§ Quantum Mechanics

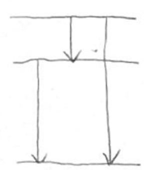
★ Historical Background

- Determinism vs Free Will
- Experimental observations

1. Stable atomic model

- classical electrodynamics ⇒ E&M radiation ⇒ { collapse of electrons / continuous spectrum

- hydrogen atom



Bohr, 1922 Nobel

$$E_n = \frac{E_1}{n^2}, \quad E_1 = -14.9\ eV$$

2. Black body radiation (thermal radiation)

- thermal radiation : thermal radiator, Draper point 525°C
  incardencent light bulb, Edison vs Tesla

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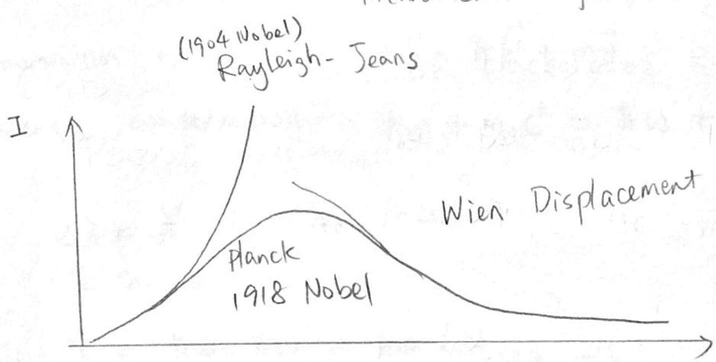


Wien Displacement Low, $\lambda_{max} T = b$, 1918 Nobel
measurement of T.

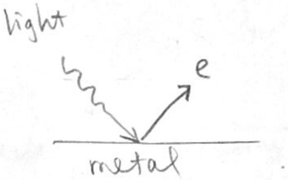
$$I(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

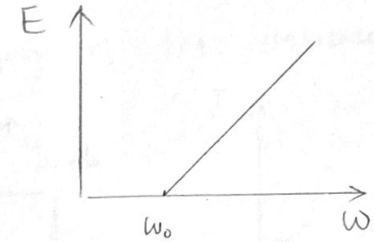
- CMB (Cosmic Microwave Background Radiation) 3K

  Penzias-Wilson at Bell lab, 1978 Nobel

  Smoot-Mather, anisotropy of CMB, 2006 Nobel

3. Photoelectric effect



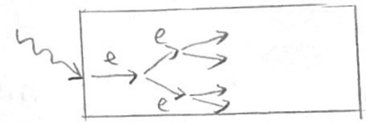


$E = \hbar(\omega - \omega_0)$ Einstein 1921 Nobel

v.s.

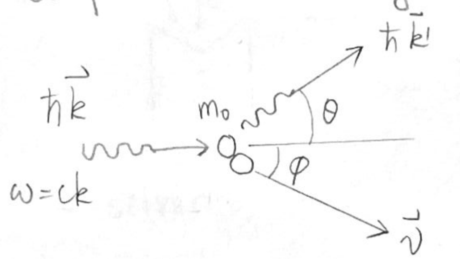
$\vec{S} = \frac{1}{\mu_0}\vec{E}\times\vec{B}$

- photomultiplier



scintillation detector

4. Compton scattering 1927 Nobel



$m = \gamma m_0 = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$.

$\begin{cases} \text{momentum conservation} & \hbar\vec{k} = \hbar\vec{k}' + m\vec{v} \\ \text{energy conservation} & \hbar\omega + m_0c^2 = \hbar\omega' + mc^2 \end{cases}$

$\Rightarrow$ $\Delta\lambda = \lambda' - \lambda = \lambda_c(1-\cos\theta)$, $\lambda_c = \frac{2\pi\hbar}{m_0 c} = 2.426\times10^{-12}\,m$ Compton wavelength

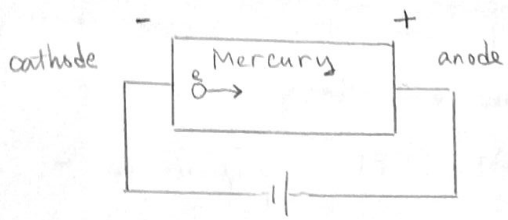
$\uparrow$ Compton shift

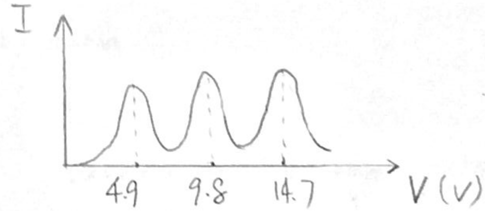
$T = \hbar\omega - \hbar\omega' = \hbar\omega\left(1 + \frac{\lambda}{2\lambda_c\sin^2\theta}\right)^{-1}$

$\uparrow$ kinetic energy of the recoil electron

5. Franck - Hertz 1926 Nobel

Nephew of the frequency Hertz

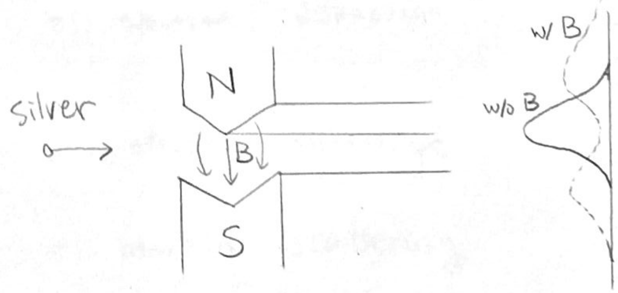




6. Stern - Gerlach

Stern → 1943 Nobel

Gerlach → Nazi Germany, no Nobel



angular momentum (directional) quantization

- silver
- electron
- nulear spin → NMR, MRI

• Wave-particle Duality

1-6: continuous $\longrightarrow$ discrete quanta

$$\begin{cases} \text{1-4: light: wave} \longrightarrow \text{particle/photon} \\ \text{1,5,6 electron: particle} \longrightarrow \text{wave} \end{cases}$$

- de Broglie. 1929 Nobel wave $\Leftrightarrow$ particle (wave packet)

$$\cdot \begin{cases} E = \hbar\omega \\ \vec{p} = \hbar\vec{k}, \quad k = \frac{2\pi}{\lambda} \end{cases}$$

wave: non-localized

$$\Psi(\vec{r}, t) = \Psi_0 e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

- electron diffraction Thomson (son of J.J. Thomson)

Davisson - Germer 1937 Nobel

electron microscope $\lambda_e = 0.122\,\text{Å}$, $E = 10$ keV

- neutron scattering Shull-Brockhouse 1994 Nobel

★ Wave Mechanics

- Bohr: If you are not confused by quantum mechanics, you haven't really understood it.

Feynman: I think I can safely say that nobody understands quantum mechanics.

- Computation is understanding.
- The level of understanding is determined by the computational complexity and accuracy.

- Operator $\hat{A}$ and physical quantity $\langle A \rangle$

$$\Psi(\vec{r},t) = \Psi_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

$$\nabla \Psi = \Psi_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} (i\vec{k}) = i\vec{k}\Psi \quad , \quad \frac{\partial \Psi}{\partial t} = \Psi_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}(-i\omega) = -i\omega\Psi$$

$$-i\hbar\nabla\Psi = \hbar\vec{k}\Psi \qquad i\hbar\frac{\partial\Psi}{\partial t} = \hbar\omega\Psi$$

$$\boxed{\hat{p} = -i\hbar\nabla} \qquad \boxed{\hat{E} = i\hbar\frac{\partial}{\partial t} = \hat{H}}$$

- Any physical quantity $A(r,p) \longrightarrow \hat{A}(\hat{r},\hat{p}) = \hat{A}(r, -i\hbar\nabla)$

e.g. $\vec{L} = \vec{r}\times\vec{p} \longrightarrow \hat{L} = \vec{r}\times(-i\hbar\nabla)$

- Hamiltonian

$$H = E = \frac{\vec{p}^2}{2m} + V(\vec{r}) \longrightarrow \boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})}$$

Schrödinger Equation $\boxed{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\Psi(\vec{r},t)}$ 1933 Nobel

Klein-Gordon Equation $E^2 = p^2c^2 + m_0^2c^4$

$$\boxed{-\hbar^2\frac{\partial^2}{\partial t^2}\Psi(\vec{r},t) = \left[-\frac{\hbar^2c^2}{2m}\nabla^2 + m_0^2c^4\right]\Psi(\vec{r},t)}$$

spin loss particle : Higgs boson

Dirac Equation $\boxed{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = [\beta mc^2 + c(\alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3)]\Psi(\vec{r},t)}$ 1933 Nobel

spin $\frac{1}{2}$ particle

- Observable $\boxed{\langle A\rangle = \int \Psi^* A \Psi \, d^3\vec{r}}$ ⇐ also see eigen states/values

① one system many times (return to initial state)

② an ensemble of many identical systems

- Hermitian operator

$\langle A\rangle$ of physical quantity must be real $\langle A\rangle^* = \langle A\rangle$

$$\left(\int \Psi^* A \Psi d^3\vec{r}\right)^* = \int (A\Psi)^* (\Psi^*)^* d^3\vec{r} = \underline{\int (A\Psi)^* \Psi d^3\vec{r} = \int \Psi^* A \Psi d^3\vec{r}}$$

[If $\int (A^+\Psi)^* \Phi \, d^3\vec{r} = \int \Psi^* A \Phi \, d^3\vec{r}$, then A^+ is the Hermitian conjugate of A

- $(A^+)^+ = A$]

$$= \underline{\int (A^+\Psi)^* \Psi d^3\vec{r}} \Rightarrow \boxed{A^+ = A}$$

- All physical quantities are represented by Hermitian operators

- Eigen states and Eigen values of Hermitian operators

$\boxed{A\Psi_n = A_n \Psi_n}$ ⓪ A_n are real. Proof: $\int \Psi_n^* A \Psi_n dx = \int \Psi_n^* A_n \Psi_n dx = A_n$

$\qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \int (A\Psi_n)^* \Psi_n dx = A_n^*$

① Normalization $\boxed{\int \Psi_n^* \Psi_n d^3\vec{r} = 1}$

② Orthogonality $\boxed{\int \Psi_n^* \Psi_m d^3\vec{r} = \delta_{nm}}$

Proof: If $n \neq m$ $A\Psi_n = A_n \Psi_n$, $A\Psi_m = A_m \Psi_m$

$$\int \Psi_n^* A \Psi_m d^3\vec{r} = \int \Psi_n^* A_m \Psi_m d^3\vec{r}$$

$$\int \Psi_n^* A \Psi_m d^3\vec{r} = \int (A\Psi_n)^* \Psi_m d^3\vec{r}, \quad \int \Psi_n^* A_m \Psi_m d^3\vec{r} = A_m \int \Psi_n^* \Psi_m d^3\vec{r}$$

$$\int (A\Psi_n)^* \Psi_m d^3\vec{r} = A_n^* \int \Psi_n^* \Psi_m d^3\vec{r} = A_n \int \Psi_n^* \Psi_m d^3\vec{r}$$

If $A_n \neq A_m$ (no degeneracy), $\int \Psi_n^* \Psi_m d^3\vec{r} = 0$

③ completeness $\boxed{\Psi = \sum C_n \Psi_n}$, $C_n = \int \Psi_n^* \Psi d^3\vec{r}$

- $\langle A\rangle = \int \Psi^* A \Psi d^3\vec{r} = \int \left(\sum C_n \Psi_n\right)^* A \left(\sum C_m \Psi_m\right) d^3\vec{r} = \boxed{\sum |C_n|^2 A_n}$

- Copenhagen / Statistical Interpretation (Bohr, Bohn, $\cdots$) $\Leftrightarrow$ Schrödinger against

$|\Psi|^2 = \Psi^* \Psi \rightarrow$ probability density : non-deterministic, guiding field

- Ψ is not unique , $\Psi \rightarrow \Psi e^{i\alpha}$ same $|\Psi|^2$
- Incompleteness, hidden variable (Einstein, de Broglie)

  Bell inequality
- Measurement, collapse

- Probability conservation

$$\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0} \qquad \rho = \Psi^* \Psi \quad , \quad \vec{J} = ?$$

$$\frac{\partial \rho}{\partial t} = \frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t}$$

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

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

$$\frac{\partial \rho}{\partial t} = \left(-\frac{i\hbar}{2m} \nabla^2 \Psi^* + \cancel{\frac{i}{\hbar} V \Psi^*}\right) \Psi + \Psi^* \left(\frac{i\hbar}{2m} \nabla^2 \Psi - \cancel{\frac{i}{\hbar} V \Psi}\right)$$

$$= -\frac{i\hbar}{2m} \left(\Psi \nabla^2 \Psi^* - \Psi^* \nabla^2 \Psi\right) = -\frac{i\hbar}{2m} \nabla \cdot \left(\Psi \nabla \Psi^* - \Psi^* \nabla \Psi\right)$$

$$\vec{J} = \frac{i\hbar}{2m} \left(\Psi \nabla \Psi^* - \Psi^* \nabla \Psi\right) = \boxed{\frac{\hbar}{m} \operatorname{Im}\{\Psi^* \nabla \Psi\}}$$

e.g. $\Psi = \Psi_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$, $\rho = |\Psi_0|^2$, $\vec{J} = \frac{\hbar}{m} \operatorname{Im}\{\Psi_0^* e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \Psi_0$

$$\vec{J} = \frac{\hbar}{m} \operatorname{Im}\{\Psi_0^* e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \Psi_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} (i\vec{k})\} = \frac{\hbar \vec{k}}{m} |\Psi_0|^2 = \rho \vec{v}$$

- Continuity & smoothness of wave function

  ① Ψ is continuous

  ② $\frac{d\Psi}{dx}$ is continuous, except at ∞ potential

- If Ψ is not continuous, $\vec{p} = -i\hbar\nabla$ gives infinite momentum

  If $\frac{d\Psi}{dx}$ " " " " , $T = \frac{\hbar^2}{2m}\nabla^2$ gives infinite kinetic energy

- Also required by Schrödinger equation

- $|\Psi|^2$ probability is continuous and smooth

- Uncertainty Principle (Heisenberg 1932 Nobel)

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2$$

- commutator $[A, B] = AB - BA$

  anti-commutator $\{A, B\} = AB + BA$

- e.g. $\boxed{[x, p_x] = i\hbar}$

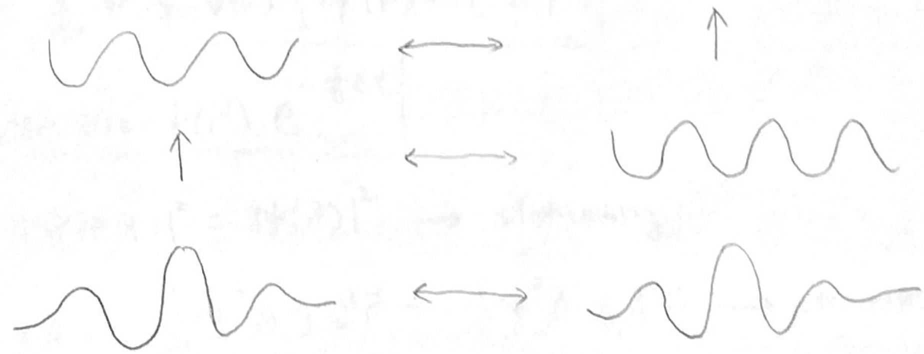
$$[x, p_x]\psi = x\left(-i\hbar \frac{\partial}{\partial x}\psi\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)(x\psi)$$

$$= -i\hbar\left(x\frac{\partial \psi}{\partial x} - \left(\psi + x\frac{\partial \psi}{\partial x}\right)\right)$$

$$= i\hbar\psi$$

- If $[A, B] \neq 0$, then $\boxed{\sigma_A \sigma_B \geqslant \frac{1}{2}\hbar}$

- Fourier transform $f(t) \xleftrightarrow{\text{F.T.}} \tilde{f}(\omega)$



JPEG

wavelet transform

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- Stationary States

(1) Energy eigen states $\hat{H}\psi = E\psi$

so $\langle H \rangle = \int \psi^* H \psi \, d^3\vec{r} = E$

$\langle H^2 \rangle = \int \psi^* H^2 \psi \, d^3\vec{r} = E^2$

$\sigma_H = 0 \longrightarrow$ stationary

(2) Time-independent Schrödinger equation

Separation of variables $\Psi(\vec{r}, t) = \psi(\vec{r})\,\phi(t)$

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r})\,\phi(t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r})\,\phi(t) + V(\vec{r})\,\psi(\vec{r})\,\phi(t)$$

$$i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(\vec{r})} \nabla^2 \psi(\vec{r}) + V(\vec{r}) = E$$

$$\boxed{\phi(t) = e^{-\frac{i}{\hbar}Et}}$$

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})}$$

$$\boxed{\Psi(\vec{r}, t) = \psi(\vec{r})\, e^{-\frac{i}{\hbar}Et}}$$

- $|\Psi(\vec{r}, t)|^2 = |\psi(\vec{r})|^2 \rightarrow$ stationary

- $\langle A \rangle = \int \Psi^* A \Psi \, d^3\vec{r} = \int \psi^* A \psi \, d^3\vec{r} \rightarrow$ stationary

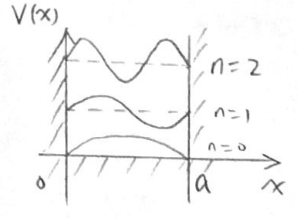
e.g. $\langle \vec{r} \rangle = \text{const}$, $\langle \vec{p} \rangle = 0$

- General solution

$$\boxed{\Psi(\vec{r}, t) = \sum C_n \psi_n(\vec{r})\, e^{-\frac{i}{\hbar}E_n t}}$$

initial condition $\Psi(\vec{r}, 0) = \sum C_n \psi_n(\vec{r}) \Rightarrow C_n = \int \Psi(\vec{r}, 0)\, \psi_n^*(\vec{r})\, d^3\vec{r}$

- 1D Infinite Square Well



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

Outside, $\psi(x) = 0$

Inside $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

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

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

continuity at $x=0$. $\psi(0) = 0 \Rightarrow B = 0$

$x = a$, $\psi(a) = 0 \Rightarrow A\sin(ka) = 0 \Rightarrow ka = n\pi \Rightarrow \boxed{k_n = \frac{n\pi}{a}}$

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}} \propto n^2$$

Localization leads to quantization.

$$\psi_n(x) = A_n \sin(k_n x)$$

Normalization $\int_0^a |\psi_n|^2 dx = 1 = \int_0^a |A_n|^2 \sin^2(k_n x)\, dx = |A_n|^2 \frac{a}{2} \Rightarrow A_n = \sqrt{\frac{2}{a}}$

$-\sqrt{\frac{2}{a}}$ doesn't affect $|\psi_n|^2$

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\sin(k_n x)}$$

- orthonormality

Kronecker δ function

$$\int_0^a \psi_n^* \psi_m\, dx = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right) dx = \delta_{nm} = \begin{cases} 0, & n=m \\ 1, & n\neq m \end{cases}$$

- Completeness

$$f(x) = \sum C_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum C_n \sin \frac{n\pi x}{a} \quad \text{Fourier series}$$

$$C_n = \int \psi_n^* f_n(x)\, dx \quad , \quad \sum |C_n|^2 = 1$$

- General solution

$$\Psi(x,t) = \sum C_n \psi_n(x)\, e^{-\frac{i}{\hbar}E_n t} = \sqrt{\frac{2}{a}} \sum C_n \sin \frac{n\pi x}{a}\, e^{-i\frac{n^2\pi^2\hbar}{2ma^2}t}$$

Initial condition $\Psi(x,0) = \sum C_n \psi_n(x) \Rightarrow C_n = \int \psi_n^* \Psi(x,0)\, dx$

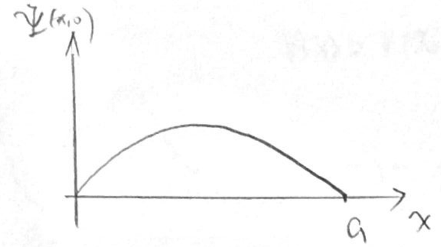
Normalization $1 = \int |\Psi|^2 dx = \int \left(\sum C_n \psi_n(x) e^{-\frac{i}{\hbar}E_n t}\right)^* \left(\sum C_m \psi_m(x) e^{-\frac{i}{\hbar}E_m t}\right) dx$

$$= \sum_n \sum_m C_n^* C_m\, e^{\frac{i}{\hbar}(E_n - E_m)t} \int \psi_n^* \psi_m\, dx = \sum_n |C_n|^2$$

Expectation value of energy

$$\langle H \rangle = \int \Psi^* H \Psi\, dx = \sum |C_n|^2 E_n$$

Ex: $\Psi(x,0) = Ax(a-x)$, $\quad 0 \le x \le a$



1) $1 = \int_0^a |\Psi(x,0)|^2 dx = |A|^2 \int_0^a x^2(a-x)^2 dx = |A|^2 \frac{a^5}{30} \Rightarrow A = \sqrt{\frac{30}{a^5}}$

2) $C_n = \int \psi_n^* \Psi(x,0)\, dx = \sqrt{\frac{2}{a}} \int_0^a \sin\frac{n\pi x}{a} \cdot \sqrt{\frac{30}{a^5}}\, x(a-x)\, dx = \begin{cases} 0, & \text{even } n \\ \frac{8\sqrt{15}}{(n\pi)^3} & \text{odd } n \end{cases}$

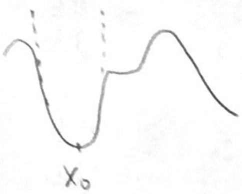
3) $|C_1|^2 = \left(\frac{8\sqrt{15}}{(n\pi)^3}\right)^2 = 0.998555 \longrightarrow$ $\Psi(x,0)$ is similar to ψ_1

$\sum |C_n|^2 = \frac{8\sqrt{15}}{\pi^3} \sum_{n=1,3,\cdots} \frac{1}{n^6} = 1$

4) $\langle H \rangle = \sum_{n=1,3,\cdots} \left(\frac{8\sqrt{15}}{(n\pi)^3}\right)^2 \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{480\hbar^2}{\pi^4 ma^2} \sum_{n=1,3,\cdots} \frac{1}{n^4} = \frac{5\hbar^2}{ma^2} \rightarrow$ close to $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$

· 1D Harmonic Oscillator

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots$$



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

Ex: UN, UO_2

(1) Analytic method

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

$$-\frac{\hbar}{m\omega}\frac{d^2\psi}{dx^2} + \frac{m\omega}{\hbar}x^2\psi = \frac{2E}{\hbar\omega}\psi$$

let $\boxed{\xi = \sqrt{\frac{m\omega}{\hbar}}\,x}$, then $-\frac{d^2\psi}{d\xi^2} + \xi^2\psi = \frac{2E}{\hbar\omega}\psi$

$$\boxed{\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi,} \qquad K = \frac{2E}{\hbar\omega} \quad \text{dimentionless}$$

- at large ξ. $\xi^2 \gg K$, $\frac{d^2\psi}{d\xi^2} = \xi^2\psi$

approximate solution $\psi(\xi) = Ae^{-\frac{\xi^2}{2}} + Be^{\frac{\xi^2}{2}}$

$$\frac{d\psi}{d\xi} = Ae^{-\frac{\xi^2}{2}}(-\xi) + Be^{\frac{\xi^2}{2}}\cdot\xi$$

$$\frac{d^2\psi}{d\xi} = Ae^{-\frac{\xi^2}{2}}(-\xi)^2 + Ae^{-\frac{\xi^2}{2}}(-1) + Be^{\frac{\xi^2}{2}}\xi^2 + Be^{\frac{\xi^2}{2}}\cdot 1 \approx \xi^2\psi$$

Normalization $\Rightarrow B = 0$.

"peal off" the exponential part $\boxed{\psi(\xi) = h(\xi)e^{-\frac{\xi^2}{2}}}$

$$\frac{d\psi}{d\xi} = \frac{dh}{d\xi}e^{-\frac{\xi^2}{2}} + he^{-\frac{\xi^2}{2}}\cdot(-\xi) = \left(\frac{dh}{d\xi} - \xi h\right)e^{-\frac{\xi^2}{2}}$$

$$\frac{d^2\psi}{d\xi^2} = \left(\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (\xi^2 - 1)h\right)e^{-\frac{\xi^2}{2}}$$

$$\boxed{\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K-1)h = 0}$$

Try Power series $h(\xi) = \sum_{j=0}^{\infty} a_j \xi^j$, Note expand $\psi(\xi)$ as power series doesn't work.

$$\frac{dh}{d\xi} = \sum_{j=1}^{\infty} j a_j \xi^{j-1}$$

$$\frac{d^2h}{d\xi^2} = \sum_{j=2}^{\infty} j(j-1) a_j \xi^{j-2} = \sum_{j=0}^{\infty} (j+2)(j+1) a_{j+2} \xi^j$$

$$\sum_{j=0}^{\infty} \left[(j+2)(j+1) a_{j+2} - 2j a_j + (k-1) a_j \right] \xi^j = 0$$

$$(j+2)(j+1) a_{j+2} - 2j a_j + (k-1) a_j = 0.$$

$$\boxed{a_{j+2} = \frac{2j+1-k}{(j+1)(j+2)} a_n}$$ recursion, determined by a_0, a_1

Normalization, for large $j=n$ $a_{j+2} \approx \frac{2}{j} a_j \Rightarrow a_j \propto \frac{1}{(j/2)!}$

then $h(\xi) \propto \sum \frac{1}{(j/2)!} \xi^j \propto \sum \frac{1}{j!} \xi^{2j} \approx e^{\xi^2} \to \infty$

So the power series must terminate beyond some $j=n$, (so $a_{j+1}=0$ and also $a_{j+1} = a_{j+3} = \cdots = 0$)

$$\Rightarrow 2n+1-k = 0 \Rightarrow k = 2n+1 \Rightarrow \boxed{E_n = (n+\tfrac{1}{2})\hbar\omega}$$

- If E is some other value, $h(\xi)$ will blow up exponentially.

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j$$

$n=0$, $k=0$ $h(\xi) = a_0$, $\psi_0(\xi) = a_0 e^{-\frac{\xi^2}{2}}$ $E_0 = \frac{1}{2}\hbar\omega$

$n=1$, $k=3$, $h(\xi) = a_1 \xi$, $\psi_1(\xi) = a_1 \xi e^{-\frac{\xi^2}{2}}$ $E_1 = \frac{3}{2}\hbar\omega$

$n=2$, $k=5$. $h(\xi) = a_0 + a_2\xi^2$. $\psi_2(\xi) = a_0(1-2\xi^2) e^{-\frac{\xi^2}{2}}$ $E_2 = \frac{5}{2}\hbar\omega$

$= a_0(1-2\xi)^2$

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

normalization

$H_0 = 1$

$H_1 = 2\xi$

$H_2 = 4\xi^2 - 2$

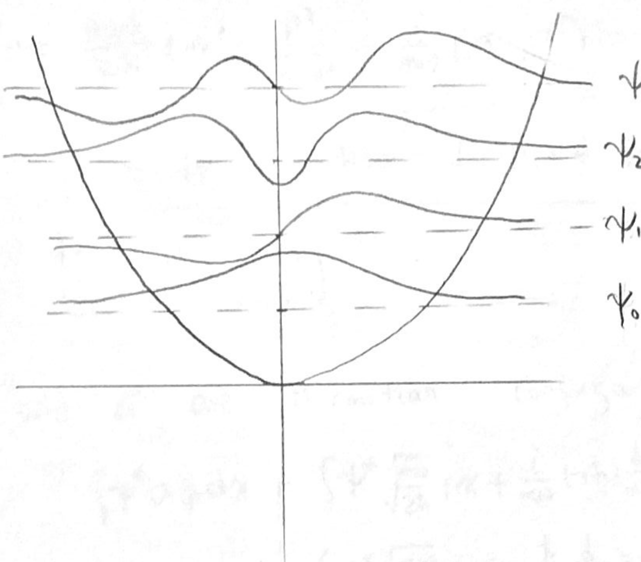
$H_3 = 8\xi^3 - 12\xi$

- $H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}$ Rodrigues formula

- $H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi)$

- $\frac{dH_n}{d\xi} = 2n H_{n-1}(\xi)$

- $e^{-z^2-2z\xi} = \sum \frac{z^n}{n!} H_n(\xi)$ generating function



$E_3 = \frac{7}{2}\hbar\omega$

$E_2 = \frac{5}{2}\hbar\omega$

$E_1 = \frac{3}{2}\hbar\omega$

$E_0 = \frac{1}{2}\hbar\omega$ Zero point energy

(2) Algebraic method

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

- Define ladder operators

$$\begin{cases} a = \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{ip}{m\omega} \right) & \text{annihilation / lowering operator} \\ a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{ip}{m\omega} \right) & \text{creation / raising operator} \end{cases}$$

$$a a^\dagger = \frac{m\omega}{2\hbar} \left(x^2 + \frac{p^2}{m^2\omega^2} - \frac{i}{m\omega} [x, p] \right) = \frac{H}{\hbar\omega} + \frac{1}{2}$$

$$a^\dagger a = \frac{m\omega}{2\hbar} \left(x^2 + \frac{p^2}{m^2\omega^2} + \frac{i}{m\omega} [x, p] \right) = \frac{H}{\hbar\omega} - \frac{1}{2}$$

$$\Rightarrow \boxed{H = (a a^\dagger - \tfrac{1}{2}) \hbar\omega = (a^\dagger a + \tfrac{1}{2}) \hbar\omega}$$

$$\boxed{[a, a^\dagger] = 1}$$

- a and $a^\dagger$ are Hermitian conjugate

Proof:

$$\int \psi^* a \phi \, dx = \int \psi^* \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{i}{m\omega} (-i\hbar) \frac{d}{dx} \right) \phi \, dx$$

$$= \int \psi^* \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{\hbar}{m\omega} \frac{d}{dx} \right) \phi \, dx$$

$$= \sqrt{\frac{m\omega}{2\hbar}} \int \left(\psi^* x \phi + \psi^* \frac{\hbar}{m\omega} \frac{d\phi}{dx} \right) dx$$

$$= \sqrt{\frac{m\omega}{2\hbar}} \int \left((x\psi)^* \phi - \frac{\hbar}{m\omega} \frac{d\psi^*}{dx} \cdot \phi \right) dx \quad \text{integrate by parts}$$

$$= \sqrt{\frac{m\omega}{2\hbar}} \int \left(\left(x - \frac{\hbar}{m\omega} \frac{d}{dx} \right) \psi \right)^* \phi \, dx$$

$$= \int (a^\dagger \psi)^* \phi \, dx$$

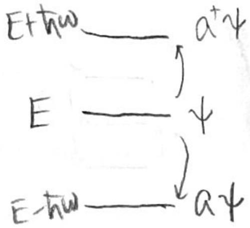
- Crucial step: If ψ is an eigen function with eigen energy E, $H\psi = E\psi$

  then $a\psi$ ... ... $E - \hbar\omega$,

  $a^+\psi$ ... ... $E + \hbar\omega$

Proof: $H(a\psi) = (aa^+ - \frac{1}{2})\hbar\omega\, a\psi = \hbar\omega(aa^+a - \frac{1}{2}a)\psi$

$= \hbar\omega\, a(a^+a - \frac{1}{2})\psi = \hbar\omega\, a(aa^+ - 1 - \frac{1}{2})\psi$



$= a(H - \hbar\omega)\psi = a(E - \hbar\omega)\psi = (E - \hbar\omega)\, a\psi$

$H(a^+\psi) = (a^+a + \frac{1}{2})\hbar\omega\, a^+\psi = \hbar\omega(a^+aa^+ + \frac{1}{2}a^+)\psi$

$= \hbar\omega\, a^+(aa^+ + \frac{1}{2})\psi = \hbar\omega\, a^+(a^+a + 1 + \frac{1}{2})\psi$

$= a^+(H + \hbar\omega)\psi = a^+(E + \hbar\omega)\psi = (E + \hbar\omega)\, a^+\psi$

- ground state $a\psi_0 = 0$

$$\sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right)\psi_0 = 0, \quad \left(x + \frac{\hbar}{m\omega}\frac{d}{dx}\right)\psi_0 = 0$$

$$\psi_0(x) = A e^{-\frac{m\omega}{2\hbar}x^2}$$

normalization $1 = \int_{-\infty}^{+\infty} |\psi_0|^2 dx = A^2 \int_{-\infty}^{+\infty} e^{-\frac{m\omega}{\hbar}x^2} dx = A^2\sqrt{\frac{\hbar\pi}{m\omega}} \Rightarrow A = \left(\frac{\hbar\pi}{m\omega}\right)^{\frac{1}{4}}$

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

$H\psi_0 = E_0\psi_0$, $\hbar\omega(a^+a + \frac{1}{2})\psi_0 = E_0\psi_0 \Rightarrow \boxed{E_0 = \frac{1}{2}\hbar\omega}$

- other states, $A_n = \frac{1}{\sqrt{n!}}$ normalization

$\boxed{\psi_n(x) = A_n (a^+)^n \psi_0(x)}$, $\boxed{E_n = (n + \frac{1}{2})\hbar\omega}$

$H\psi_n = E_n\psi_n \Rightarrow \hbar\omega(a^+a + \frac{1}{2})\psi_n = (n + \frac{1}{2})\hbar\omega\psi_n \Rightarrow a^+a\psi_n = n\psi_n$

define $\boxed{N = a^+a}$ $\boxed{N\psi_n = n\psi_n.}$

then $\boxed{aa^+ = N + 1}$

normalization ① $a^+\psi_n = c_n\psi_{n+1}$

$$\int (a^+\psi_n)^*(a^+\psi_n)dx = \int (c_n\psi_{n+1})^*(c_n\psi_{n+1})\,dx = |c_n|^2$$

$$\parallel$$

$$\int (aa^+\psi_n)^*\psi_n\,dx$$

$$\parallel$$

$$n+1 \qquad \Rightarrow \qquad c_n = \sqrt{n+1}$$

② $a\psi_n = d_n\psi_{n-1}$

$$\int (a\psi_n)^*(a\psi_n) = \int (d_n\psi_{n-1})^*(d_n\psi_{n-1})\,dx = |d_n|^2$$

$$\parallel$$

$$\int (a^+a\psi_n)^*\psi_n$$

$$\parallel$$

$$n \qquad \Rightarrow \qquad d_n = \sqrt{n}$$

$$\boxed{\begin{aligned} a\psi_n &= \sqrt{n}\,\psi_{n-1} \\ a^+\psi_n &= \sqrt{n+1}\,\psi_{n+1} \end{aligned}}$$

$$\psi_1 = \sqrt{1}\,a^+\psi_0$$

$$\psi_2 = \sqrt{2}\,a^+\psi_1 = \sqrt{2}\sqrt{1}\,(a^+)^2\psi_0$$

$$\vdots$$

$$\boxed{\psi_n = \sqrt{n!}\,(a^+)^2\psi_0}$$

- orthonormality $\boxed{\int \psi_n^* \psi_m \, dx = \delta_{nm}}$

Proof:
$$\int \psi_n^* (a^+ a) \psi_m \, dx = m \int \psi_n^* \psi_m \, dx$$
$$\shortparallel$$
$$\int (a\psi_n)^* a \psi_m \, dx$$
$$\shortparallel$$
$$\int (a^+ a \psi_n)^* \psi_m \, dx = n \int \psi_n^* \psi_m \, dx$$

- completeness

$$f(x) = \Sigma c_n \psi_n(x), \quad c_n = \int \psi_n^* f(x) \, dx, \quad \Sigma |c_n|^2 = 1$$

- general solution
$$\boxed{\Psi(x,t) = \Sigma c_n \psi_n(x) e^{-\frac{i}{\hbar} E_n t}}$$

$$\Psi(x,0) = \Sigma c_n \psi_n(x), \quad c_n = \int \psi_n^* \Psi(x,0) \, dx, \quad \Sigma |c_n|^2 = 1$$

- Other quantities
$$x = \sqrt{\frac{\hbar}{2m\omega}} (a^+ + a)$$
$$p = i \sqrt{\frac{m\omega\hbar}{2}} (a^+ - a).$$

potenitial energy $\langle V \rangle = \langle \frac{1}{2} m\omega^2 x^2 \rangle = \frac{1}{2} m\omega^2 \int \psi_n^* x^2 \psi_n \, dx$

$$= \frac{1}{2} m\omega^2 \frac{\hbar}{2m\omega} \int \psi^* (a^{+2} + a^+ a + a a^+ + a^2) \psi \, dx = \frac{1}{4} \hbar\omega (n + (n+1)) = \frac{1}{2} (n + \tfrac{1}{2}) \hbar\omega$$
$$= \frac{1}{2} E_n$$

kinetic energy $\langle T \rangle = \langle \frac{p^2}{2m} \rangle = \frac{1}{2m} \int \psi_n^* p^2 \psi_n \, dx$

$$= \frac{1}{2m} \frac{-m\omega\hbar}{2} \int \psi_n^* (a^{+2} - a^+ a - a a^+ + a^2) = \frac{1}{4} \hbar\omega (n + (n+1)) = \frac{1}{2} (n + \tfrac{1}{2}) \hbar\omega. = \frac{1}{2} E_n$$

- Free particle

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi. \qquad \frac{d^2\psi}{dx^2} = -k^2\psi \qquad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

$$\psi_k(x) = A_k e^{ikx}$$

- Orthonormality

$$\int \psi_k^*(x)\,\psi_{k'}(x)\,dx = A_k A_{k'} \int e^{-ikx} e^{ik'x}\,dx = A_k A_{k'} \int e^{-i(k-k')x}\,dx$$

$$= A_k A_{k'} \lim_{L\to\infty} \int_{-L}^{L} e^{-i(k-k')x}\,dx = A_k A_{k'} \lim_{L\to\infty} \left.\frac{e^{-i(k-k')x}}{-i(k-k')}\right|_{-L}^{L}$$

$$= A_k A_{k'} \lim_{L\to\infty} \frac{2\sin(k-k')L}{k-k'} = A_k A_{k'}\, 2\pi\,\delta(k-k')$$

$$\boxed{\lim_{L\to\infty}\frac{\sin Lx}{\pi x} = \delta(x)} \qquad A_k = A_{k'} = \frac{1}{\sqrt{2\pi}}$$

$$\boxed{\psi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}} \qquad \boxed{\int \psi_k^*(x)\,\psi_{k'}(x)\,dx = \delta(k-k')}$$

- Completeness

$$f(x) = \int \phi(k)\,\psi_k(x)\,dx = \frac{1}{\sqrt{2\pi}}\int \phi(k)\,e^{ikx}\,dx$$

$f(x) \xleftrightarrow{F.T.} \phi(k)$: momentum space wave function

$$\phi(k) = \int \psi_k^*(x)\,f(x)\,dx = \frac{1}{\sqrt{2\pi}}\int f(x)\,e^{-ikx}\,dx$$

- General solution

$$\Psi(x,t) = \int \phi(k)\,\psi_k(x)\,e^{-i\frac{E}{\hbar}t}\,dx = \frac{1}{\sqrt{2\pi}}\int \phi(k)\,e^{i(kx-\frac{E}{\hbar}t)}\,dx. \qquad E = \frac{\hbar^2 k^2}{2m} = \hbar\omega$$

initial condition $\Psi(x,0) = \int \phi(k)\,\psi_k(x)\,dx \Rightarrow \phi(k) = \int \psi_k^*(x)\,\Psi(x,0)\,dx$

$$= \frac{1}{\sqrt{2\pi}}\int \Psi(x,0)\,e^{-ikx}\,dx$$

- free particle  continuous

bound particle  discrete $\boxed{\text{Localization} \Rightarrow \text{Quantization}}$

- velocity

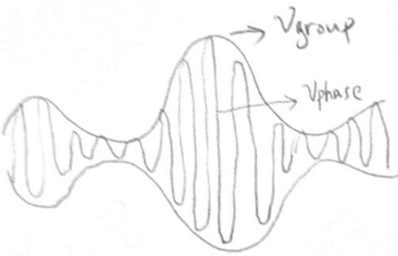
$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int \phi(k)\, e^{i(kx-\omega t)}\, dx, \qquad \omega = \omega(k) \quad \text{dispersion relation}$$

phase velocity $\quad v_{phase} = \frac{\omega}{k} \quad$ (can be larger than c)

group velocity $\quad v_{group} = \frac{d\omega}{dk} \quad$ (true velocity)

Ex: $\quad E = \frac{\hbar^2 k^2}{2m} = \hbar\omega, \quad \omega = \frac{\hbar k^2}{2m}$

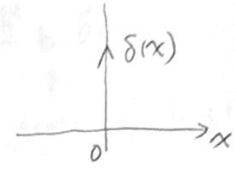
$$v_{phase} = \frac{\hbar k}{2m}, \quad v_{group} = \frac{\hbar k}{m}, \quad v_{phase} = 2 v_{group}$$



- δ function potential

- Dirac δ function

$$\delta(x) = \begin{cases} 0, & x \neq 0 \\ \infty, & x = 0 \end{cases}, \quad \int_{-\infty}^{+\infty} \delta(x)\,dx = 1$$



- Proterties of $\delta(x)$

(1) $\displaystyle\int_{-\infty}^{+\infty} \delta(ax)\,dx = \frac{1}{|a|} \Rightarrow \boxed{\delta(ax) = \frac{\delta(x)}{|a|}}$

$\boxed{\delta(-x) = \delta(x)}$

(2) $\boxed{\displaystyle\int_{-\infty}^{+\infty} \delta(x) f(x-a) = f(a)}$

$$\boxed{f(x) * \delta(x-a)} = \int_{-\infty}^{+\infty} f(\tau)\,\delta(x-a-\tau)\,d\tau$$

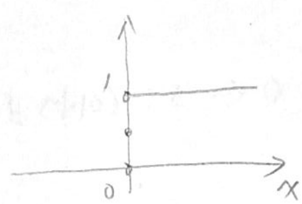
$$= \int_{-\infty}^{+\infty} f(\tau)\,\delta(\tau-(x-a))\,d\tau = \boxed{f(x-a)}$$

(3) $\boxed{\displaystyle\delta(f(x)) = \sum_i \frac{\delta(x-x_i)}{|f'(x_i)|}}$ x_i are the zero points of $f(x)$

(4) $\boxed{\delta(x) = \frac{d}{dx} H(x)}$

Heaviside step function

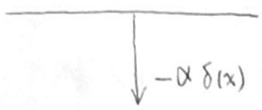
$$H(x) = \begin{cases} 1 & x > 0 \\ \frac{1}{2} & x = 0 \\ 0 & x < 0 \end{cases}$$



- dimension of $\delta(x)$: $\dfrac{1}{[x]}$

$\alpha > 0$

$V(x) = -\alpha\,\delta(x)$. $\quad [\alpha] = [x]\cdot[E]$



Ex: Fermi pseudopotential $V_F(r) = \frac{2\pi\hbar^2}{m}\, b\, \delta(r)$

$\uparrow$ bound, scattering length

(1) bound state $\quad E < 0$.

$x \neq 0 \qquad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + 0 = E\psi(x)$

$$\psi(x) = Ae^{kx} + Be^{-kx} \qquad k = \frac{\sqrt{-2mE}}{\hbar}$$

$$\psi(x) = \begin{cases} Ae^{kx}, & x < 0 \\ Be^{-kx}, & x > 0 \end{cases}$$

- Continuity ① $\psi(0^-) = \psi(0^+) \Rightarrow A = B$

② $\frac{d}{dx}\psi$ is not continuous at ∞ potential

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) - V(x)\psi(x) = E\psi(x)$$

integrate from $-\epsilon$ to ϵ

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

in the limit of $\epsilon \to 0$

$$-\frac{\hbar^2}{2m}\frac{d\psi}{dx}\Big|_{0^-}^{0^+} - \alpha\psi(0) = E\psi(0)\cdot 2\epsilon \to 0$$

$$\frac{d\psi}{dx}\Big|_{0^-}^{0^+} = -\frac{2m}{\hbar^2}\alpha A \neq 0$$

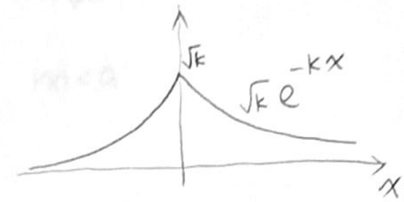
in fact $\left.\begin{aligned} \frac{d\psi}{dx}\Big|_{0^+} &= -Ak \\ \frac{d\psi}{dx}\Big|_{0^-} &= Ak \end{aligned}\right\} \Rightarrow -2Ak = -\frac{2m}{\hbar^2}\alpha A \Rightarrow k = \frac{m\alpha}{\hbar^2}$

$$k = \frac{m\alpha}{\hbar^2} = \frac{\sqrt{-2mE}}{\hbar} \Rightarrow \boxed{E = -\frac{m\alpha^2}{2\hbar^2}}$$

Only one allowed state

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

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



(2) Scattering state $E > 0$

$x \neq 0$. $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$.

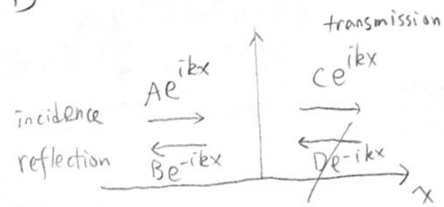
$x < 0$ $\psi(x) = Ae^{ikx} + Be^{-ikx}$ $\qquad k = \frac{\sqrt{2mE}}{\hbar}$

$x > 0$ $\psi(x) = Ce^{ikx} + De^{-ikx}$

- continuity ① $\psi(0^-) = \psi(0^+) \Rightarrow A + B = C + D$

② $-\frac{\hbar^2}{2m} \frac{d\psi}{dx}\Big|_{0^-}^{0^+} = \alpha\psi(0)$

$-\frac{\hbar^2}{2m}\, ik\left[(C-D) - (A-B)\right] = \alpha(A+B)$



Consider $D = 0$: particle comes from the left

$$\begin{cases} A + B = C \\ (1+2\beta i)A + (-1+2\beta i)B = C \end{cases} \qquad \beta = \frac{m\alpha}{k\hbar^2}$$

$$\Rightarrow \begin{cases} B(A) = \dfrac{\beta i}{1-\beta i} A \\ C(A) = \dfrac{1}{1-\beta i} A \end{cases}$$

Reflection coefficient $R = \left|\frac{B}{A}\right|^2 = \frac{\beta^2}{1+\beta^2}$

Transmission coefficient $T = \left|\frac{C}{A}\right|^2 = \frac{1}{1+\beta^2}$

$\Big\}\ R + T = 1$

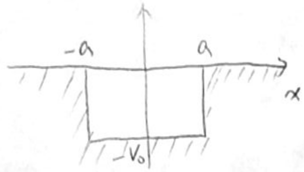
- Remarks : ① $E\uparrow$: $k\uparrow$ $\beta\downarrow$ $T\uparrow$ $R\downarrow$

② $\alpha\uparrow$: $\beta\uparrow$ $T\downarrow$ $R\uparrow$ $\qquad \alpha \to \infty$. $T \to 0$, $R \to 1$

③ If $V \to -V$: - no bound state

- scattering state remains the same vs classical

- 1D Finite Square Well



$$V(x) = \begin{cases} 0, & |x| \geq a \\ -V_0. & |x| < a \end{cases}$$

(1) Bound state $\quad E<0. \quad (E > -V_0)$

$x < -a.$ $\quad -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$

$$\psi(x) = Ae^{\kappa x} + \cancel{B}e^{-\kappa x} \xrightarrow{} 0 \qquad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

$-a < x < a$ $\quad -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - V_0\psi(x) = E\psi(x)$

$$\psi(x) = C\sin kx + D\cos kx. \qquad k = \frac{\sqrt{2m(E+V_0)}}{\hbar}$$

$x > a$ $\quad -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$

$$\psi(x) = \cancel{F}e^{\kappa x} + Ge^{-\kappa x}. \qquad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

$$\psi(x) = \begin{cases} Ae^{\kappa x} & x < -a \\ C\sin kx + D\cos kx & -a < x < a \\ Ge^{-\kappa x} & x > a \end{cases}$$

- continuity

$$Ae^{-\kappa a} = -C\sin ka + D\cos ka \quad ①$$

$$A\kappa e^{-\kappa a} = Ck\cos ka + Dk\sin ka \quad ②$$

$$Ge^{-\kappa a} = C\sin ka + D\cos ka \quad ③$$

$$-G\kappa e^{-\kappa a} = Ck\cos ka - Dk\sin ka \quad ④$$

$①^2 + \left(\frac{②}{k}\right)^2$: $\quad A^2 e^{-2\kappa a}\left(1 + \frac{\kappa^2}{k^2}\right) = C^2 + D^2$

$③^2 + \left(\frac{④}{k}\right)^2$: $\quad G^2 e^{-2\kappa a}\left(1 + \frac{\kappa^2}{k^2}\right) = C^2 + D^2$

$\Rightarrow A = \pm G.$

$A = G$: even wave function

$A = -G$, odd wave function

Even: $\quad ① - ③ \quad : \quad 0 = -2C\sin ka \Rightarrow C = 0$

$①, ③ \quad : \quad Ae^{-\kappa a} = D\cos ka$

$②, ④ \quad : \quad A\kappa e^{-\kappa a} = Dk\sin ka$

$\Rightarrow \boxed{\kappa = k\tan ka}$ quantization

Odd $\quad D = 0, \quad \boxed{\kappa = -k\cot ka}$

Notice that

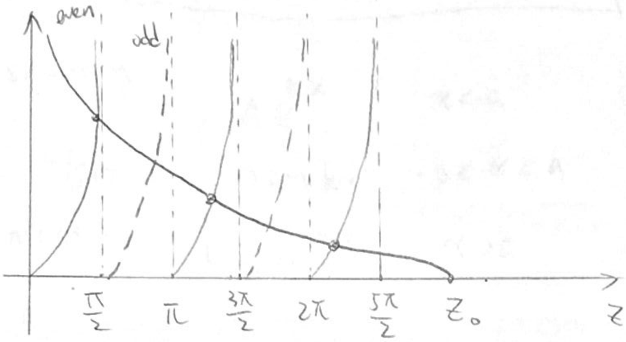
$$\kappa^2 + k^2 = \frac{2mV_0}{\hbar^2}$$

let $ka = z$, then $z^2 + \kappa^2 a^2 = \frac{2mV_0}{\hbar^2} a^2 = z_0^2$.

$$\kappa a = \sqrt{z_0^2 - z^2}.$$

then $\sqrt{z_0^2 - z^2} = z \tan z$

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}.$$



- Wide, deep $\quad z_n \approx \frac{n\pi}{2}$ $\quad n = \begin{cases} 1, 3, 5, & \text{even wave function} \\ 2, 4, 6, & \text{odd wave function} \end{cases}$

  $a \to \infty$, $V_0 \to \infty$

  $$k_n = \frac{z_n}{a} \approx \frac{n\pi}{2a}$$

  $$E_n + V_0 = \frac{k_n^2 \hbar^2}{2m} \approx \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} \quad \text{same with infinite square well}$$

- narrow, shallow $\quad$ If $z_0 < \frac{\pi}{2}$, then one bound state.

  $a \to 0$, $V_0 \to 0$

- Normalization

  even: $\quad D^2 \int_0^a \cos^2 kx \, dx + A^2 \int_a^\infty e^{-2\kappa x} dx = \frac{1}{2}$

  $$\left.\begin{aligned} & D^2 \frac{1}{k} \frac{1}{2} \left(\frac{1}{2} \sin 2ka + ka\right) + A^2 \frac{1}{2\kappa} e^{-2\kappa a} = \frac{1}{2} \\ & ①.③: \quad A e^{-\kappa a} = D \cos ka \end{aligned}\right\} \Rightarrow$$

  $$D^2 = \frac{\kappa k}{\kappa \cos^2 ka + \sin ka \cos ka + \kappa ka} = \frac{\kappa}{1 + \kappa a} \Rightarrow \boxed{D = \sqrt{\frac{\kappa}{1+\kappa a}}}$$

  $$\boxed{A = \sqrt{\frac{\kappa}{1+\kappa a}} \cos ka \, e^{\kappa a}}$$

odd

$$C^2\int_0^a \sin^2 kx\,dx + A^2\int_a^\infty e^{-2\kappa x}\,dx = \frac{1}{2}$$

$$\left.\begin{aligned} &C^2\frac{1}{k}\frac{1}{2}\left(-\frac{1}{2}\sin ka + ka\right) + A^2\frac{1}{2\kappa}e^{-2\kappa a} = \frac{1}{2} \\ &①.③:\quad Ae^{-\kappa a} = -C\sin ka \end{aligned}\right\} \Rightarrow$$

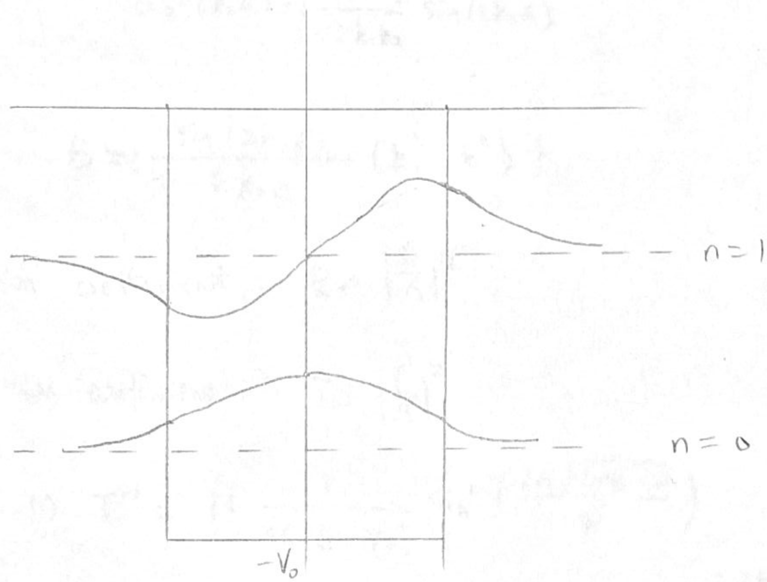
$$C^2 = \frac{k\kappa}{k^2\sin^2 ka - \sin ka\cos ka + k\kappa a} = \frac{\kappa}{1+\kappa a} \Rightarrow \boxed{C = \sqrt{\frac{\kappa}{1+\kappa a}}}$$

$$\boxed{A = -\sqrt{\frac{\kappa}{1+\kappa a}}\,\sin ka\; e^{\kappa a}}$$

- in summary

$$\psi_n(x) = \begin{cases} Ae^{\kappa x} & x<-a \\ D\cos kx, & -a<x<a \\ Ae^{-\kappa x} & x>a. \end{cases} \qquad \psi_n(x) = \begin{cases} Ae^{\kappa x} & x<-a \\ C\sin kx & -a<x<a \\ -Ae^{-\kappa x} & x>a \end{cases}$$

$n=1,3,5,\cdots$ $\qquad$ $n=2,4,6,\cdots$



(2) Scattering state $E>0$

$x<-a$, $\psi(x) = Ae^{ik_1x} + Be^{-ik_1x}$, $k_1 = \frac{\sqrt{2mE}}{\hbar}$

$-a<x<a$ $\psi(x) = C\sin k_2x + D\cos k_2x$. $k_2 = \frac{\sqrt{2m(E+V_0)}}{\hbar}$

$x>a$. $\psi(x) = Fe^{ik_1x} + \cancel{G}^{0} e^{-k_1x}$

Consider $G=0$. particle comes from the left.

- continuity
$$\begin{cases} Ae^{-ik_1a} + Be^{ik_1a} = -C\sin k_2a + D\cos k_2a \\ ik_1(Ae^{-ik_1a} - Be^{ik_1a}) = k_2(C\cos k_2a + D\sin k_2a) \\ C\sin k_2a + D\cos k_2a = Fe^{ik_1a} \\ k_2(C\cos k_2a - D\sin k_2a) = ik_1Fe^{ik_1a} \end{cases}$$

$$\Rightarrow \quad F = \frac{e^{-2ik_1a}}{\cos(2k_2a) - i\frac{k_1^2+k_2^2}{2k_1k_2}\sin(2k_2a)} A$$

$$B = i\frac{\sin(2k_2a)}{2k_2a}(k_2^2-k_1^2)F$$

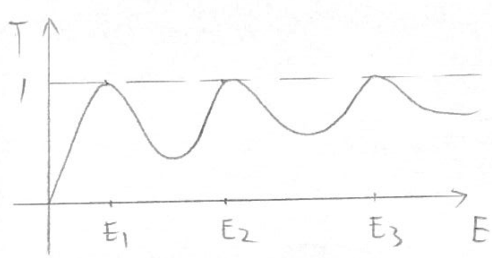
Reflection coefficient $R = \left|\frac{B}{A}\right|^2$

Transmission coefficient $T = \left|\frac{F}{A}\right|^2$

Remarks: (1) $T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a\sqrt{2m(E+V_0)}}{\hbar}\right)$

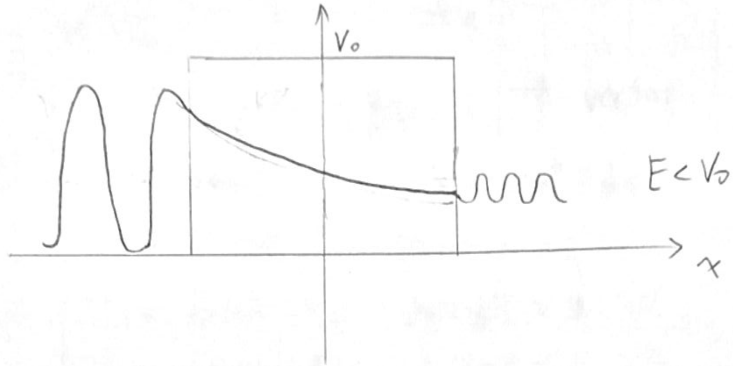
when $\frac{2a\sqrt{2m(E+V_0)}}{\hbar} = n\pi$, or $E+V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$ the eigen energies

then $T=1$, (the well becomes "transparent")



resonance

12) $V \to -V$



<u>tunneling</u>

☆ Formalism: Algebra Mechanics and Vector-Matrix Representation

- Hilbert space (∞ dimension linear space, could be discrete or continuous)
  - vector $|\psi\rangle \xrightarrow{\text{ket}} \psi(x)$ wave function
  - dual vector $\langle\psi| \xrightarrow{\text{bra}} \int \psi^*(\cdot)\, dx$
  - inner product $\langle\psi|\phi\rangle \rightarrow \int \psi^* \phi\, dx$
    - $\langle\psi|\phi\rangle^* = \langle\phi|\psi\rangle$
    - normalization $\langle\psi|\psi\rangle = 1$
    - orthogonality $\langle\psi|\phi\rangle = 0$

- Operator
  - observable $\boxed{\langle A\rangle = \langle\psi|A|\psi\rangle} \rightarrow \int \psi^* A \psi\, dx$
  - Hermitian operator

    $\langle A\rangle$ of physical quantity must be real $\langle A\rangle^* = \langle A\rangle$

    $$\langle\psi|A\psi\rangle^* = \underline{\langle A\psi|\psi\rangle = \langle\psi|A\psi\rangle}$$

    [If $\langle A^\dagger\psi|\phi\rangle = \langle\psi|A\phi\rangle$, then $A^\dagger$ is the Hermitian conjugate of A, $(A^\dagger)^\dagger = A$]

    $$= \langle A^\dagger\psi|\psi\rangle \Rightarrow \boxed{A^\dagger = A}$$

  - All physical quantities are represented by Hermitian operators.
  - Eigen states and Eigen values of Hermitian operators

    $$\boxed{A|\psi_n\rangle = A_n|\psi_n\rangle}$$

    ⓪ A_n are real.

    $$\langle\psi_n|A|\psi_n\rangle = \langle\psi_n|A_n|\psi_n\rangle = A_n$$

    $$\shortparallel$$

    $$\langle A\psi_n|\psi_n\rangle = A_n^*$$

① Normalization $\langle \psi_n | \psi_n \rangle = 1$

② orthogonality $\langle \psi_n | \psi_m \rangle = 0$ if $n = m$

$\Big\} \quad \boxed{\langle \psi_n | \psi_m \rangle = \delta_{nm}}$

Proof: $A|\psi_n\rangle = A_n|\psi_n\rangle$, $\quad A|\psi_m\rangle = A_m|\psi_m\rangle$

$$\langle \psi_n | A | \psi_m \rangle = \langle \psi_n | A_m | \psi_m \rangle = A_m \langle \psi_n | \psi_m \rangle$$

$$\parallel$$

$$\langle A\psi_n | \psi_m \rangle = A_n^* \langle \psi_n | \psi_m \rangle = A_n \langle \psi_n | \psi_m \rangle$$

If $A_n \neq A_m$, then $\langle \psi_n | \psi_m \rangle = 0$

If $A_n = A_m$ then Gram - Schmidt orthogonalization

③ completeness $\boxed{|\psi\rangle = \sum C_n |\psi_n\rangle}$ where $C_n = \langle \psi_n | \psi \rangle$

- $\boxed{|\psi\rangle =} \sum \langle \psi_n | \psi \rangle |\psi_n\rangle = \boxed{\sum |\psi_n\rangle\langle \psi_n | \psi \rangle} \Rightarrow \boxed{I = \sum |\psi_n\rangle\langle \psi_n|}$

- Projection operator $\boxed{\hat{P} = |\alpha\rangle\langle\alpha|}$. picks out the portion along $|\alpha\rangle$

- $\langle A \rangle = \langle \psi | A | \psi \rangle = \left(\sum_n C_n^* \langle \psi_n | \right) A \left(\sum_m C_m |\psi_m\rangle \right) = \boxed{\sum |C_n|^2 A_n}$

↑ probability

- Normalization $1 = \langle \psi | \psi \rangle = \sum_m C_m^* \langle \psi_m | \sum_n C_n |\psi_n\rangle = \sum_{n,m} C_m^* C_n \langle \psi_m | \psi_n \rangle = \sum |C_n|^2$

statistical intepretation

- Vector - Matrix representation

  - Heinsenberg (1932 Nobel), Born (1954 Nobel), Jordan (Nazi)

Given an operator and its eigen states $|\psi_n\rangle$.

- Vector $|\psi\rangle = \sum c_n |\psi_n\rangle \rightarrow \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix}$

- dual vector $\langle\psi| = \sum c_n^* \langle\psi_n| \rightarrow (c_1^*, \cdots, c_n^*)$

- inner product $\langle\psi|\phi\rangle = \sum c_n^* d_n$.

  - $\langle\psi|\phi\rangle^* = \langle\phi|\psi\rangle$

  - normalization $\langle\psi|\psi\rangle = 1 = \sum |c_n|^2$

  - orthogonality $\langle\psi|\phi\rangle = 0 = \sum c_n^* d_n$

- operator $A|\psi\rangle = |\phi\rangle$

$|\psi\rangle = \sum c_n |\psi_n\rangle$, $\quad |\phi\rangle = \sum d_m |\psi_m\rangle$

$$A \sum_n c_n |\psi_n\rangle = \sum_m d_m |\psi_m\rangle$$

$$\sum_n \langle\psi_m|A|\psi_n\rangle c_n = d_m$$

$$\boxed{\sum_n A_{mn} c_n = d_m}$$

$A_{mn} = \langle\psi_m|A|\psi_n\rangle$ - matrix element

$$\begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & & \vdots \\ \vdots & & \ddots & \\ A_{m1} & \cdots & & A_{mn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} d_1 \\ d_2 \\ \vdots \\ d_m \end{pmatrix}$$ - rotation

- vector representation using different bases

x: $\Psi(x,t) = \langle x|\Psi(t)\rangle$ $\qquad |\Psi(t)\rangle = \int |x\rangle\underline{\langle x|\Psi(t)\rangle}\, dx$

p: $\Phi(p,t) = \langle p|\Psi(t)\rangle$ $\qquad |\Psi(t)\rangle = \int |p\rangle\underline{\langle p|\Psi(t)\rangle}\, dx$

H: $c_n(t) = \langle n|\Psi(t)\rangle$ $\qquad |\Psi(t)\rangle = \sum |n\rangle\langle n|\Psi(t)\rangle$

$$\boxed{\begin{aligned} \Psi(x,t) &= \int \langle x|y\rangle \Psi(y,t)\, dy = \int \langle x|p\rangle \Phi(p,t)\, dp = \sum \langle x|n\rangle c_n(t) \\ &= \int \delta(x-y)\Psi(y,t)\, dy = \int \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px} \Phi(p,t)\, dp = \sum c_n(t)\, e^{-\frac{i}{\hbar}E_n t} \psi_n(x) \end{aligned}}$$

- Time evolution of an operator

- Classical mechanics

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + [A, H]$$ ← Poisson bracket

- Quantum mechanics

$$\boxed{\frac{dA}{dt} = \frac{\partial A}{\partial t} + \frac{1}{i\hbar}[A, H]}$$ ← commutator

– equivalent to Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$

Proof: $\frac{d\langle A\rangle}{dt} = \frac{d}{dt}\langle\Psi|A|\Psi\rangle$

$$= \left(\frac{\partial}{\partial t}\langle\Psi|\right)A|\Psi\rangle + \langle\Psi|\frac{\partial A}{\partial t}|\Psi\rangle + \langle\psi|A|\left(\frac{\partial}{\partial t}|\psi\rangle\right)$$

$$\left(i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \Rightarrow \frac{\partial}{\partial t}|\psi\rangle = \frac{1}{i\hbar}H|\psi\rangle, \Rightarrow \frac{\partial}{\partial t}\langle\psi| = -\frac{1}{i\hbar}\langle H\psi|\right)$$

$$= -\frac{1}{i\hbar}\langle H\Psi|A|\psi\rangle + \left\langle\frac{\partial A}{\partial t}\right\rangle + \frac{1}{i\hbar}\langle\psi|A|H\psi\rangle$$

$$= \left\langle\frac{\partial A}{\partial t}\right\rangle + \frac{1}{i\hbar}\langle\Psi|AH-HA|\Psi\rangle$$

$$= \left\langle\frac{\partial A}{\partial t}\right\rangle + \frac{1}{i\hbar}\langle[A,H]\rangle$$

- If $[A, H] = 0$, and A does not depend on t explicitly

$\frac{dA}{dt} = \frac{\partial A}{\partial t} = 0$, A is conserved

- Schrödinger picture vs Heisenberg picture

$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$, $|\psi(t)\rangle = \hat{S}|\psi(0)\rangle$

$\hat{S} = e^{-\frac{i}{\hbar}Ht}$ – S-matrix

Procedure: (1) Given H, solve $H|\psi_n\rangle = E_n|\psi_n\rangle$ to get E_n and $|\psi_n\rangle$

(2) General solution : $|\psi(t)\rangle = \sum C_n e^{-\frac{i}{\hbar}E_n t}|\psi_n\rangle$

$\uparrow$ determined by init condition

$$|\psi(0)\rangle = \sum C_n |\psi_n\rangle \Rightarrow C_n = \langle\psi_n|\psi(0)\rangle$$

(3) observable

$$\langle H\rangle = \langle\psi(t)|H|\psi(t)\rangle = \sum_n C_n^* e^{\frac{i}{\hbar}E_n t}\langle\psi_n| \sum_m E_m C_m e^{-\frac{i}{\hbar}E_m t}|\psi_m\rangle$$

$$= \sum |C_n|^2 E_n$$

$\uparrow$ probability

Example: Two - state system

① 

② nucleus — $|2\rangle$

— $|1\rangle$

③ spin $|\uparrow\rangle$

$|\downarrow\rangle$

④ bit $|0\rangle$

$|1\rangle$

⑤ schrödinger's cat

$|\text{alive}\rangle$

$|\text{dead}\rangle$

⑥ relationship

$|\text{love}\rangle$

$|\text{hate}\rangle$

⑦ exam

$|\text{pass}\rangle$

$|\text{fail}\rangle$

$$H = \begin{pmatrix} E_1 & \\ & E_2 \end{pmatrix} \Rightarrow |\psi_1\rangle = \begin{pmatrix}1\\0\end{pmatrix} = |\uparrow\rangle, \quad |\psi_2\rangle = \begin{pmatrix}0\\1\end{pmatrix} = |\downarrow\rangle$$

If $|\psi(0)\rangle = c_1|\uparrow\rangle + c_2|\downarrow\rangle = \begin{pmatrix}c_1\\c_2\end{pmatrix}$ If $c_1 = \frac{1}{2}$, $c_2 = ?$ $\frac{\sqrt{3}}{2}$

$$|\psi(t)\rangle = c_1 e^{-\frac{i}{\hbar}E_1 t}|\uparrow\rangle + c_2 e^{-\frac{i}{\hbar}E_2 t}|\downarrow\rangle = \begin{pmatrix} c_1 e^{-\frac{i}{\hbar}E_1 t} \\ c_2 e^{-\frac{i}{\hbar}E_2 t}\end{pmatrix}$$

$$\langle H\rangle = |C_1|^2 E_1 + |C_2|^2 E_2$$

· Uncertainty Principle (Heinsenberg)

- If $[A, B] = 0$, then A, B can have the same eigen state.

$$A|\psi_n\rangle = A_n|\psi_n\rangle$$

$$BA|\psi_n\rangle = A(B|\psi_n\rangle)$$

$$\parallel \qquad \Rightarrow \quad B|\psi_n\rangle = B_n|\psi_n\rangle$$

$$BA_n|\psi_n\rangle = A_n(B|\psi_n\rangle)$$

- If $[A, B] \neq 0$ then $\boxed{\sigma_A \sigma_B \geq \frac{1}{2}|\langle [A,B]\rangle|}$

$$\sigma_A^2 = \langle \Delta A|\Delta A\rangle = \langle (A - \langle A\rangle)^2 \rangle = \langle A^2 - 2A\langle A\rangle + \langle A\rangle^2\rangle = \langle A^2\rangle - \langle A\rangle^2$$

Schwarz inequality $\langle \alpha|\alpha\rangle\langle \beta|\beta\rangle \geq |\langle \alpha|\beta\rangle|^2$, $(|\alpha|^2|\beta|^2 \geq |\alpha|^2|\beta|^2\cos^2\theta)$

$$\sigma_A^2\sigma_B^2 = \langle \Delta A|\Delta A\rangle\langle \Delta B|\Delta B\rangle \geq |\langle \Delta A|\Delta B\rangle|^2$$

$$\Delta A\Delta B = \frac{1}{2}(\Delta A\Delta B - \Delta B\Delta A) + \frac{1}{2}(\Delta A\Delta B + \Delta B\Delta A) = \frac{1}{2}[\Delta A, \Delta B] + \{\Delta A, \Delta B\}.$$

$[\Delta A, \Delta B]^\dagger = (\Delta A\Delta B - \Delta B\Delta A)^\dagger = (\Delta B)^\dagger(\Delta A)^\dagger - (\Delta A)^\dagger(\Delta B)^\dagger = \Delta B\Delta A - \Delta A\Delta B = -[\Delta A, \Delta B]$ anti-Hermitian imaginary

$\{\Delta A, \Delta B\}^\dagger = (\Delta A\Delta B + \Delta B\Delta A)^\dagger = (\Delta B)^\dagger(\Delta A)^\dagger + (\Delta A)^\dagger(\Delta B)^\dagger = \Delta B\Delta A + \Delta A\Delta B = \{\Delta A, \Delta B\}$ Hermitian real

$$\sigma_A^2\sigma_B^2 \geq \frac{1}{4}|\langle[\Delta A, \Delta B]\rangle|^2$$

$$[\Delta A, \Delta B] = \Delta A\Delta B - \Delta B\Delta A = (A - \langle A\rangle)(B - \langle B\rangle) - (B - \langle B\rangle)(A - \langle A\rangle)$$

$$= (AB - \langle A\rangle B - A\langle B\rangle + \langle A\rangle\langle B\rangle) - (BA - \langle B\rangle A - B\langle A\rangle + \langle B\rangle\langle A\rangle)$$

$$= AB - BA = [A, B]$$

$\therefore \sigma_A^2\sigma_B^2 \geq \frac{1}{4}|\langle[A,B]\rangle|^2$. $\boxed{\sigma_A\sigma_B \geq \frac{1}{2}|\langle[A,B]\rangle|}$

e.g. $[x, p_x] = i\hbar$, $\sigma_x\sigma_{p_x} \geq \frac{1}{2}\hbar$

- Minimum uncertainty wave packet

$$\Delta A = ia\,\Delta B. \quad a \text{ is real}$$

For position-momentum uncertainty relation

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

$$\frac{d}{dx}\psi + \frac{a}{\hbar}x\psi - \frac{i}{\hbar}(\langle p\rangle - ia\langle x\rangle)\psi = 0$$

$x \to \infty$. $$\frac{d\psi}{dx} + \frac{a}{\hbar}x\psi = 0.$$

$$\psi(x) = C_1 e^{-\frac{a}{2\hbar}x^2}$$

let $\psi(x) = \phi(x)\, e^{-\frac{a}{2\hbar}x^2}$, then

$$\frac{d\phi}{dx}e^{-\frac{a}{2\hbar}x^2} + \cancel{\phi(x)\, e^{-\frac{a}{2\hbar}x^2}\left(-\frac{a}{\hbar}x\right)} + \cancel{\frac{a}{\hbar}x\,\phi(x)\, e^{-\frac{a}{2\hbar}x^2}}$$

$$- \frac{i}{\hbar}(\langle p\rangle - ia\langle x\rangle)\,\phi(x)\, e^{-\frac{a}{2\hbar}x^2} = 0$$

$$\frac{d\phi}{dx} - \frac{i}{\hbar}(\langle p\rangle - ia\langle x\rangle)\,\phi(x) = 0$$

$$\phi(x) = e^{\frac{i}{\hbar}(\langle p\rangle - ia\langle x\rangle)x}$$

$$\therefore \psi(x) = C_2 e^{-\frac{a}{2\hbar}x^2} e^{\frac{i}{\hbar}(\langle p\rangle - ia\langle x\rangle)x} = \boxed{C_3\, e^{-\frac{a}{2\hbar}(x-\langle x\rangle)^2}\, e^{\frac{i}{\hbar}\langle p\rangle x}}$$

Gaussian in x

- Energy-time uncertainty principle $\boxed{\sigma_H \sigma_t \geq \frac{1}{2}\hbar}$

If A doesn't depend on t explicitly, $\frac{\partial A}{\partial t} = 0$. $\frac{dA}{dt} = \frac{1}{i\hbar}[A, H]$.

$$\sigma_A \sigma_H \geq \frac{1}{2}\left|\langle [A, H]\rangle\right| = \frac{\hbar}{2}\left|\frac{d\langle A\rangle}{dt}\right|$$

define $\sigma_t = \sigma_A \Big/ \left|\frac{d\langle A\rangle}{dt}\right|$, then $\sigma_H \sigma_t \geq \frac{1}{2}\hbar$

$\sigma_A = \left|\frac{d\langle A\rangle}{dt}\right| \cdot \sigma_t$: the amount of time it takes the expectation value of A to change by one standard deviation σ_A

★ 3D Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

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

separation of variables $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$

$$\underbrace{\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]\right\}}_{=\,l(l+1)} + \underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}}_{=\,-l(l+1)} = 0$$

- The angular equation, let $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

same as solving $\nabla^2\psi = 0$

$$\underbrace{\left\{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta\right\}}_{=\,m^2} + \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{=\,-m^2} = 0$$

Φ: $\boxed{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2}$, $\Phi(\phi) = e^{im\phi}$ ($-m$ is included by allowing m to run negative)

Symmetry $\Phi(\phi) = \Phi(\phi + 2\pi)$

$$\Rightarrow e^{im\phi} = e^{im(\phi+2\pi)} \Rightarrow m = \text{int.}$$

Θ: $\boxed{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + [l(l+1)\sin^2\theta - m^2]\Theta = 0}$

$$\boxed{\Theta(\theta) = A\,P_l^m(\cos\theta)}$$

$P_l^m(x)$: associated Legendre function / polynomial

$$P_l^m(x) = (-1)^m(1-x^2)^{\frac{m}{2}}\frac{d^m}{dx^m}P_l(x), \quad m>0$$

$P_l(x)$: Legendre polynomial

$$P_l(x) = \frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l \quad \leftarrow \text{Rodrigues formula}$$

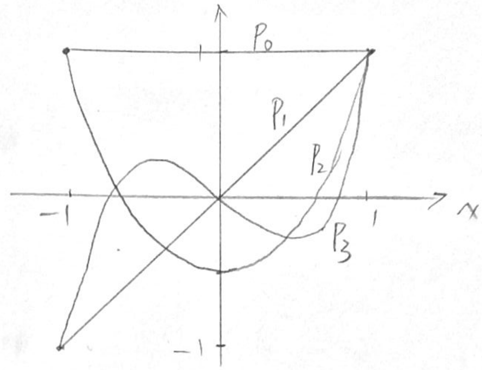
$$\boxed{P_l^{-m}(x) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(x)} \qquad \boxed{P_l^m(-x) = (-1)^{l+m}P_l^m(x)}$$

$P_0(x) = 1$

$P_1(x) = x$

$P_2(x) = \frac{1}{2}(3x^2 - 1)$

$P_3(x) = \frac{1}{2}(5x^3 - 3x)$



- If $|m| > l$, then $P_l^m = 0$, so $|m| \le l$ $m = -l, \cdots, l$ ($2l+1$ values)
- $P_l^m(x)$ is always a polynomial in $\cos\theta$ and $\sin\theta$

$P_0^0 = 1$

$P_1^0 = \cos\theta$, $P_1^1 = -\sin\theta$, $P_1^{-1} = -\frac{1}{2}P_1^1$

$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$, $P_2^1 = -3\sin\theta\cos\theta$ $P_2^2 = 3\sin^2\theta$

$P_2^{-1} = -\frac{1}{6}P_2^1$ $P_2^{-2} = \frac{1}{24}P_2^2$

$$\boxed{Y_l^m = (-1)^m \sqrt{\frac{(2l+1)(l-m!)}{4\pi\ (l+m!)}}\ P_l^m(\cos\theta)\, e^{im\phi}}$$

spherical $\underbrace{\text{harmonics}}$
↑ solution of Laplace's eq.

$$\boxed{Y_l^{-m} = (-1)^m (Y_l^m)^*}$$

- Vibration of a string sin, cos
- Vibration of a sphere Y_l^m

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

- Normalization $\int_0^\infty |R|^2 r^2 dr = 1$, $\int_0^{2\pi} d\phi \int_0^\pi d\theta (|Y|^2 \sin\theta) = 1$

- parity $\boxed{Y_l^m(\pi - \theta, \pi + \phi) = (-1)^l Y_l^m(\theta, \phi)}$

$l=0 \qquad Y_0^0 = \frac{1}{2}\sqrt{\frac{1}{\pi}}$

$l=1 \qquad Y_1^{-1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta \, e^{-i\phi}$

$\qquad\qquad Y_1^{0} = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$

$\qquad\qquad Y_1^{-1} = -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta \, e^{i\phi}$

$l=2 \qquad Y_2^{-2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2\theta \, e^{-2i\phi}$

$\qquad\qquad Y_2^{-1} = \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin\theta \cos\theta \, e^{-i\phi}$

$\qquad\qquad Y_2^{0} = \frac{1}{4}\sqrt{\frac{5}{\pi}} \left(3\cos^2\theta - 1\right)$

$\qquad\qquad Y_2^{1} = -\frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin\theta \cos\theta \, e^{i\phi}$

$\qquad\qquad Y_2^{2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2\theta \, e^{2i\phi}$

• The radial equation

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

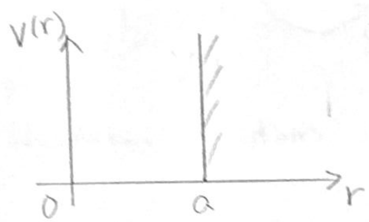
let $R(r) = \frac{u(r)}{r}$ then

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu}$$ 1-D Schrödinger equation

$$V_{eff} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$ effective potential

centrifugal term, repulsion

Ex: 3-D infinite square well



$$V(r) = \begin{cases} 0, & 0<r<a \\ \infty, & r>a \end{cases}$$

$0<r<a$: $$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}u = Eu$$

$$\frac{d^2u}{dr^2} - \left[\frac{l(l+1)}{r^2} - k^2\right]u = 0, \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

$$\boxed{u(r) = A_l r j_l(kr) + B_l r n_l(kr)}$$

where $j_l(x) = (-x)^l\left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x}$ spherical Bessel function

$n_l(x) = -(-x)^l\left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x}$ spherical Neumann function

$j_0(x) = \frac{\sin x}{x}$ $\qquad n_0(x) = -\frac{\cos x}{x}$

$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}$ $\qquad n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$

$j_2(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3}{x^2}\cos x$. $\qquad n_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x}\right)\cos x - \frac{3}{x^2}\sin x$

$x \to 0$, $j_l(x) \to \frac{2^l l!}{(2l+1)!}x^l$ $\qquad n_l(x) \to -\frac{(2l)!}{2^l l!}\frac{1}{x^{l+1}}$

$B_l = 0$ otherwise $u(r)$ is not normalizable, so $u(r) = A_l r j_l(kr)$

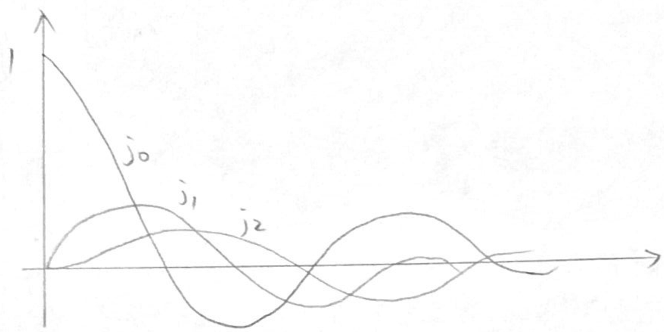
$R(r) = A_l j_l(kr)$

Continuity $R(a) = 0 \Rightarrow j_\ell(ka) = 0$.

let the zero points be $\beta_{n\ell}$. then $ka = \beta_{n\ell}$. $k = \frac{\beta_{n\ell}}{a}$. $E_n = \frac{\hbar^2}{2ma^2}\beta_{n\ell}^2$

$\psi_{n\ell m}(r,\theta,\phi) = A_{n\ell}\, j_\ell(\beta_{n\ell}\frac{r}{a})\, Y_\ell^m(\theta,\phi)$

- Each $n\ell$ energy level is $(2\ell+1)$ fold degenerate, $m = -\ell, \dots, \ell$



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

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

- Allows both continuum states $(E>0)$ and bound states $(E<0)$

bound states: $k = \frac{\sqrt{-2mE}}{\hbar}$ $E<0$

$$\frac{1}{k^2}\frac{d^2u}{dr^2} - \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2 k}\frac{1}{kr} + \frac{\ell(\ell+1)}{k^2r^2}\right]u = 0$$

let $\rho = kr$, $\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2 k}$

$$\frac{d^2u}{d\rho^2} - \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u = 0$$

$\rho \to \infty$. $\frac{d^2u}{d\rho^2} - u = 0$, $\Rightarrow u(\rho) = Ae^{-\rho} + Be^{\rho}$

$B = 0$ otherwise $u(r)$ is not normalizable. $u(\rho) \simeq Ae^{-\rho}$

$\rho \to 0$. $\frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u = 0 \Rightarrow u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$

$D = 0$. otherwise $u(r)$ is not normalizable. $u(\rho) \approx C\rho^{\ell+1}$

peel off the asymptotic behavior $u(r) = \rho^{l+1} e^{-\rho} v(\rho)$

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l+1-\rho) v + \rho \frac{dv}{d\rho} \right]$$

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho} \left\{ \left[-2(l+1) + \rho + \frac{l(l+1)}{\rho} \right] v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho \frac{d^2 v}{d\rho^2} \right\}$$

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

let $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$.

$$\frac{dv}{d\rho} = \sum_{j=1}^{\infty} c_j j \rho^{j-1} = \sum_{j=0}^{\infty} c_{j+1}(j+1)\rho^j$$

$$\frac{d^2 v}{d\rho} = \sum_{j=2}^{n} c_j j(j-1) \rho^{j-2} = \sum_{j=0}^{\infty} c_{j+1}(j+1) j \rho^{j-1}$$

$$\sum_{j=0}^{\infty} \left[j(j+1) c_{j+1} + 2(l+1)(j+1) c_{j+1} - 2j c_j + [\rho_0 - 2(l+1)] c_j \right] \rho^j = 0$$

$$\boxed{c_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2(l+1))} c_j}$$

$j \to \infty$, $c_{j+1} \to \frac{2}{j} c_j$ $\quad c_j = \frac{2^j}{j!} c_0 \quad v(\rho) = \sum \frac{2^j}{j!} c_0 \rho^j = c_0 e^{2\rho}$

$u(\rho) = c_0 \rho^{l+1} e^{\rho}$ not normalizable.

$\Rightarrow$ The power series must terminate for $j > j_{max}$, $c_{j \geq j_{max}+1} = 0$

$$2(j_{max} + l + 1) - \rho_0 = 0.$$

Define $n = j_{max} + l + 1 = \rho_0/2$ principal quantum number

$$E_n = -\frac{\hbar^2 k^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{me^2}{2\pi\epsilon_0 \hbar^2 \rho_0}\right)^2 = \boxed{-\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}} = \frac{E_1}{n^2} \quad E_1 = -13.6\,eV$$

$$k_n = \frac{me^2}{4\pi\epsilon_0 \hbar^2}\frac{1}{n} = \frac{1}{a_0 n}, \quad \boxed{a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}} = 0.529\,\text{Å} \quad \text{Bohr radius}$$

$$\boxed{R_{nl}(r) = A_{nl}\frac{u_{nl}(r)}{r} = \frac{A_{nl}}{r}\rho^{l+1} e^{-\rho} v(\rho)} \quad v(\rho) = \sum c_j \rho^j, \quad \rho = kr$$

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

$$R_{10} = 2 a_0^{-\frac{3}{2}} e^{-\frac{r}{a_0}}$$

$$R_{20} = \frac{1}{\sqrt{2}} a_0^{-\frac{3}{2}} \left(1 - \frac{1}{2}\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$R_{21} = \frac{1}{\sqrt{24}} a_0^{-\frac{3}{2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}}$$

- Degeneracy for each n, $l = 0, 1, \dots, n-1$

  for each l, $m = -l, \dots, l$

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = 2\frac{(n-1)n}{2} + n = n^2$$

- $$\boxed{R_{nl}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3}}\, e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)}$$

$L_{q-p}^{p}(x)$: associated Laguerre polynomial

$$L_{q-p}^{p}(x) = (-1)^p \frac{d^p}{dx^p} L_q(x)$$

$L_q(x)$: Laguerre polynomial

$$L_q(x) = e^x \frac{d^q}{dx^q}\left(e^{-x} x^q\right)$$

- $\boxed{\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi)}$ $|nlm\rangle$

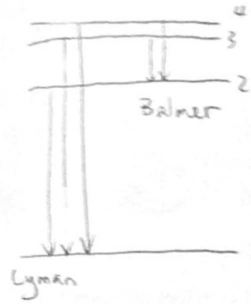
  $l = 0, \dots, n-1,$

  $m = -l, \dots, l$

- Hydrogen spectrum

$$E_\gamma = E_i - E_f = \boxed{E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)} = \hbar\omega = \frac{2\pi\hbar c}{\lambda}$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \quad R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = 1.097\times 10^{-7}\ m^{-1}$$ Rydberg const.



$n_f = 1$, Lyman series

$= 2$ Balmer series

$= 3$ Paschen series

• Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p} = \begin{pmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

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

- $\boxed{[L_x, L_y]} = [yp_z - zp_y, zp_x - xp_z]$

$$= [yp_z, zp_x] - [zp_y, zp_x] - [yp_z, xp_z] + [zp_y, xp_z]$$

$$= y[p_z, z]p_x - 0 - 0 + x[z, p_z]p_y$$

$$= -i\hbar y p_x + i\hbar x p_y = i\hbar(xp_y - yp_x) = \boxed{i\hbar L_z}$$

$\boxed{[L_y, L_z] = i\hbar L_x}$, $\boxed{[L_z, L_x] = i\hbar L_y}$

L_x, L_y, L_z cannot be determined simultaneously.

- $L^2 = L_x^2 + L_y^2 + L_z^2$

$$\boxed{[L^2, L_x]} = [L_x^2 + L_y^2 + L_z^2, L_x]$$

$$= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x]$$

$$= 0 + L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$$

$$= L_y(\cancel{-i\hbar L_z}) + (\cancel{-i\hbar L_z})L_y + L_z \cancel{i\hbar} L_y + i\hbar \cancel{L_y} L_z$$

$$\boxed{= 0}$$

$\boxed{[L^2, L_y] = [L^2, L_z] = 0} \Rightarrow [L^2, \vec{L}] = 0$

L^2 and L_z can have the same eigen state

$$L^2\psi = \lambda\psi, \quad L_z\psi = \mu\psi$$

- Define $L_\pm = L_x \pm i L_y$

$$[L^2, L_\pm] = 0$$

$$\begin{aligned}[L_z, L_\pm] &= [L_z, L_x \pm i L_y] \\ &= [L_z, L_x] \pm i [L_z, L_y] \\ &= i\hbar L_y \pm i(-i\hbar) L_x \\ &= \pm\hbar (L_x \pm i L_y) \\ &= \pm \hbar L_\pm\end{aligned}$$

- $L_\pm \psi$ is also an eigen state of L^2 with an eigen value λ

$$L^2(L_\pm\psi) = L_\pm(L^2\psi) = L_\pm(\lambda\psi) = \lambda(L_\pm\psi)$$

- $L_\pm\psi$ is also an eigen state of L_z with an eigen value $\mu \pm \lambda$

$$\begin{aligned}L_z(L_\pm\psi) &= (L_z L_\pm - L_\pm L_z)\psi + L_\pm L_z \psi \\ &= \pm\hbar L_\pm \psi + L_\pm \mu\psi \\ &= (\mu \pm \hbar) L_\pm \psi\end{aligned}$$

- $\langle L_z \rangle \leq \langle L \rangle \Rightarrow$ Consider all eigen states of L^2 with eigen value λ there is a top state ψ_t s.t. $L_+ \psi_t = 0$

let $L_z \psi_t = l\hbar \psi_t$, $L^2 \psi_t = \lambda \psi_t$

$$\begin{aligned}L_\pm L_\mp &= (L_x \pm i L_y)(L_x \mp i L_y) \\ &= L_x^2 \pm i L_y L_x \mp i L_x L_y + L_y^2 \\ &= L^2 - L_z^2 \pm i (L_y L_x - L_x L_y) \\ &= L^2 - L_z^2 \pm i(-i\hbar) L_z \\ &= L^2 - L_z^2 \pm \hbar L_z\end{aligned}$$

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$$

$$L^2\psi_t = (L_- L_+ + L_z^2 + \hbar L_z)\psi_t$$
$$= (0 + l^2\hbar^2 + \hbar l \hbar)\psi_t$$
$$= l(l+1)\hbar^2\psi_t \quad \Rightarrow \quad \lambda = l(l+1)\hbar^2$$

- bottom state ψ_b. $L_-\psi_b = 0$

let $L_z\psi_b = l'\hbar\psi_b$. $L^2\psi_b = \lambda\psi_b$

$$L^2\psi_b = (L_+ L_- + L_z^2 - \hbar L_z)\psi_b$$
$$= (0 + l'^2\hbar^2 - \hbar l'\hbar)\psi_b$$
$$= l'(l'-1)\hbar^2\psi_b \quad \Rightarrow \quad \lambda = l'(l'-1)\hbar^2$$

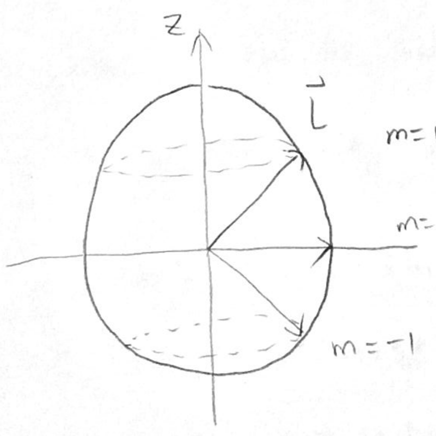
- $l(l+1) = l'(l'-1) \Rightarrow l' = -l$ or $l' = l+1$ (wrong)

$$\boxed{L^2\psi_{lm} = l(l+1)\hbar^2\psi_{lm}} \qquad \boxed{L_z\psi_{lm} = m\hbar\psi_{lm}}$$

$m = -l, \dots, l$, $\quad l = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots$

integer $\quad$ integer or half integer

$-l = l + N, \Rightarrow l = \frac{N}{2}$



- $$\vec{L} = \vec{r} \times \vec{p} = r\hat{r} \times (-i\hbar \nabla) = -i\hbar\, r\hat{r} \times \left(\hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r\sin\theta} \frac{\partial}{\partial \phi} \right)$$

$$= -i\hbar \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin\theta} \frac{\partial}{\partial \phi} \right)$$

$$\hat{\theta} = \cos\theta\cos\phi\, \hat{x} + \cos\theta \sin\phi\, \hat{y} - \sin\theta\, \hat{z}$$

$$\hat{\phi} = -\sin\phi\, \hat{x} + \cos\phi\, \hat{y}$$

$$\therefore L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial \theta} - \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right)$$

$$L_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right)$$

$$\boxed{L_z = -i\hbar \frac{\partial}{\partial \phi}}$$: azimuthal equation

$$L_\pm = L_x \pm i L_y = -i\hbar \left[(-\sin\phi \pm i\cos\phi) \frac{\partial}{\partial \theta} - \cot\theta (\cos\phi \pm i \sin\phi) \frac{\partial}{\partial \phi} \right]$$

$$= \pm \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot\theta \frac{\partial}{\partial \phi} \right)$$

$$L_+ L_- = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \cot^2\theta \frac{\partial^2}{\partial \phi^2} + i \frac{\partial}{\partial \phi} \right)$$

$$\boxed{L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right]}$$ Angular equation

Note: Here l can be half integers, but the previous separation of variables only allows integer l. (spin)

- $$\boxed{\begin{aligned} H|n\,l\,m\rangle &= E_n |n\,l\,m\rangle \\ L^2 |n\,l\,m\rangle &= l(l+1)\hbar^2 |n\,l\,m\rangle \\ L_z |n\,l\,m\rangle &= m\hbar |n\,l\,m\rangle \end{aligned}}$$

$$\boxed{\langle r\,\theta\,\phi | n\,l\,m\rangle = R_{nl}(r)\, Y_l^m(\theta, \phi)}$$

- Hydrogen spectrum

$$E_\gamma = E_i - E_f = \boxed{E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)} = \hbar\omega = \frac{2\pi\hbar c}{\lambda}$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \quad R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = 1.097 \times 10^{-7}\ m^{-1}$$ Rydberg const.

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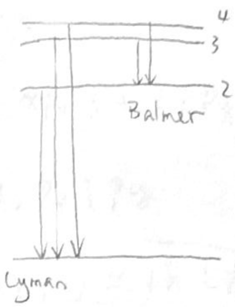

• Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p} = \begin{pmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

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

- $\boxed{[L_x, L_y]} = [yp_z - zp_y , zp_x - xp_z]$

$= [yp_z, zp_x] - [zp_y, zp_x] - [yp_z, xp_z] + [zp_y, xp_z]$

$= y[p_z, z]p_x - 0 - 0 + x[z, p_z]p_y$

$= -i\hbar yp_x + i\hbar xp_y = i\hbar(xp_y - yp_x) = \boxed{i\hbar L_z}$

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$\boxed{[L^2, L_x]} = [L_x^2 + L_y^2 + L_z^2 , L_x]$

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$= 0 + L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$

$= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z i\hbar L_y + i\hbar L_y L_z$

$\boxed{= 0}$

$\boxed{[L^2, L_y] = [L^2, L_z] = 0}$ $\Rightarrow$ $[L^2, \vec{L}] = 0$

L^2 and L_z can have the same eigen state

$L^2 \psi = \lambda \psi$, $L_z \psi = \mu \psi$

- Define $L_\pm = L_x \pm i L_y$

$$[L^2, L_\pm] = 0$$

$$[L_z, L_\pm] = [L_z, L_x \pm i L_y]$$

$$= [L_z, L_x] \pm i [L_z, L_y]$$

$$= i\hbar L_y \pm i(-i\hbar) L_x$$

$$= \pm\hbar (L_x \pm i L_y)$$

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let $L_z \psi_t = l\hbar\psi_t$, $L^2 \psi_t = \lambda\psi_t$. $\lambda = ?$

$$L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y)$$

$$= L_x^2 \pm i L_y L_x \mp i L_x L_y + L_y^2$$

$$= L^2 - L_z^2 \pm i(L_y L_x - L_x L_y)$$

$$= L^2 - L_z^2 \pm i(-i\hbar) L_z$$

$$= L^2 - L_z^2 \pm \hbar L_z$$

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$$

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$$= l(l+1)\hbar^2\psi_t \quad \Rightarrow \quad \lambda = l(l+1)\hbar^2$$

- bottom state ψ_b, $L_-\psi_b = 0$

let $L_z\psi_b = l'\hbar\psi_b$. $L^2\psi_b = \lambda\psi_b$, $\lambda = ?$

$$L^2\psi_b = (L_+L_- + L_z^2 - \hbar L_z)\psi_b$$
$$= (0 + l'^2\hbar^2 - \hbar l'\hbar)\psi_b$$
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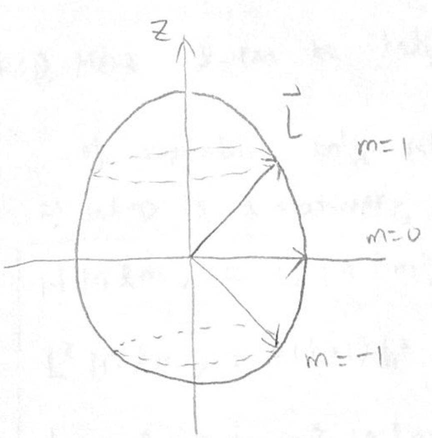
integer, integer or half integer

$-l = l + N, \Rightarrow l = \frac{N}{2}$



- $\boxed{L_\pm\psi_l^m = \hbar\sqrt{l(l+1) - m(m\pm1)}\ \psi_l^{m\pm1}}$

- $\vec{L} = \vec{r} \times \vec{p} = r\hat{r} \times (-i\hbar \nabla) = -i\hbar\, r\hat{r} \times \left(\hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi} \right)$

$$= -i\hbar \left(\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} \right)$$

$$\hat{\theta} = \cos\theta\cos\phi\, \hat{x} + \cos\theta\sin\phi\, \hat{y} - \sin\theta\, \hat{z}$$

$$\hat{\phi} = -\sin\phi\, \hat{x} + \cos\phi\, \hat{y}$$

$$\therefore \quad L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)$$

$$L_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right)$$

$\boxed{L_z = -i\hbar \frac{\partial}{\partial\phi}}$: azimuthal equation

$$L_\pm = L_x \pm i L_y = -i\hbar \left[(-\sin\phi \pm i\cos\phi)\frac{\partial}{\partial\theta} - \cot\theta\,(\cos\phi \pm i\sin\phi)\frac{\partial}{\partial\phi} \right]$$

$$= \pm\hbar e^{\pm i\phi} \left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi} \right)$$

$$L_+L_- = -\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + i\frac{\partial}{\partial\phi} \right)$$

$\boxed{L^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right]}$ Angular equation

Remark: 1) Here l can be half integers, but the previous separation of variables only allows integer l. (spin)

2) $|nlm\rangle$ is a stationary state, but has angular momentum.

- $$\boxed{\begin{aligned} H|nlm\rangle &= E_n|nlm\rangle \\ L^2|nlm\rangle &= l(l+1)\hbar^2|nlm\rangle \\ L_z|nlm\rangle &= m\hbar|nlm\rangle \end{aligned}}$$

$$\boxed{\langle r\theta\phi|nlm\rangle = R_{nl}(r)\, Y_l^m(\theta,\phi)}$$

☆ Spin

- intrinsic, relativistic effect
- inferred from Stern–Gerlach experiment
- Pauli
- Definition $[S_x, S_y] = i\hbar S_z$,

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

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

then $S^2 |s\, m\rangle = s(s+1)\hbar^2 |s\, m\rangle$

$S_z |s\, m\rangle = m_s \hbar |s\, m\rangle$

$S_\pm |s\, m\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}\ |s, m\pm 1\rangle \Rightarrow \begin{cases} S_x = \frac{1}{2}(S_+ + S_-) \\ S_y = \frac{1}{2i}(S_+ - S_-) \end{cases}$

where s can be half integers $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots$ $m = -s, \cdots, s$

- s is fixed for a given particle

  $s=0$ Higgs.

  $s=\frac{1}{2}$ electron, proton, neutron, all quarks, all leptons

  $s=1$ photon

  $s=2$ graviton

- spin $\frac{1}{2}$ $s = \frac{1}{2}$ $m = \pm\frac{1}{2}$

  Two eigen states $|\frac{1}{2}, \frac{1}{2}\rangle = |\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$

  $|\frac{1}{2}, -\frac{1}{2}\rangle = |\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}$

  General state (spinor) $|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \begin{pmatrix}a\\b\end{pmatrix}$, $a^2 + b^2 = 1$

- Matrix representation of S^2 and S_z, S_x, S_y

  $S^2 |\uparrow\rangle = \frac{3}{4}\hbar^2 |\uparrow\rangle$, $S^2|\downarrow\rangle = \frac{3}{4}\hbar^2|\downarrow\rangle$

  $\langle\uparrow| S^2 |\uparrow\rangle = \frac{3}{4}\hbar^2$

  $\langle\downarrow| S^2 |\uparrow\rangle = 0$

  $\langle\uparrow| S^2 |\downarrow\rangle = 0$

  $\langle\downarrow| S^2 |\downarrow\rangle = \frac{3}{4}\hbar^2$

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

$S_z|\uparrow\rangle = \frac{1}{2}\hbar|\uparrow\rangle \qquad S_z|\downarrow\rangle = -\frac{1}{2}\hbar|\downarrow\rangle$

$\langle\uparrow|S_z|\uparrow\rangle = \frac{1}{2}\hbar$

$\langle\downarrow|S_z|\uparrow\rangle = 0$

$\langle\uparrow|S_z|\downarrow\rangle = 0$

$\langle\downarrow|S_z|\downarrow\rangle = -\frac{1}{2}\hbar$

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

$S_+|\downarrow\rangle = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1)-(-\frac{1}{2})(-\frac{1}{2}+1)}\,|\uparrow\rangle = \hbar|\uparrow\rangle \quad , \quad S_+|\uparrow\rangle = 0$

$\Rightarrow \boxed{S_+ = \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}}$

$S_-|\uparrow\rangle = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1)-\frac{1}{2}(\frac{1}{2}-1)}\,|\downarrow\rangle = \hbar|\downarrow\rangle , \qquad S_-|\downarrow\rangle = 0$

$\Rightarrow \boxed{S_- = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}}$

$\boxed{S_x =} \frac{1}{2}(S_+ + S_-) = \boxed{\frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}}$

$\boxed{S_y =} \frac{1}{2i}(S_+ - S_-) = \boxed{\frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}}$

- Pauli matrices $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$

Hermitian

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

Pauli 1945 Nobel Chemistry

- Pauli effect

vs Ehrenfest

- Eigen states and eigen values of S_x

$\det(\lambda I - S_x) = 0$

$\begin{vmatrix}\lambda & -\frac{\hbar}{2}\\ -\frac{\hbar}{2} & \lambda\end{vmatrix} = 0 \quad , \quad \lambda = \pm\frac{\hbar}{2}$

$\lambda = \frac{\hbar}{2} \quad \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}a\\ b\end{pmatrix} \Rightarrow a = b$. normalization $a = b = \frac{1}{\sqrt{2}}$. $\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{pmatrix}$

$\lambda = -\frac{\hbar}{2} \quad \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix}a\\ b\end{pmatrix} \Rightarrow a = -b$. normalization $a = \frac{1}{\sqrt{2}},\ b = -\frac{1}{\sqrt{2}}$ or $a = -\frac{1}{\sqrt{2}},\ b = \frac{1}{\sqrt{2}}$ $\quad \pm\begin{pmatrix}\frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}}\end{pmatrix}$

general state $|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = a\begin{pmatrix}1\\0\end{pmatrix} + b\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}a\\b\end{pmatrix}$

$$= \frac{a+b}{\sqrt{2}}\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{pmatrix} + \frac{a-b}{\sqrt{2}}\begin{pmatrix}\frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}}\end{pmatrix}$$ in terms of eigen states of S_x

- start from $|\uparrow\rangle$, measure $S_x \rightarrow$ equal probability to find $\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{pmatrix}$ or $\begin{pmatrix}\frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}}\end{pmatrix}$, if $\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{pmatrix}$ measure S_z again $\rightarrow$ equal prob to find $|\uparrow\rangle$ or $|\downarrow\rangle$

• Spin in a magnetic field

- magnetic dipole moment $\vec{\mu} = \gamma \vec{S}$

$\uparrow$ gyromagnetic ratio, g-factor

$$\gamma_s = 2\gamma_l = -\frac{2e}{m}$$

- torque $\vec{\tau} = \vec{\mu} \times \vec{B}$

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

classical

$\vec{B} = B_0\hat{z}$

- Larmor procession

$$H = -\gamma B_0 S_z = -\frac{\gamma B_0 \hbar}{2}\begin{pmatrix}1 & \\ & -1\end{pmatrix}$$

so the eigen states of H are the same as S_z:

$|\uparrow\rangle$, $E_\uparrow = -\frac{\gamma B_0 \hbar}{2}$ lower energy, parallel

$|\downarrow\rangle$, $E_\downarrow = \frac{\gamma B_0 \hbar}{2}$

General time dependent solution

$$|\psi(t)\rangle = a|\uparrow\rangle e^{-\frac{i}{\hbar}E_\uparrow t} + b|\downarrow\rangle e^{-\frac{i}{\hbar}E_\downarrow t} = \begin{pmatrix}a e^{i\gamma B_0 t/2}\\ b e^{-i\gamma B_0 t/2}\end{pmatrix}$$

where a and b are determined by initial condition $|\psi(0)\rangle$

$|\psi(0)\rangle = a|\uparrow\rangle + b|\downarrow\rangle$, $a^2 + b^2 = 1$

$a = \langle\uparrow|\psi(0)\rangle$, $b = \langle\downarrow|\psi(0)\rangle$.

Write $a = \cos\frac{\alpha}{2}$, $b = \sin\frac{\alpha}{2}$, then $|\psi(t)\rangle = \begin{pmatrix}\cos\frac{\alpha}{2}\, e^{i\gamma B_0 t/2}\\ \sin\frac{\alpha}{2}\, e^{-i\gamma B_0 t/2}\end{pmatrix}$

$\sin\alpha = 2ab$

$\cos\alpha = a - b$

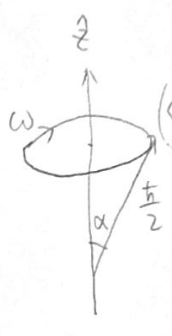
Expectation value to S_x, S_y, S_z

$$\langle S_x \rangle = \langle \psi(t) | S_x | \psi(t) \rangle = \left(\cos\frac{\alpha}{2} e^{-i\gamma B_0 t/2} \quad \sin\frac{\alpha}{2} e^{i\gamma B_0 t/2} \right) \frac{\hbar}{2} \begin{pmatrix} & 1 \\ 1 & \end{pmatrix} \begin{pmatrix} \cos\frac{\alpha}{2} e^{i\gamma B_0 t/2} \\ \sin\frac{\alpha}{2} e^{-i\gamma B_0 t/2} \end{pmatrix}$$

$$= \frac{\hbar}{2} \sin\frac{\alpha}{2} \cos\frac{\alpha}{2} \left(e^{i\gamma B_0 t} + e^{-i\gamma B_0 t} \right) = \frac{\hbar}{2} \sin\alpha \cos(\gamma B_0 t)$$

Similarly $\langle S_y \rangle = -\frac{\hbar}{2} \sin\alpha \sin(\gamma B_0 t)$

$\langle S_z \rangle = \frac{\hbar}{2} \cos\alpha$



$(\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle) \neq \vec{S}$

Larmor frequency $\boxed{\omega = \gamma B_0}$

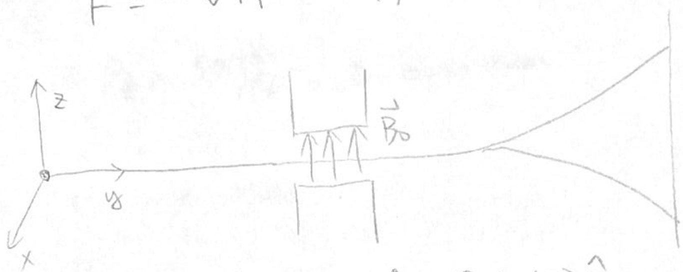
$\langle S_x \rangle^2 + \langle S_y \rangle^2 + \langle S_z \rangle^2 = \left(\frac{\hbar}{2}\right)^2$

$\langle S_x^2 + S_y^2 + S_z^2 \rangle = \frac{3}{4}\hbar^2$

Note: This figure is fundamentally different from the representation of the spin

- Stern - Gerlach experiment
  - Intuitive analysis
    Inhomogeneous magnetic field $\rightarrow$ force

$$\vec{F} = -\nabla H = \nabla(\vec{\mu} \cdot \vec{B})$$



$\vec{B} = -\alpha x \hat{x} + (B_0 + \alpha z)\hat{z}$

B_0 is a strong uniform field.

α describes a small deviation

① neutral particle $\rightarrow$ avoid Lorentz force

② heavy particle $\rightarrow$ particle trajectory can be treated classically
Silver — in fact, electron beam doesn't work

$$\vec{\mu} \cdot \vec{B} = -\alpha x \gamma S_x + (B_0 + \alpha z)\gamma S_z$$

$$\vec{F} = \gamma\alpha(-S_x \hat{x} + S_z \hat{z})$$

- Because of the Larmor procession around $\vec{B_0}$, $\langle S_x \rangle$ oscillates rapidly. $F_x = 0$

- $F_z = \gamma \alpha S_z$

Beam will split for different m_s $(2S+1$ lines$)$

$\rightarrow$ quantization of angular momentum

vs. classical continuous distribution

- More rigious analysis

$$H(t) = \begin{cases} 0 & t<0 \\ -\gamma(B_0+\alpha z)S_z, & 0\leq t\leq T \\ 0 & t>T \end{cases}$$

$t=0$, $\quad |\psi(t)\rangle = \begin{pmatrix} a \\ b \end{pmatrix} = a|\uparrow\rangle + b|\downarrow\rangle$

$0\leq t\leq T$, $\quad |\psi(t)\rangle = a|\uparrow\rangle e^{-\frac{i}{\hbar}E_\uparrow t} + b|\downarrow\rangle e^{-\frac{i}{\hbar}E_\downarrow t}$

where $E_\uparrow = -\gamma(B_0+\alpha z)\frac{\hbar}{2}$

$E_\downarrow = \gamma(B_0+\alpha z)\frac{\hbar}{2}$

$t=T$. $\quad |\psi(t)\rangle = \left(a e^{i\gamma B_0 T/2} |\uparrow\rangle\right) e^{\underset{\sim}{i\gamma\alpha T/2\, z}} + \left(b e^{-i\gamma B_0 T/2} |\downarrow\rangle\right) e^{\underset{\sim}{-i\gamma\alpha T/2\, z}}$

$P_z = \gamma\alpha T\hbar/2$ z-momentum

- prepare a pure state

- Addition of spin angular momentum (spinor, not vector)

- Two spin $\frac{1}{2}$ particles ① hydrogen atom, $e+p$

② deuteron, neutron-proton scattering $n+p$

Naively, there are four possible configurations :

$$\uparrow\uparrow, \quad \uparrow\downarrow, \quad \downarrow\uparrow, \quad \downarrow\downarrow$$

Total angular momentum eigen state $S^2 = ?$

Total z-component of the angular momentum eigen state $S_z = ?$

$$\boxed{\begin{aligned} \vec{S}^2 &= (\vec{S}_1+\vec{S}_2)^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2 \\ S_z &= S_{z1} + S_{z2} \end{aligned}}$$

- All the four states are eigen states of S_z

$$S_z|\uparrow\uparrow\rangle = S_{z1}|\uparrow\rangle|\uparrow\rangle + |\uparrow\rangle S_{z2}|\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle|\uparrow\rangle + |\uparrow\rangle\frac{\hbar}{2}|\uparrow\rangle = \hbar|\uparrow\uparrow\rangle$$

$$S_z|\uparrow\downarrow\rangle = S_{z1}|\uparrow\rangle|\downarrow\rangle + |\uparrow\rangle S_{z2}|\downarrow\rangle = \frac{\hbar}{2}|\uparrow\rangle|\downarrow\rangle + |\uparrow\rangle(-\frac{\hbar}{2})|\downarrow\rangle = 0$$

$$S_z|\downarrow\uparrow\rangle = S_{z1}|\downarrow\rangle|\uparrow\rangle + |\downarrow\rangle S_{z2}|\uparrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle|\uparrow\rangle + |\downarrow\rangle\frac{\hbar}{2}|\uparrow\rangle = 0$$

$$S_z|\downarrow\downarrow\rangle = S_{z1}|\downarrow\rangle|\downarrow\rangle + |\downarrow\rangle S_{z2}|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle|\downarrow\rangle + |\downarrow\rangle(-\frac{\hbar}{2})|\downarrow\rangle = -\hbar|\downarrow\downarrow\rangle$$

- Only $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are eigen states of S^2.

$|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ are not eigen states of S^2

① $\vec{S}^2|\uparrow\uparrow\rangle = (\vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2)|\uparrow\uparrow\rangle$

$$= S_1^2|\uparrow\rangle|\uparrow\rangle + |\uparrow\rangle S_2^2|\uparrow\rangle + 2(S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2})|\uparrow\uparrow\rangle$$

$$= \frac{3}{4}\hbar^2|\uparrow\rangle|\uparrow\rangle + |\uparrow\rangle\frac{3}{4}\hbar^2|\uparrow\rangle + 2(S_{x1}|\uparrow\rangle S_{x2}|\uparrow\rangle + S_{y1}|\uparrow\rangle S_{y2}|\uparrow\rangle + S_{z1}|\uparrow\rangle S_{z2}|\uparrow\rangle)$$

$$S_x|\uparrow\rangle = \frac{1}{2}(S_+ + S_-)|\uparrow\rangle = 0 + \frac{1}{2}\hbar|\downarrow\rangle = \frac{\hbar}{2}|\downarrow\rangle$$

$$S_y|\uparrow\rangle = \frac{1}{2i}(S_+ - S_-)|\uparrow\rangle = 0 - \frac{1}{2i}\hbar|\downarrow\rangle = \frac{i\hbar}{2}|\downarrow\rangle$$

$$S_z|\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle$$

Alternatively, use Pauli matrices

$$S_x|\uparrow\rangle = \frac{\hbar}{2}\begin{pmatrix} & 1 \\ 1 & \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}|\downarrow\rangle$$

$$S_y|\uparrow\rangle = \frac{\hbar}{2}\begin{pmatrix} & -i \\ i & \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ i \end{pmatrix} = \frac{i\hbar}{2}|\downarrow\rangle$$

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

$\therefore\ \vec{S}^2|\uparrow\uparrow\rangle = \frac{3}{4}\hbar^2|\uparrow\rangle|\uparrow\rangle + \frac{3}{4}\hbar^2|\uparrow\rangle|\uparrow\rangle + 2\left(\cancel{\frac{\hbar}{2}|\downarrow\rangle\frac{\hbar}{2}|\downarrow\rangle + \frac{i\hbar}{2}|\downarrow\rangle\frac{i\hbar}{2}|\downarrow\rangle} + \frac{\hbar}{2}|\uparrow\rangle\frac{\hbar}{2}|\uparrow\rangle\right)$

$= 2\hbar^2|\uparrow\uparrow\rangle$

② $\vec{S}^2|\downarrow\downarrow\rangle = (\vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2)|\downarrow\downarrow\rangle$

$= \vec{S}_1^2|\downarrow\rangle|\downarrow\rangle + |\downarrow\rangle\vec{S}_2^2|\downarrow\rangle + 2(S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2})|\downarrow\downarrow\rangle$

$= \frac{3}{4}\hbar^2|\downarrow\rangle|\downarrow\rangle + |\downarrow\rangle\frac{3}{4}\hbar^2|\downarrow\rangle + 2(S_{x1}|\downarrow\rangle S_{x2}|\downarrow\rangle + S_{y1}|\downarrow\rangle S_{y2}|\downarrow\rangle + S_{z1}|\downarrow\rangle S_{z2}|\downarrow\rangle)$

$S_x|\downarrow\rangle = \frac{1}{2}(S_+ + S_-)|\downarrow\rangle = \frac{1}{2}\hbar|\uparrow\rangle + 0 = \frac{\hbar}{2}|\uparrow\rangle$

$S_y|\downarrow\rangle = \frac{1}{2i}(S_+ - S_-)|\downarrow\rangle = \frac{1}{2i}\hbar|\uparrow\rangle - 0 = -\frac{i\hbar}{2}|\uparrow\rangle$

$S_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle$

Alternatively, use Pauli matrices

$S_x|\downarrow\rangle = \frac{\hbar}{2}\begin{pmatrix} & 1 \\ 1 & \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}|\uparrow\rangle$

$S_y|\downarrow\rangle = \frac{\hbar}{2}\begin{pmatrix} & -i \\ i & \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} -i \\ 0 \end{pmatrix} = -\frac{i\hbar}{2}|\uparrow\rangle$

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

$\therefore\ \vec{S}^2|\downarrow\downarrow\rangle = \frac{3}{4}\hbar^2|\downarrow\rangle|\downarrow\rangle + \frac{3}{4}\hbar^2|\downarrow\rangle|\downarrow\rangle + 2\left(\cancel{\frac{\hbar}{2}|\uparrow\rangle\frac{\hbar}{2}|\uparrow\rangle + \left(-\frac{i\hbar}{2}\right)|\uparrow\rangle\left(-\frac{i\hbar}{2}\right)|\uparrow\rangle} + \left(-\frac{\hbar}{2}\right)|\downarrow\rangle\left(-\frac{\hbar}{2}\right)|\downarrow\rangle\right)$

$= 2\hbar^2|\downarrow\downarrow\rangle$

③ $\vec{S}^2|\uparrow\downarrow\rangle = (\vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2)|\uparrow\downarrow\rangle$

$= \vec{S}_1^2|\uparrow\rangle|\downarrow\rangle + |\uparrow\rangle\vec{S}_2^2|\downarrow\rangle + 2(S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2})|\uparrow\downarrow\rangle$

$= \frac{3}{4}\hbar^2|\uparrow\rangle|\downarrow\rangle + |\uparrow\rangle\frac{3}{4}\hbar^2|\downarrow\rangle + 2(S_{x1}|\uparrow\rangle S_{x2}|\downarrow\rangle + S_{y1}|\uparrow\rangle S_{y2}|\downarrow\rangle + S_{z1}|\uparrow\rangle S_{z2}|\downarrow\rangle)$

$= \frac{3}{2}\hbar^2|\uparrow\downarrow\rangle + 2\left(\frac{\hbar}{2}|\downarrow\rangle\frac{\hbar}{2}|\uparrow\rangle + \frac{i\hbar}{2}|\downarrow\rangle\left(-\frac{i\hbar}{2}\right)|\uparrow\rangle + \frac{\hbar}{2}|\uparrow\rangle\left(-\frac{\hbar}{2}\right)|\downarrow\rangle\right)$

$= \hbar^2(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ $|\uparrow\downarrow\rangle$ is not an eigen state of $\vec{S}^2$

④ $\vec{S}^2|\downarrow\uparrow\rangle = (\vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2)|\downarrow\uparrow\rangle$

$= \vec{S}_1^2|\downarrow\rangle|\uparrow\rangle + |\downarrow\rangle\vec{S}_2^2|\uparrow\rangle + 2(S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2})|\downarrow\uparrow\rangle$

$= \frac{3}{4}\hbar^2|\downarrow\rangle|\uparrow\rangle + |\downarrow\rangle\frac{3}{4}\hbar^2|\uparrow\rangle + 2(S_{x1}|\downarrow\rangle S_{x2}|\uparrow\rangle + S_{y1}|\downarrow\rangle S_{y2}|\uparrow\rangle + S_{z1}|\downarrow\rangle S_{z2}|\uparrow\rangle)$

$= \frac{3}{2}\hbar^2|\downarrow\uparrow\rangle + 2\left(\frac{\hbar}{2}|\uparrow\rangle\frac{\hbar}{2}|\downarrow\rangle + \left(-\frac{i\hbar}{2}\right)|\uparrow\rangle\frac{i\hbar}{2}|\downarrow\rangle + \left(-\frac{\hbar}{2}\right)|\downarrow\rangle\frac{\hbar}{2}|\uparrow\rangle\right)$

$= \hbar^2(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$ $|\uparrow\downarrow\rangle$ is not an eigen state of $\vec{S}^2$

③+④ $\vec{S}^2(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = 2\hbar^2(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$

③−④ $\vec{S}^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = 0$

$\therefore$ $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ is an eigen state of S^2, with eigen value $2\hbar^2$

$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ 0

Both are also eigen states of S_z.

Summary

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

$\vec{S} = \vec{S}_1 + \vec{S}_2$

$S_z = S_{z1} + S_{z2}$

$$\boxed{\begin{aligned} s &= s_1+s_2, \cdots, |s_1-s_2| \\ m &= -s, -(s-1), \cdots, s \end{aligned}}$$

eigenstates ① $s=0$, $m=0$

$|0\,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ singlet "anti-parallel"

eigen values
S^2 : 0
S_z : 0

② $s=1$, $m=-1, 0, 1$

$$\begin{cases} |1\,1\rangle = |\uparrow\uparrow\rangle \\ |1\,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1\,-1\rangle = |\downarrow\downarrow\rangle \end{cases}$$

triplet "parallel" along xy

S^2 : $2\hbar^2$
S_z : $\hbar, 0, -\hbar$

- In general

$$\boxed{\begin{aligned} |s\,m\rangle &= \sum_{m_1+m_2=m} C^{s_1 s_2 s}_{m_1 m_2 m}\,|s_1 m_1\rangle|s_2 m_2\rangle \\ |s_1 m_1\rangle|s_2 m_2\rangle &= \sum_s C^{s_1 s_2 s}_{m_1 m_2 m}\,|s\,m\rangle \end{aligned}}$$

$C^{s_1 s_2 s}_{m_1 m_2 m}$: Clebsch–Gordon (CG) Coefficients

e.g. $s_1 = 2$, $s_1 = 1$

$$|3\,0\rangle = \frac{1}{\sqrt{5}}|2\,1\rangle|1\,-1\rangle + \sqrt{\frac{3}{5}}|2\,0\rangle|1\,0\rangle + \frac{1}{\sqrt{5}}|2\,-1\rangle|1\,1\rangle$$

- Verification $S_-|1\,1\rangle = (S_{1-} + S_{2-})|\uparrow\uparrow\rangle = \hbar|\downarrow\rangle|\uparrow\rangle + |\uparrow\rangle\hbar|\downarrow\rangle = \hbar(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$
$= \sqrt{2}\hbar\,|1\,0\rangle$

$S_-|1\,1\rangle = \hbar\sqrt{1(1+1) - 1(1-1)}\;|1\,0\rangle = \sqrt{2}\hbar\,|1\,0\rangle$