Introduction to Quantum Mechanics

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2019-6

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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:

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

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

2. Indeterminacy

3. Interpretation: Orthodox position = Copenhagen interpretation
Agnostic position

4.

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

5. Normalization

Prove: $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{-\infty}^{\infty}|\Psi(x,t)|^2\mathrm{d}x = 0$

Proof:

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

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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7.

$$< x > = \int \Psi^*(x)\Psi\mathrm{d}x$$
$$< p > = \int \Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\mathrm{d}x$$

8. The uncertainty principle:

$$p = \frac{h}{\lambda} = \hbar k$$
$$\sigma_x\sigma_p \geqslant \frac{\hbar}{2}$$

2 Time-independent Schrödinger Equation

2.1 Stationary States

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

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

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

$$\hat{H}\Psi = E\Psi \tag{2}$$

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

$$\sum_{n=1}^{\infty} |C_n|^2 = 1, \tag{3}$$

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

2.2 Infinite Square Well

In a infinite square well:

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

namely:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar}\psi = -k^2\psi \tag{5}$$

in which:

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

We know the solution to equation(5) is:

$$\psi = A\sin kx + B\cos kx. \tag{6}$$

Boundary conditions:

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

we can get $B = 0$, and $ka = 0, \pm\pi, \pm 2\pi ...$, namely:

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

Therefore,

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

$$\begin{aligned}\psi_n(x) &= \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) &(7)\\ \Psi_n(x,t) &= \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\exp\left(-i\frac{n^2\pi^2\hbar}{2ma^2}t\right). &(8)\end{aligned}$$

2.3 Harmonic Oscillator

Hooke's Law:

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

namely,

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

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:

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

2.3.1 Ladder Operator

1. Hamiltanion: $H = \frac{1}{2m}[\,p^2 + (m\omega x)^2]$, 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 Hamiltanion:

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

and Schrödinger equation (9) become:

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

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 $a_- = \frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{\partial}{\partial x} + m\omega x\right)$, 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):

$$\hbar\omega(a_+a_- + \frac{1}{2})\psi_0 = E_0\psi_0$$

$$\hbar\omega \cdot \frac{1}{2}\psi_0 = E_0\psi_0,$$

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,

$$
\begin{aligned}
a_+a_-\psi_n &= n\psi_n & (12)\\
a_-a_+\psi_n &= (n+1)\psi_n. & (13)
\end{aligned}
$$

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

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

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

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

Q. E. D.

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

Proof:

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

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

Q. E. D.

2.3.2 Analytic Method

Schrödinger equation of harmonic oscillator (9):

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

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

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

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:

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

2.4 Free Particle

Schrödinger equation with $V = 0$:

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

then

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

Solution to this equation:

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

Therefore,

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

$$k = \pm\frac{\sqrt{2mE}}{\hbar} \begin{cases} + : & \text{right;} \\ - : & \text{left.} \end{cases}$$

And

$$v_{phase} = v_{quantum} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}},$$

$$v_{class} = \frac{2E}{m} = 2v_{quantum}.$$

k is continuous spectrum, so

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

and

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

the coefficient:

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

and

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

2.5 Delta-function Potential

For different E:

$$\text{boundary state} : E < 0;$$
$$\text{scattering state} : E > 0.$$

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:

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

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 $x \to -\infty$),

similarly, $\psi(x) = Fe^{-\kappa x}$ $(x > 0)$.
The standard boundary conditions for ψ:

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

Integrating Schrödinger equation:

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

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

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

Now, we know that $B = F$, and $\left.\dfrac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-} = B\kappa,\ \left.\dfrac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{+} = -B\kappa$, so

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

then,

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

Normalizing ψ,

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

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:

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

Solution to this equation:

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

using the standard boundary conditions again:

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

and

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

so

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

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

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

The reflection coefficient R and transmission coefficient T:

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

2.6 Finite Square Well

The potential function of a finite square well is

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

(1) $E < 0$:
When $x < -a$, Schrödinger equation:

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

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

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

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:

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

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 $G = 0$ ...

3 Formalism

3.1 Hilbert Space

Square-integrable function:

$$f(x) \ \Rightarrow \ \int_a^b |f(x)|^2 \mathrm{d}x < \infty,$$

all such functions constitutes a vector space **Hilbert Space**[1].
Inner product of two functions:

$$\langle f|g\rangle = \int_a^b f(x)^* g(x) \mathrm{d}x,$$

and

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

Schwarz inequality:

$$\left|\int_a^b f(x)^* g(x) \mathrm{d}x\right| \leqslant \sqrt{\int_a^b |f(x)|^2 \mathrm{d}x \int_a^b |g(x)|^2 \mathrm{d}x}. \tag{14}$$

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

[1] Mathematicians 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

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

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 $\hat{p}$:

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

Momentum space wave function:

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

(Position space) wave function:

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

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:

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

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

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

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

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

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

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: $\Delta t\Delta E \geqslant \frac{\hbar}{2}$.
Proof:

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

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

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

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

$$\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\langle[\hat{H},\hat{Q}]\rangle. \tag{15}$$

Therefore:

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

Define

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

3.6 Dirac Notation

1. We use a vector in Hilbert Space $|\Im(t)\rangle$ 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 $|\Im(t)\rangle = \int c\,|f\rangle\,\mathrm{d}q$.

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

$$c = \Psi(x,t) = \langle x|\Im(t)\rangle\,.$$

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

$$c = \Phi(p,t) = \langle p|\Im(t)\rangle\,.$$

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

$$c_n = \langle n|\Im(t)\rangle\,.$$

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:

$$Q_{mn} = \langle e_m|\,\hat{Q}\,|e_n\rangle\,. \tag{16}$$

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:

$$[AB,C] = A[B,C] + [A,C]B. \tag{17}$$

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 $\{\phi_n\}$,*

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

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., $\forall \Phi \in$ Hilbert Space $L_2(a, b)$, $\exists c_n$ satisfy $\Phi = \sum c_n\phi_n$, we can get

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

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 $\{\phi_n\}$ 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:

Two operators commutes, $[\hat{H}, \hat{Q}] = 0$ 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 compatible 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:

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

The time-independent schrödinger equation:

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

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 $m = 0, \pm1, \pm2...$ And

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

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

The normalization condition of angular equation is:

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

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

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

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

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

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:

$$\int_0^\infty |R(r)|^2 r^2 \mathrm{d}r = 1 \;\Rightarrow\; \int_0^\infty |u|^2 \mathrm{d}r = 1,$$

and the radial function becomes:

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

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:

$$R(r) = Aj_l(kr),\; k = \frac{\sqrt{2mE}}{\hbar},$$

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 nth zero of the lth spherical Bessel function.

4.2 Hydrogen Atom

1. For hydrogen atom, potential energy:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r},$$

and the radial equation(20) says:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu.$$

Let $\kappa = \dfrac{\sqrt{-2mE}}{\hbar}$, and $\rho = \kappa r$, $\rho_0 = \dfrac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}$, we can get the famous **Bohr Formula**:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2},\; n = 1, 2, 3, \ldots \tag{21}$$

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

$$\kappa = \left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an},\text{ and } \rho = \frac{r}{an},$$

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

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \approx 0.529 \times 10^{-10} m.$$

Also $l = 0, 1, \cdots n-1$, 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.,

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \text{ where the } \textbf{Rydberg Constant} \text{ is } R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2.$$

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

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

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

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

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

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

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

$$L^2 f = \lambda f;$$
$$L_z f = \mu f,$$

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

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

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 $m = -l, -l+1, \cdots l-1, l$ and $l = 0, 1/2, 1, 3/2 \ldots$, also

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

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.

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

$$L_z f_l^m = \frac{\hbar}{i}\frac{\partial}{\partial\phi} f_l^m = \hbar m f_l^m.$$

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 seperation of variables (in spherical coordiantes, we can also get spherical harmonic solutions, cf. preceding sections), we were inadvertently constructing simultaneous eigenfunctions of the three commuting operators H, L^2 and L_z (because they share a complete set of eigenfunctions — spherical harmonics), 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,

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

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

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

where $s = 0, 1/2, 1, 3/2 \ldots$ and $m = -s, -s+1, \cdots s-1, s$, 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

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

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**:

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

Magnetic dipole momentum

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

and Hamiltanion

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

...

Two spin-1/2 particle:

$$s = 1 \text{ (triplet) } \begin{cases} |11\rangle = \uparrow\uparrow, \\ |10\rangle = \dfrac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow), \\ |1 -1\rangle = \downarrow\downarrow, \end{cases}$$

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

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

$$\begin{aligned} \text{the upper sign} &: \text{ bosons } \Rightarrow \text{ bonding,} \\ \text{the lower sign} &: \text{ fermion } \Rightarrow \text{ antibonding.} \end{aligned}$$

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:

$$E_n^1 = \langle\psi_n^0|\, H'\, |\psi_n^0\rangle\,, \tag{24}$$

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 $FineStructureConstant$:

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}.$$

6.3.1 Relativistic Correction

The relativistic kinetic energy:

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

so $H_r^1 = -\dfrac{p^4}{9m^3c^2}$. 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

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

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:

$$\begin{aligned} &(1) \text{ proton circling around electron } \Rightarrow \vec{B} \Rightarrow \text{ orbit,} \\ &(2) \text{ electron spin } \Rightarrow \vec{\mu} \Rightarrow \text{ spin,} \end{aligned}$$

(1) The magnetic field:

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

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

$$\vec{B} = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e}{mc^2r^3}\vec{L}.$$

(2) The magnetic dipole moment:

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

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

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

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

$$H'_{\text{so}} = -\vec{\mu} \cdot \vec{B} = \left(\frac{e^2}{4\pi\varepsilon_0}\right) \frac{1}{m^2c^2r^3} \vec{S} \cdot \vec{L},$$

after making a appropriate correction, it becomes:

$$H'_{\text{so}} = \left(\frac{e^2}{8\pi\varepsilon_0}\right) \frac{1}{m^2c^2r^3} \vec{S} \cdot \vec{L}.$$

The total angular momentum $\vec{J} = \vec{L} + \vec{S}$. The Hamiltanion 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 $\vec{\mu}_l = -\dfrac{e}{2m}\vec{L}$ is the dipole momentum associated with orbital motion, and $\vec{\mu}_s = -\dfrac{e}{m}\vec{S}$ 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

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

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,

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

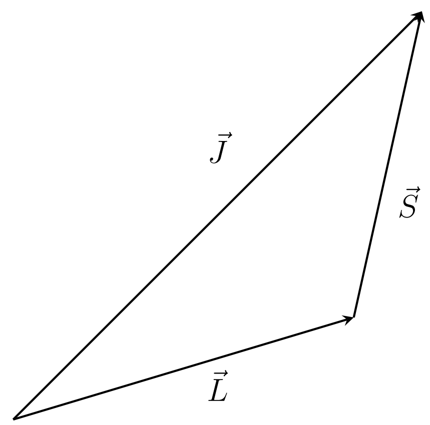

Figure 1: $\vec{J} = \vec{L} + \vec{S}$ is a constant.

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

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

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

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

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

(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:

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

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

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

therefore

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

The most common "trial" wave function is

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

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

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