

Introduction to Quantum Mechanics

—David J. Griffiths

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Abstract

To review the textbook used in Tongji University — *Introduction to Quantum Mechanics*, written by David J. Griffiths. You can browse through the contents to prepare the final exam of Quantum Mechanics. Also, it will be a good choice for you to prepare the GRE Physics Test...

1 Wave Function

1. General Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (1)$$

p.s., the energy operator is $i\hbar \frac{\partial \Psi}{\partial t}$.

2. Indeterminacy

3. Interpretation: Orthodox position = Copenhagen interpretation
Agnostic position

- 4.

$$\begin{cases} \text{Variance} \\ \text{Standarddeviation : } \sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2} \end{cases}$$

5. Normalization

Prove: $\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 0$

Proof:

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi|^2 dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\Psi|^2 dx$$

and

$$\begin{aligned} \frac{\partial}{\partial t} |\Psi|^2 &= \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \quad (\text{Schrödinger equation}) \\ &= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right) \\ &= \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \right] \end{aligned}$$

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$$\begin{aligned} \langle x \rangle &= \int \Psi^*(x) \Psi dx \\ \langle p \rangle &= \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \end{aligned}$$

8. The uncertainty principle:

$$\begin{aligned} p &= \frac{h}{\lambda} = \hbar k \\ \sigma_x \sigma_p &\geq \frac{\hbar}{2} \end{aligned}$$

2 Time-independent Schrödinger Equation

2.1 Stationary States

Solve Schrödinger equation (1) by the method of separation of variables:

$$\begin{cases} \frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi \Rightarrow \varphi = \exp(-i\frac{E}{\hbar}t) \\ -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi \end{cases}$$

and $\hat{H} = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V$ ($p \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$), namely:

$$\hat{H}\Psi = E\Psi \quad (2)$$

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

$$\sum_{n=1}^{\infty} |C_n|^2 = 1, \quad (3)$$

$$\langle H \rangle = \sum_{n=1}^{\infty} |C_n|^2 E_n. \quad (4)$$

2.2 Infinite Square Well

In a infinite square well:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi \quad (0 \leq x \leq a)$$

namely:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \quad (5)$$

in which:

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

We know the solution to equation(5) is:

$$\psi = A \sin kx + B \cos kx. \quad (6)$$

Boundary conditions:

$$\psi(0) = \psi(a) = 0,$$

we can get $B = 0$, and $ka = 0, \pm\pi, \pm2\pi, \dots$, namely:

$$k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, \dots$$

Therefore,

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

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad (7)$$

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \exp\left(-i \frac{n^2 \pi^2 \hbar}{2ma^2} t\right). \quad (8)$$

2.3 Harmonic Oscillator

Hooke's Law:

$$F = -kx = m \frac{d^2x}{dt^2},$$

namely,

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0,$$

let $\omega = \sqrt{\frac{k}{m}}$, so $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$, substituting into eq(2), we can get the Schrödinger equation of harmonic oscillator:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + \frac{1}{2}m\omega^2x^2\psi = E\psi. \quad (9)$$

2.3.1 Ladder Operator

1. Hamiltonian: $H = \frac{1}{2m}[p^2 + (m\omega x)^2]$, ladder operators: $a_{\pm} = \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x)$. And we know the commutator of x and p is $[x, p] = i\hbar$, therefore:

$$\begin{cases} a_- a_+ = \frac{1}{\hbar\omega}H - \frac{i}{2\hbar}[x, p] = \frac{1}{\hbar\omega}H + \frac{1}{2}, \\ a_+ a_- = \frac{1}{\hbar\omega}H - \frac{1}{2}. \end{cases}$$

The commutator of a_+ and a_- is: $[a_-, a_+] = a_- a_+ - a_+ a_- = 1$.

So the Hamiltonian:

$$H = \hbar\omega \left(a_{\pm} a_{\mp} \pm \frac{1}{2} \right),$$

and Schrödinger equation (9) become:

$$\hbar\omega \left(a_{\pm} a_{\mp} \pm \frac{1}{2} \right) \psi = E\psi. \quad (10)$$

2. If $H\psi = E\psi$, prove:

$$\begin{cases} H(a_+\psi) = (E + \hbar\omega)(a_+\psi), \\ H(a_-\psi) = (E - \hbar\omega)(a_-\psi). \end{cases}$$

Proof:

$$\begin{aligned} H(a_+\psi) &= \hbar\omega(a_+a_- + \frac{1}{2})(a_+\psi) \\ &= \hbar\omega a_+(a_-a_+ + \frac{1}{2})\psi \\ &= \hbar\omega a_+(\frac{1}{\hbar\omega}H + 1)\psi \\ &= a_+(H + \hbar\omega)\psi \\ &= a_+(E + \hbar\omega)\psi \\ &= (E + \hbar\omega)(a_+\psi) \end{aligned}$$

similarly, we can get

$$H(a_-\psi) = (E - \hbar\omega)(a_-\psi).$$

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3. Ground state ψ_0 satisfy: $a_-\psi_0 = 0$, where $a_- = \frac{1}{\sqrt{2\hbar m\omega}} (\hbar\frac{\partial}{\partial x} + m\omega x)$, solution:

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

Substituting ψ_0 into Schrödinger equation (10):

$$\begin{aligned} \hbar\omega(a_+a_- + \frac{1}{2})\psi_0 &= E_0\psi_0 \\ \hbar\omega \cdot \frac{1}{2}\psi_0 &= E_0\psi_0, \end{aligned}$$

Therefore,

$$E_0 = \frac{1}{2}\hbar\omega, \tag{11}$$

and

$$\begin{aligned} \psi_n &= A_n(a_+)^n\psi_0 = \frac{1}{\sqrt{n!}}(a_+)^n\psi_0, \\ E_n &= (n + \frac{1}{2})\hbar\omega. \end{aligned}$$

4. Prove $A_n = \frac{1}{\sqrt{n!}}$.

Proof: First, we have to get the Hermitian operator of the raising/lowering ladder operator:

$$a_{\pm}^{\dagger} = a_{\mp}.$$

Then, we substitute the E_n back into Schrödinger equation (10):

$$\hbar\omega(a_{\pm}a_{\mp} \pm \frac{1}{2})\psi_n = E_n\psi_n = (n + \frac{1}{2})\hbar\omega\psi_n,$$

namely,

$$a_+ a_- \psi_n = n \psi_n \quad (12)$$

$$a_- a_+ \psi_n = (n+1) \psi_n. \quad (13)$$

If $a_+ \psi_n = c_n \psi_{n+1}$ and $a_- \psi_n = d_n \psi_{n-1}$,

$$\begin{aligned} \int (a_+ \psi_n)^* (a_+ \psi_n) dx &= |c_n|^2 \int |\psi_{n+1}|^2 dx = |c_n|^2 \\ &= \int (a_- a_+ \psi_n)^* \psi_n dx = (n+1) \int |\psi_n|^2 dx = n+1 \end{aligned}$$

namely: $a_+ \psi_n = \sqrt{n+1} \psi_{n+1}$, similarly: $a_- \psi_n = \sqrt{n} \psi_{n-1}$. Therefore,

$$A_n = \frac{1}{\sqrt{n!}}.$$

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5. Prove $\int_{-\infty}^{\infty} \psi_m^* \psi_n = \delta_{mn}$ (Kronecker Delta).

Proof:

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m^* (a_+ a_-) \psi_n dx &= n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \\ &= \int_{-\infty}^{\infty} (a_+ a_- \psi_m)^* \psi_n dx = m \int_{-\infty}^{\infty} \psi_m^* \psi_n dx. \end{aligned}$$

Unless $m \neq n$, $\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0$.

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2.3.2 Analytic Method

Schrödinger equation of harmonic oscillator (9):

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

Let $\xi = \sqrt{\frac{m\omega}{\hbar}} x$ and $K = \frac{2E}{\hbar\omega}$, then:

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

Solution to this equation:

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

where $H_n(\xi)$ is Hermite polynomials:

$$H_0 = 1, \quad H_1 = 2\xi, \quad H_2 = 4\xi^2 - 2.$$

2.4 Free Particle

Schrödinger equation with $V = 0$:

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

then

$$\frac{d^2 \psi}{dx^2} = -k^2 \psi, \text{ where } k = \frac{\sqrt{2mE}}{\hbar}.$$

Solution to this equation:

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

Therefore,

$$\begin{aligned} \Psi(x, t) &= Ae^{ik(x - \frac{\hbar k}{2m}t)}, \\ k &= \pm \frac{\sqrt{2mE}}{\hbar} \begin{cases} + : \text{right;} \\ - : \text{left.} \end{cases} \end{aligned}$$

And

$$\begin{aligned} v_{\text{phase}} = v_{\text{quantum}} &= \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}, \\ v_{\text{class}} &= \frac{2E}{m} = 2v_{\text{quantum}}. \end{aligned}$$

k is continuous spectrum, so

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

and

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

the coefficient:

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

and

$$v_{\text{group}} = \frac{d\omega}{dk} = \frac{\hbar k}{m} = 2v_{\text{phase}} = v_{\text{class}}.$$

2.5 Delta-function Potential

For different E :

$$\begin{aligned} \text{boundary state} &: E < 0; \\ \text{scattering state} &: E > 0. \end{aligned}$$

For $V(x) = -\alpha\delta(x)$, Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi - \alpha\delta(x)\psi = E\psi.$$

(1) $E < 0$:

For $x < 0$, $V(x) = 0$, Schrödinger equation:

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

Solution to this equation:

$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x} = Be^{\kappa x}$ (we choose $A = 0$, for the first term blows up when $x \rightarrow -\infty$),

similarly, $\psi(x) = Fe^{-\kappa x}$ ($x > 0$).

The standard boundary conditions for ψ :

$$\begin{cases} \psi, \text{ always continuous.} \\ d\psi/dx, \text{ continuous except at point where potential is infinite.} \end{cases}$$

Integrating Schrödinger equation:

$$-\frac{\hbar^2}{2m} \int_{-\varepsilon}^{\varepsilon} \frac{\partial^2\psi}{\partial x^2} dx + \int_{-\varepsilon}^{\varepsilon} V(x)\psi dx = E \int_{-\varepsilon}^{\varepsilon} \psi dx,$$

when $\varepsilon \rightarrow 0$, $\int_{-\varepsilon}^{\varepsilon} \frac{\partial^2\psi}{\partial x^2} dx = \Delta \left(\frac{\partial\psi}{\partial x} \right)$ and $\int_{-\varepsilon}^{\varepsilon} \psi dx = 0$, therefore,

$$\Delta \left(\frac{\partial\psi}{\partial x} \right) = \frac{2m}{\hbar^2} \int_{-\varepsilon}^{\varepsilon} V(x)\psi dx = -\frac{2m}{\hbar^2} \int_{-\varepsilon}^{\varepsilon} \alpha\delta(x)\psi(x)dx = -\frac{2m\alpha}{\hbar^2}\psi(0).$$

Now, we know that $B = F$, and $\frac{d\psi}{dx}\Big|_- = B\kappa$, $\frac{d\psi}{dx}\Big|_+ = -B\kappa$, so

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

then,

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

Normalizing ψ ,

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 2 \int_0^{\infty} |B|^2 e^{-2\kappa x} dx = \frac{|B|^2}{\kappa} = 1 \Rightarrow |B| = \sqrt{\kappa},$$

namely,

$$\begin{aligned} \psi(x) &= \frac{\sqrt{m\alpha}}{\hbar} e^{-\frac{m\alpha}{\hbar^2}|x|}, \\ E &= -\frac{m\alpha^2}{2\hbar^2}. \end{aligned}$$

(2) $E > 0$:

When $x \neq 0$, Schrödinger equation:

$$\frac{\partial^2}{\partial x^2} \psi = -k^2 \psi, \quad k = \frac{\sqrt{2mE}}{\hbar}.$$

Solution to this equation:

$$\begin{aligned} \psi &= Ae^{ikx} + Be^{-ikx}, \quad x < 0; \\ \psi &= Fe^{ikx} + Ge^{-ikx}, \quad x > 0, \end{aligned}$$

using the standard boundary conditions again:

$$A + B = F + G,$$

and

$$\left. \frac{d\psi}{dx} \right|_- = ik(A - B), \quad \left. \frac{d\psi}{dx} \right|_+ = ik(F - G),$$

so

$$\Delta \left(\frac{d\psi}{dx} \right) = ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B).$$

Consider only the incident wave, namely $G = 0$, let $\beta = \frac{m\alpha}{\hbar^2 k}$, then

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

The reflection coefficient R and transmission coefficient T :

$$R = \frac{|B|^2}{|A|^2}, \quad T = \frac{|F|^2}{|A|^2}.$$

2.6 Finite Square Well

The potential function of a finite square well is

$$V(x) = \begin{cases} -V_0, & -a \leq x \leq a \\ 0, & |x| > a \end{cases}$$

(1) $E < 0$:

When $x < -a$, Schrödinger equation:

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

so, $\psi = Be^{\kappa x}$, similarly $\psi = Fe^{-\kappa x}$ ($x > a$).

When $-a < x < a$, Schrödinger equation:

$$\frac{d^2 \psi}{dx^2} = -l^2 \psi, \quad l = \frac{\sqrt{2mE - V_0}}{\hbar}.$$

Solution to this equation:

$$\psi(x) = C \sin(lx) + D \cos(lx).$$

We can assume that $\psi(x)$ is an even function, namely:

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

Applying the standard boundary conditions:

$$Fe^{-\kappa a} = D \cos(la),$$

$$-\kappa Fe^{-\kappa a} = -lD \sin(la),$$

so

$$\kappa = l \tan(la).$$

let $z = la$, then

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}, \text{ where } z_0 = \frac{\sqrt{2mV_0}}{\hbar}a.$$

(2) $E > 0$:

When $x < -a$, Schrödinger equation:

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

Solution to this equation:

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

similarly, $\psi(x) = Fe^{ikx} + Ge^{-ikx}$ ($x > a$). Schrödinger equation is the same in the square well, namely

$$\psi(x) = C \sin(lx) + D \cos(lx).$$

Consider only the incident wave, namely $G = 0 \dots$

3 Formalism

3.1 Hilbert Space

Square-integrable function:

$$f(x) \Rightarrow \int_a^b |f(x)|^2 dx < \infty,$$

all such functions constitutes a vector space **Hilbert Space**¹.

Inner product of two functions:

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

and

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

Schwarz inequality:

$$\left| \int_a^b f(x)^* g(x) dx \right| \leq \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx}. \quad (14)$$

A set of function is complete is:

$$f(x) = \sum_{n=1}^{\infty} C_n f_n(x),$$

where $\langle f_m|f_n \rangle = \delta_{mn}$ and $C_n = \langle f_n|f \rangle$.

3.2 Observables

1. Hermitian Operator

$$\langle Q \rangle = \langle \psi | \hat{Q} | \psi \rangle,$$

$$\langle Q \rangle = \langle Q \rangle^*,$$

$$\langle \psi | \hat{Q} \psi \rangle = \langle \hat{Q} \psi | \psi \rangle.$$

2. Determined States

The value is q when you measure \hat{Q} every time: $\langle \hat{Q} \rangle = q$, and

$$\begin{aligned} \sigma^2 &= 0 \\ &= \langle (\hat{Q} - \langle Q \rangle)^2 \rangle \\ &= \langle \psi | (\hat{Q} - \langle Q \rangle)^2 \psi \rangle \\ &= \langle (\hat{Q} - q) \psi | (\hat{Q} - q) \psi \rangle, \end{aligned}$$

therefore: $\hat{Q} \psi = q \psi$.

¹Mathematicians call it $L_2(a, b)$.

3.3 Discrete Spectrum

1. Prove: Hermitian Operator's eigenvalues are real.

Proof: First, we know $\hat{Q}f = qf$, and

$$\langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle,$$

and

$$\begin{aligned}\langle f|\hat{Q}f\rangle &= q\langle f|f\rangle, \\ \langle \hat{Q}f|f\rangle &= \langle qf|f\rangle = \int (qf)^* f dx = q^* \int f^* f dx = q^* \langle f|f\rangle,\end{aligned}$$

therefore: $q = q^*$.

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2. Eigenfunctions belonging to distinct eigenvalues are orthogonal.

3. The eigenfunctions of an observable operator are complete.

3.4 Continuous Spectrum

For example, the \hat{x} and \hat{p} .

1. Dirac orthonormality:

$$\langle f_m|f_n\rangle = \delta(m - n).$$

2. Eigenfunctions are not orthonormal but dirac orthonormal, and not in the Hilbert Space.

3. Eigenfunctions of \hat{x} and \hat{p} :

$$\begin{aligned}\hat{p} &\rightarrow f_p = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}, \text{ (eigenvalue is } p\text{);} \\ \hat{x} &\rightarrow g_y = \delta(x - y), \text{ (eigenvalue is } y\text{).}\end{aligned}$$

Momentum space wave function:

$$\begin{aligned}\Phi(p, t) &= \langle f_p|\Psi(x, t)\rangle \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int e^{-ipx/\hbar} \Psi(x, t) dx.\end{aligned}$$

(Position space) wave function:

$$\Psi(x, t) = \int c(p) f_p dp = \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \Phi(p, t) dp.$$

3.5 The Uncertainty Principle

1. $\sigma_A^2 = \langle (\hat{A} - \langle A \rangle) \psi | (\hat{A} - \langle A \rangle) \psi \rangle = \langle f | f \rangle$, similarly $\sigma_B^2 = \langle g | g \rangle$, where $g = \hat{B} - \langle B \rangle$. For Schwarz inequality:

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2,$$

and $|z^2| \geq \left| \frac{1}{2i}(z - z^*) \right|^2$, so

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

We know $[x, p] = i\hbar$, so $\sigma_x^2 \sigma_p^2 \geq \left(\frac{\hbar}{2} \right)^2$.

2. When $g = cf$ and $\text{Re}(\langle f | g \rangle) = 0$, where c is a constant, the inequality becomes an equality, namely:

$$\text{Re}(c \langle f | f \rangle) = 0 \Rightarrow c = ia,$$

so $g = iaf = ia(x - \langle x \rangle)$. For operators \hat{x} and \hat{p} , the minimum-uncertainty wave packet is:

$$\left(\frac{\hbar}{i} \frac{\partial}{\partial x} - \langle p \rangle \right) \psi = ia(x - \langle x \rangle) \psi.$$

3. The Energy-Time Uncertainty Principle: $\Delta t \Delta E \geq \frac{\hbar}{2}$.

Proof:

$$\frac{d}{dt} \langle Q \rangle = \frac{d}{dt} \langle \psi | \hat{Q} \psi \rangle = \langle \frac{\partial \psi}{\partial t} | \hat{Q} \psi \rangle + \langle \psi | \frac{\partial \hat{Q}}{\partial t} \psi \rangle + \langle \psi | \hat{Q} \frac{\partial \psi}{\partial t} \rangle.$$

And we know the time-dependent Schrödinger equation $i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$, so:

$$\frac{d}{dt} \langle Q \rangle = \frac{i}{\hbar} \langle \hat{H} \psi | \hat{Q} \psi \rangle - \frac{i}{\hbar} \langle \psi | \hat{Q} \hat{H} \psi \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle,$$

if \hat{Q} does not depend explicitly on time, which means $\frac{\partial \hat{Q}}{\partial t} = 0$, we can get:

$$\frac{d \langle Q \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle. \quad (15)$$

Therefore:

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

Define

$$\begin{aligned} \Delta E &= \sigma_H; \\ \Delta t &= \frac{\sigma_Q}{|d \langle Q \rangle / dt|}, \text{ namely : } \sigma_Q = \left| \frac{d \langle Q \rangle}{dt} \right| \Delta t. \end{aligned}$$

3.6 Dirac Notation

1. We use a vector in Hilbert Space $|\mathfrak{S}(t)\rangle$ to represent the state of a system (maybe not a function, such as the eigenstates of spin). Then we have $\hat{Q}|f\rangle = f|f\rangle$, so $|\mathfrak{S}(t)\rangle = \int c|f\rangle dq$.

(1) If $\hat{Q} = \hat{x}$, and $|f\rangle = |x\rangle = g_y$, then

$$c = \Psi(x, t) = \langle x | \mathfrak{S}(t) \rangle.$$

(2) If $\hat{Q} = \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$, and $|f\rangle = |p\rangle = f_p$, then

$$c = \Phi(p, t) = \langle p | \mathfrak{S}(t) \rangle.$$

(3) If $\hat{Q} = \hat{H}$, and $|f\rangle = |n\rangle$, then

$$c_n = \langle n | \mathfrak{S}(t) \rangle.$$

2. Operators (represent Observables) are linear transformations:

$$|\beta\rangle = \hat{Q}|\alpha\rangle,$$

where $|\alpha\rangle = \sum a_n |e_n\rangle$ and $|\beta\rangle = \sum b_n |e_n\rangle$. And

$$|\beta\rangle = \sum b_n |e_n\rangle = \hat{Q}|\alpha\rangle = \sum_n a_n \hat{Q} |e_n\rangle,$$

taking the inner product with $|e_m\rangle$:

$$b_m = \sum_n a_n \langle e_m | \hat{Q} | e_n \rangle = \sum_n Q_{mn} a_n,$$

namely:

$$Q_{mn} = \langle e_m | \hat{Q} | e_n \rangle. \quad (16)$$

3. Projection Operator: $\hat{P} = |\alpha\rangle \langle \alpha|$, where $|\alpha\rangle$ is a normalized vector.

$$\text{e. g. } \hat{P}|\beta\rangle = |\alpha\rangle \langle \alpha | \beta \rangle = \langle \alpha | \beta \rangle |\alpha\rangle,$$

where $\langle \alpha | \beta \rangle$ is the projection of $|\beta\rangle$ in the direction of $|\alpha\rangle$. Therefore, we know:

$$\sum_n |e_n\rangle \langle e_n| = 1,$$

for $\sum_n |e_n\rangle \langle e_n | \beta \rangle = |\beta\rangle$.

4. Commutator's property:

$$[AB, C] = A[B, C] + [A, C]B. \quad (17)$$

3.7 Physical Significance of Commutators

Theorem *If operator \hat{H} and \hat{Q} share a complete set of eigenfunctions, then these two operators commute with each other.*

Proof *If the two operators share a complete set of eigenfunctions $\{\phi_n\}$,*

$$\hat{H}\phi_n = E_n\phi_n, \text{ and } \hat{Q}\phi_n = q_n\phi_n,$$

we can get

$$[\hat{H}, \hat{Q}]\phi_n = \hat{H}\hat{Q}\phi_n - \hat{Q}\hat{H}\phi_n = E_n q_n \phi_n - q_n E_n \phi_n = 0.$$

As $\{\phi_n\}$ are complete, i.e., $\forall \Phi \in \text{Hilbert Space } L_2(a, b), \exists c_n \text{ satisfy } \Phi = \sum c_n \phi_n$, we can get

$$[\hat{H}, \hat{Q}]\Phi = \sum c_n [\hat{H}, \hat{Q}]\phi_n = 0.$$

So the two operators commute with each other. □

Theorem (converse) *If two operators commute with each other, i.e., $[\hat{H}, \hat{Q}] = 0$, operator \hat{H} and \hat{Q} share a complete set of eigenfunctions.*

Proof *If ϕ_n is a complete set of eigenfunctions of operator \hat{H} (nondegenerate), namely,*

$$\hat{H}\phi_n = E_n\phi_n,$$

and if $[\hat{H}, \hat{Q}] = 0$, we can get

$$\hat{H}\hat{Q}\phi_n - \hat{Q}\hat{H}\phi_n = 0 \Rightarrow \hat{H}\hat{Q}\phi_n = E_n\hat{Q}\phi_n.$$

So $\hat{Q}\phi_n$ is also an eigenfunction of operator \hat{H} corresponding to the same eigenvalue E_n , which means $\hat{Q}\phi_n$ and ϕ_n differ only by a constant, i.e.,

$$\hat{Q}\phi_n = c_n\phi_n.$$

So $\{\phi_n\}$ are also the eigenfunctions of operator \hat{Q} . And we can get the similar results for degenerate cases. □

Conclusion:

$[\hat{H}, \hat{Q}] = 0$ is the **Necessary and Sufficient Condition** of that operator \hat{H} and \hat{Q} share a complete set of eigenfunctions.

$[\hat{H}, \hat{Q}] = 0$ means these two observables can **be measured simultaneously**, or in another word, these two observables can **have determinate values at the same time**. (cf. section 3.5 The Uncertainty Principle).

4 Quantum Mechanics in Three Dimensions

4.1 Spherical Coordinates

Schrödinger equation $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$, and $\hat{p} = \frac{\hbar}{i}\nabla$, namely:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi. \quad (18)$$

The time-independent schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi. \quad (19)$$

In spherical coordinates:

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

where θ is the polar angle and ϕ is the azimuthal angle. Solve Schrödinger equation(19) by the method of separation of variables:

$$\psi(x, \theta, \psi) = R(r)Y(\theta, \psi), \text{ and } Y(\theta, \psi) = \Theta(\theta)\Phi(\phi),$$

and the separation constant is $l(l+1)$ and m^2 respectively. Therefore:

$$\Phi(\psi) = e^{im\phi},$$

and we know $\Phi(\phi + 2\pi) = \Phi(\phi)$, so $m = 0, \pm 1, \pm 2 \dots$ And

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

so $l > 0$, and $l \geq |m|$. For $\forall l = 0, 1, 2, \dots$, $m = \underbrace{-l, -l+1, \dots, -1, 0, 1, \dots, l-1, l}_{2l+1 \text{ terms}}$.

The normalization condition of angular equation is:

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

and the normalized angular wave function are called **Spherical Harmonics**:

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

where $\varepsilon = (-1)^m$ when $m \geq 0$, and $\varepsilon = 1$ when $m \leq 0$. And

$$\int_0^{2\pi} \int_0^\pi Y_l^m Y_{l'}^{m'} \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'},$$

where l is called azimuthal quantum number and m is called magnetic quantum number.

To solve the radial equation, let $u(r) = rR(r)$, so that the normalization condition becomes:

$$\int_0^\infty |R(r)|^2 r^2 dr = 1 \Rightarrow \int_0^\infty |u|^2 dr = 1,$$

and the radial function becomes:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu, \quad (20)$$

we can see that there exists an effective potential:

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

Then We can get the solution to the radial equation:

$$R(r) = A j_l(kr), \quad k = \frac{\sqrt{2mE}}{\hbar},$$

where $j_l(x)$ is the spherical Bessel function of order l . And the boundary conditions:

$$\begin{aligned} R(a) &= 0; \\ ka &= \beta_{nl}, \end{aligned}$$

in which β_{nl} is the n th zero of the l th spherical Bessel function.

4.2 Hydrogen Atom

1. For hydrogen atom, potential energy:

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

and the radial equation(20) says:

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

Let $\kappa = \frac{\sqrt{-2mE}}{\hbar}$, and $\rho = \kappa r$, $\rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa}$, we can get the famous **Bohr Formula**:

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots \quad (21)$$

and from $\rho_0 = 2n$ and $n \equiv j_{\max} + l + 1$, we can derive that

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{an}, \quad \text{and } \rho = \frac{r}{an},$$

and the so-called **Bohr Radius**:

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

Also $l = 0, 1, \dots, n-1$, the total degeneracy of energy level E_n is $d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2$. Therefore, the normalized hydrogen wave function is (associated Laguerre polynomial) ...

2. The spectrum of hydrogen:

$$E_\gamma = E_i - E_f = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right),$$

namely,

$$h\nu = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right), \text{ where } \hbar = \frac{h}{2\pi},$$

i.e.,

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \text{ where the **Rydberg Constant** is } R = \frac{m}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2.$$

And

n_f	Spectrum series
1	Lyman
2	Balmer
3	Paschen

4.3 Angular Momentum

Angular momentum: $\vec{L} = \vec{r} \times \vec{p}$, and

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x.$$

We can derive that

$$[r_i, r_j] = [p_i, p_j] = 0,$$

and

$$[r_i, p_j] = i\hbar \delta_{ij} = -[p_i, r_j].$$

Therefore, $[L_x, L_y] = i\hbar L_z$... And

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

namely, $\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|$... And

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0,$$

namely, $[L^2, \vec{L}] = 0$.

If

$$\begin{aligned} L^2 f &= \lambda f; \\ L_z f &= \mu f, \end{aligned}$$

let $L_{\pm} = L_x \pm iL_y$, we know $[L_z, L_{\pm}] = \pm \hbar L_{\pm}$ and $[L^2, L_{\pm}] = 0$, then

$$\begin{aligned} L^2(L_{\pm}f) &= \lambda(L_{\pm}f); \\ L_z(L_{\pm}f) &= (\mu \pm \hbar)(L_{\pm}f). \end{aligned}$$

Then $L^2 = L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z$, we can derive that:

$$\begin{aligned} L^2 f_l^m &= \hbar^2 l(l+1) f_l^m; \\ L_z f_l^m &= \hbar m f_l^m, \end{aligned}$$

where $m = -l, -l+1, \dots, l-1, l$ and $l = 0, 1/2, 1, 3/2, \dots$, also

$$L_{\pm} f_l^m = \hbar \sqrt{l(l+1) - m(m \pm 1)} f_l^{m \pm 1}. \quad (22)$$

When one tries to find the eigenfunctions of the operator L^2 and L_z , he will find that the secular equations of L^2 and L_z are precisely the **angular equation** and **azimuthal equation**, respectively.

$$\begin{aligned} L^2 f_l^m &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] f_l^m = \hbar^2 l(l+1) f_l^m. \\ L_z f_l^m &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} f_l^m = \hbar m f_l^m. \end{aligned}$$

The result is the spherical harmonics, $Y_l^m(\theta, \phi)$, *i.e.*, spherical harmonics are eigenfunctions of L^2 and L_z . When we solved the Schrödinger equation by separation of variables, we were inadvertently constructing simultaneous eigenfunctions of the three commuting operators H , L^2 and L_z , namely,

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 l(l+1)\psi, \quad L_z\psi = \hbar m\psi.$$

There is a curious final twist to this story, for the algebraic theory of angular momentum permits l (and hence also m) to take on **half-integer** values, whereas separation of variables yielded eigenfunctions only for **integer** values. You might suppose that the half-integer solutions are spurious, but it turns out that they are of profound importance (spin angular momentum), as we shall see in the following sections.

4.4 Spin

Similarly,

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y.$$

Also

$$\begin{aligned} S^2 |sm\rangle &= \hbar^2 s(s+1) |sm\rangle; \\ S_z |sm\rangle &= \hbar m |sm\rangle, \end{aligned}$$

where $|sm\rangle$ is the eigenstate of spin, and it is not a function, so we use a vector to represent it. Let $S_{\pm} = S_x \pm iS_y$, then

$$S_{\pm} |sm\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)} |s(m \pm 1)\rangle, \quad (23)$$

where $s = 0, 1/2, 1, 3/2, \dots$ and $m = -s, -s+1, \dots, s-1, s$, and there is no *priori* reason to exclude the half-integer values of s and m , which differs from what we have interpreted about the angular momentum quantum number l in the preceding section. (To be more precisely, s is exactly the half-integer values we excluded from l of last section, and the algebraically derived l actually represents a kind of more general angular momentums including both orbital and spin angular momentums.)

For $s = 1/2$, there are just two eigenstate $|\frac{1}{2} \frac{1}{2}\rangle$ and $|\frac{1}{2} (-\frac{1}{2})\rangle$, which we call spin up (\uparrow) and spin down (\downarrow). Then we can use spinor to represent the general state:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-,$$

in which $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ (\uparrow) and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ (\downarrow). Therefore:

$$S^2 \chi_+ = S^2 |\frac{1}{2} \frac{1}{2}\rangle = \hbar^2 \frac{1}{2} \times \frac{3}{2} |\frac{1}{2} \frac{1}{2}\rangle = \frac{3}{4} \hbar^2 \chi_+,$$

similarly, $S^2 \chi_- = \frac{3}{4} \hbar^2 \chi_-$, so

$$S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

And $S_z \chi_+ = \frac{1}{2} \hbar \chi_+$, $S_z \chi_- = -\frac{1}{2} \hbar \chi_-$, so

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Also $S_+ \chi_+ = S_- \chi_- = 0$, $S_+ \chi_- = \hbar \chi_+$, $S_- \chi_+ = \hbar \chi_-$, so

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix},$$

then, we can use $S_{\pm} = S_x \pm iS_y$ to get S_x and S_y .

Therefore,

$$\vec{S} = \frac{\hbar}{2} \sigma,$$

where σ is called **Pauli Spin Matrix**:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Magnetic dipole momentum

$$\vec{\mu} = \gamma \vec{S},$$

and Hamiltonian

$$H = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{B} \cdot \vec{S}.$$

...

Two spin-1/2 particle:

$$s = 1 \text{ (triplet)} \quad \left\{ \begin{array}{l} |11\rangle = \uparrow\uparrow, \\ |10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow), \\ |1-1\rangle = \downarrow\downarrow, \end{array} \right.$$

and

$$s = 0 \text{ (singlet)} : \quad |00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow).$$

5 Identical Particles

5.1 Two-Particle System

Wave function $\Psi(\vec{r}_1, \vec{r}_2, t)$ satisfy Schrödinger equation:

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

in which $H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$.

1. Distinguishable particles:

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2).$$

2. Indistinguishable particles:

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = A[\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) \pm \Psi_a(\vec{r}_2)\Psi_b(\vec{r}_1)],$$

where "+" represents **Bosons** (integer spin), and "-" represents **Fermions** (half integer spin).

3. Pauli Exclusion Principle: if $\Psi_a = \Psi_b$, then $\Psi_{-}(\vec{r}_1, \vec{r}_2) = 0$.

4. Exchange symmetric/antisymmetric: $\Psi(\vec{r}_1, \vec{r}_2) = \pm \Psi(\vec{r}_2, \vec{r}_1)$.

5. Exchange force:

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle (x_1 - x_2)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2,$$

where $\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b$, and $\langle x \rangle_{ab} = \int x \Psi_a^* \Psi_b dx$. Therefore,

the upper sign : bosons \Rightarrow bonding,

the lower sign : fermion \Rightarrow antibonding.

For electrons: the complete state is

$$\Psi(\vec{r})\chi(\vec{s}),$$

where $\Psi(\vec{r})$ is antisymmetric with respect to exchange. So if $\chi(\vec{s})$ is singlet (antisymmetric), the complete state is symmetric which should lead to *bonding* (**Covalent Bond**). And if $\chi(\vec{s})$ is triplet (symmetric), it should lead to *antibonding*.

6 Time-Independent Perturbation Theory

6.1 Nondegenerate Perturbation

1. First-Order Theory:

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle, \quad (24)$$

and $\psi_n^1 = \sum_{m \neq n} C_m^{(n)} \psi_m^0$, then

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0.$$

2. Second-Order Energies:

$$\begin{aligned} E_n^2 &= \langle \psi_m^0 | H' | \psi_n^1 \rangle \\ &= \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{(E_n^0 - E_m^0)} \\ &= \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{(E_n^0 - E_m^0)}. \end{aligned}$$

6.2 Degenerate Perturbation

The matrix elements of H' : $W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$. And $W_{ab} = W_{ba}^* = \langle \psi_a^0 | H' | \psi_b^0 \rangle$, then

$$E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right].$$

Matrix form:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

If $[A, H'] = 0$, $Af = \mu f$, and we use f as ψ_n^0 , the W matrix will automatically be diagonal.

6.3 Fine Structure of Hydrogen

Two distinct mechanisms: **Relativistic Correction** and **Spin-Orbit Coupling**. And the famous *FineStructureConstant*:

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}.$$

6.3.1 Relativistic Correction

The relativistic kinetic energy:

$$\begin{aligned} T &= \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \\ &= mc^2 \left(\sqrt{1 + \left(\frac{p}{mc} \right)^2} - 1 \right) \\ &= mc^2 \left(\frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 + \dots \right) \\ &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots \end{aligned}$$

so $H_r^1 = -\frac{p^4}{9m^3c^2}$. With equation (24),

$$E_n^1 = \langle H_r^1 \rangle = -\frac{1}{8m^3c^2} \langle \psi | p^4 | \psi \rangle = -\frac{1}{8mc^3c^2} \langle p^2 \psi | p^2 \psi \rangle,$$

and $p^2\psi = 2m(E - V)\psi$ (Schrödinger equation), then

$$E_n^1 = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} (E^2 - 2E \langle V \rangle + \langle V^2 \rangle).$$

For hydrogen atom:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a},$$

where a is Bohr radius.

6.3.2 Spin-Orbit Coupling

From electron's point of view:

- (1) proton circling around electron $\Rightarrow \vec{B} \Rightarrow$ orbit,
- (2) electron spin $\Rightarrow \vec{\mu} \Rightarrow$ spin,

(1) The magnetic field:

$$\vec{B} = \frac{\mu_0}{4\pi} \int \frac{I}{r^2} d\vec{l} = \frac{\mu_0 I}{2r},$$

where $I = \frac{e}{T}$, $L = rp = rm \frac{2\pi r}{T} = \frac{2\pi m r^2}{T}$. Therefore:

$$\vec{B} = \frac{1}{4\pi\epsilon_0} \cdot \frac{e}{mc^2 r^3} \vec{L}.$$

(2) The magnetic dipole moment:

$$\mu = I \cdot \pi r^2, \quad I = \frac{q}{T}, \quad S = \frac{2\pi m r^2}{T},$$

where S is the spin angular momentum. Therefore the **Gyromagnetic Ratio**:

$$\gamma = \frac{\mu}{S} = \frac{q}{2m},$$

namely $\vec{\mu} = \left(\frac{q}{2m}\right) \vec{S}$. For electrons, it actually is $\vec{\mu} = -\frac{e}{m} \vec{S}$.

Therefore,

$$H'_{\text{so}} = -\vec{\mu} \cdot \vec{B} = \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L},$$

after making a appropriate correction, it becomes:

$$H'_{\text{so}} = \left(\frac{e^2}{8\pi\epsilon_0}\right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}.$$

The total angular momentum $\vec{J} = \vec{L} + \vec{S}$. The Hamiltonian no longer commutes with \vec{L} and \vec{S} , H'_{so} does commutes with L^2 , S^2 and \vec{J} , and

$$\vec{L} \cdot \vec{S} = \frac{1}{2}(J^2 - L^2 - S^2) = \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)].$$

6.3.3 Zeeman Effect

For a single electron, the perturbation is

$$H'_Z = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{\text{ext}},$$

where $\vec{\mu}_l = -\frac{e}{2m}\vec{L}$ is the dipole momentum associated with orbital motion, and $\vec{\mu}_s = -\frac{e}{m}\vec{S}$ is the magnetic dipole momentum associated with electron spin. Then

$$H'_Z = \frac{e}{2m}(\vec{L} + 2\vec{S}) \cdot \vec{B}_{\text{ext}}.$$

(1) When $B_{\text{ext}} \ll B_{\text{int}}$, the fine structure dominates, H'_z is perturbation. Then

$$E_Z^1 = \frac{e}{2m}\vec{B}_{\text{ext}} \cdot \langle \vec{L} + 2\vec{S} \rangle.$$

We know that $\vec{L} + 2\vec{S} = \vec{J} + \vec{S}$, and the total angular momentum \vec{J} is a constant (see Figure 1), so the average value of \vec{S} :

$$\vec{S}_{\text{ave}} = \frac{(\vec{S} \cdot \vec{J})}{J^2} \vec{J}.$$

Therefore,

$$\begin{aligned} \langle \vec{L} + 2\vec{S} \rangle &= \langle (1 + \frac{\vec{S} \cdot \vec{J}}{J^2}) \vec{J} \rangle \\ &= \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] \langle \vec{J} \rangle \\ &= g_J \langle \vec{J} \rangle, \end{aligned}$$

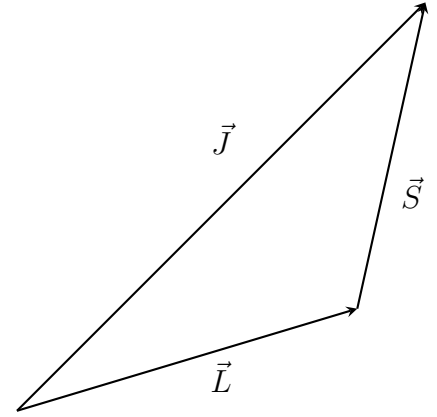


Figure 1: $\vec{J} = \vec{L} + \vec{S}$ is a constant.

where g_J is known as **Landé g-factor**. Then

$$E_Z^1 = \frac{e}{2m}g_J\vec{B}_{\text{ext}} \cdot \langle \vec{J} \rangle,$$

if we choose \vec{B}_{ext} along z -axis, then

$$E_Z^1 = \frac{e}{2m}g_JB_{\text{ext}}\hbar m_j = \mu_B g_J B_{\text{ext}} m_j,$$

where $\mu_B = \frac{e\hbar}{2m}$ is the so-called **Bohr Magnetron**.

(2) When $B_{\text{ext}} \gg B_{\text{int}}$...

(3) Neither H'_Z or H'_{fs} dominates, then $H' = H'_Z + H'_{\text{fs}}$...

7 Variational Principle

Prove:

$$E_{\text{gs}} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle.$$

Poof: we can express ψ as $\psi = \sum C_n \psi_n$, then

$$1 = \langle \psi | \psi \rangle = \left\langle \sum C_m \psi_m \middle| \sum C_n \psi_n \right\rangle = \sum_m \sum_n C_m^* C_n = \sum_n |C_n|^2,$$

therefore

$$\langle H \rangle = \sum_n E_n |C_n|^2 \geq \sum_n E_{\text{gs}} |C_n|^2 = E_{\text{gs}}.$$

The most common "trial" wave function is

$$\psi(x) = A e^{-bx^2},$$

and the ground state hydrogen atom wave function

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}.$$

8 WKB Approximation

The classic momentum of a particle is $p(x) \equiv \sqrt{2m[E - V(x)]}$, then

$$\psi(x) \approx \frac{C}{\sqrt{p(x)}} e^{\pm \frac{i}{\hbar} \int p(x) dx}.$$