan\xi$.

For odd parity, we have $A=-B$ and $C=-D$. By the continuity of $\psi(x)$ and $\psi'(x)$ at $x=\frac{a}{2}$, we have $A\left(e^{i\frac{ka}{2}}-e^{-i\frac{ka}{2}}\right)=De^{-\beta\frac{a}{2}},ikA\left(e^{i\frac{ka}{2}}+e^{-i\frac{ka}{2}}\right)=-\beta De^{-\beta\frac{a}{2}}$. Hence, we have $\cot\left(\frac{ka}{2}\right)=-\frac{\beta}{k}$. Similarly, we have $\eta=-\xi\cot\xi$ and $\xi^2+\eta^2=\frac{mV_0a^2}{\hbar^2}$.

From above, we know that even parity solutions always exist, while odd parity solutions exist only when $\sqrt{\frac{mV_0a^2}{\hbar^2}}>\frac{\pi}{2}$. When $V_0\to\infty$, the solutions converge to those of the infinite potential well.

## 2.3 Scattering State Problem

Consider a particle incident from the left on a finite potential barrier:

$$V(x) = \begin{cases} V_0 & 0 \leqslant x \leqslant a \\ 0, & x < 0 \text{ or } x > a \end{cases}$$

Assume the energy of the particle $0 < E < V_0$, then we try to solve the reflection and transmission coefficients. It's easy to determine the general solutions:

$$\psi(x) = \begin{cases} Ce^{ikx} + De^{-ikx}, & x < 0 \\ Ae^{\beta x} + Be^{-\beta x}, & 0 \leqslant x \leqslant a \\ Ee^{ikx}, & x > a \end{cases}, \quad \left( k = \frac{\sqrt{2mE}}{\hbar}, \beta = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \right).$$

Let $j_i, j_r, j_t$ be the incident, reflected and transmitted probability current densities respectively, then we hope $j_i = j_r + j_t$. Compared with the general solution, we have $j_i \leftrightarrow Ce^{ikx}, j_r \leftrightarrow De^{-ikx}, j_t \leftrightarrow Ee^{ikx}$.

**Definition 2.11.** The **reflection coefficient** $R$ and the **transmission coefficient** $T$ are defined as

$$|R|^2 = \frac{j_r}{j_i} = \frac{|D|^2}{|C|^2}, \quad |T|^2 = \frac{j_t}{j_i} = \frac{|E|^2}{|C|^2}. \tag{2.3}$$

For convenience, we let $C = 1$. By the continuity of $\psi(x)$ and $\psi'(x)$ at $x = 0$ and $x = a$, we have

$$S = \frac{2i\beta k}{(k^2 - \beta^2)\sinh(\beta a) + 2i\beta k\cosh(\beta a)} e^{-ika},$$
$$R = \frac{(\beta^2 + k^2)^2 \sinh(\beta a)}{(k^2 - \beta^2)\sinh(\beta a) + 2i\beta k\cosh(\beta a)}.$$

And

$$|S|^2 = \left( 1 + \frac{1}{\frac{4E}{V_0}\left(1 - \frac{E}{V_0}\right)} \sinh^2(\beta a) \right)^{-1}, \quad |R|^2 = \frac{(\beta^2 + k^2)^2 \sinh^2(\beta a)}{(k^2 + \beta^2)\sinh^2(\beta a) + 4\beta^2 k^2}. \tag{2.4}$$

We can verify that $|R|^2 + |S|^2 = 1$, which is what we hope.

**Proposition 2.12** (Tunneling Effect)**.** *Even if a particle with energy smaller than the potential barrier, there is still a finite probability that the particle will tunnel through the barrier and appear on the other side.*

Consider the weak scattering condition, i.e. $E \ll V_0$ and $a$ is very large. Then we have $\beta a = \frac{a}{\hbar}\sqrt{2m(V_0 - E)} \gg 1$ and $\sinh(\beta a) \approx \frac{1}{2}e^{\beta a}$. Hence, the transmission coefficient can be approximated as

$$|S|^2 \approx \frac{16E(V_0 - E)}{V_0^2} e^{-\frac{2a}{\hbar}\sqrt{2m(V_0 - E)}}. \tag{2.5}$$

This shows that the transmission coefficient decreases as $a$, $m$ and $V_0$ increase.

When $E > V_0$, the particle is still possible to be reflected. Let $\beta = i\gamma, \gamma = \frac{\sqrt{2m(E - V_0)}}{\hbar}$, then we have

$$|S|^2 = \left( 1 + \frac{1}{4}\left( \frac{k}{\gamma} - \frac{\gamma}{k} \right)^2 \sin^2(\gamma a) \right)^{-1}. \tag{2.6}$$

**Definition 2.13.** When $\sin(\gamma a) = 0$, i.e. $\gamma a = n\pi$, the transmission coefficient $|S|^2 = 1$. This phenomenon is called **resonant transmission**.

## 2.4 Harmonic Oscillator

The energy of a classical harmonic oscillator is given by $E = T + \frac{1}{2}kx^2$ with frequency $\omega = \sqrt{\frac{k}{m}}$. The Hamiltonian of a one-dimensional quantum harmonic oscillator is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2. \tag{2.7}$$

Now we try to solve the bound states of the quantum harmonic oscillator.

Let $\sqrt{\frac{\hbar}{m\omega}} = \frac{1}{\alpha}$ and $\xi = \alpha x$, then the Schrödinger equation can be written as

$$\frac{\mathrm{d}^2\Psi(\xi)}{\mathrm{d}\xi^2} - (\xi^2 - \lambda)\Psi(\xi) = 0, \quad \lambda = \frac{2E}{\hbar\omega}.$$

First consider the asymptotic behavior of $\Psi(\xi)$ as $\xi \to \pm\infty$. We have $\frac{\mathrm{d}^2\Psi(\xi)}{\mathrm{d}\xi^2} - \xi^2\Psi(\xi) = 0$, one of whose solutions is $\Psi(\xi) \sim Ae^{-\frac{\xi^2}{2}}$. Hence, for general solutions, we suppose $\Psi(\xi) = u(\xi)e^{-\frac{\xi^2}{2}}$. Then we have the Hermite equation

$$u''(\xi) - 2\xi u'(\xi) + (\lambda - 1)u(\xi) = 0.$$

Let $u(\xi) = \sum_{i=0}^{\infty} c_i\xi^i$, then we have

$$\sum_{i=0}^{\infty}(i+2)(i+1)c_{i+2}\xi^i - \sum_{i=0}^{\infty}2ic_i\xi^i + \sum_{i=0}^{\infty}c_i(\lambda-1)\xi^i = 0 \Longrightarrow c_{i+2} = \frac{2i+1-\lambda}{(i+1)(i+2)}c_i.$$

By $c_0 = 0$ and $c_1 = 0$, we have two linearly independent solutions with even parity and odd parity respectively:

$$u_1(\xi) = c_0 + c_2\xi^2 + c_4\xi^4 + \cdots, \quad u_2(\xi) = c_1\xi + c_3\xi^3 + c_5\xi^5 + \cdots.$$

Consider the Taylor series expansion of $e^{\xi^2}$, we have

$$e^{\xi^2} = \sum_{i=0}^{\infty}\frac{\xi^{2i}}{i!}.$$

When $\xi \to \infty$, it suffices to consider the case when $i$ is large enough, we have $c_{2i+2} = \frac{1}{i+1}c_{2i} \sim \frac{1}{i}c_{2i}$, which is similar to the coefficient of $u_1(\xi)$. Hence, $u_1(\xi) \sim e^{\xi^2}$ as $\xi \to \infty$. Similarly, $u_2(\xi) \sim \xi e^{\xi^2}$ as $\xi \to \infty$. Therefore, $\Psi_1(\xi) \sim e^{\frac{\xi^2}{2}}$ and $\Psi_2(\xi) \sim \xi e^{\frac{\xi^2}{2}}$ as $\xi \to \infty$, which is divergent. To make $\Psi(\xi)$ convergent, the series must terminate, i.e. there exists an integer $n$ such that $2n + 1 - \lambda = 0$. It is called the $n$-th Hermite polynomial, denoted by $H_n(\xi)$, when the series terminates at $i = n$, i.e.

$$H_n(\xi) = \begin{cases} c_1\xi + c_3\xi^3 + \cdots + c_n\xi^n, & n \text{ is odd} \\ c_0 + c_2\xi^2 + \cdots + c_n\xi^n, & n \text{ is even} \end{cases}. \tag{2.8}$$

Therefore, we have

$$\Psi(\xi) = e^{-\frac{\xi^2}{2}}H_n(\xi), \quad \psi_n(x) = \Psi(\alpha x) = \sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}}e^{-\frac{\alpha^2x^2}{2}}H_n(\alpha x). \tag{2.9}$$

By the boundary condition $2n - \lambda + 1 = 0$ and $E = \frac{1}{2}\lambda\hbar\omega$, we have

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots. \tag{2.10}$$

**Definition 2.14.** The **zero point energy** of the harmonic oscillator is defined as the lowest energy $E_0 = \frac{1}{2}\hbar\omega$.

**Proposition 2.15** (Casimir Effect)**.** *Two uncharged, parallel, perfectly conducting plates in vacuum will attract each other due to quantum vacuum fluctuations of the electromagnetic field.*

Now we briefly introduce the second quantization. Inspired by

$$\hat{H} = \hbar\omega \left(\sqrt{\frac{m\omega}{2\hbar}}\right)^2 \left(\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right)\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right)\right) - \frac{1}{2}\hbar\omega,$$

we have the following definition.

**Definition 2.16.** The **annihilation operator** $\hat{a}$ and the **creation operator** $\hat{a}^\dagger$ are defined as

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right), \quad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right). \tag{2.11}$$

It's easy to verify that $[\hat{a}, \hat{a}^\dagger] = 1$ and $\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)$, where $\hat{N} = \hat{a}^\dagger\hat{a}$. $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$ is the eigenvalue of $\hat{H}$.

$$\hat{H}|n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega|n\rangle, \quad \hat{N}|n\rangle = n|n\rangle.$$

# 3 Operators

## 3.1 Rules of Operators

The fourth postulate of quantum mechanics states that to every observable $A$ there corresponds a linear Hermitian operator $\hat{A}$ that acts on the wave functions in the Hilbert space.

**Definition 3.1.** The **Hermitian conjugate operator** $A^\dagger$ of $\hat{A}$ is defined as

$$\hat{A}^\dagger = \left(\hat{A}^*\right)^T. \tag{3.1}$$

**Definition 3.2.** Given $F(x) \in C^\infty(\mathbb{R})$ and the expansion $F(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\mathrm{d}^n F(x)}{\mathrm{d}x^n}|_{x=0} x^n$ convergent, we define the function $F(\hat{A})$ as

$$F(\hat{A}) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\mathrm{d}^n F(x)}{\mathrm{d}x^n}|_{x=0} \hat{A}^n. \tag{3.2}$$

Similarly, we can define $F(\hat{A}, \hat{B})$ for two operators $\hat{A}, \hat{B}$ as

$$F(\hat{A}, \hat{B}) = \sum_{n,m=0}^{\infty} \frac{1}{n!m!} \frac{\partial^n}{\partial x^n} \frac{\partial^m F(x,y)}{\partial y^m}|_{x=0,y=0} \hat{A}^n \hat{B}^m. \tag{3.3}$$

**Definition 3.3.** The **commutator** of two operators $\hat{A}, \hat{B}$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{3.4}$$

For example, we have $[\hat{x}, \hat{p}_x] = i\hbar$, which is called the **canonical commutation relation**.

We call $\hat{A}$ and $\hat{B}$ **commute** if $[\hat{A}, \hat{B}] = 0$; otherwise, we call them **non-commute**.

**Proposition 3.4.** *We have the following properties of commutators:*

1. $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$;
2. $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$;
3. $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$;
4. $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$;
5. $[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$.

## 3.2 Hermitian Operators

**Definition 3.5.** $\hat{A}$ is called a **Hermitian operator** if $\hat{A}^\dagger = \hat{A}$.

In fact, all observable operators are Hermitian. Recall $\hat{p}$ in Example 1.12, we have

**Theorem 3.6.** *The mean value of a Hermitian operator is always real.*

**Theorem 3.7.** *If $\hat{A}$ is a Hermitian operator, then $\overline{\Delta\hat{A}^2} \geqslant 0$.*

*Proof.*

$$\begin{aligned}\overline{\Delta\hat{A}^2} &= \int_{-\infty}^{+\infty} \psi^*(x)(\hat{A}-\overline{A})^2\psi(x)\mathrm{d}x = \int_{-\infty}^{+\infty} ((\hat{A}-\overline{A})\psi(x))^*((\hat{A}-\overline{A})\psi(x))\mathrm{d}x \\ &= \int_{-\infty}^{+\infty} |(\hat{A}-\overline{A})\psi(x)|^2\mathrm{d}x \geqslant 0.\end{aligned}$$

□

**Theorem 3.8.** *The eigenvalues of a Hermitian operator are always real.*

**Theorem 3.9.** *If $\hat{A}$ is a Hermitian operator, then $\hat{A}-\overline{A}$ is also a Hermitian operator.*

**Theorem 3.10.** *The eigenfunctions of a Hermitian operator corresponding to different eigenvalues are orthogonal.*

*Proof.* Assume $\psi_m, \psi_n$ are two eigenfunctions of $\hat{A}$ corresponding to different eigenvalues $A_m, A_n$, then we have

$$(A_m - A_n)(\psi_m, \psi_n) = (\hat{A}\psi_m, \psi_n) - (\psi_m, \hat{A}\psi_n) = 0 \Longrightarrow (\psi_m, \psi_n) = 0.$$

□

In general, the eigenfunctions of a Hermitian operator corresponding to the same eigenvalue are not necessarily orthogonal. However, we can always use the Gram-Schmidt process to orthogonalize them.

## 3.3 Non-Square Integrable Wave Functions

**Example 3.11.** The plane wave function and $\delta$-function are not square integrable. Actually, all eigenfunctions of a continuous spectrum are not square integrable.

*Proof.* Let $\psi_\alpha$ be the eigenfunction of $\hat{A}$ corresponding to the eigenvalue $\alpha$. Suppose that $(\psi_\alpha, \psi_{\alpha'}) = \delta_{\alpha\alpha'}$, then for any $\Psi$, we have $\Psi = \int C_\alpha \psi_\alpha(\boldsymbol{r})\mathrm{d}\alpha$.

$$(\Psi, \Psi) = \int C_\alpha^* \left( \int C_{\alpha'}\delta_{\alpha\alpha'}\mathrm{d}\alpha' \right) \mathrm{d}\alpha = \int C_\alpha^* \left( \lim_{\varepsilon\to 0} \int_{\alpha-\varepsilon}^{\alpha+\varepsilon} C_{\alpha'}\mathrm{d}\alpha' \right) \mathrm{d}\alpha = 0.$$

However, this is impossible. □

For eigenfunctions of a continuous spectrum, we normalize them to the $\delta$-function, i.e.

$$(\psi_\alpha, \psi_{\alpha'}) = \delta(\alpha - \alpha'). \tag{3.5}$$

Then, we have

$$(\Psi, \Psi) = \iint C_\alpha^* C_{\alpha'}\delta(\alpha-\alpha')\mathrm{d}\alpha'\mathrm{d}\alpha = \int |C_\alpha|^2\mathrm{d}\alpha. \tag{3.6}$$

**Theorem 3.12** (Completeness of Eigenfunctions of Hermitian Operators)**.** *$\hat{A}$ is a Hermitian operator. If for any $\Psi$, $\frac{(\Psi,\hat{A}\Psi)}{(\Psi,\Psi)}$ has a lower bound but no upper bound, then the eigenfunctions of $\hat{A}$ form a complete set, i.e. any wave function can be expanded as a linear combination of the eigenfunctions of $\hat{A}$.*

## 3.4 Common Eigenfunctions

**Definition 3.13.** $\psi_{mn}$ is the **common eigenfunction** of $\hat{A}$ and $\hat{B}$ if $\hat{A}\psi_{mn} = \alpha_m\psi_{mn}$ and $\hat{B}\psi_{mn} = \beta_n\psi_{mn}$, where $m$ and $n$ are the quantum numbers of $\hat{A}$ and $\hat{B}$ respectively.

**Proposition 3.14.** *Hermitian operators with common eigenfunctions commute.*

*Proof.*

$$\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi_{mn} = \hat{A}(\beta_n\psi_{mn}) - \hat{B}(\alpha_m\psi_{mn}) = (\beta_n\alpha_m - \alpha_m\beta_n)\psi_{mn} = 0 \Rightarrow [\hat{A}, \hat{B}] = 0.$$

□

Now we discuss the construction of common eigenfunctions of commutative operators. First, all the non-degenerate eigenfunctions $\psi$ of $\hat{A}$ are also eigenfunctions of $\hat{B}$, because $\hat{B}\psi$ is also an eigenfunction of $\hat{A}$, which shows that $\hat{B}\psi = \beta\psi$.

Next, for degenerate eigenfunctions $\psi_{n1}, \psi_{n2}, \cdots, \psi_{nm}$ of $\hat{A}$ corresponding to the same eigenvalue $\alpha$, we have $\hat{B}\psi_{ni} = \sum_{j=1}^{m} C_{ij}\psi_{nj}$. By the equations, we can determine the eigenfunctions of $\hat{B}$.

By the idea of common eigenfunctions and quantum numbers, we can distinguish all the degenerate states.

**Definition 3.15.** Let $\left(\hat{A}_1, \hat{A}_2, \cdots\right)$ be a set of commutative and independent Hermitian operators and their common eigenfunctions be $\psi_{a_1a_2\cdots}$, where $a_i$ is the quantum number of $\hat{A}_i$. Then, $(a_1, a_2, \cdots)$ determines the state of the particle completely and we called $(\hat{A}_1, \hat{A}_2, \cdots)$ a **complete set of commuting observables**.

**Example 3.16.** The wave function of the electron in a hydrogen atom can be expressed as $\psi_{nlm}(r, \theta, \phi)$, which is the common eigenfunction of $\hat{H}, \hat{l}^2, \hat{l}_z$. The three quantum numbers determine the state of the electron completely. Therefore, $(\hat{H}, \hat{l}^2, \hat{l}_z)$ is a complete set of commuting observables.

**Definition 3.17.** The complete set of commuting observables including the Hamiltonian is called a **complete set of conserved quantities**.

**Proposition 3.18** (Uncertainty Principle)**.** *For any wave function and $\hat{A}, \hat{B}$, we have*

$$\Delta A \cdot \Delta B \geqslant \frac{1}{2}\left|\overline{[\hat{A}, \hat{B}]}\right|. \tag{3.7}$$

*Proof.* Let $I(\alpha) = \int \left|\alpha\hat{A}\Psi + i\hat{B}\Psi\right|^2 \mathrm{d}x \geqslant 0$, then we have

$$I(\alpha) = \alpha^2\overline{\Delta A^2} + \overline{\Delta B^2} + i\alpha\overline{[\hat{A}, \hat{B}]}.$$

Since $I(\alpha)$ is real, we have $i\overline{[\hat{A}, \hat{B}]} = \beta \in \mathbb{R}$. Hence

$$I(\alpha) = \alpha^2\overline{\Delta A^2} + \overline{\Delta B^2} + \alpha\beta = \overline{\hat{A}^2}\left(\alpha^2 + \frac{\beta}{2\overline{\hat{A}^2}}\right)^2 - \frac{\beta^2}{4\overline{\hat{A}^2}} + \overline{\hat{B}^2}.$$

For every $\alpha$, $I(\alpha) \geqslant 0$, so we have $\overline{\hat{B}^2} \geqslant \frac{\beta^2}{4\overline{\hat{A}^2}}$. Since $[\hat{A} - \overline{A}, \hat{B} - \overline{B}] = [\hat{A}, \hat{B}]$, we have

$$\Delta A \cdot \Delta B \geqslant \frac{1}{2}|\overline{[\hat{A} - \overline{A}, \hat{B} - \overline{B}]} = \frac{1}{2}|\overline{[\hat{A}, \hat{B}]}|.$$

□

Specially, for $x$ and $p$, we have $\Delta x \cdot \Delta p_x \geqslant \frac{\hbar}{2}$.

## 3.5 Angular Momentum Operator

The angular momentum operator is defined as $\hat{l}_i = \varepsilon_{ijk}\hat{x}_j\hat{p}_k$ and we have $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}, [\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0$.

Recall basic properties of Levi-Civita symbol $\varepsilon_{kij}\varepsilon_{klm} = \varepsilon_{ikj}\varepsilon_{lkm} = \varepsilon_{ijk}\varepsilon_{lmk} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}$. Then we have the following commutation relations:

$$[\hat{l}_i, \hat{x}_j] = [\varepsilon_{iab}\hat{x}_a\hat{p}_b, \hat{x}_j] = \varepsilon_{iab}\hat{x}_a[\hat{p}_b, \hat{x}_j] = i\hbar\varepsilon_{ija}\hat{x}_a, \quad [\hat{l}_\alpha, \hat{p}_\beta] = i\hbar\varepsilon_{\alpha\beta\gamma}\hat{p}_\gamma, \tag{3.8}$$

$$[\hat{l}_i, \hat{l}_j] = [\varepsilon_{iab}\hat{x}_a\hat{p}_b, \varepsilon_{jcd}\hat{x}_c\hat{p}_d] = \varepsilon_{iab}\varepsilon_{jcd}\left(\hat{x}_c[\hat{x}_a, \hat{p}_d]\hat{p}_b + \hat{x}_a[\hat{p}_b, \hat{x}_c]\hat{p}_d\right) = i\hbar\varepsilon_{ijk}\hat{l}_k. \tag{3.9}$$

Therefore, we have

$$\hat{\boldsymbol{l}} \times \hat{\boldsymbol{l}} = i\hbar\hat{\boldsymbol{l}}. \tag{3.10}$$

Since

$$[\hat{l}_j^{\,2}, \hat{l}_i] = l_j[\hat{l}_j, \hat{l}_i] + [\hat{l}_j, \hat{l}_i]\hat{l}_j = i\hbar\varepsilon_{jik}(\hat{l}_j\hat{l}_k + \hat{l}_k\hat{l}_j). \tag{3.11}$$

we have

$$[\hat{\boldsymbol{l}}^2, \hat{l}_i] = 0. \tag{3.12}$$

In spherical coordinates, the angular momentum operator can be expressed as:

$$\hat{l}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right), \tag{3.13}$$

$$\hat{l}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right), \tag{3.14}$$

$$\hat{l}_z = -i\hbar\frac{\partial}{\partial\varphi}, \tag{3.15}$$

$$\hat{l}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right). \tag{3.16}$$

The Schrödinger equation in spherical coordinates is given by

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{l}^2}{\hbar^2}\right)\psi(r,\theta,\varphi) + V(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi). \tag{3.17}$$

Since $[\hat{l}^2, \hat{l}_z] = 0$, we can find their common eigenfunctions $Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$. For $\hat{l}_z$,

$$\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}\varphi}\Phi(\varphi) = \alpha\Phi(\varphi) \Rightarrow \alpha = m\hbar, \quad \Phi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}, \quad m = 0, \pm1, \pm2, \cdots. \tag{3.18}$$

For $\hat{l}^2$, denote the eigenvalue by $\lambda\hbar^2$, then we have

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

Let $x = \cos\theta$ and $y(x) = \Theta(\theta)$, then we have the associated Legendre equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\left((1-x^2)\frac{\mathrm{d}y}{\mathrm{d}x}\right) + \left(\lambda - \frac{m^2}{1-x^2}\right)y = 0 \Longrightarrow y = \sum_{k=0}^{\infty} c_k x^k, \quad c_{k+2} = \frac{k(k+1)-\lambda}{(k+1)(k+2)}c_k. \tag{3.19}$$

Since for $-1 \leqslant x \leqslant 1$, $y$ is not bounded, so the series must terminate, i.e. there exists an integer $l$ such that $l(l+1) - \lambda = 0$. Therefore, we have

$$\lambda = l(l+1), \quad l = 0, 1, 2, \cdots. \tag{3.20}$$

When $\lambda = l(l+1)$, this polynomial is called the Legendre polynomial, denoted by $P_l(x) = \sum_{k=0}^{l} c_k x^k$. When $l$ is odd, $P_l(x)$ is an odd function; when $l$ is even, $P_l(x)$ is an even function, i,e. $P_l(-x) = (-1)^l P_l(x)$. And we have Rodrigues' formula:

$$P_l(x) = \frac{1}{2^l l!} \frac{\mathrm{d}^l}{\mathrm{d}x^l}(x^2 - 1)^l. \tag{3.21}$$

Therefore, when $m = 0$, we have

$$Y_{lm}(\theta, \varphi) = P_l(\cos\theta) e^{im\varphi}, \tag{3.22}$$

where $l$ is called the **azimuthal quantum number** and $m$ is called the **magnetic quantum number**.

Using Dirac notation, we denote the eigenstate of $\hat{l}^2$ and $\hat{l}_z$ by $|l, m\rangle$, then we have

$$\hat{l}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle, \quad \hat{l}_z |l, m\rangle = m\hbar |l, m\rangle, \quad \langle x|l, m\rangle = Y_{lm}(\theta, \varphi). \tag{3.23}$$

**Definition 3.19.** The **rasing** and **lowering operators** are defined as

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y, \quad \hat{l}_- = \hat{l}_x - i\hat{l}_y. \tag{3.24}$$

We have the following properties:

1. $\hat{l}_+, \hat{l}_-$ are not Hermitian operators, but are Hermitian conjugate to each other.

2. $[\hat{l}_\pm, \hat{l}_z] = \mp\hbar\hat{l}_\pm$.

3. $\hat{l}_\pm |l, m\rangle = |l, m \pm 1\rangle$. Because $[\hat{l}_\pm, \hat{l}_z]|l, m\rangle = (\hat{l}_\pm \hat{l}_z - \hat{l}_z \hat{l}_\pm)|l, m\rangle = \mp\hbar|l, m\rangle$.

# 4 Time Evolution and Symmetries

## 4.1 Conserved Quantity and Virial Theorem

**Definition 4.1.** An observable $A$ is called a **conserved quantity** if its mean value does not change with time for any wave function, i.e.

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{A} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\Psi, \hat{A}\Psi\right) = 0. \tag{4.1}$$

**Proposition 4.2.** *The conservation condition of an observable $A$ is given by*

1. $\frac{\partial \hat{A}}{\partial t} = 0$;
2. $[\hat{A}, \hat{H}] = 0$.

*Proof.*

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\overline{A} &= \left(\frac{\partial\Psi}{\partial t}, \hat{A}\Psi\right) + \left(\Psi, \frac{\partial\hat{A}}{\partial t}\Psi\right) + \left(\Psi, \hat{A}\frac{\partial\Psi}{\partial t}\right) \\ &= \frac{1}{i\hbar}\left((\hat{H}\Psi, \hat{A}\Psi) - (\Psi, \hat{A}\hat{H}\Psi)\right) + \left(\Psi, \frac{\partial\hat{A}}{\partial t}\Psi\right) = \frac{1}{i\hbar}\overline{[\hat{A}, \hat{H}]} + \overline{\frac{\partial\hat{A}}{\partial t}}.\end{aligned}$$

□

We call the complete set of commuting observables $\{\hat{H}, \hat{A}_1, \hat{A}_2, \cdots\}$ the **complete set of conserved quantities**.

**Theorem 4.3** (Virial Theorem)**.** *For a stationary state, we have*

$$2\overline{T} = \overline{\boldsymbol{r}\cdot\nabla V(\boldsymbol{r})}. \tag{4.2}$$

*Proof.* Since $\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}$ is independent of time, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}} = \frac{1}{i\hbar}\overline{[\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}, \hat{H}]} = 0.$$

Now we calculate $[\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}, \frac{\boldsymbol{p}^2}{2m}]$ and $[\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}, V(\boldsymbol{r})]$ respectively:

$$[\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}, \boldsymbol{p}^2] = [\hat{x}\hat{p}_x, \hat{p}_x^2] + [\hat{y}\hat{p}_y, \hat{p}_y^2] + [\hat{z}\hat{p}_z, \hat{p}_z^2] = 2i\hbar\hat{p}_x^2 + 2i\hbar\hat{p}_y^2 + 2i\hbar\hat{p}_z^2 = 2i\hbar\hat{\boldsymbol{p}}^2.$$

Since $[\hat{x}\hat{p}_x, V(\boldsymbol{r})] = \hat{x}[\hat{p}_x, V(\boldsymbol{r})] = -i\hbar\hat{x}\frac{\partial V}{\partial x}$, we have

$$[\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}, V(\boldsymbol{r})] = -i\hbar\left(\hat{x}\frac{\partial V}{\partial x} + \hat{y}\frac{\partial V}{\partial y} + \hat{z}\frac{\partial V}{\partial z}\right) = -i\hbar\boldsymbol{r}\cdot\nabla V(\boldsymbol{r}).$$

By $\overline{[\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}, \hat{H}]} = 0$, we showed the theorem. □

**Example 4.4.** If the potential is spherically symmetric, i.e. $V(r,\theta,\varphi) = V(r)$, then the angular momentum of the particle is conserved.

*Proof.* It suffices to show that $[\hat{l}_x, \hat{\boldsymbol{p}}^2] = 0$.

$$[\hat{l}_x, \boldsymbol{p}^2] = [\hat{l}_x, \hat{p}_x^2] + [\hat{l}_x, \hat{p}_y^2] + [\hat{l}_x, \hat{p}_z^2] = 0 + i\hbar(\hat{p}_y\hat{p}_z + \hat{p}_z\hat{p}_y) - i\hbar(\hat{p}_z\hat{p}_y + \hat{p}_y\hat{p}_z) = 0.$$

□

Consider a infinitely small displacement $x' = x + \delta$ and $\hat{H}(x') = \hat{H}(x)$, then we have

$$\Psi(x+\delta) = \Psi(x) + \frac{i}{\hbar}\delta\hat{p}_x\Psi(x) + O(\delta^2).$$

By Schrödinger equation, we have

$$\hat{p}_x\left(i\hbar\frac{\partial}{\partial t}\Psi(x,t)\delta\right) = i\hbar\frac{\partial}{\partial t}\hat{p}_x\Psi(x,t)\delta = \hat{H}\hat{p}_x\Psi(x,t)\delta.$$

Since $\Psi$ is arbitrary, we have

$$[\hat{p}_x, \hat{H}] = 0. \tag{4.3}$$

Therefore, under an infinitely small displacement, the momentum is conserved. Similarly, we can show that under an infinitely small rotation, the angular momentum is conserved.

## 4.2 Quantum Many-Body Problem 1: Distinguishable Particles

For $N$ particles, the wave function is given by $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N, t)$ and if the Hamiltonian is independent of time, we have the stationary state

$$\Psi_n(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N, t) = \psi_n(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)e^{-\frac{i}{\hbar}E_n t}. \tag{4.4}$$

The normalization condition is given by

$$\int |\psi_n(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)|^2 \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\cdots\mathrm{d}\boldsymbol{r}_N = 1. \tag{4.5}$$

The total momentum is given by

$$\hat{\boldsymbol{P}} = \sum_{i=1}^{N}\hat{\boldsymbol{p}}_i = -i\hbar\sum_{i=1}^{N}\frac{\partial}{\partial\boldsymbol{r}_i}, \tag{4.6}$$

where every item is a **single particle operator** and the summation is a **one-body operator**. Similarly, the total angular momentum and kinetic energy are given by

$$\hat{\boldsymbol{L}} = \sum_{i=1}^{N}\hat{\boldsymbol{l}}_i = \sum_{i=1}^{N}\boldsymbol{r}_i\times\hat{\boldsymbol{p}}_i, \quad \hat{T} = \sum_{i=1}^{N}\hat{T}_i = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial r_i^2}\right) \tag{4.7}$$

The operator related to the interaction between two particles is called a **two-body operator**, such as $v(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{q_1 q_2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$.

If the particles are non-interacting, then the Hamiltonian is given by

$$\hat{H}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \sum_{i=1}^{N}\hat{h}_i(\boldsymbol{r}_i) = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial\boldsymbol{r}_i^2} + V_i(\boldsymbol{r}_i)\right). \tag{4.8}$$

After respectively solving the single-particle equation, we can construct the wave function of the whole system as

$$\Psi_{n_1,n_2,\cdots,n_N}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \phi_{n_1}(\boldsymbol{r}_1)\chi_{n_2}(\boldsymbol{r}_2)\cdots\mu_{n_N}(\boldsymbol{r}_N). \tag{4.9}$$

**Proposition 4.5.**

$$\begin{aligned}\hat{H}\phi_{n_1}(\boldsymbol{r}_1)\chi_{n_2}(\boldsymbol{r}_2)\cdots\mu_{n_N}(\boldsymbol{r}_N) &= \sum_{i=1}^{N}\hat{h}_i(\boldsymbol{r}_i)\left(\phi_{n_1}(\boldsymbol{r}_1)\chi_{n_2}(\boldsymbol{r}_2)\cdots\mu_{n_N}(\boldsymbol{r}_N)\right)\\ &= \sum_{i=1}^{N}E_{n_i}\phi_{n_1}(\boldsymbol{r}_1)\chi_{n_2}(\boldsymbol{r}_2)\cdots\mu_{n_N}(\boldsymbol{r}_N) = E\phi_{n_1}(\boldsymbol{r}_1)\chi_{n_2}(\boldsymbol{r}_2)\cdots\mu_{n_N}(\boldsymbol{r}_N),\end{aligned} \tag{4.10}$$

Consider a two-particle system, where the potential only depends on the distance between the two particles, i.e. $V(\boldsymbol{r}_1, \boldsymbol{r}_2) = V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$. Let $\boldsymbol{R} = \frac{m_1\boldsymbol{r}_1+m_2\boldsymbol{r}_2}{m_1+m_2}$ be the center of mass coordinate and $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ be the relative coordinate.

**Proposition 4.6.** *In the new coordinates, the Hamiltonian is given by*

$$\hat{H}(\boldsymbol{R}, \boldsymbol{r}) = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \boldsymbol{R}^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \boldsymbol{r}^2} + V(r). \tag{4.11}$$

*We can separate the variables as $\psi(\boldsymbol{R}, \boldsymbol{r}) = \phi(\boldsymbol{R})\varphi(\boldsymbol{r})$, where*

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \boldsymbol{R}^2}\right)\phi(\boldsymbol{R}) = E_M\phi(\boldsymbol{R}), \quad \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \boldsymbol{r}^2} + V(r)\right)\varphi(\boldsymbol{r}) = E_\mu\varphi(\boldsymbol{r}), \tag{4.12}$$

Generally, we can not separate the variables in the wave function, such as $\psi(x_1, x_2, x_3) = \sin\frac{n\pi(x_1^2+x_2x_3)}{a}$. These variables are called **entangled**.

## 4.3 Quantum Many-Body Problem 2: Identical Particles

**Definition 4.7. Identical particles** are particles with same intrinsic properties, such as mass, charge, and spin.

The exchange of two identical particles should not lead to any observable change in the system.

The fifth postulate of quantum mechanics states that identical particles can not be distinguished by any physical means.

Define the exchange operator $\hat{P}_{ij}$ as

$$\hat{P}_{ij}\Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots) = \Psi(\cdots, \boldsymbol{r}_j, \cdots, \boldsymbol{r}_i, \cdots). \tag{4.13}$$

Since $\Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots)$ and $\Psi(\cdots, \boldsymbol{r}_j, \cdots, \boldsymbol{r}_i, \cdots)$ differs only by a complex constant factor, we have

$$\hat{P}_{ij}\Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots) = \lambda\Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots). \tag{4.14}$$

Since

$$\hat{P}_{ij}^2\Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots) = \lambda^2\Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots) \equiv \Psi(\cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_j, \cdots),$$

we have $\lambda^2 = 1$, i.e. $\lambda = \pm 1$.

**Definition 4.8.** If $\lambda = 1$, the particles are called **bosons**, whose spin is integer times $\hbar$. If $\lambda = -1$, the particles are called **fermions**, whose spin is half-integer times $\hbar$.

**Proposition 4.9.** *The **Bose-Einstein distribution** and **Fermi-Dirac distribution** are given by*

$$\langle N_\lambda \rangle = \frac{1}{e^{\beta(E_\lambda-\mu)-1}}, \quad \langle N_\lambda \rangle = \frac{1}{e^{\beta(E_\lambda-\mu)}+1}. \tag{4.15}$$

When $T \gg 1$, we have $\langle N_\lambda \rangle \ll 1$, hence both distributions reduce to the classical Maxwell-Boltzmann distribution:

$$\langle N_\lambda \rangle = e^{-\beta(E_\lambda-\mu)}.$$

Consider a identical fermion system. Let $P_\alpha$ be a permutation operator, which permutes the coordinates of particles according to the permutation $\alpha$.

$$\Psi = A\sum_{\alpha=1}^{N!}\mu(\alpha)P_\alpha\left(\psi_{k_1}(\boldsymbol{r}_1)\psi_{k_2}(\boldsymbol{r}_2)\cdots\psi_{k_N}(\boldsymbol{r}_N)\right), \quad \mu(\alpha) = \begin{cases} +1, & \text{even permutation,} \\ -1, & \text{odd permutation.}\end{cases}$$

The normalization constant $A$ can be determined by

$$\begin{aligned}(\Psi,\Psi) &= |A|^2\sum_{\alpha=1}^{N!}\mu(\alpha)\sum_{\beta=1}^{N!}\mu(\beta) \\ &\quad \left(P_\alpha\left(\psi_{k_1}(\boldsymbol{r}_1)\psi_{k_2}(\boldsymbol{r}_2)\cdots\psi_{k_N}(\boldsymbol{r}_N)\right), P_\beta\left(\psi_{k_1}(\boldsymbol{r}_1)\psi_{k_2}(\boldsymbol{r}_2)\cdots\psi_{k_N}(\boldsymbol{r}_N)\right)\right) \\ &= |A|^2\sum_{\alpha=1}^{N!}\mu(\alpha)\sum_{\beta=1}^{N!}\mu(\beta)\delta_{\alpha\beta} = |A|^2 N!.\end{aligned}$$

Hence, we have the normalized wave function and Slater determinant:

$$\begin{aligned}\Psi &= \frac{1}{\sqrt{N!}}\sum_{\alpha=1}^{N!}\mu(\alpha)P_\alpha\left(\psi_{k_1}(\boldsymbol{r}_1)\psi_{k_2}(\boldsymbol{r}_2)\cdots\psi_{k_N}(\boldsymbol{r}_N)\right) \\ &= \frac{1}{N!}\begin{vmatrix}\psi_{k_1}(\boldsymbol{r}_1) & \psi_{k_1}(\boldsymbol{r}_2) & \cdots & \psi_{k_1}(\boldsymbol{r}_N) \\ \psi_{k_2}(\boldsymbol{r}_1) & \psi_{k_2}(\boldsymbol{r}_2) & \cdots & \psi_{k_2}(\boldsymbol{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{k_N}(\boldsymbol{r}_1) & \psi_{k_N}(\boldsymbol{r}_2) & \cdots & \psi_{k_N}(\boldsymbol{r}_N)\end{vmatrix}.\end{aligned} \tag{4.16}$$

Consider identical boson system. Similarly, we have

$$\begin{aligned}\Psi &= A\sum_{\alpha=1}^{N!}P_\alpha\left(\underbrace{\psi_{k_1}(\boldsymbol{r}_1)\cdots\psi_{k_1}(\boldsymbol{r}_i)}_{n_{k_1}\ \text{items}}\psi_{k_2}(\boldsymbol{r}_{i+1})\cdots\right) \\ &= A\left(n_{k_1}!n_{k_2}!\cdots n_{k_M}!\right)\sum_{\alpha=1}^{\widetilde{N}!}\widetilde{P}_\alpha\left(\underbrace{\psi_{k_1}(\boldsymbol{r}_1)\cdots\psi_{k_1}(\boldsymbol{r}_i)}_{n_{k_1}\ \text{items}}\psi_{k_2}(\boldsymbol{r}_{i+1})\cdots\right),\end{aligned}$$

where $\widetilde{N} = \frac{N!}{n_{k_1}!n_{k_2}!\cdots n_{k_M}!}$ and $\widetilde{P}_\alpha$ is the permutation operator for distinct arrangements. For normalization, we have

$$(\Psi,\Psi) = |A|^2\left(n_{k_1}!n_{k_2}!\cdots n_{k_M}!\right)^2\widetilde{N}! = 1.$$

Therefore, we have the normalized wave function:

$$\Psi = \sqrt{\frac{n_{k_1}!n_{k_2}!\cdots n_{k_M}!}{N!}}\sum_{\alpha=1}^{\widetilde{N}!}\widetilde{P}_\alpha\left(\underbrace{\psi_{k_1}(\boldsymbol{r}_1)\cdots\psi_{k_1}(\boldsymbol{r}_i)}_{n_{k_1}\ \text{items}}\psi_{k_2}(\boldsymbol{r}_{i+1})\cdots\right). \tag{4.17}$$

# 5 Central Force Field

## 5.1 General Properties of Particle Motion in a Central Force Field

In a spherical coordinate system, the Schrödinger equation of a central force field is given by

$$\left(-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\hat{l}^2}{\hbar^2 r^2}\right)+V(r)\right)\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi). \tag{5.1}$$

Since the angular momentum is conserved in a central force field, we can find the complete set of commuting observables

$$\{\hat{H},\hat{l}^2,\hat{l}_z\}.$$

Their common eigenfunctions can be expressed as $\psi_{nlm}$, where $n$ is the principal quantum number, $l$ is the azimuthal quantum number, and $m$ is the magnetic quantum number. Since the common eigenfunctions of $\hat{l}^2$ and $\hat{l}_z$ are $Y_{lm}(\theta,\varphi)$, we can separate the variables as

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi). \tag{5.2}$$

Then we have

$$\left(-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}-\frac{l(l+1)}{r^2}\right)+V(r)\right)R_{nl}(r)=ER_{nl}(r). \tag{5.3}$$

To emphasize that the equation only depends on $l$, if the radial quantum number of $\hat{H}_l$ is $n_r$, we denote $R_{nl}(r)$ by $\phi_{n_r l}(r)$ and $E$ by $E_{n_r l}$.

## 5.2 Hydrogen Atom Problem: Old Quantum Theory

The orbit needs to satisfy the angular momentum quantization condition in Bohr's theory:

$$\mu v r = n\hbar. \tag{5.4}$$

Also, it satisfies

$$\frac{e^2}{r^2}=\frac{\mu v^2}{r}. \tag{5.5}$$

Then we have

$$r=n^2\frac{\hbar^2}{\mu e^2}=n^2 a_0,\quad E_n=\frac{1}{2}\mu v^2-\frac{e^2}{r}=-\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2}, \tag{5.6}$$

where $a_0=0.529\mathring{A}$ is called the **Bohr radius** and $-\frac{\mu e^4}{2\hbar^2}=13.6\mathrm{eV}$ is a **Rydberg**.

The electromagnetic wave energy emitted when transmitting from $n$-th orbit to $m$-th orbit is given by $E_n-E_m$ and the corresponding wavenumber is

$$\tilde{\nu}_{nm}=\frac{E_n-E_m}{h}=R\left(\frac{1}{m^2}-\frac{1}{n^2}\right), \tag{5.7}$$

where $R=\frac{\mu e^4}{2\hbar^2 hc}\approx 1.097\times 10^7\mathrm{m}^{-1}$ is called the **Rydberg constant**.

We can change the special two-body problem into a one-body problem with reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$.

$$\begin{cases} -\frac{\hbar^2}{2M}\nabla^2_{\boldsymbol{R}}\Psi(\boldsymbol{R}) = E_{\boldsymbol{R}}\Psi(\boldsymbol{R}), \\ \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\boldsymbol{r}} - \frac{e^2}{r}\right)\psi(\boldsymbol{r}) = E_{\boldsymbol{r}}\psi(\boldsymbol{r}). \end{cases} \qquad \begin{cases} M = m_p + m_e, \\ \frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \approx \frac{1}{m_e}. \end{cases}$$

To solve $\phi_l$, denote

$$\chi_l(r) = r\phi_l(r) \Longrightarrow \frac{\mathrm{d}^2\chi_l}{\mathrm{d}r^2} + \left(\frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{r}\right) - \frac{l(l+1)}{r^2}\right)\chi_l = 0.$$

Now we transform the equation into a dimensionless form. Define a **Bohr** and a **Hartree** as

$$a = \frac{\hbar^2}{\mu e^2}, \quad \mathrm{Har} = \frac{\mu e^4}{2\hbar^2}.$$

And define dimensionless length $x$ and energy $\varepsilon$ as

$$x = \frac{r}{a}, \quad \varepsilon = \frac{E}{\mathrm{Har}}, \quad \chi_l(r) = y(x).$$

Then we have

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + \left(2\varepsilon + \frac{2}{x} - \frac{l(l+1)}{x^2}\right) y = 0. \tag{5.8}$$

$x = 0$ and $x = \infty$ are two singular points of the equation. Analyzing the asymptotic behavior of $y(x)$ at these two points. When $x \to 0$, the asymptotic equation is given by

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} - \frac{l(l+1)}{x^2} y = 0,$$

whose solution is

$$y^{(1)}(x) \sim x^{l+1}, \quad y^{(2)}(x) \sim x^{-l} \Longrightarrow \psi^{(1)}_{nlm} \sim r^l Y_{lm}(\theta,\varphi), \quad \psi^{(2)}_{nlm} \sim r^{-l-1} Y_{lm}(\theta,\varphi).$$

To ensure the finiteness of the wave function at $r = 0$, we have

$$y(x \to 0) \sim x^{l+1}.$$

When $x \to \infty$, the asymptotic equation is given by

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + 2\varepsilon y = 0,$$

whose solution is

$$y(x \to \infty) \sim e^{-\beta x}, \quad \beta = \sqrt{-2\varepsilon} \Longrightarrow y(x) = x^{l+1} e^{-\beta x} w(x).$$

Substituting $y(x)$ into the original equation and denoting $\xi = 2\beta x, u(\xi) = w(x)$, we have the

$$\xi\frac{\mathrm{d}^2 u}{\mathrm{d}\xi^2} + (2l + 2 - \xi)\frac{\mathrm{d}u}{\mathrm{d}\xi} + \left(\frac{1}{\beta} - l - 1\right) u = 0. \tag{5.9}$$

Consider a standard

$$\xi\frac{\mathrm{d}^2 u}{\mathrm{d}\xi^2} + (\gamma - \xi)\frac{\mathrm{d}u}{\mathrm{d}\xi} - \alpha u = 0, \tag{5.10}$$

The power series solution is given by

$$F(\alpha,\gamma,\xi)=\sum_{k=0}^{\infty}\frac{(\alpha)_k}{(\gamma)_k}\frac{\xi^k}{k!},\quad (\alpha)_k=\alpha(\alpha+1)\cdots(\alpha+k-1). \tag{5.11}$$

To ensure the finiteness of the wave function at $x=\infty$, the power series must terminate, i.e. $\alpha=0$ or $\alpha=-n_r$, where $n_r=0,1,2,\cdots$. Hence, we have

$$u_{n_rl}(\xi)=F(-n_r,2l+2,\xi). \tag{5.12}$$

$$\begin{aligned} l+1-\frac{1}{\beta}=n_r &\Longrightarrow \beta=\frac{1}{n_r+l+1}\\ &\Longrightarrow \phi_{n_rl}(r)=A_{n_rl}r^le^{-\frac{r}{(n_r+l+1)a}}F\left(-n_r,2l+2,\frac{2r}{(n_r+l+1)a}\right). \end{aligned} \tag{5.13}$$

The eigen energy is given by

$$E_{n_rl}=-\frac{\text{Har}}{2(n_r+l+1)^2}=-\frac{\mu e^4}{2\hbar^2}\frac{1}{(n_r+l+1)^2}. \tag{5.14}$$

Given energy $E_n$, the degeneracy is given by

$$g_n=\sum_{l=0}^{n-1}\sum_{m=-l}^{l}1=n^2. \tag{5.15}$$

If every quantum state can accommodate two electrons with opposite spins, we have

1. $n=1$ can accommodate 2 electrons: $1s^2$;
2. $n=2$ can accommodate 8 electrons: $2s^22p^6$;
3. $n=3$ can accommodate 18 electrons: $3s^23p^63d^{10}$;
4. $n=4$ can accommodate 32 electrons: $4s^24p^64d^{10}4f^{14}$.

The symbol of $R_{nl}(r)$ is determined by $F$, which is a $n-l-1$ order polynomial. Hence $R_{nl}(r)$ has $n-l-1$ radial nodes.

The probability density of finding the electron in the spherical shell $r\sim r+\mathrm{d}r$ is given by

$$P(r)\mathrm{d}r=\int_0^{2\pi}\int_0^{\pi}|\psi_{nlm}|^2r^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi\mathrm{d}r=|R_{nl}(r)|^2r^2\mathrm{d}r. \tag{5.16}$$

Since $R_{nl}(r)$ has $n-l-1$ radial nodes, the probability density $P(r)$ has $n-l$ peaks. Especially, for $l=n-1$, $P(r)$ has only one peak and if the peak is narrow, it is similar to the classical circular orbit in Bohr's theory.

# 6 Matrix Representation

## 6.1 From Wave Mechanics to Matrix Mechanics

Given $N$ orthonormal complete basis $\{\psi_\alpha(\boldsymbol{r})\}$, any wave function can be expressed as a linear combination of these basis functions:

$$\Psi(\boldsymbol{r}) = \sum_{\alpha=1}^{N} A_\alpha \psi_\alpha(\boldsymbol{r}) \Longleftrightarrow \Psi = \begin{pmatrix} \psi_1 & \psi_2 & \cdots & \psi_N \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix}. \tag{6.1}$$

Given $\Psi_A(\boldsymbol{r}) = \sum_{\alpha=1}^{N} A_\alpha \psi_\alpha(\boldsymbol{r})$ and $\Psi_B(\boldsymbol{r}) = \sum_{\beta=1}^{N} B_\beta \psi_\beta(\boldsymbol{r})$, we have

$$\begin{aligned} (\Psi_A, \Psi_B) &= \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} A_\alpha^* B_\beta \left(\psi_\alpha, \psi_\beta\right) = \sum_{\alpha=1}^{N} A_\alpha^* B_\alpha \\ \Longleftrightarrow (\Psi_A, \Psi_B) &= \begin{pmatrix} A_1^* & A_2^* & \cdots & A_N^* \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \\ \vdots \\ B_N \end{pmatrix} = \Psi_A^\dagger \Psi_B. \end{aligned} \tag{6.2}$$

Consider operator $\hat{O}$ acting on $\Psi_A$ such that $\hat{O}\Psi_A = \Psi_B$:

$$\hat{O}\Psi_A(\boldsymbol{r}) = \Psi_B(\boldsymbol{r}) \Longleftrightarrow \begin{pmatrix} O_{11} & O_{12} & \cdots & O_{1N} \\ O_{21} & O_{22} & \cdots & O_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ O_{N1} & O_{N2} & \cdots & O_{NN} \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \\ \vdots \\ B_N \end{pmatrix}, \tag{6.3}$$

where $O_{mn} = \left(\psi_m, \hat{O}\psi_n\right)$.

**Proposition 6.1.** *The matrix of a Hermitian operator is Hermitian.*

*Proof.*

$$O_{mn} = \left(\psi_m, \hat{O}\psi_n\right) = \left(\hat{O}\psi_m, \psi_n\right) = \left(\psi_n, \hat{O}\psi_m\right)^* = O_{nm}^*.$$

□

The eigenfunction $\hat{O}\Psi(x) = \lambda\Psi(x)$ can be expressed as

$$\mathbf{OA} = \lambda\mathbf{A}. \tag{6.4}$$

It has non-trivial solutions if and only if

$$\begin{vmatrix} O_{11}-\lambda & O_{12} & \cdots & O_{1N} \\ O_{21} & O_{22}-\lambda & \cdots & O_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ O_{N1} & O_{N2} & \cdots & O_{NN}-\lambda \end{vmatrix} = 0. \tag{6.5}$$

## 6.2 Theory Framework of Matrix Mechanics

One basis corresponds to one representation, such as the coordinate representation, momentum representation and Hamiltonian representation. Given old basis $\{\psi_n\}$ and new basis $\{\psi'_m\}$, we have

$$\psi_n(x) = \sum_m \psi'_m(x) S_{mn}, \quad S_{mn} = (\psi'_m, \psi_n) .$$

**Definition 6.2.** The matrix $\mathbf{S}$ is called the **transformation matrix** from basis $\{\psi_n\}$ to basis $\{\psi'_m\}$.

Consider $\Psi_A = \sum_{k=1}^N A_k \psi'_k = \sum_{n=1}^N A_n \psi_n$, then we have

$$\sum_{k=1}^N A'_k (\psi'_m, \psi'_k) = \sum_{n=1}^N A_n (\psi'_m, \psi_n) \Longrightarrow \sum_{k=1}^N A'_k \delta_{m'k} = \sum_{n=1}^N A_n S_{mn} \Longrightarrow \mathbf{A}' = \mathbf{S}\mathbf{A}.$$

If $\hat{O}\Psi_A = \Psi_B$ can respectively be expressed in two bases as

$$\mathbf{OA} = \mathbf{B}, \quad \mathbf{O}'\mathbf{A}' = \mathbf{B}' \Longrightarrow \mathbf{O}'\mathbf{SA} = \mathbf{SB} \Longrightarrow \mathbf{O}' = \mathbf{SOS}^{-1}.$$

## 6.3 Dirac Notation

**Definition 6.3.** The matrix of a state vector is represented by a **ket** $|\bullet\rangle$ and its Hermitian conjugate is represented by a **bra** $\langle\bullet|$.

The inner product of two state vectors $\Psi_A$ and $\Psi_B$ is represented by $\langle\Psi_A|\Psi_B\rangle$.
We often use quantum numbers or eigenvalues to label the state vectors, such as

$$\begin{aligned}
&\delta(x - x_0) \to |x_0\rangle, \quad \hat{x}|x_0\rangle = x_0|x_0\rangle, \quad \langle x_1|x_0\rangle = \delta(x_1 - x_0) \\
&\frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}p_0 x} \to |p_0\rangle, \quad \hat{p}|p_0\rangle = p_0|p_0\rangle, \quad \langle p_1|p_0\rangle = \delta(p_1 - p_0) \\
&Y_{lm} \to |lm\rangle, \quad \hat{l}^2|lm\rangle = l(l+1)\hbar^2|lm\rangle, \quad \langle l'm'|lm\rangle = \delta_{l'l}\delta_{m'm} \\
&\phi_{nl}Y_{lm} \to |nlm\rangle, \quad \hat{H}|nlm\rangle = -\frac{1}{2n^2}\frac{\mu e^4}{\hbar^2}|nlm\rangle, \quad \langle n'l'm'|nlm\rangle = \delta_{n'n}\delta_{l'l}\delta_{m'm}.
\end{aligned}$$

Dirac notation satisfies the combination rules, but not the commutation rules. FOr operators, we have

$$\langle\Psi_A|\hat{F}|\Psi_B\rangle = \langle\Psi_A|\hat{F}\Psi_B\rangle = \langle\hat{F}^\dagger\Psi_A|\Psi_B\rangle.$$

Especially, for Hermitian operator $\hat{F}$, we have

$$\langle\Psi_A|\hat{F}|\Psi_B\rangle = \langle\Psi_A|\hat{F}\Psi_B\rangle = \langle\hat{F}\Psi_A|\Psi_B\rangle.$$

There are two types of multiplication in Dirac notation. One is inner product $\langle\Psi_A|\Psi_B\rangle$ and the other is direct product $|\Psi_A\rangle\langle\Psi_B|$, which is a linear transformation.

$$|\Psi_A\rangle\langle\Psi_B| = \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} \begin{pmatrix} B_1^* & B_2^* & \cdots & B_N^* \end{pmatrix} = \begin{pmatrix} A_1B_1^* & A_1B_2^* & \cdots & A_1B_N^* \\ A_2B_1^* & A_2B_2^* & \cdots & A_2B_N^* \\ \vdots & \vdots & \ddots & \vdots \\ A_NB_1^* & A_NB_2^* & \cdots & A_NB_N^* \end{pmatrix}.$$

For a orthonormal discrete basis $\{|n\rangle\}$, we can express $|\psi\rangle$ in $\{|n\rangle\}$ as

$$|\psi\rangle = \sum_m C_m|m\rangle, \quad C_m = \langle m|\psi\rangle \Longrightarrow |\psi\rangle = \sum_m \left(\langle m|\psi\rangle\right)|m\rangle = \left(\sum_m |m\rangle\langle m|\right)|\psi\rangle.$$

Hence we have the **completeness relation of discrete basis**:

$$\sum_n |n\rangle\langle n| = 1. \tag{6.6}$$

**Definition 6.4.** $\hat{P}_n = |n\rangle\langle n|$ is called the **projection operator** onto the state $|n\rangle$.

For a orthonormal continuous basis $\{|\alpha\rangle\}$, we have the completeness relation:

$$|\Psi\rangle = \int C_\alpha|\alpha\rangle \mathrm{d}\alpha, \quad C_\alpha = \langle\alpha|\Psi\rangle \Longrightarrow \int |\alpha\rangle\langle\alpha|\mathrm{d}\alpha = 1 \tag{6.7}$$

Coordinate representation and momentum representation are two commonly used continuous representations. Consider $\langle x|\Psi\rangle$, then we have

$$\langle x|\Psi\rangle = \int\langle x|p\rangle\langle p|\Psi\rangle \mathrm{d}p \Longrightarrow \langle x|p\rangle = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}px}. \tag{6.8}$$

Now we dicuss the representation transformation of operators.

$$\mathbf{O}_{k_1k_2} = \langle k_1|\hat{O}|k_2\rangle, \quad \mathbf{O}_{n_1n_2} = \langle n_1|\hat{O}|n_2\rangle.$$

Then we have

$$O_{n_1n_2} = \sum_{k_1k_2}\langle n_1|k_1\rangle\langle k_1|\hat{O}|k_2\rangle\langle k_2|n_2\rangle = \sum_{k_1k_2} S_{n_1k_1}O_{k_1k_2}S^\dagger_{k_2n_2} \Longrightarrow \mathbf{O}' = \mathbf{SOS}^\dagger.$$

# 7 Particle Motion in a Electromagnetic Field

## 7.1 Classical Electromagnetic Theory

**Definition 7.1. d'Alembert operator** is defined as

$$\Box = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2. \tag{7.1}$$

With regular momentum $\boldsymbol{p}_m = \boldsymbol{p} - \frac{q}{c}\boldsymbol{A}(\boldsymbol{r},t)$, we have the Hamiltonian in a electromagnetic field:

$$\hat{H} = \frac{1}{2\mu}\left(\hat{\boldsymbol{p}} - \frac{q}{c}\boldsymbol{A}(\boldsymbol{r},t)\right)^2 + q\phi(\boldsymbol{r},t) = \frac{1}{2\mu}\left(\frac{\hbar}{i}\nabla - \frac{q}{c}\boldsymbol{A}(\boldsymbol{r},t)\right)^2 + q\phi(\boldsymbol{r},t). \tag{7.2}$$

Here we take the Coulomb gauge

$$\nabla\cdot\boldsymbol{A} = 0 \Longrightarrow [\boldsymbol{p},\boldsymbol{A}] = \frac{h}{i}\nabla\cdot\boldsymbol{A} = 0. \tag{7.3}$$

Since the atom is much smaller than the wavelength of the electromagnetic wave, we can assume there is a uniform electromagnetic field and we suppose

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r}. \tag{7.4}$$

Actually, we can verify that

$$\begin{aligned}\nabla\times\boldsymbol{A} &= \sum_{i=1}^{3}\boldsymbol{e}_i\varepsilon_{ijk}\frac{\partial}{\partial x_j}\boldsymbol{A}_k = \sum_{i=1}^{3}\boldsymbol{e}_i\varepsilon_{ijk}\frac{\partial}{\partial x_j}\left(\frac{1}{2}\varepsilon_{klm}B_l x_m\right)\\ &= \frac{1}{2}\sum_{i=1}^{3}\boldsymbol{e}_i\left(\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}\right)\frac{\partial B_l x_m}{\partial x_j} = \frac{1}{2}\sum_{i=1}^{3}\boldsymbol{e}_i\left(B_i\frac{\partial x_j}{\partial x_j} - B_j\frac{\partial x_i}{\partial x_j}\right) = \boldsymbol{B}.\end{aligned}$$

Suppose $\boldsymbol{B} = B\boldsymbol{e}_z$, then we have

$$\boldsymbol{A} = -\frac{i}{2}By + \frac{j}{2}Bx.$$

$$\begin{aligned}\hat{H}_m &= -\frac{q}{mc}\boldsymbol{A}\cdot\hat{\boldsymbol{p}} = -\frac{q}{2mc}\left(\boldsymbol{B}\times\boldsymbol{r}\right)\cdot\boldsymbol{p} = -\frac{q}{2mc}\boldsymbol{B}\cdot\left(\boldsymbol{r}\times\hat{\boldsymbol{p}}\right)\\ &= -\frac{q}{2mc}B\hat{l} = -\hat{\mu}_l\cdot\boldsymbol{B},\quad \hat{\mu}_l = \frac{q}{2mc}\hat{l}.\end{aligned}$$

**Definition 7.2.** $\hat{\mu}_l$ is called the **orbital magnetic moment**, and $\mu_B = \frac{e\hbar}{2mc}$ is called the **Bohr magneton**.

Hence, we have

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \hat{H}_m + \frac{q^2}{2\mu c^2}A^2 + q\phi = \frac{\hat{p}^2}{2\mu} - \frac{qB}{2\mu c}\hat{l}_z + \frac{q^2B^2}{8\mu c^2}(x^2+y^2) + q\phi.$$

Next, we discuss the probability conservation in an electromagnetic field.

$$i\hbar\frac{\partial}{\partial t}(\psi^*\psi) = \frac{1}{2\mu}\left(\psi^*\hat{p}^2\psi - \psi\hat{p}^2\psi^*\right) - \frac{q}{\mu c}\left(\psi^*\boldsymbol{A}\cdot\hat{p}\psi - \psi\boldsymbol{A}\cdot\hat{p}^*\psi^*\right).$$

Consider a gauge transformation $(\phi, \boldsymbol{A}) \to (\phi', \boldsymbol{A}')$ such that

$$\phi' = \phi - \frac{1}{c}\frac{\partial \chi}{\partial t}, \quad \boldsymbol{A}' = \boldsymbol{A} + \nabla\chi.$$

$\psi$ is the wave function before the gauge transformation, and satisfies

$$i\hbar\frac{\partial \psi}{\partial t} = \left(\left(\hat{p} - \frac{q}{c}\boldsymbol{A}\right)^2 + q\phi\right)\psi \Longrightarrow \psi' = \psi e^{if(r,t)}, \quad f(\boldsymbol{r}, t) = \frac{q}{\hbar c}\chi(\boldsymbol{r}, t).$$

Then we have

## 7.2 Normal Zeeman Effect

Neglecting the quadratic term of $\boldsymbol{B}$, we have the Hamiltonian of the electron in a hydrogen atom as

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{eB}{2\mu c}\hat{l}_z + V(r) = \hat{H}_0 + \hat{H}_M, \quad \hat{H}_M = \frac{\mu_B B}{\hbar}\hat{l}_z.$$

Since $E' = \langle nlm_l|\hat{H}_M|nlm_l\rangle = \mu_B B m_l$, the energy level splits into $2l+1$ sub-levels with equal spacing $\mu_B B$. This is called the **normal Zeeman effect**.

# 8 Spin

## 8.1 Spin Angular Momentum Operator

The magnetic field has interactive energy with the spin magnetic moment:

$$E = -\boldsymbol{\mu} \cdot \boldsymbol{B}. \tag{8.1}$$

In Stern-Gerlach experiment, the force acting on a magnetic moment in a non-uniform magnetic field is given by

$$F_z = -\frac{\partial E}{\partial z} = \mu_z \frac{\partial B_z}{\partial z}. \tag{8.2}$$

The result shows that the silver atom beam is split into two sub-beams, which indicates that the silver atom has an intrinsic angular momentum with two possible orientations.

Spin angular momentum operator $\hat{S} = \hat{s}_x i + \hat{s}_y j + \hat{s}_z k$ satisfies the same commutation relations as the orbital angular momentum operator $\hat{l}$:

$$[\hat{s}_i, \hat{s}_j] = i\hbar\varepsilon_{ijk}\hat{s}_k.$$

Take $\{\hat{s}, \hat{s}_z\}$ as the common representation and the common eigenfunctions are denoted by $\chi_{sm_s}$:

## 8.2 Basic Theory of Spin

There are two basis in the spin Hilbert space:

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |0\rangle = |-\rangle, \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{8.3}$$

$$\hat{s}_z = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix}, \quad \hat{s}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \hat{s}_x^2 = \hat{s}_y^2 = \hat{s}_z^2 = \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{8.4}$$

To compute $\hat{s}_x$ and $\hat{s}_y$, we also need to define the raising and lowering operators:

$$\hat{s}_\pm = \hat{s}_x \pm i\hat{s}_y \Longrightarrow \hat{s}_\pm|s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}|s, m_s \pm 1\rangle.$$

Then for single electron spin ($s = \frac{1}{2}, m_s = \pm\frac{1}{2}$), we have

$$\hat{s}_+|\frac{1}{2}, -\frac{1}{2}\rangle = \hbar|\frac{1}{2}, \frac{1}{2}\rangle, \quad \hat{s}_-|\frac{1}{2}, \frac{1}{2}\rangle = \hbar|\frac{1}{2}, -\frac{1}{2}\rangle.$$

**Definition 8.1. Pauli operators** are defined as

$$\hat{s} = \frac{\hbar}{2}\hat{\sigma}, \quad \hat{\sigma} = \hat{\sigma}_x i + \hat{\sigma}_y j + \hat{\sigma}_z k \Longrightarrow \hat{s}_\pm = \hbar\hat{\sigma}_\pm. \tag{8.5}$$

$$\hat{\sigma}_+ = \hat{I}\hat{\sigma}_+\hat{I} = (|0\rangle\langle 0| + |1\rangle\langle 1|)\,\hat{\sigma}_+\,(|0\rangle\langle 0| + |1\rangle\langle 1|) = |0\rangle\langle 1| = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix},$$

$$\hat{\sigma}_- = |1\rangle\langle 0| = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \Longrightarrow \hat{\sigma}_x = \hat{\sigma}_+ + \hat{\sigma}_- = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = -i(\hat{\sigma}_+ - \hat{\sigma}_-) = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},$$

$$\hat{\sigma}_z = (|0\rangle\langle 0| + |1\rangle\langle 1|)\,\hat{\sigma}_z\,(|0\rangle\langle 0| + |1\rangle\langle 1|) = |0\rangle\langle 0| - |1\rangle\langle 1| = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

**Definition 8.2.** $\hat{\sigma}_x, \hat{\sigma}_y$ and $\hat{\sigma}_z$ are called the **Pauli matrices**.

Any spin state vector can be expressed as a linear combination of the two basis vectors:

$$|\chi\rangle = a|\alpha\rangle + b|\beta\rangle = \begin{pmatrix} a \\ b \end{pmatrix}.$$

## 8.3 Spin-Orbit Coupling

In the rest frame of the electron, the nucleus revolves around the electron, generating a magnetic field $\boldsymbol{B} \propto \boldsymbol{l}$. The electron has a spin magnetic moment $\boldsymbol{M}_s$, which interacts with the magnetic field $\boldsymbol{B}$ and generates an interaction energy $-\boldsymbol{M}_s \cdot \boldsymbol{B} \propto \boldsymbol{s} \cdot \boldsymbol{l}$.

$\Psi(\boldsymbol{r}, s) = \begin{pmatrix} u(\boldsymbol{r}) \\ v(\boldsymbol{r}) \end{pmatrix}$ is the spin wave function.

**Definition 8.3.** The **total angular momentum operator** is defined as

$$\hat{\boldsymbol{j}} = \hat{\boldsymbol{l}} + \hat{\boldsymbol{s}}. \tag{8.6}$$

**Proposition 8.4.**

$$\hat{\boldsymbol{j}} \times \hat{\boldsymbol{j}} = i\hbar \hat{\boldsymbol{j}}, \quad [\hat{j}_i, \hat{j}_j] = i\hbar \varepsilon_{ijk} \hat{j}_k.$$

We find the common eigenfunctions of $\{\hat{\boldsymbol{l}}^2, \hat{\boldsymbol{j}}^2, \hat{j}_z\}$,

$$\Psi(r, \theta, \varphi, s) = R_{nlj}(r) \Phi_{ljm_j}(\theta, \varphi, s),$$

**Proposition 8.5.** *There are two kinds of* $\Phi$*:*

1.

$$\Phi(\theta, \varphi, s) = \sqrt{\frac{l+m+1}{2l+1}} Y_{lm}(\theta, \varphi) \chi_{+\frac{1}{2}}(s) + \sqrt{\frac{l-m}{2l+1}} Y_{l,m+1}(\theta, \varphi) \chi_{-\frac{1}{2}}(s), \tag{8.7}$$

*for* $j = l + \frac{1}{2}, m_j = m + \frac{1}{2}$*;*

2.

$$\Phi(\theta, \varphi, s) = \sqrt{\frac{l-m+1}{2l+1}} Y_{lm}(\theta, \varphi) \chi_{-\frac{1}{2}}(s) - \sqrt{\frac{l+m}{2l+1}} Y_{l,m-1}(\theta, \varphi) \chi_{+\frac{1}{2}}(s), \tag{8.8}$$

*for* $j = l - \frac{1}{2}, m_j = m - \frac{1}{2}$.

Define

$$\hat{j}_x = \frac{1}{2}(\hat{j}_+ + \hat{j}_-), \quad \hat{j}_y = \frac{1}{2i}(\hat{j}_+ - \hat{j}_-).$$

Then we have

$$[\hat{j}_\pm, \hat{j}^2] = 0, \quad [\hat{j}_\pm, \hat{j}_z] = \mp\hbar \hat{j}_\pm, \quad \hat{j}_+ \hat{j}_- = \hat{j}^2 - \hat{j}_z^2 + \hbar \hat{j}_z, \quad \hat{j}_- \hat{j}_+ = \hat{j}^2 - \hat{j}_z^2 - \hbar \hat{j}_z,$$

$$\hat{j}^2 |\lambda, m\rangle = \lambda \hbar^2 |\lambda, m\rangle, \quad \hat{j}_z |\lambda, m\rangle = m\hbar |\lambda, m\rangle.$$

We assume $\hat{j}_\pm |\lambda, m\rangle = c_\pm |\lambda, m \pm 1\rangle$. Since $\hat{j}_z$ gives a component of $\hat{j}$ along a certain direction, we have $m^2 \leqslant \lambda \Longrightarrow m \in [-\lambda, \lambda]$. Hence, there exists $m_0$ and $m_0 + N$ such that $\hat{j}_- |\lambda, m_0\rangle = 0$ and $\hat{j}_+ |\lambda, m_0 + N\rangle = 0$.

$$\hat{j}_+ \hat{j}_- |\lambda, m_0\rangle = 0 \Longrightarrow (\hat{j}^2 - \hat{j}_z^2 + \hbar \hat{j}_z) |\lambda, m_0\rangle = 0 \Longrightarrow \lambda = m_0(m_0 + 1).$$

$$\hat{j}_- \hat{j}_+ |\lambda, m_0 + N\rangle = 0 \Longrightarrow (\hat{j}^2 - \hat{j}_z^2 - \hbar \hat{j}_z) |\lambda, m_0 + N\rangle = 0 \Longrightarrow \lambda = (m_0 + N)(m_0 + N + 1).$$

Hence

$$m_0 = -\frac{N}{2}, \quad m_0 + N = \frac{N}{2}, \quad \lambda = \frac{N}{2}\left(\frac{N}{2} + 1\right).$$

Therefore, we denote

$$j = \frac{N}{2} \Longrightarrow m_0 = -j, \quad m_0 + N = j, \quad \lambda = j(j+1).$$

$$\hat{j}_{\pm}|j, m_j\rangle = c_{\pm}|j, m_j \pm 1\rangle, \quad \langle j, m_j|\hat{j}_{\mp} = c_{\pm}^{*}\langle j, m_j \pm 1| \Longrightarrow$$
$$\langle j, m_j|\hat{j}_{\mp}\hat{j}_{\pm}|j, m_j\rangle = |c_{\pm}|^2\langle j, m_j \pm 1|j, m_j \pm 1\rangle = |c_{\pm}|^2.$$
$$\langle j, m_j \pm 1|\hat{j}_{\mp}\hat{j}_{\pm}|j, m_j \pm 1\rangle = \frac{1}{|c_{\pm}|^2}\langle j, m_j|\hat{j}^2 - \hat{j}_z^2 \mp \hbar\hat{j}_z|j, m_j\rangle = 1 \Longrightarrow$$
$$c_{\pm} = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}.$$

Considering spin,

$$\hat{H} \approx \frac{\hat{p}^2}{2\mu} + \frac{eB}{2\mu c}\left(\hat{l}_z + 2\hat{s}_z\right) + V(r) + \xi(r)\hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}}.$$

# 9 Perturbation Theory

We consider a Hamiltonian with small perturbation:

$$\hat{H} = \hat{H}_0 + \hat{H}'. \tag{9.1}$$

## 9.1

Denote $\hat{H} = \hat{H}_0 + \lambda \hat{H}'$ and expand the energy and wave function in terms of $\lambda$:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \quad \Psi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \cdots.$$

$$\lambda^0 : \quad \hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}.$$

$$\lambda^1 : \quad \hat{H}_0 \Psi_n^{(1)} + \hat{H}' \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(1)} + E_n^{(1)} \Psi_n^{(0)} \Longleftrightarrow \left(\hat{H}_0 - E_n^{(0)}\right) \Psi_n^{(1)} = \left(E_n^{(1)} - \hat{H}'\right) \Psi_n^{(0)}.$$

$$\lambda^2 : \quad \hat{H}_0 \Psi_n^{(2)} + \hat{H}' \Psi_n^{(1)} = E_n^{(0)} \Psi_n^{(2)} + E_n^{(1)} \Psi_n^{(1)} + E_n^{(2)} \Psi_n^{(0)}$$

$$\Longleftrightarrow \left(\hat{H}_0 - E_n^{(0)}\right) \Psi_n^{(2)} = \left(E_n^{(1)} - \hat{H}'\right) \Psi_n^{(1)} + E_n^{(2)} \Psi_n^{(0)}.$$