Notes

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1 5 Key Postulates of Quantum Mechanics

- The state of a quantum system is completely described by wavefunction, which is typically denoted as $\psi(\vec{r}, t)$ [1].
- Every measurable physical quantity is represented by a Hermitian operator. Eg.

$$\vec{r} \to \vec{r}, \quad p \to \hat{p} = -i\hbar\nabla \tag{1}$$

- When a measurement of an observable is made, the wavefunction collapses to one of the eigenstates of the corresponding operator.
- The time evolution of wavefunction is determined by Schrödinger Equation:

$$i\hbar\frac{\partial\psi(\mathbf{r}, t)}{\partial t} = \hat{H}\psi(\mathbf{r}, t) \tag{2}$$

- Identical particles whose intrinsic physical properties, such as mass, charge, or spin, are the same as each other cannot be distinguished by any physical measurements.

2 Quantum Mechanics in One Dimension

2.1 The Harmonic Oscillator

In one dimension, the potential is given by:

$$V(x) = \frac{1}{2}m\omega^2x^2 \tag{3}$$

where m is the mass and ω is the angular frequency. The time-independent Schrödinger equation is:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right]\psi(x) = E\psi(x). \tag{4}$$

There are two primary methods to solve for the eigenfunctions and eigenvalues:

1. Algebraic method using ladder operators
2. Analytical method by solving the differential equation

2.1.1 Algebraic Method

We define the annihilation (a_-) and creation (a_+) operators:

$$\boxed{a_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x)} \tag{5}$$

where $p = -i\hbar\frac{d}{dx}$ is the momentum operator. These satisfy the commutation relation:

$$[a_-, a_+] = 1 \tag{6}$$

The Hamiltonian can be rewritten in terms of these operators:

$$H = \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \tag{7}$$

Let ψ_n be the nth energy eigenstate with energy E_n. The ladder operators act on these states as:

$$a_+ |n\rangle = \sqrt{n+1}\psi_{n+1}, \quad a_- |n\rangle = \sqrt{n}\psi_{n-1} \tag{8}$$

The ground state ψ_0 is found by solving $a_-\psi_0 = 0$, yielding:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-m\omega x^2/2\hbar} \tag{9}$$

The energy levels are quantized:

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, \ldots \tag{10}$$

2.1.2 Analytical Method

To simplify, we introduce the dimensionless variable:

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}} x \tag{11}$$

and express the energy in units of $\frac{1}{2}\hbar\omega$:

$$K \equiv \frac{2E}{\hbar\omega} \tag{12}$$

The Schrödinger equation then becomes:

$$\frac{d^2\psi(\xi)}{d\xi^2} = (\xi^2 - K)\psi(\xi) \tag{13}$$

For large ξ (i.e., $|\xi| \gg 1$), the term ξ^2 dominates over K, and (**??**) simplifies to:

$$\frac{d^2\psi(\xi)}{d\xi^2} \approx \xi^2\psi \tag{14}$$

The approximate solutions to this equation are:

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{+\xi^2/2} \tag{15}$$

where A and B are constants. To ensure normalizability, we discard the exponentially growing term ($B = 0$), leaving:

$$\psi(\xi) \sim e^{-\xi^2/2} \quad \text{(asymptotic solution)} \tag{16}$$

For the general solution, we assume a form that captures the asymptotic behavior and multiply by a power series $h(\xi)$:

$$\boxed{\psi(\xi) = h(\xi)e^{-\xi^2/2}} \tag{17}$$

Substituting this into (13) yields the Hermite differential equation for $h(\xi)$:

$$\frac{d\psi}{d\xi} = \left(\frac{dh}{d\xi} - \xi h \right) e^{-\xi^2/2} \tag{18}$$

We solve this using a power series expansion:

$$h(\xi) = \sum_{n=0}^{\infty} a_n \xi^n \tag{19}$$

Substituting the series into the differential equation leads to a recurrence relation for the coefficients a_n:

$$a_{n+2} = \frac{2n+1-K}{(n+2)(n+1)} a_n \tag{20}$$

To ensure normalizability, the series must terminate (i.e., $h(\xi)$ must be a polynomial). This requires:

$$2n+1-K=0 \implies K = 2n+1 \tag{21}$$

for some integer $n \geq 0$. Recalling the definition of K, the allowed energies are:

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega} \tag{22}$$

The corresponding wave functions are:

$$\boxed{\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}} \tag{23}$$

where $H_n(\xi)$ are the Hermite polynomials.

2.2 Infinite Square Well

[2]

- $V(x) =$

$$\begin{cases} 0, & 0 \leq x \leq a \\ \infty, & \text{otherwise} \end{cases} \tag{24}$$

- **Boundary conditions**

$$\begin{cases} \psi & \text{is continuous} \\ \frac{d\psi}{dx} & \text{is continuous} \end{cases} \tag{25}$$

But where the potential goes to infinity only the first of these applies.

The continuity of ψ requires that

$$\psi(0) = \psi(a) = 0 \tag{26}$$

so as to join the solution $\psi = 0$ outside the well.

- The **general solution** to the Shrodinger equation is as follows:

$$\psi(x) = A\sin kx + B\cos kx, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{27}$$

- k represents the wave vector.
- Only bound states are allowed in this case since $V(x)$ goes to ∞.
- Apply the boundary conditions to the general solution, and derive that

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3... \tag{28}$$

$$\Rightarrow \boxed{E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}} \tag{29}$$

$$\Rightarrow \boxed{\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)} \tag{30}$$

where $\sqrt{\frac{2}{a}}$ is derived by normalization, and cosine canceled out by boundary conditions.

- **Important properties**:
  (a) $\psi_n(x)$s are alternatively even or odd with respect to the center of the well.
  (b) Number of nodes $= n - 1$. e.g. ψ_1 has no node, ψ_2 has one node.
  (c) $\psi_n(x)$s are mutually **orthogonal**.

2.3 Delta Potential Well

- **Potential**: $V(x) = -\alpha\delta(x)$ $(\alpha > 0)$
- **Schrödinger Equation**:
$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi$$
- **Boundary Conditions**:
  1. ψ continuous at $x = 0$
  2. $\left.\frac{d\psi}{dx}\right|_{0^+} - \left.\frac{d\psi}{dx}\right|_{0^-} = -\frac{2m\alpha}{\hbar^2}\psi(0)$
- **Bound States** $(E < 0)$:
$$\psi(x) = \begin{cases} Ae^{kx}, & x < 0 \\ Ae^{-kx}, & x > 0 \end{cases} \quad (k = \frac{\sqrt{-2mE}}{\hbar})$$
Apply BCs:
$$k = \frac{m\alpha}{\hbar^2} \implies E = -\frac{m\alpha^2}{2\hbar^2}$$
Normalized Wave Function:
$$\psi(x) = \sqrt{\frac{m\alpha}{\hbar^2}}e^{-m\alpha|x|/\hbar^2}$$
- **Scattering States** $(E > 0)$:
$$\psi(x) = \begin{cases} e^{ikx} + Re^{-ikx}, & x < 0 \\ Te^{ikx}, & x > 0 \end{cases} \quad (k = \frac{\sqrt{2mE}}{\hbar})$$
Reflection/Transmission Coefficients:
$$R = \frac{1}{1 + \frac{2\hbar^2 E}{m\alpha^2}}, \quad T = \frac{1}{1 + \frac{m\alpha^2}{2\hbar^2 E}}$$

2.4 The Free Particle

- $V(x) = 0$ everywhere.
- General Solution:
$$\boxed{\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \text{with} \quad k = \frac{\sqrt{2mE}}{\hbar}} \tag{31}$$
- No boundary conditions to restrict the value of k and hence E, so it can take any positive energy.
- The sign in front of k determines the direction in which the wave moves.
- The wave function is not normalizable, which means the separable solutions do not represent physically realizable states. A free particle cannot exist in a stationary state (i.e. there is no such thing as a free particle with a definite energy).
- The general solution is a **superposition** of plane waves (Fourier integral):
$$\psi(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\tilde{\psi}(k)e^{ikx}\,dk \tag{32}$$
where $\tilde{\psi}(k)$ is the momentum-space wave function.
The time-dependent solution:
$$\boxed{\psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\tilde{\psi}(k)e^{i(kx-\omega t)}\,dk, \quad \omega = \frac{\hbar k^2}{2m}} \tag{33}$$
This describes wave packet dispersion.

- Plancherel's Theorem in Fourier Analysis

$$\Rightarrow \boxed{\tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} dx} \tag{34}$$

- For a free particle,

$$v_{group} = v_{classical} = 2v_{phase};\ v_{phase} = \omega/k;\ v_{group} = \frac{d\omega}{dk}$$

Notes: k is the number of wavelengths in a unit length. So $1/k$ is the wavelength ($k = 1/\lambda$). And ω (i.e. phase change in unit time) multiplied by $1/k$ gives the speed of phase.

3 Formalism

3.1 Hilbert Space

[1]

- In quantum mechanics, wavefunctions are represented as vectors, and operators act as linear transformations.
- A vector ($|\alpha\rangle$) is expressed as

$$|\alpha\rangle = \vec{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \tag{35}$$

The inner product of two vectors is defined as

$$\langle \alpha | \beta \rangle = \sum a_i^* b_i \tag{36}$$

Linear transformations are represented by matrices and can act on vectors. For example:

$$\hat{T}|\alpha\rangle = \begin{bmatrix} t_{11} & t_{12} & \cdots \\ t_{21} & t_{22} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix} \tag{37}$$

3.1.1 Vectors in Hilbert Space

- Vectors in quantum mechanics are functions living in infinite-dimensional spaces (Hilbert Space). The Hilbert Space consists of all square-integrable functions, and the inner product of two functions f and g is defined as

$$\langle f | g \rangle = \int_a^b f^* g \, dx \tag{38}$$

In particular,

$$\langle f | g \rangle = \langle g | f \rangle^* \tag{39}$$

$$\langle f | f \rangle = \int |f|^2 \, dx \geq 0 \tag{40}$$

A function is normalized $\Leftrightarrow \langle f|f\rangle = 1$.
Two functions are orthogonal $\Leftrightarrow \langle f|g\rangle = 0$.
A set of functions $\{f_n\}$ is orthonormal $\Leftrightarrow \langle f_m|f_n\rangle = \delta_{mn}$, where $\delta_{mn} = 1$ if $m = n$, or 0 otherwise (Kronecker delta).
A set of functions is complete $\Leftrightarrow$ any other function (in Hilbert space) can be expressed as a linear combination of them.

3.1.2 Example: Fourier Series

- An example of orthonormality: A function $f(x)$ can be expressed as a Fourier series because the sine and cosine functions form an orthonormal basis in the Hilbert Space. Specifically, the set $\left\{ \frac{1}{\sqrt{\pi}} \cos(nx), \frac{1}{\sqrt{\pi}} \sin(nx) \mid n \in \mathbb{N}^+ \right\}$ satisfies:

$$\left\langle \frac{1}{\sqrt{\pi}} \cos(mx) \middle| \frac{1}{\sqrt{\pi}} \cos(nx) \right\rangle = \delta_{mn} \tag{41}$$

$$\left\langle \frac{1}{\sqrt{\pi}} \sin(mx) \middle| \frac{1}{\sqrt{\pi}} \sin(nx) \right\rangle = \delta_{mn} \tag{42}$$

$$\left\langle \frac{1}{\sqrt{\pi}} \cos(mx) \middle| \frac{1}{\sqrt{\pi}} \sin(nx) \right\rangle = 0 \tag{43}$$

  This orthonormality allows the coefficients a_n and b_n to be uniquely determined by projecting $f(x)$ onto the basis functions.

3.1.3 Problems

- Show that the set of all square-integrable functions is a vector space. Is the set of all normalized functions a vector space?

  Solution: A vector space consists of a set of vectors together with a set of scalars, which is closed under vector addition and scalar multiplication [3].
  For two square-integrable functions $f(x), g(x)$, let $h(x) = f(x)+g(x)$. By the Schwarz inequality:

$$\int_a^b |h(x)|^2 \, dx = \int_a^b |f(x) + g(x)|^2 \, dx \tag{44}$$

$$= \int_a^b |f(x)|^2 \, dx + \int_a^b |g(x)|^2 \, dx + 2 \int_a^b |f(x)^* g(x)| \, dx \tag{45}$$

$$\leq \int_a^b |f(x)|^2 \, dx + \int_a^b |g(x)|^2 \, dx + 2\sqrt{\int_a^b |f(x)|^2 \, dx \int_a^b |g(x)|^2 \, dx} < \infty \tag{46}$$

  Thus, it is closed under vector addition.
  For a scalar a:

$$\int_a^b |a \cdot f(x)|^2 \, dx = a^2 \int_a^b |f(x)|^2 \, dx < \infty$$

  The set of all normalized functions is not a vector space, since $2\sqrt{\int_a^b |f(x)|^2 \, dx \int_a^b |g(x)|^2 \, dx}$ does not necessarily equal 1, implying the set is not closed under vector addition or scalar multiplication.

- Show that $\langle f|g\rangle = \int_a^b f^* g \, dx$ satisfies the conditions for an inner product.

  Solution: The inner product satisfies:

$$\langle \alpha|\beta\rangle = \langle \beta|\alpha\rangle^*; \quad \langle \alpha|\alpha\rangle \geq 0; \quad \langle \alpha|\alpha\rangle = 0 \Leftrightarrow |\alpha\rangle = 0; \quad \langle \alpha|(b|\beta\rangle + c|\gamma\rangle)\rangle = b\langle \alpha|\beta\rangle + c\langle \alpha|\gamma\rangle$$

Property 1:

$$\left(\int f^* g\,dx\right)^* = \left(\int [u(x)+iv(x)]^*[m(x)+in(x)]\,dx\right)^* \tag{47}$$

$$= \left(\int (um+vn)\,dx + i\int (un-vm)\,dx\right)^* \tag{48}$$

$$= \int (um+vn)\,dx - i\int (un-vm)\,dx \tag{49}$$

$$= \int (u-iv)(m+in)\,dx = \int g^* f\,dx \tag{50}$$

Property 2: (Assume $b \geq a$)

$$\int_a^b f^* f\,dx = \int_a^b |f|^2\,dx \geq 0, \tag{51}$$

$$\int_a^b |f|^2\,dx = 0 \Leftrightarrow f \equiv 0 \tag{52}$$

Property 3:

$$\int f^*(b\cdot g + c\cdot k)\,dx = b\int f^* g\,dx + c\int f^* k\,dx$$

- For what range of ν is $f(x) = x^\nu$ in Hilbert space on $(0,1)$? Assume ν is real.

Solution:

$$\int_{(0,1)} |x^\nu|^2\,dx < +\infty \tag{53}$$

$$\int_{(0,1)} x^{2\nu}\,dx = \lim_{x\to 1}\frac{x^{2\nu+1}}{2\nu+1} - \lim_{x\to 0}\frac{x^{2\nu+1}}{2\nu+1} \quad (\text{when } 2\nu+1>0) \tag{54}$$

$$= \frac{1}{2\nu+1} - 0 \tag{55}$$

$$\Rightarrow \nu > -\frac{1}{2} \tag{56}$$

3.2 Observables

[4]

3.2.1 Hermitian Operator

- An observable can be expressed by inner product:

$$\langle Q\rangle = \int \Psi^* \hat{Q}\Psi\,dx = \langle\Psi|\hat{Q}\Psi\rangle. \tag{57}$$

Since Q is real, $\langle Q\rangle = \langle Q\rangle^*$, implying

$$\langle\Psi|\hat{Q}\Psi\rangle = \langle\hat{Q}\Psi|\Psi\rangle, \tag{58}$$

which defines Hermitian operators. The Hermitian conjugate (adjoint) of $\hat{Q}$ is $\hat{Q}^\dagger$ satisfying

$$\langle f|\hat{Q}g\rangle = \langle\hat{Q}^\dagger f|g\rangle. \tag{59}$$

A Hermitian operator satisfies $\hat{Q} = \hat{Q}^\dagger$.

- Show that if $\langle h|\hat{Q}h\rangle = \langle \hat{Q}h|h\rangle$ for all h, then $\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$ for all f, g.

  Solution: Let $h = f + g$:

$$\int h^*\hat{Q}h\,dx = \int (f+g)^*\hat{Q}(f+g)\,dx = \int [\hat{Q}(f+g)]^*(f+g)\,dx \quad (60)$$

$$\int (f^*+g^*)(\hat{Q}f+\hat{Q}g)\,dx = \int (\hat{Q}f^*+\hat{Q}g^*)(f+g)\,dx \quad (61)$$

$$\int (f^*\hat{Q}f + f^*\hat{Q}g + g^*\hat{Q}f + g^*\hat{Q}g)\,dx = \int (\hat{Q}f^*f + \hat{Q}f^*g + \hat{Q}g^*f + \hat{Q}g^*g)\,dx \quad (62)$$

$$\Rightarrow \int f^*\hat{Q}g\,dx + \int g^*\hat{Q}f\,dx = \int \hat{Q}f^*g\,dx + \int \hat{Q}g^*f\,dx. \quad (1) \quad (63)$$

  Let $h = f + ig$:

$$\int (f+ig)^*\hat{Q}(f+ig)\,dx = \int [\hat{Q}(f+ig)]^*(f+ig)\,dx \quad (64)$$

$$\Rightarrow \int f^*\hat{Q}g\,dx - \int g^*\hat{Q}f\,dx = \int \hat{Q}f^*g\,dx - \int \hat{Q}g^*f\,dx. \quad (2) \quad (65)$$

  Adding (1) and (2):

$$\int f^*\hat{Q}g\,dx = \int \hat{Q}f^*g\,dx \Rightarrow \langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle.$$

  Key: $(ig)^* = -ig^*$.

- Under what condition (on $\alpha \in \mathbb{C}$) is $\alpha\hat{Q}$ Hermitian?

  Solution: If $\alpha\hat{Q}$ is Hermitian:

$$(\alpha\hat{Q})^\dagger = \alpha^*\hat{Q}^\dagger = \alpha\hat{Q} \Rightarrow \alpha^* = \alpha.$$

  Thus α must be real.

- Find the Hermitian conjugate of d/dx.

  Solution:

$$\left\langle f\left|\frac{d}{dx}f\right.\right\rangle = \int_{-\infty}^{\infty} f^*\frac{df}{dx}\,dx \quad (66)$$

$$= [f^*f]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f\frac{df^*}{dx}\,dx \quad (67)$$

$$\Rightarrow \left(\frac{d}{dx}\right)^\dagger = -\frac{d}{dx}. \quad (68)$$

3.2.2 Determinate States

- Every measurement Q of a determinate system is certain ($\sigma^2 = 0$, $\langle Q\rangle = q$), satisfying

$$(\hat{Q} - q)\Psi = 0. \quad (69)$$

  Thus Ψ is an eigenfunction of $\hat{Q}$ with eigenvalue q. For a determinate state Ψ, $c\Psi$ is also a determinate state.

- The collection of all eigenvalues of an operator is its spectrum. If multiple linearly independent eigenfunctions share an eigenvalue, the spectrum is degenerate.
- Example: Determinate states of total energy are eigenfunctions of the Hamiltonian operator.

3.3 Eigenfunctions of a Hermitian Operator

3.3.1 Discrete Spectra

- **Theorem 1** The eigenvalues of the normalizable eigenfunctions of a hermitian operator are real.
- **Theorem 2** Eigenfunctions belonging to distinct eigenvalues are orthogonal.
- **Theorem 3** (Axiom) The functions of an observable operator are complete (i.e., any functions in Hilbert space can be expressed as a linear combination of them).

3.3.2 Continuous Spectra

- **Theorem 1** (Dirac orthonormality)

$$\langle f_{p'}|f_p\rangle = \delta(p-p') \tag{70}$$

- **Theorem 2** (Completeness) Any function $f(x)$ in Hilbert Space can be written in the form

$$f(x) = \int_{-\infty}^{\infty} c(p) f_p(x) dp \tag{71}$$

- Note: None of the eigenfunctions of an operator of continuous spectra lives in Hilbert space, but those with real eigenvalues are Dirac orthonormalizable and complete.

3.4 Generalized Statistical Interpretation

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

- If the spectrum of $\hat{Q}$ is discrete, the probability of getting the particular eigenvalue q_n associated with the orthonormalized eigenfunction $f_n(x)$ is

$$|c_n|^2, \quad \text{where} \quad c_n = \langle f_n|\Psi\rangle \tag{72}$$

- If the spectrum is continuous, with real eigenvalues $q(z)$ and associated Dirac-orthonormalized eigenfunctions $f_z(x)$, the probability of getting a result in the range dz is

$$|c(z)|^2 dz, \quad \text{where} \quad c(z) = \langle f_z|\Psi\rangle \tag{73}$$

The expectation value of Q is

$$\langle Q\rangle = \sum_n q_n |c_n|^2 = \langle \Psi|\hat{Q}\Psi\rangle \tag{74}$$

- The momentum space wave function $\Phi(p,t)$; The position space wave function $\Psi(x,t)$.

$$\Phi(p,t) = \langle f_p|\Psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} e^{-ipx/\hbar}\Psi(x,t)dx \tag{75}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} e^{ipx/\hbar}\Phi(p,t)dp \tag{76}$$

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$$\langle Q(x,p,t)\rangle = \int \Psi^*\hat{Q}(x,-i\hbar\partial/\partial x,t)\Psi dx, \quad \text{in position space} \tag{77}$$

$$\langle Q(x,p,t)\rangle = \int \Psi^*\hat{Q}(i\hbar\partial/\partial p,p,t)\Psi dx, \quad \text{in momentum space} \tag{78}$$

3.5 Uncertainty Principle

3.5.1 Proof

- For any observable $\hat{A}$, we define the variance σ_A^2 as:

$$\sigma_A^2 = \langle(\hat{A}-\langle A\rangle)\Psi \mid (\hat{A}-\langle A\rangle)\Psi\rangle = \langle f \mid f\rangle \tag{79}$$

where $f = (\hat{A}-\langle A\rangle)\Psi$. Similarly, for another observable $\hat{B}$, the variance σ_B^2 is:

$$\sigma_B^2 = \langle g \mid g\rangle \tag{80}$$

with $g = (\hat{B}-\langle B\rangle)\Psi$.
By the Schwarz inequality, we have:

$$\sigma_A^2\sigma_B^2 \geq |\langle f \mid g\rangle|^2 \tag{81}$$

For any complex number z:

$$|z|^2 = [\mathrm{Re}(z)]^2 + [\mathrm{Im}(z)]^2 \geq [\mathrm{Im}(z)]^2 = \left(\frac{1}{2i}(z-z^*)\right)^2 \tag{82}$$

Let $z = \langle f \mid g\rangle$. Then:

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\left(\langle f \mid g\rangle - \langle g \mid f\rangle\right)\right)^2 \tag{83}$$

Now, consider the commutator of $\hat{A}$ and $\hat{B}$, defined as:

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{84}$$

We calculate $\langle f \mid g\rangle - \langle g \mid f\rangle$:

$$\langle f \mid g\rangle - \langle g \mid f\rangle = \langle(\hat{A}-\langle A\rangle)\Psi \mid (\hat{B}-\langle B\rangle)\Psi\rangle - \langle(\hat{B}-\langle B\rangle)\Psi \mid (\hat{A}-\langle A\rangle)\Psi\rangle \tag{85}$$

$$= \langle\Psi \mid (\hat{A}-\langle A\rangle)(\hat{B}-\langle B\rangle)\Psi\rangle - \langle\Psi \mid (\hat{B}-\langle B\rangle)(\hat{A}-\langle A\rangle)\Psi\rangle \tag{86}$$

$$= \langle\Psi \mid [\hat{A},\hat{B}]\Psi\rangle \tag{87}$$

Substituting, we get the generalized uncertainty principle:

$$\boxed{\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\,\langle[\hat{A},\hat{B}]\rangle\right)^2} \tag{88}$$

- As a specific example, for position $\hat{x} = x$ and momentum $\hat{p} = -i\hbar\frac{d}{dx}$, their commutator is $[\hat{x}, \hat{p}] = i\hbar$. Substituting this into the generalized uncertainty principle gives the Heisenberg uncertainty principle:

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}} \tag{89}$$

- **Incompatible observables** (i.e., a pair of observables whose operators do not commute) cannot have a complete set of common eigenfunctions.
  Compatible observables *admit* complete sets of simultaneous eigenfunctions (i.e., states that are determinate for both observables).

  e.g. In the hydrogen atom the Hamiltonian, the magnitude of angular momentum, and the z-component of angular momentum are mutually compatible observables. But there is no eigenfunction of position that is also an eigenfunction of momentum.

3.5.2 The Minimum-Uncertainty Wave Packet

Wave functions hitting the position-momentum uncertainty limit ($\sigma_x \sigma_p = \hbar/2$) (e.g., harmonic oscillator ground state, free-particle Gaussian) raise questions about the most general minimum-uncertainty form.

From the uncertainty principle proof, equality in inequalities requires:

- Schwarz inequality equality: $g(x) = cf(x)$ (c complex);
- Pure imaginary $c = ia$ (real a) to satisfy $\mathrm{Re}(i\langle f|g\rangle) = 0$, giving $g(x) = iaf(x)$.

  For position-momentum, this leads to the differential equation:

$$\left(-i\hbar\frac{d}{dx} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi \tag{90}$$

with general solution:

$$\Psi(x) = Ae^{-(x-\langle x\rangle)^2/(4\sigma^2)}e^{i\langle p\rangle x/\hbar} \tag{91}$$

Thus, the minimum-uncertainty wave packet is a Gaussian, which is consistent with earlier examples.

3.5.3 The Energy-Time Uncertainty Principle

- Generalized Ehrenfest Theorem:

$$\boxed{\frac{d}{dt}\langle Q\rangle = \frac{i}{\hbar}\langle[\hat{H}, \hat{Q}]\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle} \tag{92}$$

- According to generalized Ehrenfest theorem and uncertainty principle,

$$\sigma_H^2\sigma_Q^2 \geq \left(\frac{1}{2i}\langle[\hat{H}, \hat{Q}]\rangle\right)^2 = \left(\frac{1}{2i}\frac{\hbar}{i}\frac{d\langle Q\rangle}{dt}\right)^2 = \left(\frac{\hbar}{2}\frac{d\langle Q\rangle}{dt}\right)^2 \tag{93}$$

$$\Rightarrow \sigma_H\sigma_Q \geq \frac{\hbar}{2}\left|\frac{d\langle Q\rangle}{dt}\right|. \tag{94}$$

Define $\Delta E \equiv \sigma_H$, $\Delta t \equiv \sigma_Q/|\frac{d\langle Q\rangle}{dt}|$, therefore

$$\boxed{\Delta E\Delta t \geq \frac{\hbar}{2}}. \tag{95}$$

– Δt represents the amount of time it takes the expectation value of Q to change by one standard deviation.
– If any observable changes rapidly, the "uncertainty" in the energy must be large.

3.6 Vectors and Operators

3.6.1 Additional Notes: On "Matrix Element"

When an operator $\hat{Q}$ acts on a state $|\alpha\rangle$ to produce $|\beta\rangle = \hat{Q}|\alpha\rangle$, we want to derive the components of $|\beta\rangle$, given the components of $|\alpha\rangle$ and the transformation $\hat{Q}$.

- Original state decomposition: $|\alpha\rangle = \sum_n a_n|e_n\rangle$ where a_n is the "amount" of $|\alpha\rangle$ along basis vector $|e_n\rangle$;
- Operator's action revealed through: $Q_{mn} = \langle e_m|\hat{Q}|e_n\rangle$ showing (1) how $\hat{Q}$ redirects $a_n|e_n\rangle$ and (2) how the redirected state vector is projected on basis vector $|e_n\rangle$, or obtaining the nth-component of the transformed state vector.

  The transformation becomes clear when we write:

$$b_m = \sum_n Q_{mn}a_n \tag{96}$$

  which means the new state's m-th component combines all original components:

$$|\beta\rangle = \sum_m \left(\sum_n Q_{mn}a_n\right)|e_m\rangle \tag{97}$$

3.6.2 Bases in Hilbert Space

- Classical Analogy: A 2D vector $\mathbf{A}$ can be described via components w.r.t. different orthonormal bases (e.g., xy or $x'y'$ axes). The vector itself is independent of the basis choice.
- In quantum mechanics: A quantum state $|\mathcal{S}(t)\rangle$ "lives" in Hilbert space. It can be expanded with respect to different bases:

$$\Psi(x,t) = \langle x|\mathcal{S}(t)\rangle \tag{98}$$

$$\Phi(p,t) = \langle p|\mathcal{S}(t)\rangle \tag{99}$$

  Coefficients $c_n(t) = \langle n|\mathcal{S}(t)\rangle$ for discrete energy basis. All expansions represent the same state:

$$|\mathcal{S}(t)\rangle = \int \Psi(y,t)\,|y\rangle dy = \int \Phi(p,t)\,\frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}dp = \sum_n c_n e^{-iE_nt/\hbar}|n\rangle \tag{100}$$

- Definition: Operators (observables) transform vectors:

$$|\beta\rangle = \hat{Q}|\alpha\rangle \tag{101}$$

- Matrix Elements: With orthonormal basis $\{|e_n\rangle\}$, an operator $\hat{Q}$ is represented by matrix elements

$$Q_{mn} \equiv \langle e_m|\hat{Q}|e_n\rangle \tag{102}$$

  Taking inner product with $\langle e_m|$ on $|\beta\rangle = \hat{Q}|\alpha\rangle$ (after expanding $|\alpha\rangle, |\beta\rangle$ in basis), we get:

$$b_m = \sum_n Q_{mn}a_n \tag{103}$$

- An Example of Two-State System: Consider a system with two linearly independent states $|1\rangle = \begin{pmatrix}1\\0\end{pmatrix}$, $|2\rangle = \begin{pmatrix}0\\1\end{pmatrix}$. General state:

$$|\mathcal{S}\rangle = a|1\rangle + b|2\rangle = \begin{pmatrix}a\\b\end{pmatrix},\ |a|^2 + |b|^2 = 1 \tag{104}$$

For Hamiltonian $H = \begin{pmatrix}h & g\\g & h\end{pmatrix}$, solve time-independent Schrödinger equation $\hat{H}|s\rangle = E|s\rangle$ to find eigenvectors and eigenvalues. Expand initial state in eigenvectors, add time-dependence $e^{-iE_nt/\hbar}$ to get state at time t.

- Operators in Position/Momentum Bases: Position operator $\hat{x}$:

$$\hat{x} \to \begin{cases} x & \text{(position space)} \\ i\hbar\partial/\partial p & \text{(momentum space)} \end{cases} \tag{105}$$

Momentum operator $\hat{p}$:

$$\hat{p} \to \begin{cases} -i\hbar\partial/\partial x & \text{(position space)} \\ p & \text{(momentum space)} \end{cases} \tag{106}$$

A state's wave function $\Psi(x,t)$ is its "position-basis representation"; the state $|\mathcal{S}(t)\rangle$ is basis-independent.

3.6.3 Dirac Notation

- bra $\langle\alpha|$; ket $|\beta\rangle$.
- Bra is a linear function of vectors:

$$\langle f| = \int f^*[...]dx \tag{107}$$

- In a finite dimensional vector space, bra is expressed as row and ket is expressed as column.
- The collection of all bras is called the dual space. (duality)
- The projection operator

$$\hat{P} \equiv |\alpha\rangle\langle\alpha| \tag{108}$$

, which gives the proportion of any other vectors that lies along the direction of $|\alpha\rangle$:

$$\hat{P}|\beta\rangle \equiv (\langle\alpha|\beta\rangle)|\alpha\rangle. \tag{109}$$

- If $|e_n\rangle$ is a complete basis, then
  1. For discrete orthonormal basis,

$$\sum_n |e_n\rangle\langle e_n| = 1 \tag{110}$$

  2. For continuous orthonormal basis,

$$\int |e_n\rangle\langle e_n| dn = 1 \tag{111}$$

- Typically, functions of operators are defined by power series, e.g.

$$e^{\hat{Q}} = 1 + \hat{Q} + 1/2\hat{Q}^2 + 1/3!\hat{Q}^3 + ... \tag{112}$$

- If an operator is hermitian, its matrix elements in any orthogonal basis satisfy $Q_{mn} = Q^*_{nm}$ (see Problem 3.24). (Question: Is orthogonality condition necessary?)
- An operator can be expressed by its spectral decomposition:

$$\hat{Q} = \sum_n q_n |e_n\rangle\langle e_n| \tag{113}$$

  (see Problem 3.27)
- A function of an operator can be defined by spectral decomposition:

$$f(\hat{Q}) = \sum_n f(q_n) |e_n\rangle\langle e_n| \tag{114}$$

  , which is equivalent to the infinite series definition in case of e^Q. (Question: Universality)
-

$$[A, B] = AB - BA \tag{115}$$
$$[A, B] = -[B, A] \tag{116}$$
$$[A, B + C] = [A, B] + [A, C] \tag{117}$$
$$[A + B, C] = [A, C] + [B, C] \tag{118}$$
$$[\alpha A, B] = \alpha[A, B] = [A, \alpha B] \tag{119}$$
$$[A, BC] = [A, B]C + B[A, C] \tag{120}$$
$$[AB, C] = A[B, C] + [A, C]B \tag{121}$$
$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0 \tag{122}$$
$$[A, I] = 0 \tag{123}$$
$$[A, B^2] = [A, B]B + B[A, B] \tag{124}$$
$$[A^2, B] = A[A, B] + [A, B]A \tag{125}$$
$$[A, B] = c \implies [A, B^n] = ncB^{n-1} \tag{126}$$
$$[A, B] = c \implies [A^n, B] = ncA^{n-1} \tag{127}$$

-

$$[A^n, B] = nA^{n-1}C \quad (C = [A, B]; [A, C] = [B, C] = 0) \tag{128}$$
$$[e^{\lambda A}, B] = \lambda e^{\lambda A} C \quad (C = [A, B]; [A, C] = [B, C] = 0) \tag{129}$$

3.6.4 Changing Basis in Dirac Notation

- Most frequently used operator:

$$1 = \int dx |x\rangle\langle x| \tag{130}$$
$$1 = \int dp |p\rangle\langle p| \tag{131}$$
$$1 = \sum_n |n\rangle\langle n| \tag{132}$$

- Example: Changing basis from the position-space wave function to the momentum-space wave function.

$$\Phi(p,t) = \langle p|S(t)\rangle \tag{133}$$
$$= \langle p|(\int dx|x\rangle\langle x|)|S(t)\rangle \tag{134}$$
$$= \int \langle p|x\rangle\langle x|S(t)\rangle dx \tag{135}$$
$$= \int \langle p|x\rangle\Psi(x,t)dx \tag{136}$$
$$= \int \langle x|p\rangle^*\Psi(x,t)dx \tag{137}$$
$$= \int [f_p(x)]^*\Psi(x,t)dx \tag{138}$$
$$= \frac{1}{\sqrt{2\pi\hbar}}\int e^{-ipx/\hbar}\Psi(x,t)dx. \tag{139}$$

- Action of position operator in x basis $= \langle x|\hat{x}|S(t)\rangle = x\Psi(x,t)$
  Action of position operator in p basis $= \langle p|\hat{x}|S(t)\rangle = i\hbar\frac{\partial\Phi}{\partial p}$

3.7 Virial Theorem

$$\boxed{2\langle T\rangle = \left\langle x\frac{dV}{dx}\right\rangle} \tag{140}$$

, which can be proven by generalized Ehrenfest Theorem (Problem 3.37).

4 Quantum Mechanics in Three Dimensions

4.1 The Schrödinger Equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \tag{141}$$

The Hamiltonian operator $\hat{H}$ is derived from the classical energy by substituting $\mathbf{p} \to -i\hbar\nabla$:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) \tag{142}$$

where the Laplacian in Cartesian coordinates is

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{143}$$

The wave function Ψ and potential V are functions of $\mathbf{r} = (x,y,z)$ and t. The probability of finding the particle in the infinitesimal volume $d^3r = dxdydz$ is $|\Psi(\mathbf{r},t)|^2d^3r$, and the normalization condition is

$$\int |\Psi|^2 d^3r = 1 \tag{144}$$

with the integral over all space. For time-independent V, stationary states exist:

$$\Psi_n(\mathbf{r},t) = \psi_n(\mathbf{r})e^{-iE_nt/\hbar} \tag{145}$$

where ψ_n satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{146}$$

The general solution to the time-dependent Schrödinger equation is

$$\Psi(\mathbf{r},t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar} \tag{147}$$

with c_n determined by the initial wave function $\Psi(\mathbf{r},0)$.

4.2 Generalization of Some Conclusions in 1D

4.2.1 Canonical Commutation Relations

The canonical commutation relations for components of $\mathbf{r}$ and $\mathbf{p}$ are

$$[r_i, p_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = 0, \quad [p_i, p_j] = 0 \tag{148}$$

where $r_i = x, y, z$ and p_i are the corresponding momentum components.

4.2.2 Ehrenfest's Theorem

The three-dimensional version of Ehrenfest's theorem states

$$\frac{d}{dt}\langle \mathbf{r} \rangle = \frac{1}{m}\langle \mathbf{p} \rangle \tag{149}$$

$$\frac{d}{dt}\langle \mathbf{p} \rangle = \langle -\nabla V \rangle \tag{150}$$

4.2.3 Heisenberg's Uncertainty Principle

In three dimensions, the uncertainty principle takes the form

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2}, \quad \sigma_y \sigma_{p_y} \geq \frac{\hbar}{2}, \quad \sigma_z \sigma_{p_z} \geq \frac{\hbar}{2} \tag{151}$$

with no restriction on cross components (e.g., $\sigma_x \sigma_{p_y}$).

4.3 Infinite Cubical Well

The potential for an infinite cubical well is

$$V(x,y,z) = \begin{cases} 0, & 0 \leq x, y, z \leq a \\ \infty, & \text{otherwise} \end{cases} \tag{152}$$

The stationary states are

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \tag{153}$$

with corresponding energies

$$\boxed{E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)} \tag{154}$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$.

4.4 Spherical Coordinates

For central potentials $V(r)$, spherical coordinates (r, θ, ϕ) are used. The Laplacian in spherical coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{155}$$

The time-independent Schrödinger equation in spherical coordinates is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + V\psi = E\psi \tag{156}$$

Separable solutions $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ lead to the radial equation

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = \ell(\ell+1) \tag{157}$$

and the angular equation

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -\ell(\ell+1) \tag{158}$$

4.5 The Angular Equation

- From the time-independent Schrödinger equation in spherical coordinates, after separating radial and angular parts, the angular equation is derived as:

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -\ell(\ell+1) \tag{159}$$

  where $\ell(\ell+1)$ is the separation constant.

- The angular wave function $Y(\theta, \phi)$ is further separated into a product of functions of θ and ϕ as $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. Substituting this into the angular equation leads to two separate equations:

  1. ϕ-dependent part:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \tag{160}$$

     where m^2 is another separation constant.

  2. θ-dependent part:

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2 \tag{161}$$

- The solution to the ϕ equation is $\Phi(\phi) = e^{im\phi}$. Due to the periodicity requirement $\Phi(\phi + 2\pi) = \Phi(\phi)$, we have $e^{i2\pi m} = 1$, which implies $m = 0, \pm1, \pm2, \ldots$ (i.e., m must be an integer).

- The solution to the θ equation involves associated Legendre functions. The associated Legendre function $P_\ell^m(\cos\theta)$ is defined as:

$$P_\ell^m(x) = (-1)^m\left(1 - x^2\right)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x) \tag{162}$$

  where $P_\ell(x)$ is the Legendre polynomial given by the Rodrigues formula:

$$P_\ell(x) \equiv \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell\left(x^2 - 1\right)^\ell \tag{163}$$

  For a given ℓ, m can take values $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$, resulting in $(2\ell+1)$ possible values of m.

- The normalized angular wave functions, called spherical harmonics, are given by:

$$Y_\ell^m(\theta,\phi) = \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} e^{im\phi} P_\ell^m(\cos\theta) \tag{164}$$

They satisfy the orthogonality condition:

$$\int_0^\pi \int_0^{2\pi} [Y_\ell^m(\theta,\phi)]^* \left[Y_{\ell'}^{m'}(\theta,\phi)\right] \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'}\delta_{mm'} \tag{165}$$

4.6 The Radial Equation

- The radial part of the wave function $R(r)$ is determined by the radial equation, which is derived from the time-independent Schrödinger equation in spherical coordinates after separating the angular part. The radial equation is:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]R = \ell(\ell+1)R \tag{166}$$

where ℓ is the orbital angular momentum quantum number, m is the mass of the particle, $V(r)$ is the potential energy, and E is the energy.

- A simplification is achieved by introducing a new variable $u(r) \equiv rR(r)$. Substituting $R = u/r$ into the radial equation transforms it into:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \tag{167}$$

This equation resembles the one-dimensional time-independent Schrödinger equation, but with an effective potential V_{eff}.

- The effective potential V_{eff} is given by:

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} \tag{168}$$

The additional term $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ is called the centrifugal term, which acts like a repulsive potential, tending to push the particle away from the origin.

- The normalization condition for the radial wave function, in terms of $u(r)$, becomes:

$$\int_0^\infty |u|^2 dr = 1 \tag{169}$$

This is a result of normalizing $R(r)$ and $Y(\theta,\phi)$ separately, where the radial normalization condition for $R(r)$ is $\int_0^\infty |R|^2 r^2 dr = 1$ and substituting $R = u/r$ leads to the above expression.

4.7 Infinite Spherical Well

- Potential function:

$$V(r) = \begin{cases} 0, & r \le a; \\ \infty, & r \ge a. \end{cases} \tag{170}$$

- This is a spherical symmetric potential, so the angular solution is spherical harmonics. The only task needed is solving the radial equation:

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2\right] u \tag{171}$$

, where $k \equiv \frac{\sqrt{2mE}}{\hbar}$.

- The general solution to the radial equation of infinite spherical well reads

$$u(r) = Arj_l(kr) + Brn_l(kr), \tag{172}$$

where $j_l(x)$ is the spherical Bessel function of order l:

$$j_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x} \tag{173}$$

, and $n_l(x)$ is the spherical Neumann function of order l:

$$n_l(x) = -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x}. \tag{174}$$

However, Neumann function blows up at the origin, hence $B = 0$, and

$$R(r) = Aj_l(kr). \tag{175}$$

- Applying the boundary condition $R(a) = 0$:

$$k \cdot a = \beta_{Nl} \Rightarrow k = \frac{1}{a}\beta_{Nl}, \tag{176}$$

where β_{Nl} is the N-th zero of lth order spherical Bessel function. The allowed energies, then, are given by

$$E_{Nl} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2ma^2}\beta_{Nl}^2 \quad , \tag{177}$$

and the wave function is

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_l \left(\beta_{Nl}\frac{r}{a}\right) Y_l^m(\theta, \phi), \tag{178}$$

where A_{nl} is the normalization constant.

- Characteristics

  1. The wavefunction has $N - 1$ radial nodes
  2. The energy levels are determined by both n's and l's.
  3. Each energy level is $(2l+1)$-fold degenerate: a specific pair of n and l determines an energy level, and there are $(2l + 1)$ distinct values of m.

4.8 The Hydrogen Atom

- The potential function:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{179}$$

- This is also a spherical symmetric well, so we only need to solve the radial equation:

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[-\frac{e^2}{4\pi\epsilon_0 r}+\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]u=Eu \quad . \tag{180}$$

Define

$$\kappa\equiv\sqrt{-2m_eE}/\hbar \tag{181}$$

, and divide by E, we have

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2}=\left[1-\frac{m_ee^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r}+\frac{l(l+1)}{(\kappa r)^2}\right]u \tag{182}$$

Let $\rho=\kappa r$, and $\rho_0=m_ee^2/(2\pi\epsilon_0\hbar^2\kappa)$ (both are dimensionless), so that

$$\frac{d^2u}{dr^2}=\left[1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}\right]u \tag{183}$$

- Next, we examine the asymptotic behavior. As $\rho\to\infty$,

$$\frac{d^2u}{d\rho^2}=u. \tag{184}$$

The general solution (which does not blow up as p goes infinity) is

$$u(\rho)\sim Ae^{-\rho}. \tag{185}$$

Similarly, as $\rho\to 0$, we have

$$\frac{d^2u}{d\rho^2}=\frac{l(l+1)}{\rho^2}u. \tag{186}$$

The general solution (which does not blow up as ρ approaches 0) is

$$u(\rho)\sim C\rho^{l+1}. \tag{187}$$

Therefore,

$$u(\rho)=\rho^{l+1}e^{-\rho}v(\rho) \tag{188}$$

Substitute into the radial equation, we derive

$$\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}+[\rho_0-2(l+1)]v=0 \tag{189}$$

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

$$v(\rho)=\sum_{j=0}^{\infty}c_j\rho^j \tag{190}$$

Expressing the radial equation in power series, we have

$$\sum_{j=0}^{\infty}j(j+1)c_{j+1}\rho^j+2(l+1)\sum_{j=0}^{\infty}j(j+1)c_{j+1}\rho^j-2\sum_{j=0}^{\infty}jc_j\rho^j+[\rho_0-2(l+1)]\sum_{j=0}^{\infty}c_j\rho^j=0. \tag{191}$$

Hence,

$$j(j+1)c_{j+1}+2(l+1)(j+1)c_{j+1}-2jc_j+[\rho_0-2(l+1)]c_j=0 \tag{192}$$

$$\Rightarrow c_{j+1}=\left\{\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right\}c_j. \tag{193}$$

For large j, the solution blows up (see Page 189 of the textbook), so the power series must terminate:

$$c_{N-1}\neq 0 \quad \text{but} \quad c_N=0. \tag{194}$$

- According to the recursion formula we derived,

$$2(N+l)-\rho_0=0. \tag{195}$$

Defining $n \equiv N+l$, we have $\rho_0 = 2n$ and hence the energy level

$$E=-\frac{\hbar^2\kappa^2}{2m}=-\frac{m_e e^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2} \tag{196}$$

$$\Rightarrow E_n=-\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}=E_1/n^2 \quad (n=1,2,3,...) \tag{197}$$

This is called Bohr Formula.

- The characteristic length of the hydrogen atom is called Bohr radius:

$$a \equiv 1/\kappa = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529\times 10^{-10}\text{m}. \tag{198}$$

- The wave function of the hydrogen atom is

$$\psi_{nlm}=R_{nl}(r)Y_l^m(\theta,\phi) \tag{199}$$

, where c_0 in the recursion formula determined by normalization.

- Characteristics

1. The degeneracy of each energy level is n^2. (See Page 191 of the textbook).
2. For a specific n, possible values of l are $l = 0, 1, 2, ..., n-1$.
3. In the hydrogen atom model, different values of l carry the same energy for a given n, which gives the model extra degeneracy compared to the infinite spherical well model.
4. For bound states of the hydrogen atom, $E < 0$, with corresponding n's from 1 to ∞. For scattering states, $E > 0$. $E_\infty = 0$ separates bound states and scattering states.
5. All $|\psi|^2$ is of azimuthal symmetry. (For more about nodes, see Page 195 of the textbook)

- The polynomial $v(\rho)$ can be written as

$$v(\rho)=L_{n-l-1}^{2l+1}(2\rho) \tag{200}$$

, where

$$L_q^p(x)\equiv(-1)^p\left(\frac{d}{dx}\right)^p L_{p+q}(x) \tag{201}$$

is an associated Laguerre polynomial, and

$$L_q(x)\equiv\frac{e^x}{q!}\left(\frac{d}{dx}\right)^q(e^{-x}x^q) \tag{202}$$

is the q-th Laguerre polynomial.

- The normalized hydrogen atom wave functions are

$$\psi_{nlm}=\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n(n+l)!}}e^{-r/na}\left(\frac{2r}{na}\right)^l\left[L_{n-l-1}^{2l+1}(2r/na)\right]Y_l^m(\theta,\phi). \tag{203}$$

- Orthogonality:

$$\int\psi_{nlm}^*\psi_{n'l'm'}r^2drd\Omega=1 \tag{204}$$

- Question: Can electron enters the nuclei? (as the solution does not rule out this possibility)?

5 2-Dimensional Harmonic Oscillator & Infinite Square Well

5.1 Harmonic Oscillator

[?]

- Potential:

$$V(x,y) = \frac{1}{2}m\omega^2(x^2+y^2) \tag{205}$$

- Time-independent Shrodinger equation:

$$-\frac{\hbar^2}{2m}(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2})+\frac{1}{2}m\omega(x^2+y^2)\psi = E\psi \tag{206}$$

- Using separation of variables, we assume that the solution ψ can be expressed as the product of the wave function of x and the wave function of y:

$$\psi = X(x)Y(y) \tag{207}$$

Substituting into the Shrodinger equation:

$$-\frac{\hbar^2}{2m}(Y\frac{\partial^2 X}{\partial x^2}+X\frac{\partial^2 Y}{\partial y^2})+\frac{1}{2}m\omega(x^2+y^2)XY = EXY \tag{208}$$

$$\Rightarrow -\frac{\hbar^2}{2m}(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2})+\frac{1}{2}m\omega(x^2+y^2) = E \tag{209}$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{2}m\omega x^2\right]+\left[-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{2}m\omega y^2\right] = E \tag{210}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{2}m\omega x^2 = E_x\ , \tag{211}$$

$$-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{2}m\omega y^2 = E_y\ , \tag{212}$$

$$E = E_x + E_y \tag{213}$$

The x-dependent and y dependent equations are exactly the same as Schrodinger equation of HM in 1-D. Using the result obtained previously,

$$X(x) = A\frac{1}{\sqrt{2^{n_x}n_x!}}H_{n_x}(\xi_x)e^{-\xi_x^2/2}\ ; \tag{214}$$

$$Y(y) = B\frac{1}{\sqrt{2^{n_y}n_y!}}H_{n_y}(\xi_y)e^{-\xi_y^2/2}\ , \tag{215}$$

$$\text{where}\ \ \xi_{(x,y)} = \sqrt{\frac{m\omega}{\hbar}}\cdot(x,y)\ . \tag{216}$$

Therefore,

$$\psi(x,y) = C\cdot\frac{1}{\sqrt{2^{n_x}n_x!}}H_{n_x}(\xi_x)e^{-\xi_x^2/2}\cdot\frac{1}{\sqrt{2^{n_y}n_y!}}H_{n_y}(\xi_y)e^{-\xi_y^2/2}\ ; \tag{217}$$

$$E = \hbar\omega(n_x+n_y+1) = \hbar\omega(N+1). \tag{218}$$

5.2 Infinite Square Well

- Potential function:

$$V(x,y) = \begin{cases}0, & 0\le x,y\le a\\ \infty, & \text{otherwise}\end{cases} \tag{219}$$

- Solution:

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right); \tag{220}$$

$$\psi(y) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_y \pi}{a} y\right); \tag{221}$$

$$\psi(x,y) = \psi(x)\psi(y) = \frac{2}{a} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \tag{222}$$

References

[1] David J. Griffiths. Introduction to Quantum Mechanics (The Third Edition). pages 119–121, 2018.

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[4] David J. Griffiths. Introduction to Quantum Mechanics (The Third Edition). pages 123–124, 2018.