Introduction to Quantum Mechanics

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Contents

Abstract

To review the *Introduction to Quantum Mechanics*...

1 Wave Function

1. Schrödinger equation:

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

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:

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

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

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

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

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,

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

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

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

2.3 Harmonic Oscillator

Hooke's Law:

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

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

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:

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

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,

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

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

Proof:

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

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

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2.3.2 Analytic Method

Schrödinger equation of harmonic oscillator (9):

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

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:

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

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 $\beta = \frac{m\alpha}{\hbar^2 k}$, 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 $\hat{p}$:

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

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 $\frac{\mathrm{d}\hat{Q}}{\partial t} = 0$, 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 $|\Im(t)\rangle = \displaystyle\int c\,|f\rangle\,\mathrm{d}q$.

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

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

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

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

2. Operators (representint 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.

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

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:

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

4 Quantum Mechanics in Three Dimensions

4.1 Spherical Coordinates

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

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

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:

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

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

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

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

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 $l = 0, 1, \ldots n-1$, 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,

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

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

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

$$L_\pm f_l^m = \hbar\sqrt{l(l+1) - m(m \pm 1)} f_l^{m\pm1}. \tag{22}$$

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

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

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

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

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

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

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:

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

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:

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

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 $\langle x\rangle_{ab} = \int x\Psi_a^*\Psi_b \mathrm{d}x$. Therefore,

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

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 momentum:

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

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

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

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

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

We know $\vec{L}+2\vec{S} = \vec{J}+\vec{S}$, 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,

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

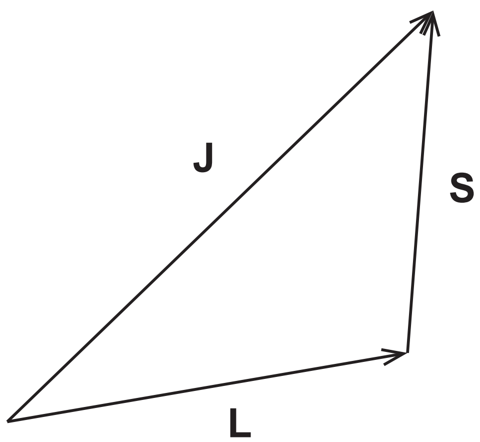

Figure 1: $\vec{J} = \vec{L} + \vec{S}$

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

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

:wqif 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 $\mu_B = \frac{e\hbar}{2m}$ 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

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

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

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