Quantum Mechanics Note by CHESTNUT

He Yingqiu

July 16, 2024

Preface

I got BSc degree from Zhejiang University of Technology, China, in 2024. You can visit my website at heyingqiu.github.io. It would be an honor if you took the time to explore it.
The notes begin with a review of Classical Mechanics and Classical Electrodynamics, providing a background and an introduction for comparison and mastery from an overview. For a more in-depth study of Classical Mechanics, you can refer to my other notes, which are also based on a video uploaded on Bilibili. I find the teaching in this video to be exceptional. Following this review, the notes progress to fundamental concepts such as representation and symbols.
Reference books:

- Modern Quantum Mechanics (Third Edition) by J.J. Sakurai and Jim Napolitano

Reference video:

- Peking University - Quantum Mechanics Lecture (Guo Hong)

Feel free to communicate with me about anything you would like. You can contact me at he.yingqiu@hotmail.com. Thanks again for visiting!

Yingqiu He 🌰
Zhejiang, home
2024.07.16

Contents

Chapter 1

Preliminaries

1.1 Classical Mechanics

Newtonian Mechanics

Euclidean space (physical space)
Cartesian coordiante: $\vec{x}$

- Momentum force
$$\frac{\mathrm{d}\vec{p}}{\mathrm{d}t} = \vec{F}; \quad \vec{p} = m\vec{v}$$
- Angular momentum torque
$$\frac{\mathrm{d}\vec{L}}{\mathrm{d}t} = \vec{N}; \quad \vec{L} = \vec{x} \times \vec{p}$$
- Relation
$$\vec{N} = \vec{x} \times \vec{F}$$

Proof. $\frac{\mathrm{d}\vec{L}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}(\vec{x} \times \vec{p}) = \frac{\mathrm{d}x}{\mathrm{d}t} \times \vec{p} + \vec{x} \times \frac{\mathrm{d}\vec{p}}{\mathrm{d}t} = \cancel{\vec{v} \times m\vec{v}} + \vec{x} \times \vec{F}$ □

Mass point - mass point system - rigid body

- Inertia of mass: m; Inertia of rotation: mr^2

Lagrangian Mechanics

$3N$ dependent coordiantes $x_1, \cdots, x_{3N}$ $\to$ D independent generalized coordinates $q_1, \cdots, q_D$, $\partial q_i / \partial q_j = 0 \quad (i \neq j)$

- Holonomic constraint $f(x,t) \equiv 0$
- Non-holonomic constraint $f(x, \dot{x}, t) \equiv 0$

Coordinates and Space

- Generalized coordiantes $q_\alpha(t) \quad (\alpha = q, \cdots, D) \quad D \leqslant 3N$
- in Configuration space (Abstract space)
- Functional
  - e.g. Lagrangian: $L(q_\alpha(t), \dot{q}_\alpha(t); t)$, Hamiltonian: $H(q_\alpha(t), p_\alpha(t); t)$, Action: $S[q(t)] = \int_{t_1}^{t_2} L\mathrm{d}t$
  - Dimensions of these functionals:
    $[L] = [H] =$ [Energy], $[S] =$ [Energy] · [Time] = [Length] · [Momentum] = $[\hbar]$

Table 1.1: Comparison

	Space	Coordinates	dimensional
Newtonian Mechanics	Physical Space	$\vec{x}_\alpha(t)$	3N
Lagrangian Mechanics	Configuration Space	$q_\alpha(t)$	D
Hamiltonian Mechanics	Phase Space	$q_\alpha(t), p_\alpha(t)$	2D

Principle of Least Action

Consider $f(q, \dot{q}, t)$,

- Differentiate: $\Delta f = f(x_2) - f(x_1) = \dfrac{\partial f}{\partial q}\Delta q + \dfrac{\partial f}{\partial \dot{q}}\Delta \dot{q}$
- Differential: $\Delta f \xrightarrow{\Delta x \to 0} \mathrm{d}f = \dfrac{\partial f}{\partial q}\mathrm{d}q + \dfrac{\partial f}{\partial \dot{q}}\mathrm{d}\dot{q}$
- Variation: $\mathrm{d}f \xrightarrow{\mathrm{d}\to\delta} \delta f = \dfrac{\partial f}{\partial q}\delta q + \dfrac{\partial f}{\partial \dot{q}}\delta \dot{q}$

Usually $\delta q(t_1) = \delta q(t_2) = 0,\ \delta t = 0$ and use $\delta\dot{q} = \delta(\mathrm{d}q/\mathrm{d}t) = \mathrm{d}(\delta q)/\mathrm{d}t$, principle of least action tell us

$$0 \equiv \delta S = \delta\int_{t_1}^{t_2} L(q,\dot{q},t)\mathrm{d}t = \int_{t_1}^{t_2}\left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta\dot{q}\right)\mathrm{d}t = \int_{t_1}^{t_2}\left\{\frac{\partial L}{\partial q}\delta q + \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}}\right)\delta q\right\}\mathrm{d}t$$
$$= \int_{t_1}^{t_2}\left(\frac{\partial L}{\partial q} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}}\right)\delta q\mathrm{d}t + \left.\frac{\partial L}{\partial \dot{q}}\delta q\right|_{t_1}^{t_2} \quad \Rightarrow$$

Euler-Lagrangian's Equation:

$$\frac{\partial L}{\partial q_\alpha} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_\alpha}\right) \qquad (\alpha = 1, \cdots, D)$$

Hamiltonian Mechanics

Hamilton's Canonical Transformations

$$\dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha}, \qquad \dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha}$$

Legendre's Transformation:

$$\begin{cases} p_\alpha = \dfrac{\partial L}{\partial \dot{q}_\alpha}, \\ H(q,p,t) = \displaystyle\sum_\alpha p_\alpha \dot{q}_\alpha - L(q,\dot{q},t) \end{cases}$$

Methods of proof:

1. since H is $\dot{q}$-independent, and L is p-independent, then
$$\frac{\partial H}{\partial \dot{q}_\alpha} = p_\alpha - \frac{\partial L}{\partial \dot{q}_\alpha} \equiv 0, \qquad \frac{\partial L}{\partial p_\alpha} = \dot{q}_\alpha - \frac{\partial H}{\partial p_\alpha} \equiv 0, \quad \text{and} \quad \dot{p}_\alpha = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_\alpha}\right) = \frac{\partial L}{\partial q_\alpha} = -\frac{\partial H}{\partial q_\alpha}$$
2. $\mathrm{d}H = \dfrac{\partial H}{\partial t}\mathrm{d}t + \dfrac{\partial H}{\partial q}\mathrm{d}q + \dfrac{\partial H}{\partial p}\mathrm{d}p$, on the other hand $\mathrm{d}H = \mathrm{d}(p\dot{q} - L(q,\dot{q},t)) = \dot{q}\mathrm{d}p - \dot{p}\mathrm{d}q - \dfrac{\partial L}{\partial t}\mathrm{d}t$
3. $0 \equiv \delta S = \delta\displaystyle\int (p\dot{q} - H(q,p,t))\mathrm{d}t$ (under)

Poisson's Bracket (Classical Canonical Commutator)

$\forall f(q,p,t)$, then

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial f}{\partial p_\alpha}\dot{p}_\alpha = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial q_\alpha}\frac{\partial H}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial H}{\partial q_\alpha} = \frac{\partial f}{\partial t} + [f,H]_{\mathrm{PB}}$$

where

$$[f,H]_{\mathrm{PB}} = \frac{\partial f}{\partial q_\alpha}\frac{\partial H}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial H}{\partial q_\alpha}, \quad \text{or} \quad [A,B]_{\mathrm{PB}} = \frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha}\frac{\partial B}{\partial q_\alpha}$$

- $[q_\alpha, p_\beta]_{\mathrm{PB}} = \delta_{\alpha\beta},\ [q_\alpha, q_\beta]_{\mathrm{PB}} = [p_\alpha, p_\beta] \equiv 0$
- In QM, similarly, Heisenberg's equation and Ehrenfest's theorem are

$$\frac{\mathrm{d}\hat{f}}{\mathrm{d}t} = \frac{\partial \hat{f}}{\partial t} + \frac{1}{i\hbar}[\hat{f}, \hat{H}] \qquad \frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{f} \right\rangle = \left\langle \frac{\partial \hat{f}}{\partial t} \right\rangle + \frac{1}{i\hbar}\left\langle [\hat{f}, \hat{H}] \right\rangle$$

quantum canonical commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

- if $f(q,p,t) = q_\alpha$, then $\dot{q_\alpha} = \dfrac{\partial q_\alpha}{\partial t} + [q_\alpha, H]_{\mathrm{PB}} = \dfrac{\partial H}{\partial p_\alpha}$; if $f(q,p,t) = p_\alpha$, then $\dot{p}_\alpha = \dfrac{\partial p_\alpha}{\partial t} + [p, H]_{PB} = -\dfrac{\partial H}{\partial q_\alpha}$

Properties:

1. $[A, B]_{\mathrm{PB}} = -[B, A]_{\mathrm{PB}}$
2. $[A + B, C]_{\mathrm{PB}} = [A, C]_{\mathrm{PB}} + [B, C]_{\mathrm{PB}}$
3. $[A, BC]_{\mathrm{PB}} = [A, B]_{\mathrm{PB}} C + B[A, C]_{\mathrm{PB}}$
4. $[A, B^n]_{\mathrm{PB}} = n[A, B]_{\mathrm{PB}} B^{n-1}$
5. $[A, f(B)]_{\mathrm{PB}} = [A, B]_{\mathrm{PB}} \dfrac{\partial f(B)}{\partial B}$

Hamilton-Jacobis Equation

We have discussed principle of least action with fixed $q(t)$, now we ask for $q(t)$ not fixed ($\delta q(t) \neq 0,\ \delta q(t_0) = 0$), then

$$\delta S = \frac{\partial L}{\partial \dot{q}} \delta q \bigg|_{t_0}^{t} = p\delta q = \frac{\partial S}{\partial q}\delta q \quad \Rightarrow \quad p = \frac{\partial S}{\partial q}$$

and

$$p\dot{q} - H = L = \frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\partial S}{\partial t} + \frac{\partial S}{\partial q}\dot{q} = \frac{\partial S}{\partial t} + p\dot{q} \quad \Rightarrow \quad \frac{\partial S}{\partial t} + H(q, \frac{\partial S}{\partial q}, t) = 0$$

1.2 Classical Electrodynamics Mechanics

Vector Analysis

$$\vec{v} = v_1 \vec{e}_1 + v_2 \vec{e}_2 + v_3 \vec{e}_3 = \sum_i v_i \vec{e}_i = v_i \vec{e}_i \qquad (i = 1, 2, 3)$$

Kronecker Tensor

$$\delta_{ij} = \begin{cases} 1, & (i = j) \\ 0, & (i \neq j) \end{cases}$$

- $\vec{e}_i \cdot \vec{e}_j = \delta_{ij}$

Levi-Civite Tensor

$$\varepsilon_{ijk} = \begin{cases} +1, & \text{(even permutation)} \\ -1, & \text{(odd permutation)} \\ 0, & \text{(no permutation)} \end{cases}$$

- $\vec{e}_i \times \vec{e}_j = \varepsilon_{ijk} \vec{e}_k$
- $\vec{e}_i \cdot (\vec{e}_j \times \vec{e}_k) = \varepsilon_{ijk}$
- $\varepsilon_{ijk}\varepsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}$

Vector Algebra

- Dot product (Inner product):

$$\vec{A}\cdot\vec{B} = A_i\vec{e}_i\cdot B_i\vec{e}_j = (A_iB_j)(\vec{e}_i\times\vec{e}_j) = A_iB_j\delta_{ij} = A_iB_j$$

- Gross product:

$$\vec{A}\times\vec{B} = A_i\vec{e}_i\times B_i\vec{e}_j = (A_iB_j)(\vec{e}_i\times\vec{e}_j) = A_iB_j\varepsilon_{ijk}\vec{e}_k = (\vec{A}\times\vec{B})_k\vec{e}_k$$

- $(\vec{A}\times\vec{B})\cdot(\vec{C}\times\vec{D}) = (\vec{A}\cdot\vec{C})(\vec{B}\cdot\vec{D}) - (\vec{A}\cdot\vec{D})(\vec{B}\cdot\vec{C})$
- $[L_i, L_j]_{\text{PB}} = \varepsilon_{ijk}L_k$

  Proof. $\varepsilon_{iab}\varepsilon_{jcd}[x_ap_b, x_cp_d] = \varepsilon_{iab}\varepsilon_{jcd}(x_cp_b\delta_{ad} - x_ap_d\delta_{bc}) = (\delta_{bj}\delta_{ic} - \delta_{bc}\delta_{ij})x_cp_b + (\delta_{ij}\delta_{ad} - \delta_{id}\delta_{aj})x_ap_d = x_ip_j - x_jp_i$ □

- $[L_i, \vec{L}^2]_{PB} \equiv 0$

  Proof. $= [L_i, L_j]L_j + L_j[L_i, L_j] = \varepsilon_{ijk}(L_jL_k + L_kL_j)$ (Anti-symmetric · Symetrix $\equiv 0$) □

- $[L_i, x_j] = \varepsilon_{ijk}x_k$, $[L_i, p_j] = \varepsilon_{ijk}p_k$

Vector Calculus

$(\vec{\nabla})_i = \dfrac{\partial}{\partial x_i} = \partial_i \quad (i = 1, 2, 3)$

1. Gradient:

$$\vec{\nabla}\phi = (\partial_i\phi)\vec{e}_i = \frac{\partial\phi}{\partial x_i}\vec{e}_1 + \frac{\partial\phi}{\partial x_2}\vec{e}_2 + \frac{\partial\phi}{\partial x_3}\vec{e}_3$$

2. Divergence:

$$\vec{\nabla}\cdot\vec{A} = \partial_iA_i = \frac{\partial}{\partial x_i}A_1 + \frac{\partial}{\partial x_2}A_2 + \frac{\partial}{\partial x_3}A_3$$

3. Curl:

$$\vec{\nabla}\times\vec{A} = (\vec{e}_i\partial_i)\times\vec{e}_jA_j = \varepsilon_{ijk}\vec{e}_k\partial_iA_j = (\varepsilon_ijk\partial_iA_j)\vec{e}_k = (\vec{\nabla}\times\vec{A})_k\vec{e}_k$$

   - $(\vec{\nabla}\times\vec{A})_i = \varepsilon_{ijk}\partial_jA_k$

Example:

1. $\vec{\nabla}\times\vec{\nabla}\phi \equiv 0; \quad \vec{\nabla}\cdot(\vec{\nabla}\times\vec{A}) \equiv 0$ curl-free for gradient field and divergence-free for curl field

   Proof. $(\vec{\nabla}\times\vec{\nabla}\phi)_i = \varepsilon_{ijk}\partial_j(\vec{\nabla}\phi)_k = \varepsilon_{ijk}\partial_j\partial_k\phi \equiv 0$ ($\vec{E} = -\vec{\nabla}\phi$ static electric field)
   $\vec{\nabla}\cdot(\vec{\nabla}\times\vec{A}) = \partial_i\varepsilon_{ijk}\partial_jA_k = \varepsilon_{ijk}\partial_i\partial_jA_k \equiv 0$ ($\vec{B} = \vec{\nabla}\times\vec{A}, \vec{\nabla}\cdot\vec{B} \equiv 0$) □

2. $\vec{\nabla}\times(\vec{\nabla}\times\vec{A}) = \vec{\nabla}(\vec{\nabla}\cdot\vec{A}) - \nabla^2\vec{A}$

   Proof. $\left[\vec{\nabla}\times(\vec{\nabla}\times\vec{A})\right]_i = \varepsilon_{ijk}\partial_j\varepsilon_{klm}\partial_lA_m = (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})\partial_j\partial_lA_m = \partial_j\partial_iA_j - \partial_j\partial_jA_i = \partial_i(\vec{\nabla}\cdot\vec{A}) - \nabla^2A_i$ □

3. $\vec{v}\times(\vec{\nabla}\times\vec{A}) = \vec{\nabla}(\vec{v}\cdot\vec{A}) - (\vec{v}\cdot\vec{\nabla})\vec{A}$

   Proof. $[\vec{v}\times(\vec{\nabla}\times\vec{A})]_i = \varepsilon_{ijk}v_j\varepsilon_{klm}\partial_lA_m = v_j\partial_lA_j - v_j\partial_jA_i = \partial_i(v_jA_j) - v_j\partial_jA_i$ □

4. $\vec{A}\cdot(\vec{B}\times\vec{C}) = \vec{B}\cdot(\vec{C}\times\vec{A}) = \vec{C}\cdot(\vec{A}\times\vec{B})$

   Proof. $\vec{A}\cdot(\vec{B}\times\vec{C}) = A_i(\vec{B}\times\vec{C})_i = A_i\varepsilon_{ijk}B_jC_k = (\varepsilon_{jki}C_kA_i)B_j = (\varepsilon_{kij}A_iB_j)C_k$ □

Generalized Stokes Theorem

$$\int_{\Omega} \mathrm{d}\omega = \int_{\partial\Omega} \omega$$

- Newton-Leibmig's formula:

$$\int_a^b \mathrm{d}f = f(b) - f(a)$$

- Green's theorem:

$$\oint_L f\mathrm{d}x + g\mathrm{d}y = \iint_S \left(\frac{\partial g}{\partial x} - \frac{\partial f}{\partial y}\right)\mathrm{d}x\mathrm{d}y$$

- Stokes's theorem:

$$\oint_L \vec{F} \cdot \mathrm{d}\vec{l} = \iint_S (\vec{\nabla} \times \vec{F}) \cdot \mathrm{d}\vec{S}$$

- Gauss's theorem:

$$\oiint_S \vec{F} \cdot \mathrm{d}\vec{S} = \iiint_V (\vec{\nabla} \cdot \vec{F})\mathrm{d}^3\vec{x}$$

Helmholtz's Theorem

$\forall\vec{F}$ continuous differentiable, $\vec{F} = \vec{F}_{\perp} + \vec{F}_{\parallel}$

1. $\vec{F}_{\perp}$:tranverse component, $\vec{\nabla} \cdot \vec{F}_{\perp} = 0$ or equivalently $\vec{F}_{\perp} = \vec{\nabla} \times \vec{A}$
2. $\vec{F}_{\parallel}$: longitudiral component, $\vec{\nabla} \times \vec{F}_{\parallel} = 0$ or equivalently $\vec{F}_{\parallel} = -\vec{\nabla}\phi$

Experimental Laws and Maxwell's Equations

*Gauss Units [1]

$$\begin{aligned}
\vec{\nabla} \cdot \vec{E} &= 4\pi\rho(\vec{x}) \\
\vec{\nabla} \cdot \vec{B} &= 0 \\
\vec{\nabla} \times \vec{B} &= \frac{4\pi}{c}\vec{j} + \frac{1}{c}\frac{\partial\vec{E}}{\partial t} \\
\vec{\nabla} \times \vec{E} &= -\frac{1}{c}\frac{\partial\vec{B}}{\partial t}
\end{aligned}$$

1. Coulomb's law:

$$\vec{E}(\vec{x}) = \int_{V'} \frac{\rho(\vec{x}')(\vec{x} - \vec{x}')}{|\vec{x} - \vec{x}'|^3}\mathrm{d}^3\vec{x}' = -\nabla\phi(\vec{x}), \quad \phi(\vec{x}) = \int_{V'} \frac{\rho(\vec{x}')}{|\vec{x} - \vec{x}'|}\mathrm{d}^3\vec{x}'$$

2. Biat-Savarts' law:

$$\vec{B}(\vec{x}) = \frac{1}{c}\int_{V'} \frac{\vec{j}(\vec{x}') \times (\vec{x} - \vec{x}')}{|\vec{x} - \vec{x}'|}\mathrm{d}^3\vec{x}' = \vec{\nabla} \times \vec{A}(\vec{x}), \quad \vec{A}(\vec{x}) = \int_{V'} \frac{\vec{j}(\vec{x}')}{|\vec{x} - \vec{x}'|}\mathrm{d}^3\vec{x}'$$

3. Ampere's law of circuit:

$$\oint_L \vec{B} \cdot \mathrm{d}\vec{l} = \frac{4\pi}{c}\iint_S \vec{j} \cdot \mathrm{d}\vec{S}$$

4. Faraday's law in induction:

$$\oint_L \vec{E} \cdot \mathrm{d}\vec{l} = -\frac{1}{c}\frac{\mathrm{d}}{\mathrm{d}t}\iint_S \vec{B} \cdot \mathrm{d}\vec{S}$$

5. Conversation of electric charge:

$$\frac{\partial\rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0, \quad \vec{j} = \rho\vec{v}$$

[1] $\vec{\nabla}\left(\frac{1}{r}\right) = \frac{-\vec{r}}{r^3}$, $\vec{\nabla} \cdot \vec{\nabla}\left(\frac{1}{r}\right) = \nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(\vec{x})$, $\int_V \vec{\nabla} \cdot \frac{\vec{r}}{r^3}\mathrm{d}^3\vec{r} = \oiint_S \frac{\vec{r}}{r^3} \cdot \mathrm{d}\vec{S} = \oiint_S \frac{\vec{r}}{r^3}\vec{r}^0 r^2 \sin\theta\mathrm{d}\theta\mathrm{d}\phi = 4\pi$

Properties

Conversations, Invariance Covariance

Invariance Gauge

$\vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$, $\quad \vec{B} = \vec{\nabla} \times \vec{A}$, after Gauge transformation, we have $\vec{E}' = \vec{E}$, $\vec{B}' = \vec{B}$

$$\phi \to \phi' = \phi + \vec{\nabla}\chi \qquad \vec{A} \to \vec{A}' = \vec{A} - \frac{1}{c}\frac{\partial}{\partial t}\chi$$

1. Columb's gauge: $\vec{\nabla} \cdot \vec{A} = 0$
2. Lorenz's gauge: $\vec{\nabla} \cdot \vec{A} + \frac{1}{c}\frac{\partial}{\partial t}\phi = 0$

Multiexpansion

$\phi(\vec{x}) = \phi^{(0)} + \phi^{(1)} + \phi^{(2)} + \cdots, \quad \vec{A}(\vec{x}) = \vec{A}^{(0)} + \vec{A}^{(1)} + \vec{A}^{(2)} + \cdots$ monopole + dipole + quadrapole

$\vec{E} = \vec{E}^{(0)} + \vec{E}^{(1)} + \vec{E}^{(2)}, \quad \vec{B} = 0 + \vec{B}^{(1)} + \vec{B}^{(2)} + \cdots$

Charged Particle in EM field

Newtonian Lorentz Equations:

$$\vec{f}_{\text{Lorentz}} = q\left(\vec{E} + \frac{\vec{v}}{c} \times \vec{B}\right) = m\ddot{\vec{x}}$$

Lagrangian Mechanics

1. Euler-Lagrangian's equation: $\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_\alpha} = \frac{\partial L}{\partial q_\alpha}$
2. d'Alembert's virtual work principle: $\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{q}_\alpha}\right) - \frac{\partial T}{\partial q_\alpha} = Q_\alpha$ (generalized force)

If $L = T - V$, then take it into and find out $V(q, \dot{q}, t)$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial V}{\partial \dot{q}_\alpha}\right) - \frac{\partial V}{\partial q_\alpha} = Q_\alpha = (\vec{f}_{\text{Lorentz}})_\alpha = q\left[\vec{E}_\alpha + \left(\frac{\vec{v}}{c} \times \vec{B}\right)_\alpha\right]$$

Since $E_\alpha = \left(-\vec{\nabla}\phi - \frac{1}{c}\frac{\partial}{\partial t}\vec{A}\right)_\alpha$, $q\left(\frac{\vec{v}}{c} \times \vec{B}\right)_\alpha = \frac{q}{c}\varepsilon_{\alpha\beta\gamma}v_\beta(\varepsilon_{\gamma ab}\partial_a A_b) = \frac{q}{c}[v\beta\partial_\alpha A_\beta - v_\beta\partial_\beta A_\alpha]$, we have

$$Q_\alpha = -q\partial_\alpha\phi - \frac{q}{c}\partial_t A_\alpha + \frac{q}{c}\Big[\partial_\alpha(\vec{v} \cdot \vec{A}) - (\vec{v} \cdot \vec{\nabla})A_\alpha\Big] = -q\partial_\alpha\Big[\phi - \frac{1}{c}(\vec{v} \cdot \vec{A})\Big] - \frac{q}{c}\partial_t A_\alpha + (\vec{v} \cdot \vec{\nabla})A_\alpha$$

and $\frac{\mathrm{d}}{\mathrm{d}t}\vec{A}(\vec{x}, t) = \frac{\partial \vec{A}}{\partial t} + \frac{\mathrm{d}\vec{x}}{\mathrm{d}t}\frac{\partial \vec{A}}{\partial \vec{x}} = \frac{\partial \vec{A}}{\partial t} + (\vec{v} \cdot \vec{\nabla})\vec{A}$, therefore

$$Q_\alpha = -q\partial_\alpha\Big[\phi - \frac{1}{c}(\vec{v} \cdot \vec{A})\Big] - \frac{q}{c}\frac{\mathrm{d}}{\mathrm{d}t}A_\alpha$$

Construct an effective potential $V(\vec{x}, \dot{\vec{x}}, t) = q\Big[\phi - \frac{1}{c}(\vec{v} \cdot \vec{A})\Big]$, check:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial V}{\partial \dot{\vec{x}}}\right) = -\frac{q}{c}\frac{\mathrm{d}\vec{A}}{\mathrm{d}t}, \quad \frac{\partial V}{\partial \vec{x}} = q\frac{\partial \phi}{\partial \vec{x}} - \frac{q}{c}(\vec{v} \cdot \vec{\nabla})\vec{A}$$

then $L = T - V = \frac{m\ddot{x}^2}{2} - q\Big[\phi - \frac{1}{c}\Big(\vec{v} \cdot \vec{A}\Big)\Big]$, canonical momentum: $\vec{p} = \frac{\partial L}{\partial \dot{\vec{x}}} = m\dot{\vec{x}} + \frac{q}{c}\vec{A}$

$$H = \vec{p}\,\dot{\vec{x}} - L = \frac{m\dot{\vec{x}}^2}{2} + q\phi = \frac{1}{2m}\Big(\vec{p} - \frac{q}{c}\vec{A}\Big)^2 + q\phi$$

Chapter 2

Introduction

2.1 Fundamental Postulates (Axion) of Quantum Mechanics

$$SOME \quad IS$$

Postulate 1: State

$\diamondsuit$ *Description of the state of a system: At a fixed time t_0, the state of an isolated physical system is defined by specifying a ket $|\psi(t_0)\rangle$ belonging to the state space $\mathcal{E}$.*
System ↔ State Vector ket: $|\psi\rangle$; bra: $\langle\psi|$

$$\text{Hermiltian Conjugate:} \quad (|\psi\rangle)^\dagger = \langle\psi| \qquad (\dagger : \text{adjoint})$$

Postulate 2: Operator

$\diamondsuit$ *Description of physical quantities: Every measurable physical quantity A is described by an operator $\hat{A}$ acting in state space $\mathcal{E}$; this operator if an observable.*
Physical quantity ↔ Observables ↔ Operator $\hat{A}$ (Linear & Hermiltian)

Postulate 3: Measurement

$\diamondsuit$ *The measurement of physical quantities: The only possible result of the measurement of a physical quantity A is one of the eigenvalues of the corresponding observable $\hat{A}$*
Measurement outcome of $\hat{A}$ (uncertian; certain). The eigenvalue equation is

$$\hat{A}\,|\psi_n\rangle = A_n\,|\psi_n\rangle$$

- $\hat{A}$ operator, q-number
- A_n eigenvalue, c-number
- ”eigen”: ”proper”, ”characteristic”

Probability of finding A_n when A is measured in $|\psi\rangle$:

$$\mathcal{P}(A_n) = |\langle\psi_n|\psi\rangle|^2$$

Postulate 4: Evolution

$\diamondsuit$ *Time evolution of systems: The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger’s equation or Heisenberg’s equation.*

Schrödinger's Picture

(State: change; observable: no change) Schrödinger's equation:

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle = \hat{H}(t)\left|\psi(t)\right\rangle$$

- $\hat{H}$ is called Hamiltonian operator of the system, associated with the total energy of the system

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{\vec{p}}^2}{2m} + \hat{V}(\hat{\vec{x}})$$

- $\left|\psi(t=0)\right\rangle = \left|\psi_0\right\rangle$

Heisenberg's Picture

(State: no change; observable: change) Heisenberg's equation:

$$\frac{\mathrm{d}\hat{F}}{\mathrm{d}t} = \frac{\partial\hat{F}}{\partial t} + \frac{1}{i\hbar}\left[\hat{F}, \hat{H}\right]$$

Postulate 5: Identical Particle and Symmetrization

$$\left.\begin{array}{r}\text{Symmetric}\\ \text{Anti-symmetric}\end{array}\right\}\ \text{State}\ \left\{\begin{array}{l}\text{Boson (integer spin) Bose-Einstein Statistics}\\ \text{Fermion (half-integer spin) Femi-Diracs Statistics}\end{array}\right.$$

2.2 Vector and Operator

2.2.1 State Vector

Vector in Euclidean Space $\leftrightarrow$ State Vector in Hilbert Space

- $\left|\psi\right\rangle$: ket $\in \mathbb{H} \leftrightarrow \begin{bmatrix}\psi_1\\ \psi_2\\ \vdots\end{bmatrix}$; $\quad \left\langle\psi\right| = (\left|\psi\right\rangle)^\dagger$: bra $\in \mathbb{H} \leftrightarrow \left[\psi_1^*, \psi_2^*, \cdots\right]$
- Conjugate ($\dagger$): Transverse($\top, \sim$) + Complex conjugate ($*$) $\quad\Rightarrow\quad \left\langle\psi|\phi\right\rangle = \left\langle\phi|\psi\right\rangle^\dagger = \left\langle\phi|\psi\right\rangle^*$
- Orthonormality: $\vec{e}_i \cdot \vec{e}_j = \delta_{ij} \leftrightarrow \left\langle u_m|u_n\right\rangle = \delta_{mn}$
- Completeness: $\sum_i \vec{e}_i \cdot \vec{e}_j = \mathbb{1}, \leftrightarrow \sum_n \left|u_m\right\rangle\left\langle u_n\right| = \mathbb{1}$

1. Vector addition: $\left|\psi_1\right\rangle + \left|\psi_2\right\rangle = \left|\psi_2\right\rangle + \left|\psi_1\right\rangle$
2. Scale multiplication: $a(\left|\psi_1\right\rangle + \left|\psi_2\right\rangle) = a\left|\psi_1\right\rangle + a\left|\psi_2\right\rangle$, $ab\left|\psi\right\rangle = ba\left|\psi\right\rangle$
3. Inner product: $\left\langle\psi|\phi\right\rangle = c \in \mathbb{C} \quad\Rightarrow\quad \left\langle\psi|\psi\right\rangle = r \in \mathbb{R} \geqslant 0$, $\left\langle\phi|\psi\right\rangle = (\left\langle\psi|\phi\right\rangle)^* = c^*$
4. Dyadic product of motion: $(\left|\psi\right\rangle\left\langle\phi\right|)^\dagger = \left|\phi\right\rangle\left\langle\psi\right| = \begin{bmatrix}\phi_1\\ \phi_2\\ \vdots\end{bmatrix}\begin{bmatrix}\psi_1 & \psi_2 & \cdots\end{bmatrix}$
5. Basis: for Hermiltian operator
   (a) Discrete: $\hat{A}\left|\psi_n\right\rangle = A_n\left|\psi_n\right\rangle \qquad \left\langle\psi_n|\psi_m\right\rangle = \delta_{nm}, \sum_n \left|\psi_n\right\rangle\left\langle\psi_n\right| = \mathbb{1}$
   (b) Continuous: $\hat{A}\left|a\right\rangle = a\left|a\right\rangle \qquad \left\langle a|a'\right\rangle = \delta(a-a'), \int \mathrm{d}a\left|a\right\rangle\left\langle a\right| = \mathbb{1}$

2.2.2 Operator

Consider

$$\hat{A}\left|\psi\right\rangle = \left|\phi\right\rangle$$

Linear Operator

$\forall |\psi_1\rangle, |\psi_2\rangle, \forall a, b \in \mathbb{1}$, if $\hat{A}(a|\psi_1\rangle + b|\psi_2\rangle) = a\hat{A}|\psi_1\rangle + b\hat{A}|\psi_2\rangle$, then $\hat{A}$ is a linear operator,
otherwise if $\hat{A} = (a|\psi_1\rangle + b|\psi_2\rangle) = a^*\hat{A}|\psi_1\rangle + b^*\hat{A}|\psi_2\rangle$, then $\hat{A}$ is a anti-linear operator.
Two kinds of operators in GM:

1. Observables: linear, Hermiltian
$$\hat{H}^\dagger = \hat{H}$$
2. Transformation: restricted to linear unitary transformation
$$\hat{U}^\dagger = \hat{U}^{-1} \quad \text{or} \quad \hat{U}^\dagger\hat{U} = \hat{U}\hat{U}^\dagger = \mathbb{1}$$

Rules

0. $\forall |\psi\rangle$, if $\hat{A}|\psi\rangle = \hat{B}|\psi\rangle$, then $\hat{A} = \hat{B}$
1. $\hat{A} + \hat{B} = \hat{B} + \hat{A}$, $(\hat{A} + \hat{B}) + \hat{C} = \hat{A} + (\hat{B} + \hat{C})$. $\forall |\psi\rangle$, $\hat{A}|\psi\rangle + \hat{B}|\psi\rangle = (\hat{A} + \hat{B})|\psi\rangle$
2. $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, commutation: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$
3. Adjoint (Hermiltian conjugate): $\langle\phi|\hat{A}^\dagger = \left(\hat{A}|\phi\rangle\right)^\dagger$

Properties

- Identity: $\forall |\psi\rangle, \exists \mathbb{1}, \mathbb{1}|\psi\rangle = |\psi\rangle$
- Inverse: $\hat{A}|\psi\rangle \to |\psi\rangle = \hat{A}^{-1}|\phi\rangle$, $(\hat{A}_1\hat{A}_2\cdots\hat{A}_n)^{-1} = \hat{A}_n^{-1}\cdots\hat{A}_2^{-1}\hat{A}_1^{-1}$
- $(\hat{A}_1\hat{A}_2\cdots\hat{A}_n)^\dagger = \hat{A}_n^\dagger\cdots\hat{A}_2^\dagger\hat{A}_1^\dagger$

2.3 Overview of Quantum Mechanics

Many "Two" s : POSE P$\cdots$M

1. Roles: State vector; Operator
2. Operator: Observables; Transformation. Hermiltian; Unitary
3. State: ket(vector); bra(dual vector)
4. Eigenspectrum: Discrete(bound state); Continuous(unbound state)
5. Properties: Wave particles dulity
   (a) Problems: Eigenvalues; Evolution
   (b) Pictures: Schrödinger; Heisenberg
   (c) Particles: Boson; Fermion
   (d) Perturbation theories: non-degenrate; degenerate
   (e) Angular momentum: Orbit; Spin
6. Mechanics: wave function; matrix form

2.4 Wave Mechanics and Matrix Mechanics

2.4.1 Wave Mechanics

Old wave function (WF) interpretation: matter wave / probabilistic wave
New wave function interpretation: projection of state vector in representation (basis)

- Discrete: wave function in $\{|u_n\rangle\}$-basis

$$|\psi\rangle = \mathbb{1}\,|\psi\rangle = \left(\sum_n |u_n\rangle\langle u_n|\right)|\psi\rangle = \sum_n c_n\,|u_n\rangle\,, \quad \text{WF:} \quad c_n = \langle u_n|\psi\rangle$$

  - energy-representation: $|\psi\rangle = \sum_n c_n\,|\psi_n\rangle\,, \quad c_n = \langle\psi_n|\psi\rangle\,, \quad \hat{A}\,|\psi_n\rangle = A_n\,|\psi_n\rangle$

- Continuous: wave function in $\{|a\rangle\}$-basis

$$|\psi\rangle = \mathbb{1}\,|\psi\rangle = \left(\int \mathrm{d}a\,|a\rangle\langle a|\right)|\psi\rangle = \int \psi(a)\,|a\rangle\,\mathrm{d}a, \quad \text{WF:} \quad \psi(a) = \langle a|\psi\rangle$$

  - in $\hat{\vec{x}}$-representation:

$$\hat{\vec{x}}\,|\vec{x}\rangle = \vec{x}\,|\vec{x}\rangle\,, \qquad |\psi\rangle = \int \mathrm{d}^3\vec{x}\,\psi(\vec{x})\,|\vec{x}\rangle$$

    * orthonomal: $\langle\vec{x}|\vec{x}'\rangle = \delta(\vec{x}-\vec{x}')$; $\quad \int \mathrm{d}^3\,|\vec{x}\rangle\langle\vec{x}| = \mathbb{1}$
    * left ($|x\rangle$) is eigenstate, right ($\vec{x}$) is eigenvalue
    * wave function:
  - in $\hat{\vec{p}}$-representation

$$\hat{\vec{p}}\,|\vec{p}\rangle = \vec{p}\,|\vec{p}\rangle\,, \qquad |\psi\rangle = \int \mathrm{d}^3\vec{p}\,\tilde{\psi}(\vec{p})\,|p\rangle$$

    * orthonomal: $\langle\vec{p}|\vec{p}'\rangle = \delta(\vec{p}-\vec{p}')$; $\quad \int \mathrm{d}^3\,|\vec{p}\rangle\langle\vec{p}| = \mathbb{1}$

Wave function in $\hat{\vec{x}}$ and $\hat{\vec{p}}$-representation:

$$\psi(\vec{x}) = \langle\vec{x}|\psi\rangle\,, \qquad \tilde{\psi}(\vec{p}) = \langle\vec{p}|\psi\rangle$$

Relation of $\psi(\vec{x})$ and $\tilde{\psi}(\vec{p})$:

$$\begin{aligned}\tilde{\psi}(\vec{p}) &= \langle\vec{p}|\psi\rangle = \langle\vec{p}|\mathbb{1}|\psi\rangle = \left\langle \vec{p}\left|\left(\int \mathrm{d}^3\vec{x}\,|x\rangle\langle x|\right)\right|\psi\right\rangle = \int \mathrm{d}^3\vec{x}\,\langle\vec{p}|\vec{x}\rangle\,\psi(\vec{x}) \\ &= \int \psi(\vec{x})\psi^*_{\vec{p}}(\vec{x})\mathrm{d}^3\vec{x} \quad \text{where} \quad \psi_{\vec{p}}(\vec{x}) = \langle\vec{p}|\vec{x}\rangle = \left(\frac{1}{2\pi\hbar}\right)^{\frac{3}{2}} \exp\left\{-i\frac{\vec{p}\cdot\vec{x}}{\hbar}\right\}\end{aligned}$$

IN $\hat{\vec{x}}$-REPRESENTATION, the Schrödinger's equation is

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle\,,\ \hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(\hat{\vec{x}}) \quad \Rightarrow \quad i\hbar\frac{\partial}{\partial t}\psi(\vec{x},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)$$

- $\psi(\vec{x},t) = \langle\vec{x}|\psi(t)\rangle\,,\ \hat{\vec{x}} = \hat{\vec{x}},\ \hat{\vec{p}} = -i\hbar\vec{\nabla},\ \int \mathrm{d}^3x\,|\vec{x}\rangle\langle\vec{x}| = \mathbb{1}$

same as IN $\hat{\vec{p}}$-REPRESENTATION, the Schrödinger's equation is

$$\Rightarrow \quad i\hbar\frac{\partial}{\partial t}\tilde{\psi}(\vec{p},t) = \frac{\hat{\vec{p}}^2}{2m}\tilde{\psi}(\vec{p},t) + V\left(i\hbar\frac{\partial}{\partial\hat{p}}\right)\tilde{\psi}(\vec{p},t)$$

- $\tilde{\psi}(\vec{p},t) = \langle\vec{p}|\psi(t)\rangle\,,\ \hat{\vec{p}} = \hat{\vec{p}},\ \hat{\vec{x}} = i\hbar\frac{\partial}{\partial\vec{p}},\ \int \mathrm{d}^3p\,|\vec{p}\rangle\langle\vec{p}| = \mathbb{1}$

Ajoint (Hermiltian Conjugate)

$$\langle\psi|\hat{A}^\dagger|\phi\rangle = \left(\langle\phi|\hat{A}|\psi\rangle\right)^* \quad \Rightarrow \quad \hat{A}^\dagger = \left(\hat{A}^\top\right)^*$$

Proof. Let $|\psi\rangle = \sum_m c_m |u_m\rangle$, $|\phi\rangle = \sum_n d_n |u_n\rangle$, then $\langle\psi|\hat{A}^\dagger|\phi\rangle = \sum_{m,n} d_n c_m^* \hat{A}^\dagger_{mn}$, and

$$\left(\langle\phi|\hat{A}|\psi\rangle\right)^* = \left[\left(\sum_n d_n^* \langle u_n|\right)\hat{A}\left(\sum_m c_m |u_m\rangle\right)\right]^* = \left(\sum_{n,m} d_n^* c_m \langle u_n|\hat{A}|u_m\rangle\right)^* = \sum_{n,m} d_n c_m^* \hat{A}^*_{nm}$$

Therefore, $\sum_{m,n} d_n c_m^* \hat{A}^\dagger_{mn} = \sum_{m,n} d_n c_m^* \hat{A}^*_{nm} \quad \Rightarrow \quad \left(\hat{A}^\dagger\right)_{mn} = \left(\hat{A}^*\right)_{nm} = \left(\hat{A}^\top\right)^*_{nm} \quad \Rightarrow$ □

If $\hat{A}^\dagger = \hat{A}$, then

- Eigenvalues is $\mathbb{R}$
- Eigenfunction is orthonomal and complete

Proof. Definition of ajoint: $\left(\hat{A}^\dagger |\psi\rangle\right)^\dagger = \langle\psi|\,\hat{A}^\dagger \quad \Leftrightarrow \quad \langle\psi|\hat{A}^\dagger|\phi\rangle = \left(\langle\phi|\hat{A}|\psi\rangle\right)^*$
Let $\hat{A}|\psi_n\rangle = A_n|\psi_n\rangle$, $\hat{A}|\psi_m\rangle = A_m|\psi_m\rangle$ (non-degenerate, discrete, spectrum),

$$\langle\psi_n|\hat{A}|\psi_n\rangle = \left(\langle\psi_n|\hat{A}|\psi_n\rangle\right)^* = \left(\langle\psi_n|A_n|\psi_n\rangle\right)^* = A_n^*\langle\psi_n|\psi_n\rangle; \quad \langle\psi_n|\hat{A}|\psi_n\rangle = \langle A_n|\psi_n|A_n\rangle = A_n\langle\psi_n|\psi_n\rangle$$

Therefore $A_n = A_n^* \quad \Rightarrow \quad A_n \in \mathbb{R}$.

$$\langle\psi_n|\hat{A}^\dagger|\psi_m\rangle = \left(\langle\psi_m|\hat{A}|\psi_n\rangle\right)^* = A_n^*\langle\psi_m|\psi_n\rangle^* = A_n\langle\psi_n|\psi_m\rangle$$
$$\left\langle\psi_n\middle|\hat{A}\middle|\psi_m\right\rangle = A_m\langle\psi_n|\psi_m\rangle$$

Therefore $(A_n - A_m)\langle\psi_n|\psi_m\rangle = 0$. Since $n \neq m$, so $A_n \neq A_m$, $\langle\psi_n|\psi_m\rangle \equiv 0 \quad \Rightarrow \quad |\psi_n\rangle \perp |\psi_m\rangle$ □

Remark: degenerate $\hat{A}\left|\psi_n^i\right\rangle = A_n\left|\psi_n^i\right\rangle$, $i = 1, 2, \cdots, g_n$ (g_n:degeneracy)

2.5 Matrix Mechanics

The state vector is

$$|\psi\rangle = \mathbb{1}|\psi\rangle = \sum_n c_n |u_n\rangle = \mathbb{1}$$

- $|u_n\rangle = \begin{bmatrix}\cdots & 1 & \cdots\end{bmatrix}^\top, \quad \langle u_n| = \begin{bmatrix}\cdots & 1 & \cdots\end{bmatrix} \quad \Rightarrow \quad |\psi\rangle \to \begin{bmatrix}c_1 & c_2 & \cdots & c_n & \cdots\end{bmatrix}^\top$

Observable is

$$\hat{A} = \mathbb{1}\hat{A}\mathbb{1} = \left(\sum_n |u_n\rangle\langle u_n|\right)\hat{A}\left(\sum_m |u_m\rangle\langle u_m|\right) = \sum_{n,m}\langle u_n|\hat{A}|u_m\rangle\left(|u_n\rangle\langle u_m|\right)$$
$$= \sum_{n,m} A_{nm}|u_n\rangle\langle u_m| = \begin{bmatrix} \cdot & \cdots & \cdot & \cdot \\ \vdots & \ddots & \vdots & \vdots \\ \cdot & \cdots & A_{nm} & \cdot \\ \cdot & \cdots & \cdot & \cdot \end{bmatrix}$$

2.6 Commutation Relation of Observables

Commutation

- q-number: $\hat{A}\hat{B} \neq \hat{B}\hat{A}$ (QM)
- c-number: $AB = BA$ (CM)

Definition of commutor:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Compare it to Classical canonical commutor:

$$[A, B]_{\mathrm{PB}} = \sum_\alpha \left(\frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha}\frac{\partial B}{\partial q_\alpha}\right)$$

The relation is

$$[A,B]_{\mathrm{PB}} \quad \leftrightarrow \quad \left(\frac{1}{i\hbar}\right)\left[\hat{A},\hat{B}\right]$$

Properties of Commutation

1. $\left[\hat{A},\hat{B}\right]\neq 0$, then it means uncertainty relation $\Delta\hat{A}\cdot\Delta\hat{B}\geqslant\frac{|\langle[\hat{A},\hat{B}]\rangle|}{2}$;
   otherwise $\left[\hat{A},\hat{B}\right]=0$, then it means common (simultaneous) eigenstates
2. Linearity: $\left[a\hat{A},b\hat{B}+c\hat{C}\right]=ab\left[\hat{A},\hat{B}\right]+ac\left[\hat{A},\hat{C}\right]$
3. Leibniz rule: $\left[\hat{A},\hat{B}\hat{C}\right]=\left[\hat{A},\hat{B}\right]\hat{C}+\hat{B}\left[\hat{A},\hat{C}\right]$, $\quad\left[\hat{A}\hat{B},\hat{C}\right]=\left[\hat{A},\hat{C}\right]\hat{B}+\hat{A}\left[\hat{B},\hat{C}\right]$
4. Power related: $\left[\hat{A},\hat{B}^n\right]=n\left[\hat{A},\hat{B}\right]\hat{B}^{n-1}$, provided by $\left[\hat{B},[\hat{A},\hat{B}]\right]=0$

   Proof. For $n=1$, $[\hat{A},\hat{B}]=[\hat{A},\hat{B}^1]=1[\hat{A},\hat{B}]\,\hat{B}^{1-1}$, suppose $[\hat{A},\hat{B}^n]=k[\hat{A},\hat{B}]\,\hat{B}^{k-1}$, then, when $n=k+1$, one has $[\hat{A},\hat{B}^{k+1}]=[\hat{A},\hat{B}^k\hat{B}]=[\hat{A},\hat{B}^k]\,\hat{B}+\hat{B}^k[\hat{A},\hat{B}]=k[\hat{A},\hat{B}]\,\hat{B}^{k-1}\hat{B}+\hat{B}^k[\hat{A},\hat{B}]=(k+1)[\hat{A},\hat{B}]\,\hat{B}^k \quad\Rightarrow$ □

5. Function related: $\left[\hat{A},f(\hat{B})\right]=\left[\hat{A},\hat{B}\right]\frac{\partial f}{\partial\hat{B}}$, provided by $\left[\hat{B},[\hat{A},\hat{B}]\right]=0$

   Proof. $\left[\hat{A},f(\hat{B})\right]=\left[\hat{A},\sum_n\frac{f^{(n)}(0)}{n!}\hat{B}^n\right]=\sum_n\frac{f^{(n)}(0)}{n!}\left[\hat{A},\hat{B}^n\right]=\sum_n\frac{f^{(n)}(0)}{n!}n\hat{B}^{n-1}\left[\hat{A},\hat{B}\right]\quad\Rightarrow$ □

6. Jacobi's identity:
   (a) CM: $[A,[B,C]]_{\mathrm{PB}}+[B,[C,A]]_{\mathrm{PB}}+[C,[A,B]]_{\mathrm{PB}}=0$
   (b) Vector analysis: $\vec{A}\times\left(\vec{B}\times\vec{C}\right)+\vec{B}\times\left(\vec{C}\times\vec{A}\right)+\vec{C}\times\left(\vec{A}\times\vec{B}\right)=0$
   (c) CED: $F_{\mu\nu,\lambda}+F_{\nu\lambda,\mu}+F_{\lambda\mu,\nu}=0$
   (d) QM: $\left[\hat{A},[\hat{B},\hat{C}]\right]+\left[\hat{B},[\hat{C},\hat{A}]\right]+\left[\hat{C},[\hat{A},\hat{B}]\right]=0$

Fundamental Commutation Relation

Review the fundamental commutation relation in classical mechanics: $[x_i,p_j]_{\mathrm{PB}}=\delta_{ij}$, $[x_i,x_j]=[p_i,p_j]\equiv 0$, similarly

Fundamental commutation relation:

$$[\hat{x}_i,\hat{p}_j]=i\hbar\delta_{ij},\qquad[\hat{x}_i,\hat{x}_j]=[\hat{p}_i,\hat{p}_j]\equiv 0$$

Proof. In $\hat{\vec{x}}$-representation, we have $\hat{x}=\hat{x}$, $\hat{p}_x=-i\hbar\,\partial/\partial x$, then for $\forall\psi(x)$

$$(\hat{x}\hat{p}_x-\hat{p}_x\hat{x})\psi(x)=\left[x\left(-i\hbar\frac{\partial}{\partial x}\right)-\left(-i\hbar\frac{\partial}{\partial x}\right)x\right]\psi(x)=-i\hbar\left(x\frac{\partial}{\partial x}\psi(x)-\frac{\partial}{\partial x}x\psi(x)\right)=i\hbar\psi(x)$$

Therefore, $[\hat{x},\hat{p}_x]=i\hbar$, since the equality is established for $\forall\psi(x)$. □

Commutation Relation of Orbital Angular Momentum

According to fundamental commutation relation, we have

Commutation relation of orbital angular momentum:

$$\text{from}\quad\hat{\vec{L}}=\hat{\vec{x}}\times\hat{\vec{p}}\Leftrightarrow\hat{L}_i=\varepsilon_{ijk}\hat{x}_j\hat{p}_k\quad\text{then}\quad\left[\hat{L}_i,\hat{L}_j\right]=i\hbar\varepsilon_{ijk}\hat{L}_k\Leftrightarrow\hat{\vec{L}}\times\hat{\vec{L}}=i\hbar\hat{\vec{L}}$$

1. $\left[\hat{L}_i,\hat{L}_j\right]=i\hbar\varepsilon_{ijk}\hat{L}_k\quad\Rightarrow\quad\hat{\vec{L}}\times\hat{\vec{L}}=i\hbar\hat{\vec{L}}$

Proof. $\left[\hat{L}_i, \hat{L}_j\right] = [\varepsilon_{iab}\hat{x}_a\hat{p}_b, \varepsilon_{jmn}\hat{x}_m\hat{p}_n]$

$$\left(\hat{\vec{L}} \times \hat{\vec{L}}\right)_i = \varepsilon_{ijk}\hat{L}_j\hat{L}_k = \frac{1}{2}\varepsilon_{ijk}\hat{L}_j\hat{L}_k + \frac{1}{2}\varepsilon_{ikj}\hat{L}_k\hat{L}_j = \frac{1}{2}\varepsilon_{ijk}\left(\hat{L}_j\hat{L}_k - \hat{L}_k\hat{L}_j\right) = \frac{1}{2}\varepsilon_{ijk}\left[\hat{L}_j, \hat{L}_k\right]$$
$$= \frac{1}{2}\varepsilon_{ijk} i\hbar\varepsilon_{jkl}\hat{L}_l = \frac{i\hbar}{2}(\delta_{il}\delta_{jj} - \delta_{jl}\delta_{ij})\hat{L}_l = \frac{i\hbar}{2}(2\delta_{il})\hat{L}_i = i\hbar\hat{L}_i$$ □

2. $\hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}} \quad \Rightarrow \quad \left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k$

   Proof. $\left(\hat{\vec{L}} \times \hat{\vec{L}}\right)_i = i\hbar\hat{L}_i \to \varepsilon_{abi}\varepsilon_{ijk}\hat{L}_j\hat{L}_k = i\hbar\varepsilon_{abi}\hat{L}_i$. l.h.s $= (\delta_{aj}\delta_{bk} - \delta_{ak}\delta_{bj})\hat{L}_j\hat{L}_k = \hat{L}_a\hat{L}_b - \hat{L}_b\hat{L}_a = \left[\hat{L}_a, \hat{L}_b\right]$ □

3. $\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \quad \Rightarrow \quad \left[\hat{L}_z, \hat{\vec{L}}^2\right] \equiv 0$

   Proof. $\left[\hat{L}_z, \hat{\vec{L}}^2\right] = \left[\hat{L}_i, \hat{L}_j\hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k\hat{L}_j + i\hbar\varepsilon_{ijk}\hat{L}_j\hat{L}_k = i\hbar\varepsilon_{ijk}(\hat{L}_k\hat{L}_j + \hat{L}_j\hat{L}_k) \equiv 0$ □

4. $\left[\hat{L}_i, \hat{x}_j\right] = i\hbar\varepsilon_{ijk}\hat{x}_k \quad \Leftrightarrow \quad \hat{\vec{L}} \times \hat{\vec{x}} + \hat{\vec{x}} \times \hat{\vec{L}} = 2i\hbar\hat{\vec{x}}$

   Proof. $\left[\hat{L}_i, \hat{x}_j\right] = [\varepsilon_{iab}\hat{x}_a\hat{p}_b, \hat{x}_j] = \varepsilon_{iab}\hat{x}_a[\hat{p}_b, \hat{x}_j] = -i\hbar\varepsilon_{iaj}\hat{x}_a = i\hbar\varepsilon_{ijk}\hat{x}_k \quad \Rightarrow \quad \hat{L}_i\hat{x}_j = \hat{x}_j\hat{L}_i + i\hbar\varepsilon_{ijk}\hat{x}_k$

$$\left(\hat{\vec{L}} \times \hat{\vec{x}} + \hat{\vec{x}} \times \hat{\vec{L}}\right)_i = \varepsilon_{ijk}\left(\hat{L}_j\hat{x}_k + \hat{x}_j\hat{L}_k\right) = \varepsilon_{ijk}\left(\hat{x}_k\hat{L}_j + i\hbar\varepsilon_{jkl}\hat{x}_l + \hat{x}_j\hat{L}_k\right) = \varepsilon_{ijk}\left(\hat{x}_k\hat{L}_j + \hat{x}_j\hat{L}_k\right) + i\hbar(\varepsilon_{ijk}\varepsilon_{jkl}\hat{x}_l)$$
$$= 0 + i\hbar(\delta_{il}\delta_{jj} - \delta_{ij}\delta_{jl})\hat{x}_l = i\hbar(2\delta_{il})\hat{x}_l = 2i\hbar\hat{x}_i$$ □

5. $\left[\hat{L}_i, \hat{p}_j\right] = i\hbar\varepsilon_{ijk}\hat{p}_k \quad \Leftrightarrow \quad \hat{\vec{L}} \times \hat{\vec{p}} + \hat{\vec{p}} \times \hat{\vec{L}} = 2i\hbar\hat{\vec{p}}$

6. $\forall$ vector $\vec{v} \quad \Leftrightarrow \quad i\hbar\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{\vec{v}}_k \quad \Leftrightarrow \quad \hat{\vec{L}} \times \hat{\vec{v}} + \hat{\vec{v}} \times \hat{L} = 2i\hbar\hat{\vec{v}}$

7. For $V(\vec{x}) = V(r)$, $r = \sqrt{x^2 + y^2 + z^2} \quad \Rightarrow \quad \left[\hat{L}_i, \hat{V}(r)\right] \equiv 0$

   Proof. $[L_i, V(r)] = \left[\hat{L}_i, \hat{x}_j\right]\frac{\partial V}{\partial x_j} = (i\hbar\varepsilon_{ijk}\hat{x}_k)\frac{\mathrm{d}V}{\mathrm{d}r}\frac{\mathrm{d}x_j}{\mathrm{d}r} = \left(\frac{i\hbar}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\right)\varepsilon_{ijk}\hat{x}_k\hat{x}_j \equiv 0$ □

8. For $\hat{T} = \dfrac{\hat{\vec{p}}^2}{2m} \quad \Rightarrow \quad \left[\hat{L}_i, \hat{T}\right] \equiv 0$

   Proof. $\left[\hat{L}_i, \hat{\vec{p}}^2\right] = \left[\hat{L}_i, \hat{p}_j\right]\hat{p}_j + \hat{p}_j\left[\hat{L}_i, \hat{p}_j\right] = i\hbar\varepsilon_{ijk}(\hat{p}_k\hat{p}_j + \hat{p}_j\hat{p}_k) \equiv 0$ □

9. For $\hat{H} = \hat{T} + V(r) \quad \Rightarrow \quad \left[\hat{L}_i, \hat{H}\right] \equiv 0$, $\left[\hat{\vec{L}}^2, \hat{H}\right] = 0$

2.7 Eigenvalues Problem in QM

2.7.1 Observables

1. Position (canonical):

$$\hat{\vec{x}} = \begin{cases} \hat{\vec{x}}, & (\hat{\vec{x}}\text{-representation}) \\ +i\hbar\dfrac{\partial}{\partial\vec{p}}, & (\hat{\vec{p}}\text{-representation}) \end{cases}$$

2. Momentum (canonical)

$$\hat{\vec{p}} = \begin{cases} -i\hbar\dfrac{\partial}{\partial\vec{x}}, & (\hat{\vec{x}}\text{-representation}) \\ \hat{\vec{p}}, & (\hat{\vec{p}}\text{-representation}) \end{cases}$$

3. Orbital angular momentum
$$\hat{\vec{L}} = \hat{\vec{x}} \times \hat{\vec{p}}, \quad \text{or} \quad \hat{L}_i = \varepsilon_{ijk}\hat{x}_j\hat{p}_k$$
$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \quad \Rightarrow \quad \left[\hat{L}_i, \hat{\vec{L}}^2\right] \equiv 0 \quad \text{and} \quad \hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}}$$
   Note: $\hat{\vec{L}} \times \hat{\vec{L}} \neq 0$, but $\hat{\vec{L}} = \hat{\vec{x}} \times \hat{\vec{p}} = -\hat{\vec{p}} \times \hat{\vec{x}}$, $\left(\hat{\vec{x}} \times \hat{\vec{p}}\right)_i = \varepsilon_{ijk}\hat{x}_k\hat{p}_j$, $\hat{x}_k\hat{p}_j + \hat{p}_j\hat{x}_k = [\hat{x}_k, \hat{p}_j] = i\hbar\delta_{kj} = 0$
   Consider vector $\vec{v}$, then $\hat{\vec{L}} \times \hat{\vec{v}} + \hat{\vec{v}} \times \hat{\vec{L}} = 2i\hbar\hat{\vec{v}}$, $\left[\hat{L}_i, \hat{v}_j\right] = i\hbar\varepsilon_{ijk}\hat{v}_k$
4. Intrinsic angular momentum
$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\varepsilon_{ijk}\hat{S}_k \quad \Leftrightarrow \quad \hat{\vec{S}} \times \hat{\vec{S}} = i\hbar\hat{\vec{S}}$$
$$\left[\hat{L}_i, \hat{S}_j\right] = 0$$
5. Hamiltonian
$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{\vec{p}}^2}{2m} + V(\hat{\vec{x}})$$
   The kinetic energy only depend on $\hat{\vec{p}}$, and the potential only depend on $\hat{\vec{x}}$
6. Energy
$$\hat{E} = i\hbar\frac{\partial}{\partial t} \quad \text{or} \quad \hat{E} = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}$$
   Note: in non-relactivistic QM, time t is not observable
   Schrödinger's equation: $\hat{E}\psi(\vec{x}, t) = \hat{H}\psi(\vec{x}, t), \psi(\vec{x}, t) = \mathrm{e}^{i(\vec{p}\cdot\vec{x}-Et)/h} \quad \Rightarrow \quad \hat{H}\psi(\vec{x}) = E\psi(\vec{x})$

2.7.2 Eigenvalues and Eigenstates

Position

Eigenvalue equation is
$$\hat{\vec{x}}\left|\vec{x}'\right\rangle = \vec{x}'\left|\vec{x}'\right\rangle$$

- Orthonomalism: $\left\langle\vec{x}'\middle|\vec{x}''\right\rangle = \delta\left(\vec{x}' - \vec{x}''\right)$
- Revolution identity: $\int \mathrm{d}\vec{x}\,|\vec{x}\rangle\langle\vec{x}| = \mathbb{1}$

Multiply both sides with $\int |\vec{x}\rangle\langle\vec{x}|\,\mathrm{d}\vec{x}$, then
$$\text{l.h.s} \quad = \int |\vec{x}\rangle\left(\langle\vec{x}|\hat{\vec{x}}|\vec{x}'\rangle\right) = \quad \text{r.h.s} \quad = \int |\vec{x}\rangle\,\vec{x}'\left\langle\vec{x}\middle|\vec{x}'\right\rangle \quad \Rightarrow \quad \langle\vec{x}|\hat{\vec{x}}|\vec{x}'\rangle = \vec{x}' = \delta\left(\vec{x} - \vec{x}'\right)$$

In $\hat{\vec{x}}$-representation, wave function of $|\vec{x}\rangle$ is [1]
$$\left\langle\vec{x}'\middle|\vec{x}\right\rangle = \delta\left(\vec{x} - \vec{x}'\right) \quad \text{and} \quad \hat{\vec{x}}\delta\left(\vec{x} - \vec{x}'\right) = \vec{x}'\delta\left(\vec{x} - \vec{x}'\right)$$

Momentum

Eigenvalue equation is
$$\hat{\vec{p}}\left|\vec{p}'\right\rangle = \vec{p}'\left|\vec{p}'\right\rangle$$

- Orthonomalism: $\left\langle\vec{p}'\middle|\vec{p}''\right\rangle = \delta\left(\vec{p}' - \vec{p}''\right)$
- Revolution identity: $\int \mathrm{d}\vec{p}\,|\vec{p}\rangle\langle\vec{p}| = \mathbf{1}$

In $\hat{\vec{p}}$-representation, wave function of $|\vec{p}\rangle$ is
$$\left\langle\vec{p}'\middle|\vec{p}\right\rangle = \delta\left(\vec{p} - \vec{p}'\right) \quad \text{and} \quad \hat{\vec{p}}\delta\left(\vec{p} - \vec{p}'\right) = \vec{p}'\delta\left(\vec{p} - \vec{p}'\right)$$

Note: "Spectrum" - set of eigenvalues of observable is eigenspectrum for this condition is continuous spectrum

[1] $f(x)\delta(x-a) = f(a)\delta(x-a)$

Relation of between wave function in two representation

The state and wave function are

$$|\psi\rangle = \mathbb{1}\,|\psi\rangle = \begin{cases} \text{in } \hat{\vec{x}}\text{-rep:} & \int \mathrm{d}\vec{x}\,|\vec{x}\rangle\langle\vec{x}|\psi\rangle = \int \mathrm{d}\vec{x}\,|\vec{x}\rangle\,\psi(\vec{x}) \\ \text{in } \hat{\vec{p}}\text{-rep:} & \int \mathrm{d}\vec{p}\,|\vec{p}\rangle\langle\vec{p}|\psi\rangle = \int \mathrm{d}\vec{p}\,|\vec{p}\rangle\,\tilde{\psi}(\vec{p}) \end{cases}, \qquad \begin{cases} \psi(\vec{x}) = \langle\vec{x}|\psi\rangle \\ \tilde{\psi}(\vec{p}) = \langle\vec{p}|\psi\rangle \end{cases}$$

Steps of asking relation of $\psi(\vec{x})$ and $\tilde{\psi}(\vec{p})$:

1. Multiply $\int \mathrm{d}\vec{x}\,|\vec{x}\rangle\langle\vec{x}|$ to two rep of $|\psi\rangle$, then $\psi(\vec{x}) = \langle\vec{x}|\vec{p}\rangle\tilde{\psi}(\vec{p}) = \psi_{\vec{p}}(\vec{x})\tilde{\psi}(\vec{p})$, hence, we need to ask $\psi_{\vec{p}}(x)$
2. Multiply $\int \mathrm{d}\vec{x}\,|\vec{x}\rangle\langle\vec{x}|$ to both side of $\hat{\vec{p}}\,|\vec{p}\rangle = \vec{p}\,|\vec{p}\rangle$, it can be conosidered as changing $\hat{\vec{p}}$-rep to $\hat{\vec{x}}$-rep, therefore

$$\langle\vec{x}|\hat{\vec{p}}|\vec{p}\rangle = \vec{p}\,\langle\vec{x}|\vec{p}\rangle \quad\Rightarrow\quad -i\hbar\frac{\partial}{\partial\vec{x}}\psi_{\vec{p}}(\vec{x}) = \vec{p}\,\psi_{\vec{p}}(\vec{x}) \quad\Rightarrow\quad \psi_{\vec{p}}(\vec{x}) = N\mathrm{e}^{i\,\vec{p}\cdot\vec{x}/\hbar}$$

   Note: for 1-D we have $-i\hbar\,\mathrm{d}\psi_p(x)/\mathrm{d}x = p\psi_p(x) \Rightarrow \psi_p(x) = N\mathrm{e}^{ipx/\hbar}$. Then, normalization is needed to ask N.
3. Consider orthonomalism, take into the terms [2]

$$\int \mathrm{d}\vec{x}\,\psi^*_{\vec{p}'}(\vec{x})\psi_{\vec{p}}(\vec{x}) = \int \mathrm{d}\vec{x}\,\langle\vec{p}'|\vec{x}\rangle\langle\vec{x}|\vec{p}\rangle = \left\langle\vec{p}'\middle|\left(\int \mathrm{d}\vec{x}\,|\vec{x}\rangle\langle\vec{x}|\right)\middle|\vec{p}\right\rangle = \langle\vec{p}'|\vec{p}\rangle = \delta(\vec{p}-\vec{p}')$$
$$= \int \mathrm{d}\vec{x}\,|N^2|\mathrm{e}^{i(\vec{p}-\vec{p}')\cdot\vec{x}/\hbar} = |N^2|(2\pi)^3\delta\left(\frac{\vec{p}-\vec{p}'}{\hbar}\right) = |N^2|(2\pi\hbar)^2\delta(\vec{p}-\vec{p}')$$

   Therefore, $|N^2| = \left(\frac{1}{2\pi\hbar}\right)^3$, and we finished.

The relation between $\psi(\vec{x})$ and $\tilde{\psi}(\vec{p})$

$$\psi(\vec{x}) = \psi_{\vec{p}}(\vec{x})\tilde{\psi}(\vec{p}) \quad\Rightarrow\quad \psi_{\vec{p}}(\vec{x}) = \langle\vec{x}|\vec{p}\rangle = \left(\frac{1}{2\pi\hbar}\right)^{\frac{3}{2}}\mathrm{e}^{i\,\vec{p}\cdot\vec{x}/\hbar},$$
$$\tilde{\psi}(\vec{p}) = \psi_{\vec{x}}(\vec{p})\psi(\vec{x}) \quad\Rightarrow\quad \psi_{\vec{x}}(\vec{p}) = \langle\vec{p}|\vec{x}\rangle = \left(\frac{1}{2\pi\hbar}\right)^{\frac{3}{2}}\mathrm{e}^{-i\,\vec{p}\cdot\vec{x}/\hbar}$$

2.8 Uncertainty Principle

2.8.1 Generalized Uncertainty Principle

1. Heisenberg's uncertainty principle

$$\Delta\hat{x}\cdot\Delta\hat{p} \geqslant \frac{\hbar}{2}$$

2. Generalized uncertainty principle

$$\text{when}\quad \left[\hat{A},\hat{B}\right] \neq 0, \quad\text{then}\quad \Delta\hat{A}\cdot\Delta\hat{B} \geqslant \frac{1}{2}\left|\left\langle[\hat{A},\hat{B}]\right\rangle\right|$$

Expectation value:

$$\left\langle\hat{O}\right\rangle_\psi = \left\langle\psi\middle|\hat{O}\middle|\psi\right\rangle$$

Deviation: (mean square / root deviation)

$$\Delta\hat{A} = \sqrt{\Delta A^2} = \left\langle\left(\hat{A}-\langle\hat{A}\rangle^2\right)\right\rangle^{\frac{1}{2}} = \left(\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2\right)^{\frac{1}{2}}$$

[2] $\int_{-\infty}^{+\infty}\mathrm{e}^{\pm ikx}\mathrm{d}k = 2\pi\delta(x)$, $\quad\int_{-\infty}^{+\infty}\mathrm{e}^{\pm i\vec{k}\cdot\vec{x}}\mathrm{d}\vec{k} = \int_{-\infty}^{+\infty}\mathrm{e}^{\pm ik_xx}\mathrm{d}k_x\int_{-\infty}^{+\infty}\mathrm{e}^{\pm ik_yy}\mathrm{d}k_y\int_{-\infty}^{+\infty}\mathrm{e}^{\pm ik_zz}\mathrm{d}k_z = (2\pi)^3\delta(x)\delta(y)\delta(z) = (2\pi)^3\delta(\vec{x})$

Proof of Generalized Uncertainty Principle

Deviation operator:

$$\hat{\sigma}_A = \hat{A} - \left\langle \hat{A} \right\rangle, \quad \hat{\sigma}_B = \hat{B} - \left\langle \hat{B} \right\rangle$$

Properties of $\hat{\sigma}_A,\, \hat{\sigma}_B$

1. Hermitz: $\hat{\sigma}_A^\dagger = \hat{\sigma}_A \quad \Rightarrow \quad \hat{\sigma}_A^\dagger \hat{\sigma}_A = \hat{\sigma}_A^2$
2. Commutator: $[\hat{\sigma}_A, \hat{\sigma}_B] = \left[\hat{A}, \hat{B}\right]$
3. $\hat{\sigma}_A \hat{\sigma}_B = \frac{1}{2}[\hat{\sigma}_A, \hat{\sigma}_B] + \frac{1}{2}\{\hat{\sigma}_A, \hat{\sigma}_B\}$
4. Expectation value of $[\hat{\sigma}_A, \hat{\sigma}_B]$ and $\{\hat{\sigma}_A, \hat{\sigma}_B\}$
   (a) $[\hat{\sigma}_A, \hat{\sigma}_B]^\dagger = (\hat{\sigma}_A\hat{\sigma}_B - \hat{\sigma}_B\hat{\sigma}_A)^\dagger = \hat{\sigma}_B\hat{\sigma}_A - \hat{\sigma}_A\hat{\sigma}_B = -[\hat{\sigma}_A, \hat{\sigma}_B]$ (skew-hermitian) [3]
   (b) $\{\hat{\sigma}_A, \hat{\sigma}_B\}^\dagger = (\hat{\sigma}_A\hat{\sigma}_B + \hat{\sigma}_B\hat{\sigma}_A)^\dagger = \{\hat{\sigma}_A, \hat{\sigma}_B\}$ (hermitian)

   Therefore, $|\langle\hat{\sigma}_A\hat{\sigma}_B\rangle| = \frac{1}{2}|\langle[\hat{\sigma}_A, \hat{\sigma}_B] + \{\hat{\sigma}_A, \hat{\sigma}_B\}\rangle| = \frac{1}{2}|\langle[\hat{\sigma}_A, \hat{\sigma}_B]\rangle + \langle\{\hat{\sigma}_A, \hat{\sigma}_B\}\rangle| \geqslant \frac{1}{2}|\langle[\hat{\sigma}_A, \hat{\sigma}_B]\rangle| = \frac{1}{2}\left|\left\langle[\hat{A}, \hat{B}]\right\rangle\right|$

We need to prove $\left\langle\sigma_A^2\right\rangle\left\langle\sigma_B^2\right\rangle \geqslant \frac{1}{4}\left|\langle[\hat{\sigma}_A, \hat{\sigma}_B]\rangle\right|^2$
Cauchy-Schwarz Inequality:

1. $\left(\sum_n a_n^2\right)\left(\sum_n b_n^2\right) \geqslant \left(\sum_n a_n b_n\right)^2$
2. $u = |\vec{u}|,\, v = |\vec{v}| \to uv \geqslant \vec{u}\cdot\vec{v};\, |\vec{u}||\vec{v}| \geqslant |\vec{u}||\vec{v}|\cos\theta;\, |\vec{u}| + |\vec{v}| \geqslant |\vec{u} + \vec{v}| \Rightarrow \vec{u}^2 \cdot \vec{v}^2 \geqslant (\vec{u}\cdot\vec{v})^2$
3. $u^2 \leftrightarrow \langle u|u\rangle,\, v^2 \leftrightarrow \langle v|v\rangle,\, \vec{u}\cdot\vec{v} \leftrightarrow \langle u|v\rangle \quad \Rightarrow \quad \langle u|u\rangle\langle v|v\rangle \geqslant (\langle u|v\rangle)^2$ equality iff $|u\rangle = C\,|v\rangle$

$$\begin{aligned}\left\langle\sigma_A^2\right\rangle\left\langle\sigma_B^2\right\rangle &= \langle\psi|\hat{\sigma}_A^2|\psi\rangle\,\langle\psi|\hat{\sigma}_B^2|\psi\rangle = \langle\psi|\hat{\sigma}_A^\dagger\hat{\sigma}_A|\psi\rangle\,\langle\psi|\hat{\sigma}_B^\dagger\hat{\sigma}_B|\psi\rangle = \langle\psi_A|\psi_A\rangle\langle\psi_B|\psi_B\rangle \\ &\geqslant |\langle\psi_A|\psi_B\rangle|^2 = \left|\langle\psi|\hat{\sigma}_A^\dagger\hat{\sigma}_B|\psi\rangle\right|^2 = |\langle\psi|\hat{\sigma}_A\hat{\sigma}_B|\psi\rangle|^2\end{aligned}$$

Since $\Delta\hat{A} = \left\langle\hat{\sigma}_A^2\right\rangle^{\frac{1}{2}}$, therefore

$$\Delta\hat{A}\cdot\Delta\hat{B} \geqslant \sqrt{|\langle\hat{\sigma}_A\hat{\sigma}_B\rangle|^2} \geqslant \sqrt{\left(\frac{1}{2}\left|\left\langle[\hat{A}, \hat{B}]\right\rangle\right|\right)^2} = \frac{1}{2}\left|\left\langle[\hat{A}, \hat{B}]\right\rangle\right|$$

2.8.2 Minimum Uncertainty Wavepacket

$$\exists\,|\psi\rangle \quad \Rightarrow \quad \Delta\hat{A}\cdot\Delta\hat{B} = \frac{1}{2}\left|\left\langle[\hat{A}, \hat{B}]\right\rangle\right| \quad \text{(minimum uncertainty state)}$$

Proof with $\hat{x}, \hat{p}$

Let $\hat{\sigma}_x = \hat{x} - \langle\hat{x}\rangle,\, \hat{\sigma}_p = \hat{p} - \langle\hat{p}\rangle$,

$$|\alpha\rangle = (\hat{\sigma}_x + i\lambda\hat{\sigma}_p)\,|\psi\rangle$$

satisfy MUW ($\lambda \in \Re$). Therefore, $\langle\alpha|\alpha\rangle \geqslant 0$ equality iff $|\alpha\rangle = \vec{0}$, take into the term,

$$\langle\alpha|\alpha\rangle = \langle\psi|(\hat{\sigma}_x - i\lambda\hat{\sigma}_p)(\hat{\sigma}_x + i\lambda\hat{\sigma}_p)|\psi\rangle = \left\langle\hat{\sigma}_p^2\right\rangle\lambda^2 - \hbar\lambda + \left\langle\hat{\sigma}_x^2\right\rangle \geqslant 0$$

Therefore, $\Delta = (-\hbar)^2 - 4\left\langle\hat{\sigma}_p^2\right\rangle\left\langle\hat{\sigma}_x^2\right\rangle \leqslant 0 \quad \Rightarrow \quad \left\langle\hat{\sigma}_x^2\right\rangle\left\langle\hat{\sigma}_p^2\right\rangle \geqslant \frac{\hbar^2}{4} \quad \Rightarrow \quad \Delta\hat{x}\Delta\hat{p} \geqslant \frac{\hbar}{2}$ (HUP).
When $\Delta = 0$, $\Delta\hat{x}\Delta\hat{p} = \frac{\hbar}{2}$, $\lambda = \frac{\hbar}{2\left\langle\hat{\sigma}_p^2\right\rangle} = \frac{2\Delta\hat{x}^2}{\hbar} \quad \Rightarrow \quad \lambda\hbar = \Delta\hat{x}^2$

[3] Hermitian: $\hat{A}^\dagger = \hat{A},\, \left\langle\hat{A}\right\rangle = C \in \Re$; skew-hermitian: $\hat{A}^\dagger = -\hat{A},\, \left\langle\hat{A}\right\rangle = C \in \Im$.

Wave function in MUS

Since $|\alpha\rangle \equiv 0$, $\langle x|\alpha\rangle = 0$, and in $\hat{x}$-rep, $\hat{x} = x,\ \hat{p} = -i\hbar\ \mathrm{d}/\mathrm{d}x$, then

$$\langle x|(\hat{\sigma}_x + i\lambda\hat{\sigma}_p)|\psi\rangle = \left[(\hat{x} - \langle\hat{x}\rangle) + \lambda\hbar\frac{\mathrm{d}}{\mathrm{d}x} - i\lambda\langle\hat{p}\rangle\right]\psi(x) = 0$$

Consider $\psi(x) = u(x - \langle x\rangle)\exp\{i\langle\hat{p}\rangle x/\hbar\}$, let $q = x - \langle x\rangle$, the equation become

$$\left[q + \lambda\hbar\frac{\mathrm{d}}{\mathrm{d}q}\right]u(q) = 0 \quad\Rightarrow\quad \int\frac{\mathrm{d}u(q)}{u(q)} = \int -\frac{q}{\lambda\hbar}\mathrm{d}q \quad\Rightarrow\quad u(q) = A\exp\left\{-\frac{q^2}{2\lambda\hbar}\right\}$$

Since $\lambda\hbar = \Delta\hat{x}^2$, then the wave function is a Gauss function

$$\psi(x) = A\exp\{i\langle\hat{p}\rangle x/\hbar\}\exp\left\{-\frac{1}{2}\left(\frac{x - \langle x\rangle}{\Delta x}\right)^2\right\} \quad\Rightarrow\quad |\psi(x)|^2 \sim \exp\left\{-\left(\frac{x - \langle x\rangle}{\Delta x}\right)^2\right\}$$

Remarks:

1. Uncertainty principle always holds, provided that $[\hat{A}, \hat{B}] \neq 0$, conjugate observables $[\hat{A}\cdot\hat{B}] \sim [\hbar]$ (dimension)
2. $\exists\,|\psi\rangle$ (Gauss classical state) $\quad\Rightarrow\quad$ Minimum uncertainty state

2.8.3 Energy-Time Uncertainty Principe

$$\Delta E\cdot\Delta T \geqslant \frac{\hbar}{2}$$

However, time is not observable.

Proof. Since Ehrenfest theorem (Eq: 4.1), then $\Delta\hat{A}\cdot\hat{H} \geqslant \dfrac{1}{2}\left|\left\langle[\hat{A}, \hat{H}]\right\rangle\right| = \dfrac{\hbar}{2}\left|\dfrac{\mathrm{d}}{\mathrm{d}t}\langle\hat{A}\rangle\right|$, $\qquad$ ($\partial\hat{A}\big/\partial t \equiv 0,\ [\hat{A}, \hat{H}] \neq 0$)

let $\dfrac{\Delta\hat{A}}{\left|\mathrm{d}\langle\hat{A}\rangle\big/\mathrm{d}t\right|} = \Delta T$ and $\Delta\hat{H} = \Delta E \quad\Rightarrow$ $\square$

Chapter 3

Theory of Angular Momentum

3.1 Orbital Angular Momentum

3.1.1 Eigenvalue Probelm of AM

We have already known that $\left[\hat{\vec{L}}, \hat{L}_i\right] = 0$, which means $\hat{\vec{L}}$, $\hat{L}_i$ are compatible observables, and they have common eigenstates. Suppose z-axis as quantum axis which is the $\vec{B}$ direction, then

$$\left[\hat{\vec{L}}^2, \hat{L}_z\right] \equiv 0$$

In the later note, we can get

$$\hat{\vec{L}}^2 |lm\rangle = \hbar^2 l(l+1) |lm\rangle, \qquad \hat{L}_z |lm\rangle = \hbar m |lm\rangle$$

where $|lm\rangle$ is the eigenstate, e.g. for a fixed l, $m = -l, -l+1, \cdots, l-1, l$, there are $|l, -l\rangle, |l, -l+1\rangle, \cdots, |l, l-1\rangle, |l, l\rangle$, $(2l-1)$ eigenstates. We call one eigenvalue corresponding to multi-eigenstates as degeneracy.

- Orthonomality (ON): $\langle lm|l'm'\rangle = \delta_{ll'}\delta_{mm'}$
- Resolution of identity completeness (RI): $\sum_{l,m} |lm\rangle\langle lm| = \mathbb{1}_l$

3.1.2 Ladder Operator

Define the ladder operator as

$$\hat{L}_\pm = L_x \pm i\hat{L}_y$$

- Raising operator: $\hat{L}_+$; Lowing operator: $\hat{L}_-$
- $\hat{L}_x = \dfrac{\hat{L}_+ + \hat{L}_-}{2}, \quad \hat{L}_y = \dfrac{\hat{L}_+ - \hat{L}_-}{2i}$
- $\left[\hat{L}_\pm, \hat{\vec{L}}^2\right] = 0$
- $\left[\hat{L}_\pm, \hat{L}_z\right] = -i\hbar\hat{L}_y \pm i \cdot i\hbar\hat{L}_x = \mp\hbar\hat{L}_\pm \quad \Rightarrow \quad \hat{L}_z\hat{L}_\pm = \hat{L}_\pm\hat{L}_z \pm \hbar\hat{L}_\pm$

Then, we find

$$\hat{L}_z\hat{L}_\pm |lm\rangle = \left(\hat{L}_\pm\hat{L}_z \pm \hbar\hat{L}_\pm\right) |lm\rangle = \hbar m\hat{L}_\pm |lm\rangle \pm \hbar\hat{L}_\pm |lm\rangle = \hbar(m+1)\hat{L}_\pm |lm\rangle$$

which means $\hat{L}_\pm |lm\rangle$ is the eigenstate of $\hat{L}_z$, corresponding to eigenvalue of $\hbar(m+1)$, therefore, we can asuume

$$\hat{L}_\pm |l, m\rangle = C_\pm |l, m\pm 1\rangle \quad \text{where} \quad C_\pm = \hbar\sqrt{l(l+1) - m_l(m_l \pm 1)}$$

Quantum numbers (qn) Summary:

- Principal qn: $n \leftrightarrow \hat{H}$
- Orbital angular qn: $l \leftrightarrow \hat{\vec{L}}^2$; Spin angular qn: $s \leftrightarrow \hat{\vec{S}}^2$
- Magnetic qn: $m_l \leftrightarrow \hat{L}_z$; spin magnetic qn: $m_s \leftrightarrow \hat{S}_z$

3.2 Spin and Pauli Matrices

3.2.1 The Stern-Gerlach Experiment

- Quantumzation of spatial orienration of angular momentum
- Intrisic angular momentum (Spin)
- SGE
    1. Silver neutral atom beam: no Lorentz force
    2. Magnetic field: Inhomogeneous, $\vec{F} = -\vec{\nabla} W_m,\ W_m = -\vec{\mu}\cdot\vec{B} \quad \Rightarrow \quad \vec{F} = \vec{\mu}\vec{\nabla}\cdot\vec{B}, \quad \vec{\mu}\propto\vec{L}$
    3. Deflection: two vector, up(50%), down (50%)
    4. Further: $\vec{v}$ is small, $\vec{p}$ is small, $\vec{L} = \vec{x}\times\vec{p}$ is small, $\vec{\mu}$ is small, so intrisic freedom?

NEED insert picture and the caption.
Significances of spin:

1. Spin is an intrisic angular momentum
2. Spin is an eigenstate to disdinguish two families
    (a) Spin is integer: $s = 0, 1, 2, \cdots$,
    bosons: Bose-Einstein statistics; permutation $\psi_s(\cdots x_i, \cdots, x_j, \cdots) = \psi_s(\cdots x_j, \cdots, x_i, \cdots)$ unchanged
    (b) Spin is half-integer: $s = 1/2, 3/2, \cdots$
    Fermion: Fermi-Dirac statistics; permutaiton $\psi_s(\cdots x_i, \cdots, x_j, \cdots) = -\psi_s(\cdots x_j, \cdots, x_i, \cdots)$ opposite spin

3.2.2 Spin Angular Momentum

Similar to orbital angular momentum, we have

$$\left[\hat{\vec{S}}^2, \hat{S}_i\right] \equiv 0 \quad \Leftrightarrow \quad \left[\hat{S}_i, \hat{S}_j\right] = i\hbar\varepsilon_{ijk}\hat{S}_k \quad \Leftrightarrow \quad \hat{\vec{S}}\times\hat{\vec{S}} = i\hbar\hat{\vec{S}}$$

Eigen function is with common eigenstates $|s, m_s\rangle$

$$\begin{cases} \hat{\vec{S}}^2 |s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle \\ \hat{S}|s, m_s\rangle = \hbar m_s |s, m_s\rangle \end{cases}$$

Spin 1/2

Consider $s = \dfrac{1}{2}$, it stands for electron, proton, neutron. Then $s(s+1) = \dfrac{3}{4}$, $m_s = \pm\dfrac{1}{2}$, and define two states as

$$\begin{matrix} \text{UP:} & \left|s = \dfrac{1}{2}, m_s = +\dfrac{1}{2}\right\rangle = |+\rangle = |\uparrow\rangle = |0\rangle = \begin{bmatrix}1\\0\end{bmatrix} \\ \text{DOWN:} & \left|s = \dfrac{1}{2}, m_s = -\dfrac{1}{2}\right\rangle = |-\rangle = |\downarrow\rangle = |1\rangle = \begin{bmatrix}0\\1\end{bmatrix} \end{matrix} \quad \Rightarrow \quad \begin{cases} |0\rangle\langle 0| + |1\rangle\langle 1| = \mathbb{1}_2 \\ \langle 0|0\rangle = \langle 1|1\rangle = 1 \\ \langle 0|1\rangle = \langle 1|0\rangle = 0 \end{cases}$$

Therefore, we have the eigen function of in $\hat{S}_z$-representation, and define Pauli matrix as

$$\begin{matrix} \hat{S}_z|0\rangle = +\dfrac{\hbar}{2}|0\rangle \\ \hat{S}_z|1\rangle = -\dfrac{\hbar}{2}|1\rangle \end{matrix} \quad \Rightarrow \quad \hat{\vec{S}} = \frac{\hbar}{2}\hat{\vec{\sigma}} \quad \Rightarrow \quad \begin{matrix} \hat{\sigma}_z|0\rangle = +1|0\rangle \\ \hat{\sigma}_z|1\rangle = -1|1\rangle \end{matrix}$$

Discussion:

1. $\hat{\sigma}_i^2 = \mathbb{1}_2 \quad (i = 1, 2, 3), \qquad \hat{\vec{S}}^2 = \dfrac{3}{4}\hbar^2\mathbb{1}_2 \quad \Rightarrow \quad \hat{\vec{\sigma}}^2 = 3\mathbb{1}_2$
2. $\hat{\sigma}_z = \begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$

Proof. $\hat{\sigma}_z = \mathbb{1}_2 \cdot \hat{\sigma}_z \cdot \mathbb{1}_2 = (|0\rangle\langle 0| + |1\rangle\langle 1|)\hat{\sigma}_z(|0\rangle\langle 0| + |1\rangle\langle 1|) = |0\rangle\langle 0| - |1\rangle\langle 1|$ ☐

3. $[\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\hat{\sigma}_k$

   Proof. $\left[\hat{S}_i, \hat{S}_j\right] = [\hbar\hat{\sigma}_i/2, \hbar\hat{\sigma}_j/2] = i\hbar\varepsilon_{ijk}\hat{S}_k = i\hbar\varepsilon_{ijk}(\hbar\hat{\sigma}_k/2)$ ☐

4. $\{\hat{\sigma}_i, \hat{\sigma}_j\} = 2\delta_{ij}\mathbb{1}_2$

   Proof. $\hat{\sigma}_i(\hat{\sigma}_i\hat{\sigma}_j - \hat{\sigma}_j\hat{\sigma}_i) = \hat{\sigma}_i 2i\varepsilon_{ijk}\hat{\sigma}_k \quad \Rightarrow \quad \hat{\sigma}_j - \hat{\sigma}_i\hat{\sigma}_j\hat{\sigma}_i = 2i\varepsilon_{ijk}\hat{\sigma}_i\hat{\sigma}_k$ minus [1]
   $(\hat{\sigma}_j\hat{\sigma}_i - \hat{\sigma}_i\hat{\sigma}_j)\hat{\sigma}_i = 2i\varepsilon_{jik}\hat{\sigma}_k\hat{\sigma}_i \quad \Rightarrow \quad \hat{\sigma}_j - \hat{\sigma}_i\hat{\sigma}_j\hat{\sigma}_i = -2i\varepsilon_{ijk}\hat{\sigma}_k\hat{\sigma}_i \quad \Rightarrow \quad 0 = \varepsilon_{ijk}(\hat{\sigma}_k\hat{\sigma}_i + \hat{\sigma}_i\hat{\sigma}_k)$ ☐

5. $\hat{\sigma}_i\hat{\sigma}_j = \delta_{ij}\mathbb{1}_2 + i\varepsilon_{ijk}\hat{\sigma}_k$

Similar to the orbitla angular momentum ladder operator, in spin

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y, \quad \hat{S}_\pm |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\, |s, m_s \pm 1\rangle$$

Apply the ladder operator to each case of spin 1/2,

$$\hat{S}_+ |1\rangle = \hbar |0\rangle, \quad \hat{S}_- |0\rangle = \hbar |1\rangle$$

Use the relation, we can also define Pauli ladder operator by /

$$\begin{aligned} (|0\rangle\langle 1|)\, |1\rangle = |0\rangle \quad &\leftrightarrow \quad \hat{S}_+ = \hbar\, |0\rangle\langle 0| = \hbar\hat{\sigma}_+ \\ (|1\rangle\langle 0|)\, |0\rangle = |1\rangle \quad &\leftrightarrow \quad \hat{S}_- = \hbar\, |1\rangle\langle 0| = \hbar\hat{\sigma}_- \end{aligned}$$

Therefore, we have

$$\hat{S}_\pm = \hbar\hat{\sigma}_\pm, \quad \hat{\sigma}_\pm = \frac{1}{2}(\hat{\sigma}_x \pm i\hat{\sigma}_y), \quad \begin{cases} \hat{\sigma}_+ = |0\rangle\langle 1| \\ \hat{\sigma}_- = |1\rangle\langle 0| \end{cases}, \quad \begin{cases} \hat{\sigma}_x = \hat{\sigma}_+ + \hat{\sigma}_- \\ \hat{\sigma}_y = (-i)(\hat{\sigma}_+ - \hat{\sigma}_-) \end{cases}$$

Pauli matrix ($\hat{S}_z$-representation):

$$\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \hat{\sigma}_z \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \hat{\sigma}_0 = \mathbb{1}_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Properties of Pauli matrix:

1. $\hat{\sigma}_i = \begin{bmatrix} \delta_{i3} & \delta_{i1} - i\delta_i 2 \\ \delta_{i1} + i\delta_{i2} & \delta_{i3} \end{bmatrix}$
2. $\mathrm{Tr}(\hat{\sigma}_i) = 0$
3. $\det(\hat{\sigma}_i) = -1$
4. $\left(\hat{\vec{\sigma}} \cdot \hat{\vec{A}}\right)\left(\hat{\vec{\sigma}} \cdot \hat{\vec{B}}\right) = \left(\hat{\vec{A}} \cdot \hat{\vec{B}}\right)\mathbb{1}_2 + i\hat{\vec{\sigma}} \cdot \left(\hat{\vec{A}} \times \hat{\vec{B}}\right)$

   e.g $\left(\hat{\vec{\sigma}} \cdot \hat{\vec{p}}\right)^2 = \hat{\vec{p}}^2 \cdot \mathbb{1}_2, \quad \left[\hat{\vec{\sigma}} \cdot \left(\hat{\vec{p}} - \frac{q}{c}\hat{\vec{A}}\right)\right]^2 = \left(\hat{\vec{\sigma}} \cdot \hat{\vec{\Pi}}\right)^2 = \hat{\vec{\Pi}} \cdot \mathbb{1} + i\hat{\vec{\sigma}} \cdot \left(\hat{\vec{\Pi}} \times \hat{\vec{\Pi}}\right)$

3.3 Algebra Method in QM

Summary of orbital angular momentum eigenvalue problem:

$$\begin{aligned} &[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}, \quad [\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] \equiv 0, \quad \hat{\vec{L}} = \hat{\vec{x}} \times \hat{\vec{p}} \quad \text{or} \quad \hat{L}_i = \varepsilon_{ijk}\hat{x}_j\hat{p}_k \\ &\Rightarrow \quad \left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \quad \Leftrightarrow \quad \hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}} \\ &\Rightarrow \quad \left[\hat{\vec{L}}^2, \hat{L}_i\right] \equiv 0 \quad \Rightarrow \quad \begin{cases} \hat{\vec{L}}^2 |l, m_l\rangle = \hbar^2 l(l+1)\, |l, m_l\rangle \\ \hat{L}_z\, |l, m_l\rangle = \hbar m_l\, |l, m_l\rangle \end{cases} \quad (m_l = -l, -l+1, \cdots, l-1, l) \end{aligned}$$

[1] i: no Einstein convention

Generalize to intrisic angular momentum ⇔ SGE

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\varepsilon_{ijk}\hat{S}_k \quad\Leftrightarrow\quad \vec{S}\times\vec{S} = i\hbar\vec{S} \quad\Rightarrow\quad \left[\hat{\vec{S}}^2, \hat{S}_i\right] \equiv 0$$

$$\Rightarrow\quad \begin{cases} \hat{\vec{S}}^2\left|s, m_s\right\rangle = \hbar^2 s(s+1)\left|s, m_s\right\rangle \\ \hat{S}_z\left|s, m_s\right\rangle = \hbar m_s\left|s, m_s\right\rangle \end{cases}$$

SEG

Generalize to arbitrary angular momentum

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

Commutation:

1. $\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\epsilon_{ijk}\hat{J}_k$

   Proof. $[\hat{J}_i, \hat{J}_j] = [\hat{L}_i + \hat{S}_i, \hat{L}_j + \hat{S}_j] = [\hat{L}_i, \hat{S}_j] + [\hat{S}_i, \hat{S}_j] = i\hbar\varepsilon_{ijk}(\hat{L}_k + \hat{S}_k) = i\hbar\varepsilon_{ijk}\hat{J}_k \quad [\hat{L}_i, \hat{L}_j] \equiv 0$ □

2. $\left[\hat{\vec{J}}^2, \hat{J}_i\right] \equiv 0 \quad (i = 1, 2, 3)$
3. $\left[\hat{\vec{J}}^2, \hat{J}_\pm\right] = 0$ define ladder operator $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$

   Proof. $[\hat{J}_z, \hat{J}_\pm] = [\hat{J}_z, \hat{J}_x \pm i\hat{J}_y] = i\hbar\hat{J}_y \pm i(-i\hbar)\hat{J}_x = \pm(\hat{J}_x \pm i\hbar\hat{J}_y)$ □

4. $\left[\hat{J}_z, \hat{J}_\pm\right] = \pm\hbar\hat{J}_\pm$
5. $\hat{J}_+\hat{J}_- = \hat{\vec{J}}^2 - \hat{J}_z^2 + \hbar\hat{J}_z$
6. $\hat{J}_\pm^\dagger = \hat{J}_\mp$

Next, ask for the eigenvalue problem. Assume

$$\begin{cases} \hat{\vec{J}}^2\left|\lambda, m\right\rangle = \hbar^2\lambda\left|\lambda, m\right\rangle \\ \hat{J}_z\left|\lambda, m\right\rangle = \hbar m\left|\lambda, m\right\rangle \end{cases}$$

Since $[\hat{\vec{J}}^2, \hat{J}_\pm] \equiv 0$, then

$$\hat{\vec{J}}^2\Big(\hat{J}_\pm\left|\lambda, m\right\rangle\Big) = \hat{J}_\pm\hat{\vec{J}}^2\left|\lambda, m\right\rangle = \lambda\hbar^2\Big(\hat{J}_\pm\left|\lambda, m\right\rangle\Big)$$

Since $\hat{J}_z\hat{J}_\pm = \hat{J}_\pm\hat{J}_z \pm \hbar\hat{J}_\pm$, then

$$\hat{J}_z\Big(\hat{J}_\pm\left|\lambda, m\right\rangle\Big) = \Big(\hat{J}_\pm\hat{J}_z \pm \hbar\hat{J}_\pm\Big)\left|\lambda, m\right\rangle = (m\pm 1)\hbar\Big(\hat{J}_\pm\left|\lambda, m\right\rangle\Big)$$

which means $\hat{J}_\pm\left|\lambda, m\right\rangle$ is eigen state of $\hat{J}_z$ with eigen value of $(m\pm 1)\hbar$. Therefore,

$$\hat{J}_\pm\left|\lambda, m\right\rangle = C_\pm\left|\lambda, m\pm 1\right\rangle \quad\Rightarrow\quad \hat{J}_\pm^n\left|\lambda, m\right\rangle = P_\pm\left|\lambda, m\pm n\right\rangle$$

And

$$\left.\begin{array}{rl} \langle\hat{\vec{J}}^2\rangle = \langle\lambda, m|\hat{\vec{J}}^2|\lambda, m\rangle = \lambda\hbar^2 & \langle\hat{\vec{J}}^2\rangle \geqslant \langle\hat{\vec{J}}_z^2\rangle \\ \langle\hat{\vec{J}}_z^2\rangle = \langle\lambda, m|\hat{\vec{J}}_z^2|\lambda, m\rangle = m^2\hbar^2 & \lambda \geqslant m^2 \end{array}\right\}$$

Therefore, $\exists m_0$ (minimal), $\exists N$ (integer), $m_0 + N$ is the maximal, let

$$\hat{J}_-\left|\lambda, m_0\right\rangle \equiv 0, \quad \hat{J}_+\left|\lambda, m_0 + N\right\rangle \equiv 0$$

Since $\hat{J}_\mp\hat{J}_\pm = \hat{\vec{J}}^2 - \hat{J}_z^2 \mp \hbar\hat{J}_z$,

$$0 \equiv \hat{J}_+\Big(\hat{J}_-\left|\lambda, m_0\right\rangle\Big) = \hbar^2(\lambda - m_0^2 + m_0), \quad 0 \equiv \hat{J}_-\Big(\hat{J}_+\left|\lambda, m_0 + N\right\rangle\Big) = \hbar^2\big(\lambda - (m_0+N)^2 - (m_0+N)\big)$$

Minus each other, we got $(1+N)(2m_0+N)=0$, then

$$m_0=-\frac{N}{2},\quad m_0=\frac{N}{2},\quad \lambda=\frac{N}{2}\left(\frac{N}{2}+1\right)$$

let $j=\dfrac{N}{2}$, therefore

$$\lambda=j(j+1),\quad m_j=-j,-j+1,\cdots,j-1,j$$

Eigenvalue equations:

$$\begin{cases}\hat{\vec{J}}^2\left|j,m_j\right\rangle=\hbar^2 j(j+1)\left|j,m_j\right\rangle & (j\geqslant 0)\\ \hat{J}_z\left|j,m_j\right\rangle=\hbar m_j\left|j,m_j\right\rangle & (m_j=-j,-j+1,\cdots,+j)\end{cases}$$

Next, ask for $C_\pm$

$$\hbar^2\big(j(j+1)-m_j^2\mp m_j\big)\langle j,m_j|j,m_j\rangle=\langle j,m_j|\hat{\vec{J}}^2-\hat{J}_z^2\mp\hbar\hat{J}_z|j,m_j\rangle=\langle j,m_j|\hat{J}_\mp\hat{J}_\pm|j,m_j\rangle=|C_\pm|^2\langle j,m_j|j,m_j\rangle$$

For simplicity, $C_\pm\in\mathbb{R}$, therefore

$$C_\pm=\hbar\sqrt{j(j+1)-m_j(m_j\pm 1)}$$

Ladder operation:

$$\hat{J}_\pm\left|j,m_j\right\rangle=\hbar\sqrt{j(j+1)-m_j(m_j\pm 1)}\left|j,m_j\pm 1\right\rangle$$

Remark: $\hat{J}_+\left|j,j\right\rangle\equiv 0, \hat{J}_-\left|j,-j\right\rangle\equiv 0$

- j: azimuthal quantum number
- m_j: magnetic quantum number

Consider

$$H=\frac{\vec{p}^{\,2}}{2m}+V(r)+\xi(r)\vec{L}\cdot\vec{S}$$

- $\xi(r)\vec{L}\cdot\vec{S}\to\vec{L}-\vec{S}$ coupling $\leftrightarrow$ fine structrue
- $V(r)\to$ central potential

Since $[\hat{L}_i,\hat{p}_j]=i\hbar\varepsilon_{ijk}\vec{p}_k$,

$$[\hat{L}_i,\hat{\vec{p}}^2]\equiv 0,\ [\hat{S}_i,\hat{\vec{p}}^2]\equiv 0,\ [\hat{J}_i,\hat{\vec{p}}^2]\equiv 0,\ [\hat{L}_i,\hat{V}(r)]\equiv 0,\ [\hat{S}_i,\hat{V}(r)]\equiv 0,\ [\hat{J}_i,\hat{V}(r)]\equiv 0$$

and

$$[\hat{L}_i,\hat{\vec{L}}\cdot\hat{\vec{S}}]=[\hat{L}_i,\hat{L}_j\hat{S}_j]=i\hbar\varepsilon_{ijk}\hat{L}_k\hat{S}_j\neq 0,\quad [\hat{\vec{L}}^2,\hat{\vec{L}}\cdot\hat{\vec{S}}]=[\hat{L}_i\hat{L}_i,\hat{L}_j\hat{S}_j]=i\hbar\varepsilon_{ijk}(\hat{L}_k\hat{L}_i+\hat{L}_i\hat{L}_k)\hat{S}_j\equiv 0$$

Similar to $\hat{\vec{S}}$ and $\hat{\vec{J}}$

$$[\hat{S}_i,\hat{\vec{L}}\cdot\hat{\vec{S}}]\neq 0,[\hat{\vec{L}}^2,\hat{\vec{L}}\cdot\hat{\vec{S}}]\equiv 0,\quad [\hat{J}_i,\hat{\vec{L}}\cdot\hat{\vec{S}}]\equiv 0,\quad [\hat{\vec{J}}\cdot\hat{\vec{S}}]\equiv 0$$

Therefore, $\left(\hat{\vec{L}}^2,\ \hat{\vec{S}}^2,\ \hat{\vec{J}}^2,\ \hat{J}_i\right)$ commutes with $\hat{H}$.

3.4 Addition of Angular Momenta

3.4.1 Basis

Consider $\hat{\vec{J}}_1$ and $\hat{\vec{J}}_2$, then $\hat{\vec{J}}=\hat{\vec{J}}_1+\hat{\vec{J}}_2$, $\hat{J}_z=\hat{J}_{1z}+\hat{J}_{2z}$, eigenvalue equations are (same as $\hat{\vec{J}}_2$)

$$\begin{cases}\hat{\vec{J}}_1^2\left|j_1,m_1\right\rangle=\hbar^2 j_1(j_1+1)\left|j_1,m_1\right\rangle\\ \hat{J}_{1z}\left|j_1,m_1\right\rangle=\hbar m_1\left|j_1,m_1\right\rangle\end{cases}\qquad\begin{cases}\langle j_1m_1|j_1'm_1'\rangle=\delta_{j_1j_1'}\delta_{m_1m_1'} & \text{(ON)}\\ \sum\limits_{m_1}|j_1m_1\rangle\langle j_1m_1|=\mathbb{1}_{2j_1+1} & \text{(RI)}\end{cases}$$

Commutation: $(i,j,k=x,y,z;\ \alpha,\beta=1,2)$

1. $[\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k, \quad [\hat{J}_{\alpha i}, \hat{J}_{\beta j}] = i\hbar\delta_{\alpha\beta}\varepsilon_{ijk}\hat{J}_{\alpha k}$

   Proof. $[\hat{J}_i, \hat{J}_j] = [\hat{J}_{1i} + \hat{J}_{2i}, \hat{J}_{1j} + \hat{J}_{2j}] = i\hbar\varepsilon_{ijk}\hat{J}_{1k} + i\hbar\varepsilon_{ijk}\hat{J}_{2k}$ □

2. $[\hat{\vec{J}}^2, \hat{J}_i] \equiv 0, \quad [\hat{\vec{J}}^2, \hat{\vec{J}}_i^2] \equiv 0, \quad [\hat{\vec{J}}^2{}_\alpha, \hat{J}_{\alpha i}] \equiv 0, \quad [\hat{\vec{J}}^2, \hat{J}_{\alpha i}] \neq 0$

   Proof. $[\hat{\vec{J}}^2, \hat{J}_{\alpha i}] = [\hat{\vec{J}}_1^2 + \hat{\vec{J}}_2^2 + 2\hat{\vec{J}}_1 \cdot \hat{\vec{J}}_1, \hat{J}_{\alpha i}] = 2[\hat{J}_{1j}\hat{J}_{2j}, \hat{J}_{\alpha i}] = 2i\hbar\varepsilon_{jik}\hat{J}_{1k}\hat{J}_{2j} \neq 0 \quad (\alpha = 1)$ □

Therefore, $\hat{J}_{1z},\ \hat{J}_{2z}$ don't commute with $\hat{\vec{J}}^2$; $\hat{\vec{J}}_1,\ \hat{\vec{J}}_2$ commute with $\hat{\vec{J}}^2$.
Complete set of commuting observables (CSCO): $\left(\vec{J}_1^2, \vec{J}_2^2, \hat{J}_z, \hat{\vec{J}}^2\right)$
Related good quantum number (GQN): (j_1, j_2, m, j)

3.4.2 Two Representation

Uncoupled Basis

Tensor product: $\otimes$

$$|j_1 m_1\rangle \otimes |j_2 m_2\rangle = |j_1 m_1 j_2 m_2\rangle$$

- $\left(\vec{J}_1 + \vec{J}_2\right)|j_1 j_2 m_1 m_2\rangle = \left(\vec{J}_1 + \vec{J}_2\right)|j_1 m_1\rangle \otimes |j_2 m_2\rangle = \left(\vec{J}_1 |j_1 m_1\rangle\right) \otimes |j_2 m_2\rangle + |j_1 m_1\rangle \otimes \left(\vec{J}_2 |j_2 m_2\rangle\right)$
- ON: $\langle j_1 m_1 j_2 m_2 | j_1' m_1' j_2' m_2'\rangle = \delta_{j_1 j_1'}\delta_{j_1, j_2'}\delta_{m_1 m_1'}\delta_{m_2 m_2'}$, for fixed j_1, j_2, $\langle j_1 m_1 j_2 m_2 | j_1' m_1' j_2' m_2'\rangle = \delta_{m_1 m_1'}\delta_{m_2 m_2'}$
- RI: $\sum_{m_1, m_2} |j_1 m_1 j_2 m_2\rangle\langle j_1 m_1 j_2 m_2| = \mathbb{1}_{(2j_1+1)(2j_2+1)}$
- Dimension of tensor product: $\dim|j_1 m_1\rangle = 2j_1 + 1$, $\dim|j_1 m_1\rangle \otimes |j_2 m_2\rangle = (2j_1+1)(2j_2+1)$

Coupled Basis

$$|j_1 j_2 j m\rangle = |jm\rangle, \quad \text{for fixed } j_1, j_2$$

since $-j_1 \leqslant m_1 \leqslant j_1,\ -j_2 \leqslant m_2 \leqslant j_2,\ -j \leqslant m \leqslant j$, and $-j_1 \leqslant m - m_2 \leqslant j_1,\ -j_2 \leqslant m - m_1 \leqslant j_2$,
choose $m_1 = j_1,\ m_2 = j_2,\ m = j$, then $j_2 - j_1 \leqslant j \leqslant j_1 + j_2,\ j_1 - j_2 \leqslant j \leqslant j_1 + j_2$, therefore

$$|j_2 - j_1| \leqslant j \leqslant j_1 + j_2, \quad m = -j, -j+1, \cdots, j-1, j$$

- Dimensionality: $\dim|jm\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2}(2j+1)$

3.4.3 Clebsch Gordan Coefficient

$$\begin{aligned} |j_1 j_2 j m\rangle = |jm\rangle = \mathbb{1}_{(2j_1+1)(2j_2+1)} \cdot |jm\rangle &= \left[\sum_{m_1=-j_1}^{j_1}\sum_{m_2=-j_2}^{j_2} |j_1 m_1 j_2 m_2\rangle\langle j_1 m_2 j_2 m_2|\right]|jm\rangle \\ &= \sum_{m_1=-j_1}^{j_1}\sum_{m_2=-j_2}^{j_2} \left(\langle j_1 m_1 j_2 m_2 | jm\rangle\right)|j_1 m_1 j_2 m_2\rangle \end{aligned}$$

Define Clebsch Gordan coefficient $C^j_{m_1 m_2}$:

$$|j_1 j_2 j m\rangle = \sum_{m_1 + m_2 = m} C^j_{m_1 m_2}|j_1 m_1 j_2 m_2\rangle$$

Proof. $\hat{J}_z|jm\rangle = m\hbar|jm\rangle = (\hat{J}_{1_z} + \hat{J}_{2z})\sum_{m_1 m_2} C^j_{m_1 m_2}|j_1 m_2 j_2 m_2\rangle = \sum_{m_1 m_2} C^j_{m_1 m_2}(m_1 + m_2)\hbar|j_1 m_2 j_2 m_2\rangle$
Then $m_1 + m_2 = m \quad \Rightarrow \quad \sum_{m_1 + m_2 = m}$ □

An example of Spin 1/2 $\times$ Spin 1/2

Consider spins of two electron, we have $j_1 = \frac{1}{2}, m_1 = \pm\frac{1}{2}$ and $j_2 = \frac{1}{2}, m_2 = \pm\frac{1}{2}$

$$\begin{aligned}\Big\{|j_1 m_1\rangle \otimes |j_2 m_2\rangle\Big\} &= \Big\{|m_1\rangle \otimes |m_2\rangle\Big\} = \Big\{ |-\frac{1}{2}\rangle \otimes |-\frac{1}{2}\rangle,\ |-\frac{1}{2}\rangle \otimes |\frac{1}{2}\rangle,\ |\frac{1}{2}\rangle \otimes |-\frac{1}{2}\rangle,\ |\frac{1}{2}\rangle \otimes |\frac{1}{2}\rangle\Big\} \\ &= \Big\{ |1\rangle \otimes |1\rangle,\ |1\rangle \otimes |0\rangle,\ |0\rangle \otimes |1\rangle,\ |0\rangle \otimes |0\rangle\Big\} \\ &= \Big\{|1\,1\rangle,\ |1\,0\rangle,\ |0\,1\rangle,\ |0\,0\rangle\Big\}\end{aligned}$$

Since $|j_2 - j_1| \leqslant j \leqslant j_1 + j_2$, therefore $j = 0, 1$ and $m = 0, -1, 1$, $\prod_j (2j+1) = (2j_1+1)(2j_2+1) = 4$

Note: $C^j_{m_1 m_2}$; $m_1 + m_2 = m$; $|+\frac{1}{2}\rangle = |0\rangle = |\uparrow\rangle = |+\rangle$

1. Singlet: $j = 0, m = 0$

$$|j, m\rangle = |0\,0\rangle = C^0_{-\frac{1}{2}\,\frac{1}{2}}\,|-\frac{1}{2}\,\frac{1}{2}\rangle + C^0_{\frac{1}{2}-\frac{1}{2}}\,|\frac{1}{2}\ -\frac{1}{2}\rangle = \frac{1}{\sqrt{2}}\,|1\rangle_1 \otimes |0\rangle_2 - \frac{1}{\sqrt{2}}\,|0\rangle_1 \otimes |1\rangle_2 = \frac{1}{\sqrt{2}}(|1\,0\rangle - |0\,1\rangle)$$

2. Triplet: $j = 1, m = 0, \pm 1$

$$\begin{aligned}|1\ -1\rangle &= C^1_{-\frac{1}{2}-\frac{1}{2}}\,|-\frac{1}{2}\ -\frac{1}{2}\rangle = |1\rangle_1 \otimes |1\rangle_2 = |1\,1\rangle \\ |1\,0\rangle &= C^1_{-\frac{1}{2}\,\frac{1}{2}}\,|-\frac{1}{2}\,\frac{1}{2}\rangle + C^1_{\frac{1}{2}-\frac{1}{2}}\,|\frac{1}{2}\ -\frac{1}{2}\rangle = \frac{1}{\sqrt{2}}\,|1\rangle_1 \otimes |0\rangle_2 + \frac{1}{\sqrt{2}}\,|0\rangle_1 \otimes |1\rangle_2 = \frac{1}{\sqrt{2}}(|1\,0\rangle + |0\,1\rangle) \\ |1\ +1\rangle &= C^1_{\frac{1}{2}\,\frac{1}{2}}\,|-\frac{1}{2}\ -\frac{1}{2}\rangle = |0\rangle_1 \otimes |0\rangle_2 = |0\,0\rangle\end{aligned}$$

Entangled state: cannot written tensor product state.

Chapter 4

Quantum Dynamics and Symmetry

4.1 The Schrödinger's Equation

4.1.1 Wave Function

Schrödinger's Equation (SE):

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle = \hat{H}\left|\psi(t)\right\rangle, \quad \text{where} \quad \hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(\vec{x})$$

Remarks:

1. Pure state
2. Closed system: $\langle\psi(t)|\psi(t)\rangle = 1 \quad \xrightarrow{\vec{x}-\text{representation}} \quad \int |\psi(\vec{x},t)|^2 \mathrm{d}^3\vec{x} = 1$
3. Non-relativistic Quantum Mechanics
4. Initial value problem (IVP): $|\psi(t=t_0)\rangle = |\psi(t_0)\rangle$; stationary SE: $\psi(\vec{x}, t=t_0) = \psi(\vec{x}, t_0)$, with normalization.
5. Schrödinger's picture: $\dfrac{\mathrm{d}\hat{A}}{\mathrm{d}t} \equiv 0, \quad \hat{A}$: observables

In $\hat{\vec{x}}$-representation, we have

$$\hat{\vec{p}} = i\hbar\vec{\nabla}, \quad \langle\vec{x}|\psi(t)\rangle = \psi(\vec{x},t)$$

Therefore, the wave function in $\hat{\vec{x}}$-representation is

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{x},t) = -\left(\frac{\hbar}{2m}\nabla^2 + V(\hat{\vec{x}})\right)\psi(\vec{x},t)$$

Generally, $\dfrac{\partial\hat{\vec{A}}}{\partial t} \equiv 0, \quad \dfrac{\partial\hat{H}}{\partial t} \equiv 0$

4.1.2 Time Evolution Operator in SE

Operator $\hat{U}$

$$\left|\psi(t)\right\rangle = \hat{U}(t,t_0)\left|\psi(t_0)\right\rangle$$

then take it into SE, we have

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Big[\hat{U}(t,t_0)\left|\psi(t_0)\right\rangle\Big] = \hat{H}\Big[\hat{U}(t,t_0)\left|\psi(t_0)\right\rangle\Big] \quad \Rightarrow \quad i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}(t,t_0) = \hat{H}\hat{U}(t,t_0) \quad \Rightarrow \quad \frac{\mathrm{d}\hat{U}(t,t_0)}{\hat{U}(t,t_0)} = -\frac{i}{\hbar}\hat{H}(t,t_0)\mathrm{d}t$$

If $\partial\hat{H}\Big/\partial t \equiv 0$, which means a conservation system, then

$$\hat{U}(t,t_0) = \exp\left\{-\frac{i}{\hbar}\hat{H}(t-t_0)\right\}$$

Properties of $\hat{U}(t, t_0)$

1. $\hat{U}^\dagger(t, t_0) = \hat{U}^{-1}(t, t_0) = \hat{U}(t_0, t)$ or $\hat{U}^\dagger(t, t_0)\hat{U}(t_0, t) = 1$
2. $\hat{U}(t, t_1)\hat{U}(t_1, t_0) = \hat{U}(t, t_0) \quad \Rightarrow$ Chain rule: $\hat{U}(t, t_n)\hat{U}(t_n, t_{n-1})\cdots\hat{U}(t_2, t_1)\hat{U}(t_1, t_0) \equiv \hat{U}(t, t_0)$
3. $\hat{U}(t, t_0) = \hat{U}(t - t_0) = \hat{U}(\tau), \quad (\tau = t - t_0)$ and $\hat{U}(t_0, t_0) = \mathbb{1}$ and Dysen series: If $\partial\hat{U}\big/\partial t \neq 0$, then
   $\hat{U}(t, t_0) = \mathbb{1} - \frac{i}{\hbar}\int \hat{U}(t', t_0)\mathrm{d}t' = \mathbb{1} - \frac{i}{\hbar}\int\left[\mathbb{1} - \frac{i}{\hbar}\int \hat{U}(t_1, t_0)\right]\mathrm{d}t_1 = \cdots$

4.1.3 Continuity Equation

If $V^*(\vec{x}) = V(\vec{x})$, which means potential $\in \Re$,

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

then we multiply ψ^* (ψ for second one) in each side of the equation, and move $i\hbar$ ($-i\hbar$ for second one) to the other side. Then, sum up the two equations of each sides, we got

$$\text{l.h.s} = \psi^*\frac{\partial}{\partial t}\psi + \psi\frac{\partial}{\partial t}\psi^* = \frac{\partial}{\partial t}(\psi^*\psi)$$
$$\text{r.h.s} = -\frac{\hbar}{2mi}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] = -\frac{\hbar}{2mi}\vec{\nabla}\cdot\left[\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right]$$

Therefore,

$$\frac{\partial}{\partial t}(\psi^*\psi) + \frac{\hbar}{2mi}\vec{\nabla}\cdot\left[\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right] = 0$$

we can rewrite the equation as

Continuity equation:

$$\boxed{\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot\vec{j} \equiv 0}$$

define Probability density:

$$\rho(\vec{x}, t) = \psi^*(\vec{x}, t)\psi(\vec{x}, t) = |\psi(\vec{x}, t)|^2$$

Probability current density:

$$\vec{j} = \frac{\hbar}{2mi}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right) = \frac{1}{m}\,\mathrm{Re}(\psi^*\frac{\hbar}{i}\vec{\nabla}\psi)$$

- If $Q = \int_V \rho(\overrightarrow{x, t})\mathrm{d}^2\vec{x}$, the continuity equation is $\frac{\mathrm{d}Q}{\mathrm{d}t} \equiv 0$

4.1.4 Ehrenfest's Theorem

From $\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \frac{\hat{H}}{i\hbar}|\psi(t)\rangle$, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)| = -\frac{\hat{H}}{i\hbar}\langle\psi(t)|$, $\langle\hat{O}\rangle = \langle\psi(t)|\hat{O}|\psi(t)\rangle$, we have

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\hat{O}\right\rangle(t) &= \left(\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)|\right)\hat{O}|\psi(t)\rangle + \left\langle\psi(t)\middle|\frac{\mathrm{d}}{\mathrm{d}t}\hat{O}\middle|\psi(t)\right\rangle + \langle\psi(t)|\hat{O}\left(\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle\right)\\ &= -\frac{1}{i\hbar}\left\langle\psi(t)\middle|\hat{H}\hat{O}\middle|\psi(t)\right\rangle + \left\langle\psi(t)\middle|\frac{\mathrm{d}}{\mathrm{d}t}\hat{O}\middle|\psi(t)\right\rangle + \frac{1}{i\hbar}\left\langle\psi(t)\middle|\hat{O}\hat{H}\middle|\psi(t)\right\rangle\\ &= \left\langle\frac{\partial}{\partial t}\hat{O}\right\rangle + \frac{1}{i\hbar}\left\langle[\hat{O}, \hat{H}]\right\rangle\end{aligned}$$

- Conserved quantity (constant of motion): $\partial\hat{O}\big/\partial t \equiv 0$; $[\hat{O}, \hat{H}] \equiv 0$
- Classical mechanics:

$$\frac{\mathrm{d}}{\mathrm{d}t}O = \frac{\partial O}{\partial t} + [O, H]_{\mathrm{PB}} \quad\to\quad m\frac{\mathrm{d}^2}{\mathrm{d}t^2}x = -V'(x)$$

- Quantum mechanics:

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{O}_H = \left(\frac{\partial \hat{O}_s}{\partial t}\right)_H + \frac{1}{i\hbar}\Big[\hat{O}_H, \hat{H}\Big]$$

Ehrenfest's theorem:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{O} \right\rangle(t) = \left\langle \frac{\partial}{\partial t}\hat{O} \right\rangle + \frac{1}{i\hbar}\left\langle [\hat{O}, \hat{H}] \right\rangle \tag{4.1}$$

Example: for 1-dim, $\hat{x},\, \hat{p},\, \hat{H} = \dfrac{\hat{p}^2}{2m} + V(x)$, then

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{x} \rangle &= \frac{1}{i\hbar}\left\langle [\hat{x}, \hat{H}] \right\rangle = \frac{1}{i\hbar}\left\langle [\hat{x}, \frac{\hat{p}^2}{2m}] \right\rangle = \frac{\langle \hat{p} \rangle}{m} \\
\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{p} \rangle &= \frac{1}{i\hbar}\left\langle [\hat{p}, \hat{H}] \right\rangle = \frac{1}{i\hbar}\langle [\hat{p}, V(x)] \rangle = \frac{1}{i\hbar}\left\langle [\hat{p}, \hat{x}] V'(x) \right\rangle = -\left\langle V'(x) \right\rangle
\end{aligned}$$

for 3-dim, $\vec{F} = -\vec{\nabla} V(x)$, consider 2nd differentiation,

$$\frac{\mathrm{d}^2 \langle \hat{x} \rangle}{\mathrm{d}t^2} = \frac{1}{m}\frac{\mathrm{d}\langle \hat{p} \rangle}{\mathrm{d}t} = -\frac{1}{m}\left\langle V'(x) \right\rangle \quad \Rightarrow \quad m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle \hat{x} \rangle = -\left\langle V'(x) \right\rangle$$

QM: $\left\langle V'(x) \right\rangle$ v.s. CM $V'(x)\Big|_{x=\langle x \rangle}$,
assume $V(x) = \sum_n V_n \hat{x}^n$, then $V'(x) = \sum_n V_n n \hat{x}^{n-1}$, which means $\left\langle V'(x) \right\rangle = \sum_n V_n \left\langle \hat{x}^{n-1} \right\rangle$ v.s. $V'(x)\Big|_{x=\langle x \rangle} = \sum_n V_n \langle \hat{x} \rangle^{n-1}$,
then compare $\left\langle \hat{x}^{n-1} \right\rangle$ v.s. $\langle \hat{x} \rangle^{n-1}$

- $n = 0$: $V(x) = const \quad \Rightarrow \quad \vec{F} = 0 \quad \Rightarrow$ CM $\sim$ QM
- $n = 1$: $\left\langle \hat{x}^{n-1} \right\rangle = 1$ v.s. $\langle \hat{x} \rangle^0 = 1 \quad \Rightarrow$ CM $\sim$ QM, $\quad V(x) = x$
- $n = 2$: $\langle \hat{x} \rangle$ v.s. $\langle \hat{x} \rangle \quad \Rightarrow$ CM $\sim$ QM, $\quad V(x) = x^2$
- $n \geqslant 3$: $\left\langle \hat{x}^3 - 1 \right\rangle$ v.s. $\langle \hat{x} \rangle^2 \quad \Rightarrow$ CM $\nsim$ QM,
  (QM) $\left\langle V'(x) \right\rangle = \int \psi^*(x,t) V'(x) \psi(x,t) \mathrm{d}x = V'(\langle x \rangle) \int \psi^* \psi \mathrm{d}x = V'(\langle x \rangle) = V'(x)\Big|_{x=\langle x \rangle}$ (CM)

4.2 The Schrödinger Versus the Heisenberg Picture

In Schrödinger picture, the observables don't change with time

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle_S = \hat{H}_S \left|\psi(t)\right\rangle_S, \qquad \frac{\mathrm{d}}{\mathrm{d}t}\hat{A}_S(t) \equiv 0$$

In Heisenberg Picture, the state vector don't change with time

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{F}_H = \left(\frac{\partial}{\partial t}\hat{F}_S\right)_H + \frac{1}{i\hbar}\Big[\hat{F}_H, \hat{H}\Big], \qquad \frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle_H \equiv 0$$

Time Evolution Operator

To prove $S \Leftrightarrow H$, we have

$$\left|\psi(t)\right\rangle_S = \hat{U}(t)\left|\psi(t)\right\rangle_H, \quad \hat{U}(t) = \exp\left\{-\frac{i}{\hbar}\hat{H}t\right\}$$

Since ${}_S\langle \psi(t)|\psi(t)\rangle_S = {}_H\langle \psi(t)|\psi(t)\rangle_H \quad \Rightarrow \quad {}_H\langle \psi(t)|\hat{U}^\dagger \hat{U}|\psi(t)\rangle_H = {}_H\langle \psi(t)|\psi(t)\rangle_H$,
$\hat{F}_S,\, \hat{F}_H$ are observables under Schrödinger and Heisenberg picture, similarly

$${}_S\left\langle \psi(t) \middle| \hat{F}_S \middle| \psi(t) \right\rangle_S = {}_H\left\langle \psi(t) \middle| \hat{F}_H \middle| \psi(t) \right\rangle_H \quad \Rightarrow \quad {}_H\left\langle \psi(t) \middle| \hat{U}^\dagger \hat{F}_S \hat{U} \middle| \psi(t) \right\rangle_H = {}_H\left\langle \psi(t) \middle| \hat{F}_H \middle| \psi(t) \right\rangle_H$$

Therefore,

$$\hat{F}_H = \hat{U}^\dagger \hat{F}_S \hat{U} \quad \text{or} \quad \hat{F}_S = \hat{U}\hat{F}_H\hat{U}^\dagger$$

Remind $\mathrm{d}\hat{F}_S\Big/\mathrm{d}t \equiv 0,\ \mathrm{d}/\mathrm{d}t\ \hat{U} = (-i\hat{H}/\hbar)\hat{U},\ \hat{H}_H = \hat{U}^\dagger\hat{H}_S\hat{U} = \hat{H}_S$, then

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\hat{F}_H &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\hat{U}^\dagger\hat{F}_S\hat{U}\right) = \frac{i}{\hbar}\hat{U}^\dagger\hat{F}_S\hat{U} + \hat{U}^\dagger\left(\frac{\partial\hat{F}_S}{\partial t}\right)\hat{U} - \frac{i}{\hbar}\hat{F}_S\hat{H}\hat{U} \\
&= \left(\frac{\partial\hat{F}_S}{\partial t}\right)_H + \frac{1}{i\hbar}\left(\hat{U}^\dagger\hat{F}_S\hat{U}\hat{U}^\dagger\hat{H}\hat{U} - \hat{U}^\dagger\hat{H}\hat{U}\hat{U}^\dagger\hat{F}_S\hat{U}\right) \\
&= \left(\frac{\partial\hat{F}_S}{\partial t}\right)_H + \frac{1}{i\hbar}\left[\hat{F}_H, \hat{H}_H\right] \\
\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle_H &= \frac{\mathrm{d}}{\mathrm{d}t}\hat{U}^\dagger\left|\psi(t)\right\rangle_S = \left(\frac{\mathrm{d}\hat{U}^\dagger}{\mathrm{d}t}\right)\left|\psi(t)\right\rangle_S + \hat{U}^\dagger\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle_S \\
&= \frac{i}{\hbar}\hat{U}^\dagger\hat{H}_S\left|\psi(t)\right\rangle_S + \frac{1}{i\hbar}\hat{U}^\dagger\hat{H}_S\left|\psi(t)\right\rangle_S \equiv 0
\end{aligned}
$$

4.3 Symmetry Transformation

Different to symmetric transformation
Wigner's Theorem

- Unitary: Space translation, space reflection, time translation, permatation
- Anti-unitary: time reversal

State Vector

Transfer $|\psi\rangle$

$$
\begin{aligned}
|\psi\rangle &\xrightarrow{\quad\hat{U}\quad} \left|\psi'\right\rangle = \hat{U}\left|\psi\right\rangle \\
|\phi\rangle &\xrightarrow{\quad\hat{U}\quad} \left|\phi'\right\rangle = \hat{U}\left|\phi\right\rangle
\end{aligned}
$$

Invariance:

$$\langle\psi|\phi\rangle \xrightarrow{\quad\hat{U}\quad} \left\langle\psi'\middle|\phi'\right\rangle = \langle\psi|\phi\rangle$$

Inner product invariance:

$$\langle\psi|\hat{U}^\dagger\hat{U}|\phi\rangle = \langle\psi|\phi\rangle \quad\Rightarrow\quad \hat{U}^\dagger\hat{U} = \mathbb{1} \quad \text{or} \quad \hat{U}^\dagger = \hat{U}^{-1}$$

Operator (observabes)

$$\langle\psi|\hat{A}|\phi\rangle \xrightarrow{\quad\hat{U}\quad} \left\langle\psi'\middle|\hat{A}'\middle|\phi'\right\rangle = \langle\psi|\hat{A}|\phi\rangle$$

Inner product invariance:

$$\langle\psi|\hat{U}^\dagger\hat{A}'\hat{U}|\phi\rangle = \langle\psi|\hat{A}|\phi\rangle \quad\Rightarrow\quad \hat{U}^\dagger\hat{A}'\hat{U} = \hat{A} \quad \text{or} \quad \hat{A}' = \hat{U}\hat{A}\hat{U}^\dagger$$

Linear unitary transformation:

$$
\begin{aligned}
\left|\psi'\right\rangle = \hat{U}\left|\psi\right\rangle &\quad\Leftrightarrow\quad \text{Invariance of} \quad \langle\psi|\phi\rangle \\
\hat{A}' = \hat{U}\hat{A}\hat{U}^\dagger &\quad\Leftrightarrow\quad \text{Invariance of} \quad \langle\psi|\hat{A}|\phi\rangle
\end{aligned}
$$

Hamilton

If $\hat{H} \xrightarrow{\hat{U}} \hat{H}' = \hat{U}\hat{H}\hat{U}^\dagger$, then one yields $\hat{U}\hat{H}\hat{U}^\dagger\hat{H} \quad\Rightarrow\quad \hat{U}\hat{H} = \hat{H}\hat{U} \quad\Rightarrow\quad \left[\hat{U}, \hat{H}\right] \equiv 0$

4.4 Symmetry & Conservation in QM

1. Discrete Symmetry

(a) Space Reflection

$$|\vec{x}\rangle \xrightarrow{\hat{\pi}} |\vec{x}'\rangle = \hat{\pi}\,|\vec{x}\rangle = |-\vec{x}\rangle \quad \Rightarrow \quad \hat{\vec{x}} \to \hat{\vec{x}}' = \hat{\pi}\hat{\vec{x}}\hat{\pi}^\dagger = -\hat{\vec{x}}, \quad \left\{\hat{\vec{x}}, \hat{\pi}\right\} = 0$$

If $[\hat{\pi}, \hat{H}] = 0$, then $\hat{\pi}$ is a conserved quantity, which called parity, and $\hat{\pi}^\dagger = \hat{\pi}$.

(b) Pomutation (transposition)

$$\hat{T}_{ij}\,|\cdots u_i, \cdots, u_j \cdots\rangle = |\cdots u_j, \cdots, u_i \cdots\rangle = \pm\,|\cdots u_i, \cdots, u_j \cdots\rangle$$

2. Continuous Symmetry

In CM:

(a) Space translation ↔ Conservation of momentum
(b) Time translation ↔ Conservation of energy
(c) Space rotation ↔ Conservation of angular momentum

In QM: Infinitesimal transformation ($\hat{U}^\dagger\hat{U} = \hat{U}\hat{U}^\dagger = \mathbb{1}$)

$$\hat{U}(\varepsilon) = \mathbb{1} - i\varepsilon\hat{F} \qquad (\varepsilon \ll 1)$$

Then $(\mathbb{1} + i\varepsilon\hat{F}^\dagger)\mathbb{1} - i\varepsilon\hat{F} = \mathbb{1} \quad \Rightarrow \quad \mathbb{1} + i\varepsilon(\hat{F}^\dagger - \hat{F}) + \mathcal{O}(\varepsilon^2) = \mathbb{1}$

- $\hat{U}$: group
- $\hat{F}$: generator/observable (Hermitian)
- ε/a: parameter (like space translation quantity)

Let $N\varepsilon = a,\ N \gg 1$,

$$\underbrace{\hat{U}(\varepsilon)\cdots\hat{U}}_{N} = \hat{U}^N(\varepsilon) = \left(\mathbb{1} - i\varepsilon\hat{F}\right)^N = \left[\mathbb{1} - \frac{1}{N}\left(-ia\hat{F}\right)\right]^N \xrightarrow{N\to\infty} \mathrm{e}^{-ia\hat{F}}$$

Summary:

Lie Group: $\hat{U}(a) = \mathrm{e}^{-ia\hat{F}}$

Lie Algebra: $\hat{u}(\varepsilon) = \mathbb{1} - i\varepsilon\hat{F}$

Nother's Theorem

Space Translation

Define

$$\hat{T}(a)\,|x\rangle = |x + a\rangle \Leftrightarrow \langle x|\,\hat{T}^\dagger(a) = \langle x + a|\,, \quad \hat{T}(-a)\,|x\rangle = |x - a\rangle \Leftrightarrow \langle x|\,\hat{T}^\dagger(-a) = \langle x - a|$$

Since $\langle x + a|y + a\rangle = \delta_{(x-y)} \quad \Rightarrow \quad \langle x'|y'\rangle = \langle x|\hat{T}^\dagger(a)\hat{T}(a)|y\rangle = \langle x|y\rangle$, then $\hat{T}^\dagger(a)\hat{T}(a) = \mathbb{1}$ or $\hat{T}^\dagger(a) = \hat{T}^{-1}(a)$,
Since $\hat{T}(-a)\hat{T}(a)\,|x\rangle = \hat{T}(-a)\,|x + a\rangle = |x\rangle \quad \Rightarrow \quad \hat{T}(-a) = \hat{T}^{-1}(a)$, therefore

$$\hat{T}^\dagger(a) = \hat{T}^{-1}(a) = \hat{T}(-a)$$

Consider $\hat{x}\hat{T}(a)\,|x\rangle = \hat{x}\,|x + a\rangle = (x + a)\,|x + a\rangle\,,\ \hat{T}(a)\hat{x}\,|x\rangle = \hat{T}(a)x\,|x\rangle = x\hat{T}(a)\,|x\rangle = x\,|x + a\rangle$, then

$$\left[\hat{x}, \hat{T}(a)\right]|x\rangle = a\,|x + a\rangle = a\hat{T}(a)\,|x\rangle \quad \Rightarrow \quad \left[\hat{x}, \hat{T}(a)\right] = a\hat{T}(a)$$

so that $\hat{x}\hat{T}(a) = \hat{T}(a)\hat{x} + a\hat{T}(a) \quad \Rightarrow \quad \hat{x} = \hat{T}(a)\hat{x}\hat{T}^\dagger(a) + a\mathbb{1}$, therefore

$$\hat{x}' = \hat{T}(a)\hat{x}\hat{T}^\dagger(a) = \hat{x} - a\cdot\mathbb{1}$$

Taylor series: compare to $\hat{F}$

$$\hat{T}(a) = \hat{T}(0) + a\frac{\mathrm{d}\hat{T}(a)}{\mathrm{d}a}\bigg|_{a=0} + \cdots = \mathbb{1} + a\frac{\mathrm{d}\hat{T}(a)}{\mathrm{d}a}\bigg|_{a=0} + \cdots = \mathbb{1} - ia\hat{k}$$

So that $\hat{k} = i\ a\ \mathrm{d}\hat{T}(a)\Big/\mathrm{d}a\ \Big|_{a=0}$, then

$$\frac{\mathrm{d}\hat{T}(a)}{\mathrm{d}a} = \lim_{\epsilon\to 0}\hat{T}(a+\epsilon) - \hat{T}(a) = \lim_{\epsilon\to 0}\frac{\hat{T}(\epsilon)\hat{T}(a) - \hat{T}(a)}{\epsilon} = \lim_{\epsilon\to 0}\frac{\hat{T}(\epsilon) - \mathbb{1}}{\epsilon}\cdot\hat{T}(a) = -i\hat{k}\hat{T}(a)$$

solve the differntiate function, got

$$\hat{T}(a) = \hat{T}(0)\exp\left\{-ia\hat{k}\right\} = \exp\left\{-ia\hat{k}\right\}$$

Since $\left[\hat{x}, \hat{T}(a)\right] = a\hat{T}(a)$, take it into and got $[\hat{x}, \hat{k}] = i$. Since $[\hat{x}, \hat{p}] = i\hbar$, therefore $\hat{k} = \dfrac{\hat{p}}{\hbar}$, and

$$\hat{T}(a) = \exp\left\{\frac{i\vec{a}\cdot\hat{\vec{p}}}{\hbar}\right\}$$

if $[\hat{T}(a), \hat{H}] = 0$, then $[\hat{p}, \hat{H}] = 0 \quad\Rightarrow\quad \hat{p}$ is conserved.

Time Translation

$$\hat{U}(\tau) = \exp\left\{\frac{i\tau\hat{H}}{\hbar}\right\} \quad\Leftrightarrow\quad \left[\hat{H}, \hat{H}\right] \equiv 0 \quad\Rightarrow\quad \text{Energy is conseved.}$$

Space Rotation

- Rotation axis: $\hat{\boldsymbol{n}}$
- Rotation angle: θ

Rodrigues rotation formula:

$$\vec{x}' = \vec{x}\cos\theta + (1-\cos\theta)(\vec{x}\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}} + (\hat{\boldsymbol{n}}\times\vec{x})\sin\theta$$

Proof. $\vec{x} = \vec{x}_{\parallel} + \vec{x}_{\perp},\ \vec{x}_{\parallel} = (\vec{x}\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}},\ \vec{x}_{\perp} = \vec{x} - \vec{x}_{\parallel} = \vec{x} - (\vec{x}\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}$,
$\vec{x}' = \vec{x}'_{\parallel} + \vec{x}'_{\perp},\ \vec{x}'_{\parallel} = \vec{x}_{\parallel} = (\vec{x}\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}},\ \vec{x}'_{\perp} = \vec{x}_{\perp}\cos\theta + (\hat{\boldsymbol{n}}\times\vec{x}_{\perp})\sin\theta$, take into □

when $\theta \ll 1,\ \cos\theta\sim 1,\ \sin\theta\sim\theta$, then $\vec{x}' = \vec{x} + \theta(\hat{\boldsymbol{n}}\times\vec{x}) = \vec{x} + \delta\vec{x},\ \delta\vec{x} = \vec{x}' - \vec{x} = \theta(\hat{\boldsymbol{n}}\times\vec{x})$, similarly

$$\begin{aligned}\hat{u}(\theta) &= \mathbb{1} - i\delta\vec{x}\cdot\frac{\vec{p}}{\hbar} = \mathbb{1} - i\theta(\hat{\boldsymbol{n}}\times\vec{x})\cdot\frac{\vec{p}}{\hbar} = \mathbb{1} - i\theta(\vec{x}\times\vec{p})\cdot\frac{\hat{\boldsymbol{n}}}{\hbar} = \mathbb{1} - i\theta\left(\vec{L}\cdot\hat{\boldsymbol{n}}\right)/\hbar \\ \Rightarrow\quad \hat{U}(\hat{\boldsymbol{n}},\theta) &= \exp\left\{-i\theta\left(\hat{\boldsymbol{n}}\cdot\hat{\vec{L}}\right)/\hbar\right\}\end{aligned}$$

If $[\hat{U}(\hat{\boldsymbol{n}},\theta), \hat{H}] \equiv 0$, then $[\hat{\vec{L}}, \hat{H}] \equiv 0 \quad\Rightarrow\quad \vec{L}$ is conserved.

Summary (QM)

1. Space translation

$$\begin{cases}\hat{T}(\vec{a}) = \exp\left\{-i\vec{a}\cdot\hat{\vec{p}}/\hbar\right\} \\ \hat{t}(\vec{\varepsilon}) = \mathbb{1} - i\vec{\varepsilon}\cdot\vec{p}/\hbar\end{cases} \quad\Rightarrow\quad \hat{\vec{p}}\ \text{is conserved.}$$

2. Time translation

$$\begin{cases}\hat{U}(\tau) = \exp\left\{+i\tau\hat{H}/\hbar\right\} \\ \hat{u}(\varepsilon) = \mathbb{1} - i\varepsilon\hat{H}/\hbar\end{cases} \quad\Rightarrow\quad E\ \text{is conserved.}$$

3. Space rotation

$$\begin{cases}hU(\hat{\boldsymbol{n}},\theta) = \exp\left\{-i\theta\left(\hat{\boldsymbol{n}}\cdot\hat{\vec{L}}\right)/\hbar\right\} \\ \hat{u}(\hat{\boldsymbol{n}},\theta) = \mathbb{1} - i\varepsilon\left(\hat{\boldsymbol{n}}\cdot\hat{\vec{L}}\right)/\hbar\end{cases} \quad\Rightarrow\quad \hat{\vec{L}}\ \text{is conserved.}$$

Chapter 5

The One-dimensional Stationary Schrödinger's Equations

5.1 Stationary Schrödinger's Equation

Take a general discussion first,

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle=\hat{H}\left|\psi(t)\right\rangle,\quad \text{if}\quad \frac{\partial\hat{H}}{\partial t}\equiv 0,\quad \text{then}\quad \left|\psi(t)\right\rangle=\mathrm{e}^{i\hat{H}t/\hbar}\left|\psi(0)\right\rangle$$

Stationary Schrödinger's equation (SSE) or Time-independent Schrödinger's equation or Energy eigenvalue equation:

$$\hat{H}\left|\psi(0)\right\rangle=E\left|\psi(0)\right\rangle,\quad \text{or at a moment}\quad \hat{H}\left|\psi(t)\right\rangle=E\left|\psi(t)\right\rangle$$

- For $\forall\hat{A}$ observables, the expectation is

$$\left\langle\psi(t)\middle|\hat{A}\middle|\psi(t)\right\rangle=\left\langle\psi(0)\middle|\mathrm{e}^{iEt/\hbar}\hat{A}\mathrm{e}^{-iEt/\hbar}\middle|\psi(0)\right\rangle=\left\langle\psi(0)\middle|\hat{A}\middle|\psi(0)\right\rangle$$

  Therefore, $\langle\hat{A}\rangle(t)=\langle\hat{A}\rangle(t=0)$, e.g. $\langle\hat{H}\rangle(t)=\langle\hat{H}\rangle(t=0)$

- The probability of one of eigenvalues A_k of $\hat{A}$

$$p(A_k;t)=\left|\langle u_k|\psi(t)\rangle\right|^2=\left|\langle u_k|\mathrm{e}^{-iEt/\hbar}|\psi(0)\rangle\right|^2=\left|\langle u_k|\psi(0)\rangle\right|^2=p(A_k;t=0)$$

- Consider $\hat{H}=E$, then $\left|\psi(t)\right\rangle=\mathrm{e}^{-iEt/\hbar}\left|\psi(0)\right\rangle$, the wave function is

$$\psi(\vec{x},t)=\langle\vec{x}|\psi(t)\rangle=\left\langle\vec{x}\middle|\mathrm{e}^{-iEt/\hbar}\middle|\psi(0)\right\rangle=\mathrm{e}^{-iEt/\hbar}\psi(\vec{x},t=0)$$

  Take it into the Schrödinger's equation, we can get the stationary Schrödinger's equation

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

* Remember that $\dfrac{\partial\hat{H}}{\partial t}\equiv 0\Leftrightarrow\dfrac{\partial V}{\partial t}\equiv 0$ here
* Consider $\rho(\vec{x},t)=\psi^*(\vec{x},t)\psi(\vec{x},t)=\mathrm{e}^{iEt/\hbar}\psi^*(\vec{x})\mathrm{e}^{-iEt/\hbar}\psi(\vec{x})=|\psi(\vec{x})|^2\quad\Rightarrow\quad\dfrac{\partial\rho}{\partial t}=0$,
  since continuity equation, we have $\vec{\nabla}\cdot\vec{j}\equiv 0$

Comparison: conserved quantity v.s. stationary state

1. (a) If $[\hat{A},\hat{H}]\equiv 0$, then $\hat{A}$ is conserved quantity
   (b) $\forall\hat{A}$, if in stationary state, then $\langle\hat{A}\rangle(t)=\langle\hat{A}\rangle(t=0)$

2. If $\hat{A}$, $\hat{B}$ are conserved quantities, and $[\hat{A},\hat{B}] \neq 0$, then the system is mostly degenerate;
   If $[\hat{A},\hat{H}] = [\hat{B},\hat{H}] \equiv 0, [\hat{A},\hat{B}] \neq 0$, then degenerate happen,
   e.g. $[\hat{L}_x,\hat{H}] = [\hat{L}_y,\hat{H}] \equiv 0, [\hat{L}_x,\hat{L}_y] \neq 0$, then degenrate, $|lm_l\rangle$ has $(2l+1)$ degeneracy, except $|l=0,m=0\rangle$
   * The relation between symmetry, conservation and degeneracy.
3. More on Ehrenfest's theorem:
$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{\vec{x}}\cdot\hat{\vec{p}}\right\rangle = \frac{1}{m}\left\langle \hat{\vec{p}}^{\,2}\right\rangle - \left\langle \hat{\vec{x}}\cdot\vec{\nabla}V\right\rangle$$

Proof. $\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{\vec{x}}\cdot\hat{\vec{p}}\right\rangle = \frac{1}{i\hbar}\left\langle [\hat{\vec{x}}\cdot\hat{\vec{p}},\hat{H}]\right\rangle = \frac{1}{i\hbar}\left\langle \left[\hat{\vec{x}}\cdot\hat{\vec{p}},\frac{\hat{\vec{p}}^{\,2}}{2m}+V(\hat{\vec{x}})\right]\right\rangle = \frac{1}{i\hbar}\left\langle \frac{1}{2m}[\hat{x}_i,\hat{p}_j]2\hat{p}_j\hat{p}_i + \hat{x}_i[\hat{p}_i,\hat{x}_i]\frac{\partial V}{\partial x_j}\right\rangle$ □

If $|\psi(t)\rangle$ is stationary state, then $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\vec{x}}\cdot\hat{\vec{p}}\rangle \equiv 0$, hence $\frac{1}{m}\langle\hat{\vec{p}}^{\,2}\rangle = \langle\vec{x}\cdot\vec{\nabla}V\rangle$, since $\hat{T} = \frac{\hat{\vec{p}}^{\,2}}{2m}$,

$$\text{Virial Theorem:}\quad 2\left\langle \hat{T}\right\rangle = \left\langle \vec{x}\cdot\vec{\nabla}V\right\rangle$$

e.g. If $V(\vec{x}) = V(a\vec{x}) = a^n V(\vec{x}) \quad\Rightarrow\quad 2\langle T\rangle = n\langle\hat{V}\rangle$

Harmonic oscillation: $V(x) = \frac{1}{2}m\omega^2x^2 \Rightarrow \langle T\rangle = \langle\hat{V}\rangle$; Coulomb's potential: $V(r) = -\frac{e^2}{r} \Rightarrow \langle T\rangle = \frac{-\langle\hat{V}\rangle}{2}$

Stationary Schrödinger's Equation in 1D

One-dimensional stationary Schrödinger's equation:

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V(x)\right]\psi(x) = E\psi(x) \quad\Rightarrow\quad \psi''(x) = -\frac{2m}{\hbar^2}[E-V(x)]\psi(x)$$

- $\psi(x)$ is dependent on $V(x)$
- ψ is continuous integrable, and
$$\int_{-\infty}^{+\infty}|\psi(x)|^2\mathrm{d}x < \infty$$
- Three choices of $V(x)$
  - $V(x)$ is continuous, then $\psi(x),\psi'(x),\psi''(x)$ are continuous;
  - $V(x)$ has a number of discontinuous, and $V(x)$ contains no derivatives of δ-function, then ψ'' maybe contain $\delta(x)$, but $\psi'(x),\psi(x)$ don't contain $\delta(x)$, so $\psi(x),\psi'(x)$ are continuous;
  - $V(x)$ constains hard walls (e.g. infinite square wall), then $\psi(x)=0$ at boundary point, and beyond the wall.
- Definition for solving SSE, we usually define afterwords
$$k^2 = \frac{2m}{\hbar^2}E,\quad\text{and}\quad \kappa^2 = -\frac{2m}{\hbar^2}E,\quad\text{and}\quad k'^2 = \frac{2m}{\hbar^2}[E-V(x)]$$

5.2 Potential Well Problem

5.2.1 Infinite Square Well

Consider
$$V(x) = \begin{cases} 0, & -a/2 < x < a/2 \\ \infty, & |x| \geqslant a/2 \end{cases}$$

Beacasue of hard wall, $\psi(x) \xrightarrow{x\to\infty} 0$, and
$$\psi(x) = 0 \quad\text{for}\quad |x| \geqslant a/2$$

Inside the wall, $V(x)=0$, and use Eq.(**??**), SSE becomes
$$\psi''(x) = -k^2\psi(x) \quad\text{where}\quad k^2 = \frac{2mE}{\hbar^2}$$

The solution of the equation with two coefficient is

$$\psi(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx}$$

Consider boundary condition: $\psi(x)$ is continuous, so

$$\left.\begin{aligned}\text{for}\quad \psi\left(\frac{a}{2}\right) = 0, \quad A\mathrm{e}^{ika/2} + B\mathrm{e}^{-ika/2} = 0\\ \text{for}\quad \psi\left(-\frac{a}{2}\right) = 0, \quad A\mathrm{e}^{-ika/2} + B\mathrm{e}^{ika/2} = 0\end{aligned}\right\} \quad k_n a = n\pi, \quad \text{and} \quad A = (-1)^{n+1}B, \quad (n = 1, 2, \cdots)$$

Typical bound state ⇔ discret energy spectrum

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

- Ground state energy:

$$E_g = \frac{\hbar^2\pi^2}{2ma^2}$$

After normalization, we have the wave function inside the wall

$$\psi_n(x) = \begin{cases}\sqrt{\dfrac{2}{a}}\cos\left(\dfrac{n\pi}{a}x\right), & \text{even } n\\ \sqrt{\dfrac{2}{a}}\sin\left(\dfrac{n\pi}{a}x\right), & \text{odd } n\end{cases}$$

We can find out that since $V(x) = V(-x)$ which is even function, therefore $\psi_n(x)$ has the property of even function when n is even (odd function when n is odd). So if $\hat{H}$ is even function, $\psi(x)$ has explicit parity.
*Node theorem: $\psi(x) = 0$ points, except $x = \pm\dfrac{a}{2}$ boundary points, there are $(n-1)$ nodes for $\psi_n(x)$.

5.2.2 Finite Square Well (need learn again)

Consider potential is

$$V(x) = \begin{cases}-V_0, & -a/2 < x < a/2\\ 0, & |x| \geqslant a/2\end{cases}$$

Since it is boundary state, we can know the result is discrete energy spectrum. And the SSE is
Boundary condition: $\psi(x)$, $\psi'(x)$ are both continuous.

$$\xi^2 = ka^2, \quad ,\eta = \kappa a^2, \quad z_0^2 = \frac{2mV_0a^2}{\hbar^2}$$

$$\text{Even solution:}\quad \xi^2 + \eta^2 = z_0^2, \quad \xi = \eta\tan\eta$$
$$\text{Odd solution:}\quad \xi^2 + \eta^2 = z_0^2, \quad \xi = -\eta\cot\eta$$

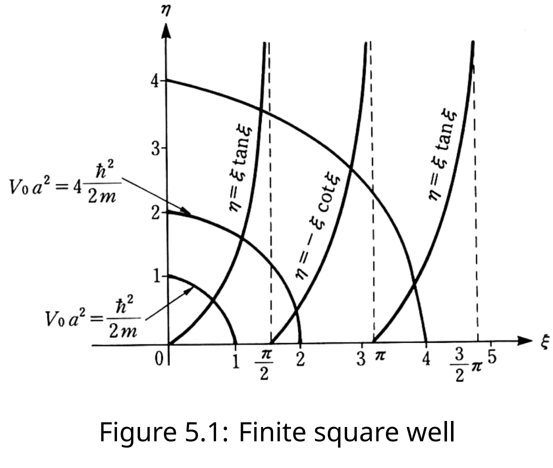

Figure 5.1: Finite square well

5.2.3 Harmonic Oscillation

Classical Harmonic Oscillation

In Classical Mechanics, the Harmiltonian of harmonic oscillation is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

If $E = H$, then we can got a ellipse equation

$$\frac{x^2}{\left(\sqrt{\frac{2E}{m\omega^2}}\right)^2} + \frac{p^2}{\left(\sqrt{2mE}\right)^2} = 1 \quad \Rightarrow \quad S = \pi\left(\sqrt{\frac{2E}{m\omega^2}}\right)\left(\sqrt{2mE}\right) = \frac{2\pi E}{\omega}$$

If $E = n\hbar\omega$, then

$$S = \frac{2\pi n\hbar\omega}{\omega} = hn, \quad n = 1, 2, 3\cdots$$

If $E = (n + 1/2)\hbar\omega,\ n = 1, 2, 3\cdots$, then (WKB approximation)

$$S = \frac{2\pi\left(n + \frac{1}{2}\right)\hbar\omega}{\omega} = h\left(n + \frac{1}{2}\right)$$

From these we can also have Sommerfield Quantzation:

$$S = \oint p\mathrm{d}x \quad \Rightarrow \quad \oint p\mathrm{d}q = hn \quad \text{or} \quad \oint p\mathrm{d}q = h\left(n + \frac{1}{2}\right)$$

Since $a^2 + b^2 = (a + ib)(a - ib)$, when $E = \hbar\omega$, we have

$$\frac{x}{\sqrt{\frac{2E}{m\omega^2}}} + i\frac{p}{\sqrt{2mE}} \to \alpha \equiv \sqrt{\frac{m\omega}{2\hbar}}x + i\frac{p}{\sqrt{2m\hbar\omega}} \quad \Rightarrow \quad \alpha\alpha^* = 1$$

Quantum Harmonic Oscillation

Similarly, in QM, we can have $\alpha \to \hat{a},\ \alpha^* \to \hat{a}^\dagger$, i.e.

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}, \qquad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}$$

Since $[\hat{x}, \hat{p}] = i\hbar$, therefore we got the commutation relation between $\hat{a}$ and $\hat{a}^\dagger$:

$$\left[\hat{a}, \hat{a}^\dagger\right] = 1$$

- $\hat{a}$: annihilation operator
- $\hat{a}^\dagger$: creation operator

In QM, we have the Harmiltonian of harmonic oscillation:

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

Define occupation number operator as:

$$\hat{N} = \hat{a}^\dagger\hat{a}, \quad \to \quad \begin{cases} [\hat{N}, \hat{a}] = -\hat{a} & \Rightarrow \quad \hat{N}\hat{a} = \hat{a}\hat{N} - \hat{a} \\ [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger & \Rightarrow \quad \hat{N}\hat{a}^\dagger = \hat{a}^\dagger\hat{N} + \hat{a}^\dagger \end{cases}$$

Let $\hat{N}\left|\lambda\right\rangle = \lambda\left|\lambda\right\rangle$, we have

$$\hat{N}(\hat{a}\left|\lambda\right\rangle) = (\hat{a}\hat{N} - \hat{a})\left|\lambda\right\rangle = \lambda\hat{a}\left|\lambda\right\rangle - \hat{a}\left|\lambda\right\rangle = (\lambda - 1)(\hat{a}\left|\lambda\right\rangle) \quad \Rightarrow \quad \begin{array}{l} \hat{a}\left|\lambda\right\rangle = c_-\left|\lambda - 1\right\rangle \\ \left\langle\lambda\right|\hat{a}^\dagger = c_-^*\left\langle\lambda - 1\right| \end{array}$$

Then, ask for normalization

$$\begin{aligned}\left\langle\lambda\middle|\hat{a}^\dagger\hat{a}\middle|\lambda\right\rangle &= |c_-|^2\left\langle\lambda-1|\lambda-1\right\rangle = |c_-|^2 \\ &= \left\langle\lambda\middle|\hat{N}\middle|\lambda\right\rangle = \lambda\left\langle\lambda|\lambda\right\rangle = \lambda\end{aligned} \quad\Rightarrow\quad |c_-|^2 = \lambda \quad\to\quad c_- = \sqrt{\lambda}$$

Therefore, we can get series of state

$$\hat{a}\left|\lambda\right\rangle = \sqrt{\lambda-1} \quad\Rightarrow\quad \hat{a}\left|0\right\rangle = \sqrt{0}\left|0-1\right\rangle = 0 \quad\Rightarrow\quad \hat{a}\left|0\right\rangle = 0,\ \hat{a}\left|1\right\rangle = \left|0\right\rangle,\ \hat{a}\left|2\right\rangle = \sqrt{2}\left|1\right\rangle,\ \cdots$$

We can assume $|\lambda\rangle = |n\rangle$, therefore

$$\hat{N}\left|n\right\rangle = n\left|n\right\rangle, \qquad \hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle \qquad (n = 0, 1, 2, \cdots)$$

Similarly, for creation operator we have

$$\hat{N}\hat{a}^\dagger\left|n\right\rangle = (\hat{a}^\dagger\hat{N} + \hat{a}^\dagger)\left|n\right\rangle = (n+1)\hat{a}^\dagger\left|n\right\rangle \quad\Rightarrow\quad \hat{a}^\dagger\left|n\right\rangle = c_+\left|n+1\right\rangle \quad \text{where} \quad c_+ = \sqrt{n+1}$$

For the ground state, we can write it in

$$\left|n\right\rangle = \frac{\hat{a}^\dagger}{\sqrt{n}}\left|n-1\right\rangle = \frac{\hat{a}^\dagger}{\sqrt{n}}\cdot\frac{\hat{a}^\dagger}{\sqrt{n-1}}\left|n-2\right\rangle = \cdots = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\left|0\right\rangle$$

Summary:

1. $\left[\hat{a}, \hat{a}^\dagger\right] = 1$
2. $\hat{N} = \hat{a}^\dagger\hat{a}, \quad \left[\hat{N}, \hat{a}\right] = -\hat{a}, \quad \left[\hat{N}, \hat{a}^\dagger\right] = \hat{a}^\dagger$
3. $\hat{N}\left|n\right\rangle = n\left|n\right\rangle, \quad \hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle, \quad \hat{a}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle \qquad (n = 0, 1, 2, \cdots)$
4. $\hat{a}\left|0\right\rangle = 0$
5. $\left|n\right\rangle = \dfrac{(a^\dagger)^n}{\sqrt{n!}}\left|0\right\rangle$
6. ON: $\langle n|m\rangle = \delta_{nm}$, RI: $\displaystyle\sum_{n=0}^{\infty}|n\rangle\langle n| = \mathbb{1}$
7. $\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \dfrac{1}{2}\right), \quad \hat{H}\left|n\right\rangle = \hbar\omega\left(n + \dfrac{1}{2}\right), \quad \hat{H} = \hbar\omega\left(\hat{N} + \dfrac{1}{2}\right), \quad \hat{H}\left|0\right\rangle = \dfrac{1}{2}\hbar\omega\left|0\right\rangle$ (zero point energy)

In vaccume, since $\Delta\hat{x}^2 + \Delta\hat{p}^2 = \hbar^2/4$ is the minimum uncertainty,

$$\langle 0|\hat{x}^2|0\rangle = \left(\langle 0|\hat{x}|0\rangle\right)^2 = \Delta\hat{x}^2, \quad \langle 0|\hat{p}^2|0\rangle = \left(\langle 0|\hat{p}|0\rangle\right)^2 = \Delta\hat{p}^2$$

which means $|0\rangle$ is minimum uncertainty state.
Next, discuss wave function of $|0\rangle$ in $\hat{x}$-rep: from $\langle x|\hat{a}|0\rangle = 0$

$$\langle x|\left(\sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{\mathrm{d}}{\mathrm{d}x}\right)|0\rangle = 0$$

since $\psi_0(x) = \langle x|0\rangle$, take into

$$x\psi_0(x) + \frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\psi_0(x) = 0 \quad\to\quad \frac{\mathrm{d}\psi_0(x)}{\psi_0(x)} = -\frac{m\omega}{\hbar}x\mathrm{d}x \quad\to\quad \psi_0(x) = A\exp\left\{-\frac{m\omega x^2}{2\hbar}\right\} \xrightarrow{\text{normalization}} A = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$$

Expand to $\psi_n(x)$,

$$\begin{aligned}\psi_n(x) = \langle x|n\rangle &= \langle x|\frac{(\hat{a})^n}{\sqrt{n!}}|0\rangle = \langle x|\frac{1}{\sqrt{n!}}\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{\hat{p}}{2m\hbar}\right)^n|0\rangle = \frac{1}{\sqrt{2^n n!}}\langle x|\left(\sqrt{\frac{m\omega}{\hbar}}x - \sqrt{\frac{\hbar}{m\omega}}\frac{\mathrm{d}}{\mathrm{d}x}\right)^n|0\rangle \\ &= \frac{1}{\sqrt{2^n n!}}\langle x|\left(z - \frac{\mathrm{d}}{\mathrm{d}z}\right)^n|0\rangle = \frac{1}{\sqrt{2^n n!}}\left(z - \frac{\mathrm{d}}{\mathrm{d}z}\right)^n\psi_0(x) \qquad \text{let } z = \alpha x = \sqrt{m\omega/\hbar}x \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\frac{1}{\sqrt{2^n n!}}\left(z - \frac{\mathrm{d}}{\mathrm{d}z}\right)^n\mathrm{e}^{-z^2/2}\end{aligned}$$

Let

$$\left(z - \frac{\mathrm{d}}{\mathrm{d}z}\right)^n\mathrm{e}^{-z^2/2} = H_n(z)\mathrm{e}^{-z^2/2}, \qquad \psi_n(x) \sim H_n(\alpha x)\mathrm{e}^{-\alpha^2x^2/2}$$

- $H_n(z)$ is Hermitian polynomical
- $H_n(-z) = (-1)^n H_n(z)$, when n is even wave function is even.

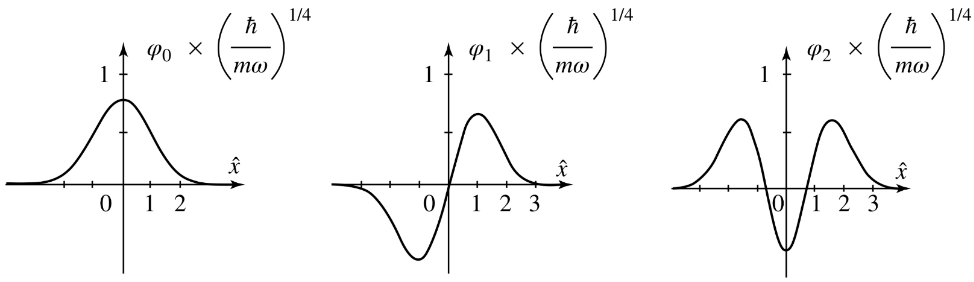

Figure 5.2: Wave function

A discussion about boundary condition of SSE

Integrate $\psi''(x) = -\frac{2m}{\hbar^2}(E - V(x))\psi(x)$ of each side,

$$\begin{aligned}\text{l.h.s} &= \int_{x_0-\epsilon}^{x_0+\epsilon}\frac{\mathrm{d}}{\mathrm{d}x}\psi'(x)\mathrm{d}x = \psi'(x)\Big|_{x_0-\epsilon}^{x_0+\epsilon} = \psi'(x_0+\epsilon) - \psi'(x_0-\epsilon) = \Delta x_0\psi'(x) \\ \text{r.h.s} &= -\frac{2m}{\hbar}\int_{x_0-\epsilon}^{x_0+\epsilon}(E - V(x))\psi(x)\mathrm{d}x = -\frac{2m}{\hbar^2}(E - V(\xi))\psi(\xi)\cdot(2\epsilon)\end{aligned}$$

When $\epsilon \to 0$, $\Delta x_0\psi'(x) = 0$, then $\psi'(x)$ is continuous. However, if $V(x)$ is infinite, $V(x) = -a\delta(x - x_0)$,

$$\text{r.h.s} = -\frac{2m}{\hbar^2}\int_{x_0-\epsilon}^{x_0+\epsilon}a\delta(x - x_0)\psi(x)\mathrm{d}x = -\frac{2ma}{\hbar^2}\psi(x_0) \quad \Rightarrow \quad \Delta x_0\psi'(x) = \frac{2m}{\hbar^2}\psi(x_0)$$

To proof $\psi'(x)$ is continuous, unless $V(x) \to \infty$,
suppose $\psi(x)$ is discontinuous, wave function has a break point, and $\psi'(x) = \delta(x)$, then

$$\begin{aligned}\left\langle\hat{T}\right\rangle \sim \langle\hat{p}^2\rangle \sim \int\psi^*\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi &= \int\psi^*\frac{\mathrm{d}}{\mathrm{d}x}\psi'\mathrm{d}x = \int\psi^*\frac{\mathrm{d}}{\mathrm{d}x}\delta(x)\mathrm{d}x = \int\psi^*\mathrm{d}\delta(x) \\ &= \psi^*\delta(x)\Big|_{-\infty}^{\infty} - \int\delta(x)\frac{\mathrm{d}\psi^*}{\mathrm{d}x}\mathrm{d}x = 0 - \int_{-\infty}^{\infty}\delta(x)\delta(x)\mathrm{d}x \sim \delta(0) = \infty\end{aligned}$$

5.3 Delta Potential

Potential

$$V(x) = -a\delta(x) \qquad (a > 0)$$

When $E < 0$: (Bound state)

The wave function is

$$\psi''(x) = \kappa^2\psi(x) \quad \Rightarrow \quad \psi(x) = A\mathrm{e}^{\kappa x} + B\mathrm{e}^{-\kappa x}, \qquad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

For region I: $x \to -\infty$, $\psi_{\mathrm{I}}(x) \to 0 \quad \Rightarrow \quad \psi_{\mathrm{I}} = A\mathrm{e}^{\kappa x}$. Similarly in region II, $\psi_{\mathrm{II}}(x) = B\mathrm{e}^{-\kappa x}$.
Consider boundary condition, since $\psi(x)$ is continuous, $\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0)$, then $A = B$.
For $\psi'(x)$,

$$\begin{aligned}
&\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}\left(-\frac{\hbar^2}{2m}\psi''(a) - a\delta(x)\psi(x)\right)\mathrm{d}x = \lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon} E\psi(x)\mathrm{d}x \\
\Rightarrow \quad & -\frac{\hbar^2}{2m}\psi'(x)\bigg|_{-\epsilon}^{+\epsilon} - a\psi(0) = E\psi(0)\cdot 2\epsilon \;\to\; 0 \\
\Rightarrow \quad & \psi'_{\mathrm{II}}(0) - \psi'_{\mathrm{I}}(0) = -\frac{2ma}{\hbar^2}\psi(0) \quad \Rightarrow \quad -A\kappa - A\kappa = -\frac{2ma}{\hbar^2}A; \qquad \psi(0) = A
\end{aligned}$$

Therefore,

$$\kappa = \frac{ma}{\hbar^2}, \qquad E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{ma^2}{2\hbar^2}$$

Normalization, $\displaystyle\int_{-\infty}^{0}|A|^2\mathrm{e}^{2\kappa x}\mathrm{d}x + \int_{0}^{\infty}|A|^2\mathrm{e}^{-2\kappa x}\mathrm{d}x = 1 \quad \Rightarrow \quad A = \sqrt{\kappa} = \frac{\sqrt{ma}}{\hbar}$.

Bound state solution:

$$E = -\frac{ma^2}{2\hbar^2}; \quad \psi(x) = \frac{\sqrt{ma}}{\hbar}\exp\left\{-\frac{\sqrt{ma}}{\hbar}|x|\right\}$$

When $E > 0$: (Scattering state)

The wave function is

$$\psi''(x) = -k^2\psi(x) \quad \Rightarrow \quad \begin{cases}\psi_{\mathrm{I}}(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx} \\ \psi_{\mathrm{I}}(x) = F\mathrm{e}^{ikx} + G\mathrm{e}^{-ikx}\end{cases}, \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

Since no reflection in region II, then $G = 0$.
Consider boundary condition, since $\psi(x)$ is continuous, $A + B = F$. Next, for $\psi'(x)$,

$$\begin{aligned}
&\psi'_{\mathrm{II}}(0) - \psi'_{\mathrm{I}}(0) = -\frac{2ma}{\hbar^2}\psi(0) \quad \Rightarrow \quad ik(F - G) - ik(A - B) = -\frac{2ma}{\hbar^2}(A + B) \\
\Rightarrow \quad & F - G = A(1 + 2i\beta) - B(1 - 2i\beta) \quad \text{where} \quad \beta = \frac{ma}{\hbar^2 k}
\end{aligned}$$

Compare the relations, we got

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

- Reflection coefficient: $R = \left|\dfrac{B}{A}\right|^2 = \dfrac{\beta^2}{1 + \beta^2}$
- Transmission coefficient: $T = \left|\dfrac{F}{A}\right|^2 = \dfrac{1}{1 + \beta^2}$

NOTE: δ-well $(a > 0)$ & δ-barrier $a < 0$

5.4 Barrier Problem

5.4.1 Step Barrier

Consider

$$V(x) = \begin{cases}0, & x < 0 \\ V_0, & x \geqslant 0\end{cases}$$

When $E > V_0$:

$$\text{for} \quad x < 0, \quad \psi'' = -k^2\psi, \quad \psi(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx}, \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}$$
$$\text{for} \quad x \geqslant 0, \quad \psi'' = -k'^2\psi, \quad \psi(x) = C\mathrm{e}^{ik'x}, \quad \text{where} \quad k' = \frac{\sqrt{2m(E-V_0)}}{\hbar}$$

Boundary condition:

$$\left.\begin{aligned} \psi(0^+) = \psi(0^-) \quad &\Rightarrow \quad A + B = C \\ \psi'(0^+) = \psi'(0^-) \quad &\Rightarrow \quad ik(A-B) = ik'C \end{aligned}\right\} \quad \frac{B}{A} = \frac{k-k'}{k+k'}, \quad \frac{C}{A} = \frac{2k}{k+k'} \quad \text{and} \quad A, B, C \in \Re$$

When $E = V_0$:

$$\psi(x) = \begin{cases} 2A\cos(kx), & (x \neq 0) \\ 2A, & (x > 0) \end{cases}$$

Using the probability current density: $\vec{\nabla} \cdot \vec{j} = 0,\ \partial\rho/\partial t \equiv 0$

$$\vec{j} = \frac{\hbar}{2mi}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right) = \frac{1}{m}\,\mathrm{Re}\left(\psi^*\frac{\hbar}{i}\vec{\nabla}\psi\right)$$

$j_A \leftrightarrow \psi_A,\ j_B \leftrightarrow \psi_B,\ j_C \leftrightarrow \psi_C,\ j_l \leftrightarrow (\psi_A + \psi_B),\ j_r \leftrightarrow \psi_C$, take wave function expression into it, we got

$$j_A = \frac{\hbar k}{m}|A|^2,\ j_B = \frac{\hbar k}{m}|B|^2,\ j_l = j_A - j_B = \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right),\ j_C = j_r = \frac{\hbar k'}{m}|C|^2$$

since $\mathrm{d}j/\mathrm{d}x = 0$, then $j_l = j_r$,

$$k\left(|A|^2 - |B|^2\right) = k'|C|^2$$

- Reflection coefficient: $R = \dfrac{j_B}{j_A} = \dfrac{|B|^2}{|A^2|} = \dfrac{|k-k'|^2}{|k+k'|^2} \neq 1$
- Transmission coefficient: $T = \dfrac{j_C}{j_A} = \dfrac{k'|C|^2}{k|A|^2} = \dfrac{4kk'}{(k+k')^2}$
- Reflection+Transmission: $R + T = 1$

When $E < V_0$:

$$\text{for} \quad x < 0, \quad \psi'' = -k^2\psi, \quad \psi(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx}, \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}$$
$$\text{for} \quad x \geqslant 0, \quad \psi'' = \kappa^2\psi, \quad \psi(x) = C\mathrm{e}^{\kappa x}, \quad \text{where} \quad \kappa = \frac{\sqrt{2m(V_0-E)}}{\hbar}$$

Introduce $\theta(E)$, [PICTURE of theta]

$$\theta(E) = \arg(\kappa + ik) = \tan^{-1}\left(\frac{k}{\kappa}\right) = \tan^{-1}\sqrt{\frac{E}{V_0 - E}}, \qquad \theta'(E) = \frac{1}{2}\sqrt{\frac{1}{E(V_0-E)}}$$

From boundary condition got

$$\frac{B}{A} = \frac{k - i\kappa}{k + i\kappa} = -\frac{\kappa + ik}{\kappa - ik} = -e^{2i\theta(E)}, \qquad \kappa + ik = \sqrt{\kappa^2 + k^2}\mathrm{e}^{i\theta(E)}$$

Probability current: $j_A = j_B = \dfrac{\hbar k}{m}(k^2\kappa^2),\ j_C = 0 \quad \Rightarrow \quad T = 0,\ R = 1$.
For $x < 0$,

$$\psi^2(x) = \left[A\mathrm{e}^{i\theta(E)}\left(\mathrm{e}^{-i\theta(E)}\mathrm{e}^{ikx} + \mathrm{e}^{i\theta(E)}\mathrm{e}^{-ikx}\right)\right]^2 = 4A^2\sin^2(kx - \theta(E))$$

When $\psi(x_0) = 0$, $kx_0 = \theta(E)$.

Tunneling effect [NEED RECTIFY]

Penetrate depth:

$$d_p \sim \frac{1}{\kappa}$$

General discussion of SSE

1. If $V \in \Re$, then $\psi(x)$ can be chosen to be real.

   Proof. $\psi'' + \frac{2m}{\hbar^2}(E - V(x))\psi = 0$, $\psi^{*\prime\prime} + \frac{2m}{\hbar^2}(E - V(x))\psi^* = 0 \quad \Rightarrow \quad \psi, \psi^*$ are both solution;
   $\psi_R = \frac{1}{2}(\psi + \psi^*)$, $\psi_I = \frac{1}{2i}(\psi + \psi^*)$ are both solution. □

2. If $V(-x) = V(x)$, then $\psi(x)$ can be chose to be even/odd.

5.4.2 Finite Square Barrier

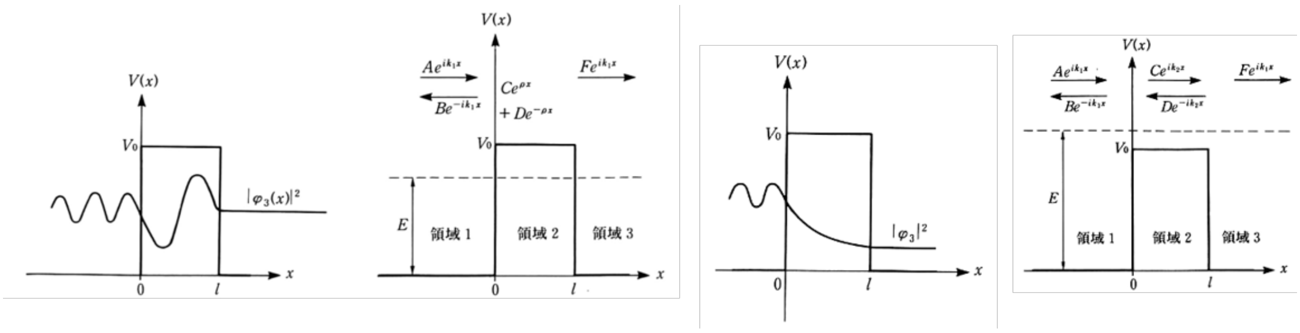

Figure 5.3: Wave function

Chapter 6

Central Potential and The Hydrogen Atom

6.1 Stationary States of a Particle in a Central Potential

Review basis:

1. $V(\vec{x}) = V(r) \quad \Rightarrow \quad \left[\hat{\vec{L}}, \hat{H}\right] \equiv 0 \quad \Rightarrow \quad \left[\hat{L}_i, \hat{H}\right] \equiv 0, \left[\hat{\vec{L}}^2, \hat{H}\right] \equiv 0 \quad \Rightarrow \quad \hat{\vec{L}}^2, \hat{L}_z$ are conserved quantities
2. Simultaneous eigenstates with $\hat{H}$: CSCO $\hat{\vec{L}} \leftrightarrow l$; $\hat{L}_z \leftrightarrow m_l \quad \Rightarrow \quad |l, m_l\rangle$
3. Angular momentum: $\vec{L} = \vec{x} \times \vec{p}$, $\hat{L}_i = \varepsilon_{ijk}\hat{x}_j\hat{p}_k$.
4. Eigenvalue equation for $\hat{\vec{L}}^2$, $\hat{L}_z$: $\hat{\vec{L}}^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle$; $\hat{L}_z |l, m_l\rangle = \hbar m_l |l, m_l\rangle$
5. Orthonormality + Completeness: $\langle lm|l'm'\rangle = \delta_{ll'}mm'$; $\sum_n |lm\rangle\langle ml| = \mathbb{1}$

6.1.1 Spherical Harmonic Function

Consider spherical coordinate,

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}, \quad \hat{\vec{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Since $|l, m_l\rangle$ in $\vec{x}$-rep is

$$\langle\vec{x}|l, m_l\rangle = \langle\theta, \phi|l, m_l\rangle = Y_{lm}(\theta\phi)$$

By solving eigen equations in spherical coordinate,

$$\hat{\vec{L}}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi), \qquad \hat{L}_z Y_{lm}(\theta, \phi) = \hbar m_l Y_{lm}(\theta, \phi)$$

We got [1]

$$Y_{lm}(\theta, \phi) \propto P_l^m(\theta, \phi)\mathrm{e}^{im\phi} \qquad \hat{L}_z\mathrm{e}^{im\phi} = \hbar m\mathrm{e}^{im\phi}$$

or Spherical Harmonic function:

$$\begin{aligned} Y_{lm}(\theta, \phi) &= (-1)^m\sqrt{\frac{(2l+1)!(l-m)!}{4\pi(l+m)!}}\mathrm{e}^{im\phi}P_l^m(\cos\theta) \\ &= \frac{(-1)^l}{2l!}\sqrt{\frac{(2l+1)!(l-m)!}{4\pi(l+m)!}}\mathrm{e}^{im\phi}(\sin\theta)^m\frac{\mathrm{d}^{l-m}}{\mathrm{d}(\cos\theta)^{l-m}}(\sin\theta)^{2l} \end{aligned}$$

Need to remember:

- $Y_{00}(\theta, \phi) = \dfrac{1}{\sqrt{4\pi}}$
- $Y_{10}(\theta, \phi) = \sqrt{\dfrac{3}{4\pi}}\cos\theta = \sqrt{\dfrac{3}{4\pi}}\left(\dfrac{z}{r}\right)$

[1] $P_l^m(\theta, \phi)$: associated Lagandre function

- $Y_{1\pm 1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta \mathrm{e}^{\pm i\phi} = \mp\sqrt{\frac{3}{8\pi}}\left(\frac{x \pm iy}{r}\right)$

and Orthonomality:

$$\int \langle lm|\vec{x}\rangle\langle\vec{x}|l'm'\rangle\,\mathrm{d}\vec{x}' = \int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\mathrm{d}\theta Y_{lm*}(\theta\phi)Y_{l'm'}(\theta,\phi) = \delta_{ll'}\delta_{mm'}$$

6.1.2 Radical Wave Function

Wave function of eigen state of Harmonic:

$$\hat{H}\,|nlm\rangle = E_{nlm}\,|nlm\rangle, \quad \left\langle\hat{\vec{x}}\middle|nlm\right\rangle = \psi_{nlm}(r,\theta,\phi), \quad \psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

- $R_{nl}(r)$: radical wave function
- $r \leftrightarrow$ radial; $\theta,\phi \leftrightarrow$ azimuthal

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(r) = \frac{\hat{p}_r^2}{2m} + \frac{\hat{\vec{L}}^2}{2mr} + V(r)$$

Take $\hat{H}$ into SSE,

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}r\right)\right] + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right\}R_{nl}(r) = E_{nl}R_{nl}(r)$$

Rewrite $R_{nl}(r)$ and define effective potential as

$$R_{nl}(r) = \frac{1}{r}u_{nl}(r), \qquad V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$$

Then

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + V_{\text{eff}}(r)\right]u_{nl}(r) = E_{nl}u_{nl}(r)$$

- $l(l+1)\hbar^2/2mr^2 \to$ azimuthal kinetic energy
- $-(\hbar^2/2m)\,\mathrm{d}^2/\mathrm{d}r^2 \to$ radical kinetic energy

If coloumb potential $V(r) \sim 1/r$, $V_{\text{eff}} \sim -A/r + B/r^2$. [PICTURE, Veff(r)]

Asymptotic analysis

$r \to 0$, require that $|u(r)| \ll N$, assume that $V(r) \sim 1/r$ or faster, $r^2V(r) \to 0$, then SSE become

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}u_{nl}(r) = \frac{l(l+1)}{r^2}u_{nl}(r)$$

If $u_{nl}(r) = r^\alpha$,

$$\frac{\mathrm{d}^2u_{nl}}{\mathrm{d}r^2} \sim \alpha(\alpha-1)r^{\alpha-2}, \qquad \frac{l(l+1)}{r^2}u_{nl} \sim l(l+1)r^{\alpha-2}$$

Therefore, $\alpha(\alpha-1) = l(l+1)$, and

$$\begin{cases}\alpha = l+1 & \Rightarrow \quad u_{nl}(r) = r^{l+1}\\ \alpha = -l & \Rightarrow \quad u_{nl}(r) = r^{-l}\end{cases}$$

If $R_{nl}(r) = r^{-l-1}$, since $\nabla^2(1/r) = -4\pi\delta(x)$, then $\nabla^2\left(r^{-(l+1)}\right) \sim \delta^{(l)}$, ψ is not conserved, give up it. $R_{nl}(r) = r^l$ is adopted. When $r \to 0$, $R_{nl}(r) \to 0$,

$$\psi(r,\theta,\phi) = Nr^lY_{lm}(\theta,\phi)$$

Normalization:

$$\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\mathrm{d}\theta|Y_{lm}(\theta,\phi)|^2\int_0^{\infty}r^2\mathrm{d}r|R_{nl}(r)|^2 = 1$$

6.2 The Hydrogen Atom

6.2.1 Center-of-Mass System: Two Body

Central potential and kinetic energy:

$$\hat{V}(\vec{x}) = \hat{V}(r) \quad \Rightarrow \quad \left[\hat{\vec{L}}, \hat{H}\right] = 0$$

$$\hat{T} = \frac{\hat{\vec{p}}^2}{2m} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{\vec{L}}^2}{2mr^2}$$

Suppose $m_1, \vec{x}_1, \vec{p}_1$ and $m_2, \vec{x}_2, \vec{p}_2$, then

$$\hat{H} = \frac{\hat{\vec{p}}_1^2}{2m} + \frac{\hat{\vec{p}}_1^2}{2m} + V(|\vec{x}_1 - \vec{x}_2|)$$

Define center of mass and other valuables:

$$\vec{X} = \frac{m_1\vec{x}_1 + m_2\vec{x}_2}{m_1 + m_2}, \quad \vec{P} = \vec{p}_1 + \vec{p}_2, \quad \vec{x} = \vec{x}_1 - \vec{x}_2, \quad \vec{p} = \alpha\vec{p}_1 - \beta\vec{p}_2$$

And $\vec{p}_1(\vec{P}, \vec{p}),\ \vec{p}_2(\vec{P}, \vec{p}),\ \vec{x}_1(\vec{X}, \vec{x}),\ \vec{x}_2(\vec{X}, \vec{x})$, satisfy commutation relations

$$[\hat{x}_{ai}, \hat{x}_{bj}] = [\hat{p}_{ai}, \hat{p}_{bj}] \equiv 0, \quad [\hat{x}_{ai}, \hat{p}_{bj}] = i\hbar\delta_{ab}\delta_{ij},$$

particle: $a, b = 1, 2$
coordinate: $i, j, k = 1, 2, 3$

Therefore,

$$\alpha = \frac{\mu}{m_1}, \quad \beta = \frac{\mu}{m_2} \quad \text{and} \quad \hat{H} = \frac{\hat{\vec{p}}^2}{2\mu} + \frac{\hat{\vec{P}}^2}{2M} + V(r)$$

- Reduced mass: $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$; total mass: $M = m_1 + m_2$
- $r = |\vec{x}_1 - \vec{x}_2| = |\vec{x}|$

Two body → One body, if $m_1 \ll m_2$, then $\mu = m_1$.
The center of mass and relative SSE are:

$$\frac{\hat{\vec{P}}^2}{2m}\Psi_{\text{CM}} = E_{\text{CM}}\Psi_{\text{CM}}$$

$$\left[\frac{\hat{\vec{p}}^2}{2\mu} + V(|\vec{x}|)\right]\Psi_{\text{rel}} = E_{\text{rel}}\Psi_{\text{rel}}$$

6.2.2 Hydrogen Atom

Bohr Model (Semi-Classical)

Potential:

$$V(r) = -\frac{e^2}{r}$$

- Hydrogen-like: $-Ze^2/r$

Bohr-radius:

$$a_0 = \frac{\hbar^2}{me^2} \sim 0.05\text{nm}$$

- Length scale: since $\dfrac{p^2}{2m} \sim \dfrac{1}{2m}\hbar^2\nabla^2 \sim \dfrac{\hbar^2}{ma_0^2}$ and $V(r) \sim \dfrac{e^2}{a_0}$, then $\dfrac{e^2}{a_0} = \dfrac{\hbar^2}{ma_0^2} \quad \Rightarrow \quad a_0 = \dfrac{\hbar^2}{me^2}$

From $T = V/2$, the energy is

$$E_1 = -\frac{e^2}{2a_0} \sim -13.6\text{eV}, \qquad E_n = E_1 \cdot \frac{1}{n^2} = -\frac{me^4}{2\hbar^2 n^2} \sim \alpha^2 \cdot (mc^2)$$

where fine structure constance define as (Gauss-unit)

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$$

- Sommerfield constant: $\alpha^2 = 1/19000$

Besides, $E_n \leftrightarrow \psi_{nlm}(r,\theta,\phi)$, if no spin considered, the number of state are $\sum_l (2l+1) = n^2$; if considered, then $2n^2$.
Since under Coloumb field, electron is bounded with nuclei, then $E<0$. $u(r) = R(r)/r$, the SSE is

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

Let $x = 2r/a_0$, then

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{l(l+1)}{x^2} - \frac{1}{x}\right]u(x) = -\kappa u(x), \qquad \kappa = \frac{-E}{2e^2/a_0}$$

- When $x \to \infty$,

$$\frac{\mathrm{d}^2 u}{\mathrm{d}x^2} = \kappa u \quad \Rightarrow \quad u \sim \mathrm{e}^{\pm\kappa x}$$

Let $\rho = \kappa x$, then

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

- When $\rho \to \infty$, $u \sim \mathrm{e}^{-\rho}$
- When $\rho \to 0$, $u \sim \rho^{l+1}$

Therefore, we can write $u(\rho)$ with polynominal function as

$$u(\rho) = \mathrm{e}^{-\rho}\rho^{l+1}W(\rho), \qquad W(\rho) = \sum_{k=0}^{n_r} a_k\rho^k$$

- $\exists k_{\max}, \forall k > k_{\max}, a_k = 0$
- n_r: number of nodes $n = n_r + l + 1 \quad \Rightarrow \quad n_r = n-1, n-2, \cdots, 0$
- Associated Leguared function (polynominal):

$$W(\rho) = L^{2l+1}n_r(\rho) = a_0\rho^0 + a_1\rho^1 + \cdots + a_{n_r}\rho^{n_r}$$

The solution of SSE for hydrogen atom is:

$$E_n = -\kappa^2\frac{2e^2}{a_0} = -\frac{1}{(n_r+l+1)^2}\cdot\frac{e^2}{2a_0} = -\frac{1}{n^2}\cdot E_1 = -13.6\mathrm{eV}\cdot\frac{1}{n^2}$$

$$\Psi_{nlm}(r,\theta,\phi) = N\cdot\left(\frac{r}{a_0}\right)^l L_{n_r}^{2l+1}\mathrm{e}^{-r/na_0}Y_{lm}(\theta,\phi) = \sqrt{\frac{2}{(na_0)^3}\frac{(n-l-1)!}{2n(l+1)!}}\mathrm{e}^{-\rho}\rho^l L_{n_r}^{2l+1}(\rho)\mathrm{e}^{-r/na_0}Y_{lm}(\theta,\phi)$$

where $\quad \rho = \dfrac{r}{na_0}$

[energy picture]

Chapter 7

Approximation Methods

7.1 Variational Theory and Helium Atom

Raleign-Ritz Variational Principle

Expection value of energy is

$$\left\langle \hat{H} \right\rangle = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \quad \Rightarrow \quad \delta\left\langle \hat{H} \right\rangle - \lambda\delta(\langle\psi|\psi\rangle) = 0$$

where λ is Lagrange multiplier.

Ritz Variational Principle

1. Trial wave function $|\psi(c_i)\rangle \quad i = 1, 2, 3\cdots$ as parameter
2. $\langle\hat{H}\rangle = \dfrac{\langle\psi(c_i)|\hat{H}|\psi(c_i)\rangle}{\langle\psi(c_i)|\psi(c_i)\rangle}$
3. $\delta\langle\hat{H}\rangle = 0 \quad \Rightarrow \quad \sum_i \dfrac{\partial\langle\hat{H}\rangle}{\partial c_i}\delta c_i = 0 \quad \Rightarrow \quad \dfrac{\partial}{\partial c_i}\langle\hat{H}\rangle(c_i) = 0 \quad \Rightarrow \quad c_i \quad \Rightarrow \quad \hat{H},\, |\psi(c_i)\rangle$

Helium Atom

The Harmiltonian of helium atom is

$$\hat{H} = \left(-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{2e^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m_2}\nabla_1^2 - \frac{2e^2}{r_2}\right) + \frac{e^2}{r_{12}} = \hat{H}_{01} + \hat{H}_{02} + \hat{H}_z$$

Trivial wavefunction:

$$\Psi(\vec{x}_2, \vec{x}_2) = \Psi_{100}(\vec{x}_1)\Psi_{100}(\vec{x}_2) = \left\{\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \mathrm{e}^{-\frac{Zr_1}{a_0}}\right\}\left\{\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \mathrm{e}^{-\frac{Zr_2}{a_0}}\right\} = \frac{Z^3}{\pi a_0^3}\mathrm{e}^{-\frac{Z}{a_0}(r_1+r_2)}$$

Take it into the expectation of $\hat{H}$,

$$\left\langle \hat{H} \right\rangle = \int \mathrm{d}^3\vec{x}_1 \int \mathrm{d}^3\vec{x}_2 \Psi^*(\vec{x}_1, \vec{x}_2)\hat{H}\Psi(\vec{x}_1, \vec{x}_2) = \frac{e^2Z^2}{a_0} - \frac{4e^2Z}{a_0} + \frac{5e^2Z}{8a_0}$$

As the variational principle, $\partial\langle\hat{H}\rangle\Big/\partial Z = 0$, then $Z = 27/16 \approx 1.69$, therefore the eigenvalue and eigen funciton of ground state are

$$E_{\text{ground}} = \frac{e^2}{a_0}\left(Z^2 - 4Z + \frac{5}{8}Z\right) \cong -2.85\left(\frac{e^2}{a_0}\right) \approx -77\text{eV}$$

$$\Psi_{\text{ground}} = \left(\frac{27}{16}\right)^3 \frac{1}{\pi a_0^3}\exp\left\{-\frac{27}{16}(r_1 + r_2)\right\}$$

- V.S. perturbation: $E_{\text{ground}} \cong -2.75\left(\dfrac{e^2}{a_0}\right) =\approx -75\text{eV}$

7.2 Scattering Theory

Background:

- Elastic collision: $A+B \to A+B$, potential sacttering $V(\vec{x}) = V(r)$
- Inelastic collision: $A+B \to A^* + B$ (relativistic QM, QFT)
- Reaction: $A+B \to C+D+E+\cdots$

Quantities:

$$[\rho] = [\rho]^2 = [L]^{-3},\ [\vec{j}] = [\rho][T]^{-1}[L] = [L]^{-2}[T]^{-1}$$

- Equation of continuity: $\partial\rho/\partial t + \vec{\nabla}\cdot\vec{j} = 0$
- Probability density: $\rho = \psi^*\psi$
- Probability current density: $\vec{j} = \dfrac{\hbar}{2mi}\Big(\psi^*\vec{\nabla}\psi - \quad \text{c.c.} \quad\Big) = \mathrm{Re}\left[\psi^*\left(-\dfrac{i\hbar}{m}\vec{\nabla}\right)\psi\right]$

SSE + Boundary condition

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\vec{x}) = E\psi(\vec{x}) \qquad (E>0)$$

The wave function can be written as

$$\psi(\vec{x}) = \psi_{\text{incident}} + \psi_{\text{scattering}}$$

- $\psi_{\text{incident}} = \mathrm{e}^{ikz}$
- $\psi_{\text{scattering}} = \dfrac{e^{ikr}}{r}f(\theta,\phi) + \mathcal{O}\left(\dfrac{1}{r^2}\right)$
  - $\dfrac{e^{ikr}}{r}$: ideal spherical wave function
  - $f(\theta,\phi)$: scattering amplitute

Probability current potential

When $r\to\infty$, the probability current density of scattering and incident is [1]

$$\vec{j}_{\text{sca}} = \hat{\boldsymbol{e}}_r\left(\frac{\hbar k}{m}\right)\left|\frac{f(\theta,\phi)}{r}\right|^2 = \hat{\boldsymbol{e}}_r v\left|\frac{f(\theta,\phi)}{r}\right|^2$$
$$\vec{j}_{\text{inc}} = \hat{\boldsymbol{e}}_z\frac{\hbar k}{m} = v\hat{\boldsymbol{e}}_z$$

Since $\displaystyle\int_V \vec{\nabla}\cdot\vec{j}\,\mathrm{d}^3\vec{x} = \oiint_S \vec{j}\cdot\mathrm{d}\vec{S} = 0$, then

$$\vec{j}_{\text{inc}}\cdot\mathrm{d}\vec{\sigma}_{\text{in}} = \vec{j}_{\text{sca}}\cdot\mathrm{d}\vec{\sigma}_{\text{sca}}$$

Since $\mathrm{d}\vec{S} = \hat{\boldsymbol{n}}\cdot r^2\mathrm{d}\Omega$, $\displaystyle\int_{\delta\Omega}\vec{j}_{\text{sca}}\mathrm{d}\vec{S} = \int_{\delta\Omega}\vec{j}_{\text{sca}}\cdot\hat{\boldsymbol{n}}\cdot r^2\mathrm{d}\Omega = 0$,

$$\vec{j}_{\text{sca}}\cdot\mathrm{d}\vec{\sigma}_{\text{sca}} = \int_{\delta\Omega}\frac{|f(\theta,\phi)|^2}{r^2}\cdot v\cdot r^2\mathrm{d}\Omega\Big/\delta\Omega = v\hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z\mathrm{d}r$$

We get differential scattering cross-section:

$$\sigma(\theta,\phi) = \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta,\phi)|^2$$

[1]Spherical coordinate: $\vec{\nabla} = \hat{\boldsymbol{e}}_r\dfrac{\partial}{\partial r} + \hat{\boldsymbol{e}}_\theta\dfrac{1}{r} + \hat{\boldsymbol{e}}_\phi\dfrac{1}{r\sin\theta\frac{\partial}{\partial\phi}}$, $\quad \nabla^2 = \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial}{\partial r}\right) + \dfrac{1}{r^2\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial}{\partial\theta}\right) + \dfrac{1}{r^2\sin\theta^2}\dfrac{\partial^2}{\partial\phi^2}$

- When $r\to\infty$, $\vec{\nabla}\to\hat{\boldsymbol{e}}_r\dfrac{\partial}{\partial r}$, $\quad \nabla^2 \to \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial}{\partial r}\right) + \mathcal{O}\left(\dfrac{1}{r^2}\right) = \dfrac{\partial^2}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial}{\partial r}$

Suppose the solution as

$$\psi(r,\theta)=\sum_{l=0}^{\infty}a_l P_l(\cos\theta)R_{nl}(r)$$

- Plane wave: $\mathrm{e}^{ikz}=\mathrm{e}^{ikr\cos\theta}=\sum_{l=0}^{\infty}(2l+1)i^l j_l(kr)P_l(\cos\theta)\xrightarrow{k_r\to\infty}\sum_{l=0}^{\infty}\frac{(2l+1)}{2ikr}\left[(-1)^{l+1}\mathrm{e}^{-ikr}+\mathrm{e}^{ikr}\right]P_l(\cos\theta)$

When $k_r\to\infty$,

$$\begin{aligned}\psi(r,\theta)=\psi_{\text{inc}}+\psi_{\text{sca}}\quad\to\quad&\sum_{l=0}^{\infty}a_l\frac{(-i)^l\mathrm{e}^{-2i\delta_l}}{ir}\left[(-1)^{l+1}\mathrm{e}^{-ikr}+\mathrm{e}^{ikr}\right]P_l(\cos\theta)\\&+\sum_{l=0}^{\infty}a_l\frac{(-i)^l\mathrm{e}^{-i\delta_l}}{ir}\left(\mathrm{e}^{i\delta_l}-1\right)\mathrm{e}^{ikr}P(\cos\theta)\\=&\mathrm{e}^{ikr}+\frac{\mathrm{e}^{ikr}}{r}\sum_{l=0}^{\infty}\left(\frac{2l+1}{2ik}\right)\left(\mathrm{e}^{2i\delta_l-1}-1\right)P_l(\cos\theta)\end{aligned}$$

Therefore $f(\theta)=\frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(\mathrm{e}^{2i\delta_l-1}-1\right)P_l(\cos\theta)=\sum_{l=0}^{\infty}f_l(\theta)$

- $l=0$: s-wave
- $l=1$: p-wave
- $l=2$: d-wave
- δ_l: phase-shift. $l=0$, dominates; $\delta_0=-ka$, $\delta_{l>1}\to(ka)^{2l+1}\to 0$

$$\delta_l=\frac{-(ka)^{2l+1}}{(2l-1)!!(2l+1)!!}$$

Then we can got the sacttering cross-section

$$\sigma=\int_{\Omega}|f(\theta)|^2\mathrm{d}\Omega=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l=\sum_{l=0}^{\infty}\sigma_l$$

Hard sphere scattering

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

1. $ka\ll 1$, $\lambda_{\text{dB}}\gg a$ [2]

   Then $f(\theta)\cong -a$, $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}=a^2$, $\sigma=\int_{\Omega}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\mathrm{d}\Omega=4\pi a^2$,

   Therefore, the biggest contribution is from $l=0$ potential wave (partial wave).

2. $ka\gg 1$, $\lambda_{\text{dB}}\ll a$

   $\mathrm{e}^{2i\delta_l}=\mathrm{e}^{-(ika-i(l+1)\pi)}\quad\Rightarrow\quad\delta_l=\frac{l\pi}{2}-ka$,

??????????????????? don't underst and

7.3 Perturbation Theory

7.3.1 Non-degenerate

If Harmiltonian can be written as

$$\hat{H}(\lambda)=\hat{H}^{(0)}+\lambda\delta\hat{H}\qquad(\lambda\in[0,1])$$

[2] $k=2\pi/\lambda_{\text{dB}}$

- $\hat{H}^{(0)}$: origin Harmiltonian, and the origin SSE is

$$\hat{H}^{(0)}\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle$$

- λ: dimensionless and natural, artificial

and for non-degenerate, for applying perturbation theory, we need

1. $\hat{H}^{(0)}\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle$
2. $\left|\delta\hat{H}\right| \ll \left|\hat{H}^{(0)}\right| \quad \Rightarrow \quad \begin{cases} \langle\psi_n^{(0)}|\delta\hat{H}|\psi_n^{(0)}\rangle \ll E_n^{(0)} \\ \langle\psi_n^{(0)}|\delta\hat{H}|\psi_n^{(0)}\rangle \ll \left|E_n^{(0)} - E_m^{(0)}\right| \end{cases}$

Consider such SSE states and its solution (target!)

$$\begin{cases} \hat{H}(\lambda)\left|\psi_n(\lambda)\right\rangle = E_n(\lambda)\left|\psi_n(\lambda)\right\rangle \\ \left|\psi_n(\lambda)\right\rangle = \sum_m C_m(\lambda)\left|\psi_m^{(0)}\right\rangle \end{cases} \qquad \begin{cases} C_m(\lambda) = \lambda^0 C_m^{(0)} + \lambda^1 C_m^{(1)} + \lambda^2 C_m^{(2)} + \cdots \\ E_n(\lambda) = \lambda^0 E_n^{(0)} + \lambda^1 E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \end{cases}$$

- or $\quad \left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \sum_{m\neq n} C_m\left|\psi_m^{(0)}\right\rangle$
- $\delta\hat{H}_{nk} = \left\langle\psi_n^{(0)}\middle|\delta\hat{H}\middle|\psi_k^{(0)}\right\rangle$

Take the terms into SSE, then

$$\left(\hat{H}^{(0)} + \lambda\delta\hat{H}\right)\sum_m C_m(\lambda)\left|\psi_m^{(0)}\right\rangle = E_n(\lambda)\sum_m C_m(\lambda)\left|\psi_m^{(0)}\right\rangle$$

and multiply each side with $\left\langle\psi_k^{(0)}\right|$, we have

$$\begin{aligned}
\text{l.h.s.} \quad &= \left\langle\psi_k^{(0)}\middle|\hat{H}^{(0)}\sum_m C_m(\lambda)\middle|\psi_m^{(0)}\right\rangle + \left\langle\psi_k^{(0)}\middle|\lambda\delta\hat{H}\sum_m C_m(\lambda)\middle|\psi_m^{(0)}\right\rangle = E_k^{(0)}C_k(\lambda) + \sum_m \lambda\delta\hat{H}_{km}C_m(\lambda) \\
&= E_k^{(0)}\left(C_k^{(0)} + \lambda C_k^{(1)} + \lambda^2 C_k^{(2)} + \cdots\right) + \lambda\sum_m \delta\hat{H}_{km}\left(C_m^{(0)} + \lambda C_m^{(1)} + \lambda^2 C_m^{(2)} + \cdots\right) \\
&= E_k^{(0)}C_k^{(0)} + \lambda\left(E_k^{(0)}C_k^{(1)} + \sum_m \delta\hat{H}_{km}C_m^{(0)}\right) + \lambda^2\left(E_k^{(0)}C_k^{(2)} + \sum_m \delta\hat{H}_{km}C_m^{(1)}\right) + \cdots \\
\text{r.h.s.} \quad &= \sum_m \left\langle\psi_k^{(0)}\middle|\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(C_m^{(0)} + \lambda C_m^{(1)} + \lambda^2 C_m^{(2)} + \cdots\right)\middle|\psi_m^{(0)}\right\rangle \\
&= E_n^{(0)}C_k^{(0)} + \lambda\left(E_n^{(0)}C_k^{(1)} + E_n^{(1)}C_k^{(0)}\right) + \lambda^2\left(E_n^{(2)}C_k^{(0)} + E_n^{(1)}C_k^{(1)} + E_n^{(0)}C_k^{(2)}\right) + \cdots
\end{aligned}$$

Then we got λ series

1. $\mathcal{O}(\lambda^0)$: $\quad E_k^{(0)}C_k^{(0)} = E_n^{(0)}C_k^{(0)} \quad \rightarrow \quad \left(E_n^{(0)} - E_k^{(0)}\right)C_k^{(0)} = 0 \quad \Rightarrow \quad \boxed{C_k^{(0)} = \delta_{nk}}$
2. $\mathcal{O}(\lambda^1)$: $\quad E_k^{(0)}C_k^{(1)} + \sum_m \delta\hat{H}_{km}C_m^{(0)} = E_n^{(0)}C_k^{(1)} + E_n^{(1)}C_k^{(0)}$
   - for $k = n$: $\quad \sum_m \delta\hat{H}_{nm}\delta_{nm} = E_n^{(1)}\delta_{nn} \quad \Rightarrow \quad \boxed{E_n^{(1)} = \delta\hat{H}_{nn}}$
   - for $k \neq n$: $\quad E_k^{(0)}C_k^{(1)} + \sum_m \delta\hat{H}_{km}\delta_{nm} = E_n^{(0)}C_k^{(1)} \quad \rightarrow \quad \left(E_n^{(0)} - E_k^{(0)}\right)C_k^{(1)} = \delta\hat{H}_{kn} \quad \Rightarrow \quad \boxed{C_k^{(1)} = \frac{\delta\hat{H}_{kn}}{E_n^{(0)} - E_k^{(0)}}}$
3. $\mathcal{O}(\lambda^2)$: $\quad E_k^{(0)}C_k^{(2)} + \sum_m \delta\hat{H}_{km}C_m^{(1)} = E_n^{(2)}C_k^{(0)} + E_n^{(1)}C_k^{(1)} + E_n^{(0)}C_k^{(2)}$
   - for $k = n$: $\quad \sum_m \delta\hat{H}_{nm}C_m^{(1)} = \delta\hat{H}_{nm}C_n^{(1)} + E_n^{(2)} \quad \Rightarrow \quad \boxed{E_n^{(2)} = \sum_{m\neq n}\frac{\left|\delta\hat{H}_{nm}\right|^2}{E_n^{(0)} - E_m^{(0)}}}$

- for $k \neq n$: $C_k^{(2)} = \sum_{m\neq n}\left[\frac{\delta\hat{H}_{km}\delta\hat{H}_{mn}}{\left(E_n^{(0)}-E_k^{(0)}\right)\left(E_n^{(0)}-E_m^{(0)}\right)} - \frac{\delta\hat{H}_{mn}\delta\hat{H}_{kn}}{\left(E_n^{(0)}-E_k^{(0)}\right)^2}\right]$ need to be checked.

1-st order and 2nd-order $(\lambda = 1)$

$$|\psi_n\rangle \approx \left|\psi_n^{(0)}\right\rangle + \sum_{k\neq n}\frac{\delta\hat{H}_{kn}}{E_n^{(0)}-E_k^{(0)}}\left|\psi_k^{(0)}\right\rangle, \qquad E_n \approx E_n^{(0)} + \delta\hat{H}_{nn} + \sum_{m\neq n}\frac{\left|\delta\hat{H}_{nm}\right|^2}{E_n^{(0)}-E_m^{(0)}}$$

* $\delta\hat{H}_{nn}$ is diagonal; the others are off-diagonal

Example of one-dim an harmonic oscillator

Review of the background:

$$\hat{H} = \hat{H}^{(0)} + \delta\hat{H}, \quad \hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \quad \hat{H}^{(0)}\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle$$

the solution are

$$\hat{H}^{(0)} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right); \quad E_n^{(0)} = \hbar\omega\left(n+\frac{1}{2}\right), \quad (n = 0,1,2,\cdots)$$

$$\left|\psi_n^{(0)}\right\rangle = |n\rangle \quad \text{Occupation number state, Fock state}$$

$$\hat{a}^\dagger\hat{a}\,|n\rangle = \hat{N}\,|n\rangle = n\,|n\rangle; \quad \hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle; \quad \hat{a}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}; \quad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\hbar\omega}}\hat{p} \quad \Rightarrow \quad \hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}+\hat{a}^\dagger\right)$$

If there is small magnetic field come in,

$$\delta\hat{H} = -q\mathcal{E}\hat{x} = -\alpha_0\hbar\omega\left(\hat{a}+\hat{a}^\dagger\right)$$

where $\alpha_0 = \sqrt{\frac{m\omega}{2\hbar}}x_0,\ x_0 = \frac{q\mathcal{E}}{m\omega^2}$.
Since $\langle n|\hat{a}|m\rangle = \sqrt{m}\delta_{n,m-1},\ \langle n|\hat{a}^\dagger|m\rangle = \sqrt{m+1}\delta_{n,m+1}$,

$$E_n^{(1)} = \delta\hat{H}_{nn} = \left\langle\psi_n^{(0)}\middle|\delta\hat{H}\middle|\psi_n^{(0)}\right\rangle = \langle n|-\alpha_0\hbar\omega\left(\hat{a}+\hat{a}^\dagger\right)|n\rangle \equiv 0$$

$$\delta\hat{H}_{kn} = \left\langle\psi_k^{(0)}\middle|\delta\hat{H}\middle|\psi_n^{(0)}\right\rangle = \langle k|-\alpha_0\hbar\omega(\hat{a}+\hat{a}^\dagger)|n\rangle = (-\alpha_0\hbar\omega)\left[\sqrt{n}\delta_{k,n-1} + \sqrt{n+1}\delta_{k,n+1}\right]$$

Diagnal: $\delta\hat{H}_{nn} \equiv 0$; off-diagonal: $\delta\hat{H}_{kn} \neq 0\,(k = n\pm 1)$. When $k = n\pm 1$

$$E_k^{(2)} = \sum_{k\neq n}\frac{\left|\hat{H}_{nk}\right|^2}{E_n^{(0)}-E_k^{(0)}} = \frac{\left|\hat{H}_{n,n-1}\right|^2}{\hbar\omega} + \frac{\left|\hat{H}_{n,n+1}\right|^2}{-\hbar\omega} = \frac{(-\alpha_0\hbar\omega)^2 n}{\hbar\omega} + \frac{(-\alpha_0\hbar\omega)^2(n+1)}{-\hbar\omega} = -\alpha_0^2\hbar\omega$$

$$C_k^{(1)} = \frac{\delta\hat{H}_{kn}}{E_n^{(0)}-E_k^{(0)}} = \frac{(-\alpha_0\hbar\omega)(\sqrt{n}\delta_{k,n-1}+\sqrt{n+1}\delta_{k,n+1})}{(n-k)\hbar\omega}, \quad C_{n-1}^{(1)} = -\alpha_0\sqrt{n}, \quad C_{n+1}^{(1)} = \alpha_0\sqrt{n+1}$$

$$|\psi_n\rangle = \left|\psi_n^{(0)}\right\rangle + \sum_{k\neq n}C_k^{(1)}\left|\psi_k^{(0)}\right\rangle = |n\rangle + \left(-\alpha_0\sqrt{n}\right)|n-1\rangle + \left(\alpha_0\sqrt{n+1}\right)|n+1\rangle$$

$$\langle\hat{x}\rangle = \langle\psi_n|\hat{x}|\psi_n\rangle = \left[\langle n| + \alpha_0(\sqrt{n+1}\,\langle n+1| - \sqrt{n}\,\langle n-1|)\right]\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger)\left[|n\rangle + \alpha_0\left(\sqrt{n+1}\,|n+1\rangle - \sqrt{n}\,|n-1\rangle\right)\right] = \frac{q\mathcal{E}}{m\omega^2}$$

$$P = |q|\,\langle\hat{x}\rangle - (-|q|)\,\langle x\rangle = 2|q|\,\langle\hat{x}\rangle = \frac{2q^2\mathcal{E}}{m\omega} = \chi\mathcal{E} \quad \text{(Polarization)}$$

Therefore, in summarize

$$
\begin{aligned}
E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{q^2\mathcal{E}^2}{2m\omega^2} \\
|\psi_n\rangle &= |n\rangle + \alpha_0\big(\sqrt{n+1}\,|n+1\rangle - \sqrt{n}\,|n-1\rangle\big), \quad \text{where} \quad \alpha_0 = \sqrt{\frac{m\omega}{2\hbar}}\frac{q\mathcal{E}}{m\omega^2} \\
\hat{H} &= \hat{H}^{(0)} + \delta\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) - \hbar\omega\alpha_0\big(\hat{a} + \hat{a}^\dagger\big) = \hbar\omega\left[\big(\hat{a}^\dagger - \alpha_0\big)\big(\hat{a} - \alpha_0\big) + \frac{1}{2}\right] - \hbar\omega\alpha_0^2
\end{aligned}
$$

7.3.2 Degenerate

For degenerate consideration, similarly, we have

1. $\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda\delta\hat{H}, \qquad (\lambda \in [0,1])$
2. $\hat{H}^{(0)}\,|n\nu\rangle = E_n^{(0)}\,|n\nu\rangle, \qquad (\nu = 1, 2, \cdots, \nu_n)$ * ν_n is the degeneracy when in n's eigenvalue
3. orthonomality+Completeness of $\{|n\nu\rangle\}$:
   - $\langle n'\nu'|n\nu\rangle = \delta_{nn'}\delta_{\nu\nu'}$
   - $\sum\limits_{n\nu} |n\nu\rangle\langle n\nu| = \mathbb{1}$

And the SSE and states

$$
\begin{cases} \hat{H}\,|\psi_k\rangle = E_k\,|\psi_k\rangle \\ |\psi_k\rangle = \sum\limits_{m\mu} C_{m\mu}\,|m\mu\rangle \end{cases} \qquad \begin{cases} C_{m\mu} = \lambda^0 C_{m\mu}^{(0)} + \lambda^1 C_{m\mu}^{(1)} + \lambda^2 C_{m\mu}^{(2)} + \cdots \\ E_k = \lambda^0 E_k^{(0)} + \lambda^1 E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots \end{cases}
$$

Notes:

- $C_{m\mu} = \langle m\mu|\psi_k\rangle$
- $\delta\hat{H}_{m\mu,n\nu} = \langle m\mu|\delta\hat{H}|n\nu\rangle$
- ν, μ means degeneracy

multiply the SSE with $|m\mu\rangle$, then the two side are

$$
\begin{aligned}
\text{l.h.s.} \quad &= \langle m\mu|\hat{H}_0 + \lambda\delta\hat{H}|\psi_k\rangle = E_m^{(0)}\langle m\mu|\psi_k\rangle + \sum_{n\nu}\langle m\mu|\lambda\delta\hat{H}|n\nu\rangle\langle n\nu|\psi_k\rangle = E_m^{(0)}C_{m\mu} + \sum_{n\nu}\lambda\delta\hat{H}_{m\mu,n\nu}C_{n\nu} \\
&= E_m^{(0)}\left(\lambda^0 C_{m\mu}^{(0)} + \lambda^1 C_{m\mu}^{(1)} + \cdots\right) + \sum_{n\nu}\lambda\delta\hat{H}_{m\mu,n\nu}\left(\lambda^0 C_{n\nu}^{(0)} + \lambda^1 C_{n\nu}^{(1)} + \cdots\right) \\
&= E_m^{(0)}C_{m\mu}^{(0)} + \lambda\left(E_m^{(0)}C_{m\mu}^{(1)} + \sum_{n\nu}\delta\hat{H}_{m\mu,n\nu}C_{n\nu}^{(0)}\right) + \cdots \\
\text{r.h.s.} \quad &= \langle m\mu|E_k|\psi_k\rangle = E_k C_{m\mu} = \left(\lambda^0 E_k^{(0)} + \lambda^1 E_k^{(1)} + \cdots\right)\left(\lambda^0 C_{m\mu}^{(0)} + \lambda^1 C_{m\mu}^{(1)} + \cdots\right) \\
&= E_k^{(0)}C_{m\mu}^{(0)} + \lambda\left(E_k^{(0)}C_{m\mu}^{(1)} + E_k^{(1)}C_{m\mu}^{(0)}\right) + \cdots
\end{aligned}
$$

Then we got λ series:

1. $\mathcal{O}(\lambda^0)$: $\quad E_m^{(0)}C_{m\mu}^{(0)} = E_k^{(0)}C_{m\mu}^{(0)} \quad \Rightarrow \quad \boxed{C_{m\mu}^{(0)} = a_\mu\delta_{km}}$
2. $\mathcal{O}(\lambda^1)$: $\quad E_m^{(0)}C_{m\mu}^{(1)} + \sum\limits_{n\nu}\delta\hat{H}_{m\mu,n\nu}C_{n\nu}^{(0)} = E_k^{(0)}C_{m\mu}^{(1)} + E_k^{(1)}C_{m\mu}^{(0)}$ some mistakes here...
   - for $k = m$: $\quad \sum\limits_{\nu}\delta\hat{H}_{k\mu,n\nu}a_\nu - E_k^{(1)}a_\mu = 0$, let $\delta\hat{H}_{k\mu,k\nu} = \delta\hat{H}_{\mu\nu} \quad \Rightarrow \quad \sum\limits_{\mu\nu}\left(\delta\hat{H}_{\mu\nu} - E_k^{(1)}\delta_{\mu\nu}\right)a_\nu = 0$, therefore

$$
\det\left|\sum_{\mu\nu}\left(\delta\hat{H}_{\mu\nu} - E_k^{(1)}\delta_{\mu\nu}\right)\right|_{\nu_n\times\nu_n} = 0 \tag{7.1}
$$

We can got $E_{k\alpha}^{(1)}$, $(\alpha = 1, \cdots, \alpha_k)$

- $\alpha_k = \nu_k$, then degeneracy completely lifted
- $\alpha_k = 1$, then degeneracy not broken
- $1 < \alpha_k < \nu_k$, then partically lifted

Finally, we can got the state in zero-th order, and engery in first order

$$|\psi_{k\alpha}\rangle = \sum_{\alpha} a_{\mu\alpha} |ka\rangle$$

7.4 Application to Perterbation

7.4.1 Stark Effect

Phenomenon: when there is electric field

$$\vec{E} = \mathcal{E}\hat{e}_z$$

come in to the Hydrogen atom. Normally, $n = 2$, $l = 0\,(m = 0)$, $l = 1\,(m = 0, \pm 1)$, for four energy line, however, there only three. Denote four state:

$$\begin{aligned}
&2S : \quad |2\,0\,0\rangle \to |1\rangle ; \\
&2P_0 : \quad |2\,1\,0\rangle \to |2\rangle ; \qquad 2P_1 : \quad |2\,1\,1\rangle \to |3\rangle ; \qquad 2P_{-1} : \quad |2,\,1,\,-1\rangle \to |4\rangle ;
\end{aligned}$$

Because for degeneracy, $\nu_n = 4$ Normally SSE is

$$\hat{H}^{(0)} |2lm\rangle = E_2^{(0)} |2lm\rangle , \quad E_n = -\frac{e^2}{2a_0} = -12.6\mathrm{eV}/n^2$$

Then, adding perturbation

$$\lambda\delta\hat{H} = e\mathcal{E}r\cos z = \left(\frac{e\mathcal{E}a_0}{e^2/a_0}\right)\left(\frac{e^2}{a_0^2} r\cos\theta\right) \quad \Rightarrow \quad \lambda = \frac{W_{\text{ext}}}{W_{col}} \ll 1$$

1. $W_{\text{ext}} = e\mathcal{E}a_0$: energy of electric field
2. $W_{\text{col}} = e^2/a_0$: energy of self
3. e^2/a_0^2: Column force

Ask $\delta H_{\mu\nu} \quad (\nu, \mu = 1, 2, 3, 4)$ $(\delta\hat{H}_{\mu\nu} = \delta\hat{H}_{k\mu,k\nu},\ k = 2)$ a 4×4 matrixel.
Since $\left[\hat{L}_z, \hat{z}\right] = 0$ which means $\hat{L}_z, \hat{z}$ have simultaneous eigenvalue, and suppose $|lm\rangle$ is eigenstate of $\hat{z}$, then

$$\left\langle lm' \middle| \hat{z} \middle| lm \right\rangle \quad \propto \quad \delta_{m'm}$$

which means a selection rule for m:

$$\Delta m = m - m' = 0$$

Similarly,

$$\left\langle lm \middle| \delta\hat{H} \middle| lm' \right\rangle \sim \delta_{l+1,l'} \quad \Rightarrow \quad \Delta l = l' - l = \pm 1$$

Since $z = r\cos\theta \sim Y_{10}(\theta, \phi)$, we have already the solution is

$$\cos\theta Y_{lm}(\theta,\phi) \quad \propto \quad a \cdot Y_{l+1,m}(\theta,\phi) + b \cdot Y_{l-1,m}(\theta,\phi) \quad \text{where} \quad Y_{lm}(\theta,\phi) = |lm\rangle$$

Hence,

$$\left\langle l'm \middle| \cos\theta \middle| lm \right\rangle \quad \sim \quad a\left\langle l' \middle| l+1 \right\rangle + \left\langle l' \middle| l-1 \right\rangle$$

> Selection rule for l and m on $\hat{z}$:
>
> $$\Delta l = \pm 1, \quad \Delta m = 0$$

Therefore, $|1\rangle$ and $|2\rangle$ have degenerated. NEED PUT PICTURE, NOT SURE THE RESULTS.

$$\langle 1|\lambda\delta\hat{H}|2\rangle = \langle 2|\lambda\delta\hat{H}|1\rangle \quad \text{and} \quad \langle 2\,0\,0|\lambda\delta\hat{H}|2\,1\,0\rangle = \int \psi_{200}^*(\theta,\phi)\lambda\delta\hat{H}\psi_{210}(\theta,\phi) r^2 \mathrm{d}r \sin\theta \mathrm{d}\phi = -3ea_0\mathcal{E}$$

Then from Eq.(7.1), we have

$$\begin{vmatrix} -E_2^{(1)} & -3ea_0\mathcal{E} & 0 & 0 \\ -3ea_0\mathcal{E} & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \quad \Rightarrow \quad E_2^{(1)} = 0, \pm 3a_0e\mathcal{E}$$

Therefore, for we have the state and the corresponding enery are

$$|\psi_k\rangle \quad = \quad \begin{cases} |2\,1\,1\rangle, \quad |2\,1\,-1\rangle & \to E_2^{(0)} + 0 \\ \frac{1}{\sqrt{2}}(|2\,0\,0\rangle + |2\,1\,0\rangle) & \to E_2^{(0)} - 3ea_0\mathcal{E} \\ \frac{1}{\sqrt{2}}(|2\,0\,0\rangle - |2\,1\,0\rangle) & \to E_2^{(0)} + 3ea_0\mathcal{E} \end{cases}$$

* The degeneracy is from multi observables have communicated with $\hat{H}$, then the observable is conerved and have multi same eigenstates. The perturbation break the symmetry, and dismiss degeneracy, and revised.

7.4.2 Charged Particles in Magnetic Field

Review the classical electromagnetic theory, we know that the Harmilton's canonical equations of motion can get Newton-Lorentz's equation: [3]

$$H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right) + q\phi \quad \Rightarrow \quad \begin{cases} m\ddot{\vec{x}} = q\left(\vec{E} + \frac{\vec{v}}{c} \times \vec{B}\right), & A_i = A_i(\vec{x}, t) \\ \vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\mathrm{d}}{\mathrm{d}t}\vec{A}, \quad \vec{B} = \vec{\nabla} \times \vec{A}. & \phi = \phi(\vec{x}, t) \end{cases}$$

Proof. Since $H = \frac{1}{2m}\left(p_i - \frac{q}{c}\right)\left(p_i - \frac{q}{c}A_i\right) + q\phi$, and $\dot{A}_i = \frac{\partial A_i}{\partial t} + \frac{\partial A_i}{\partial x_j}\frac{\mathrm{d}x_j}{\mathrm{d}t} = \partial_t A_i + v_j\partial_j A_i$

then $\dot{x}_i = \frac{\partial H}{\partial p_i} = \frac{1}{m}\left(p_i - \frac{q}{c}A_i\right) = v_i$, $\dot{p} = -\frac{\partial H}{\partial x_i} = -\frac{1}{m}\left(p_j - \frac{q}{c}A_j\right)\left(-\frac{q}{c}\frac{\partial A_j}{\partial x_i}\right) - q\partial_i\phi = -q\partial_i\phi + \frac{q}{c}v_j\partial_i\dot{A}_j$,

therefore

$$\begin{aligned} m\ddot{x}_i =& \dot{p}_i - \frac{q}{c}\dot{A}_i = -q\partial_i\phi + \frac{q}{c}v_j\partial_i A_j - \frac{q}{c}\partial_t A_i - \frac{q}{c}v_i\partial_j A_i \\ =& q\left(-\partial_i\phi - \frac{1}{c}\partial_t A_i\right) + \frac{q}{c}v_j(\partial_i A_j - \partial_j A_i) = qE_i + q\left(\frac{\vec{v} \times \vec{B}}{c}\right)_i \end{aligned}$$

since $\left(\vec{v} \times \vec{B}\right)_i = \varepsilon_{ijk}v_jB_j = \varepsilon_{ijk}v_j\varepsilon_{klm}\partial_l A_m = v_j\partial_i A_j - v_j\partial_j A_i$ □

Non-Relativistic QM (NO-SPIN)

Since $[\hat{p}_i, A_j(\hat{\vec{x}})] = [\hat{p}_i, \hat{x}_\alpha]\partial_\alpha A_j = -i\hbar\partial_i A_j$, then

$$\hat{p}_i A_i = A_i\hat{p}_i - i\hbar\partial_i A_i \quad \Rightarrow \quad \hat{\vec{p}} \cdot \vec{A} = \vec{A} \cdot \hat{\vec{p}} - i\hbar\vec{\nabla} \cdot \vec{A}$$

Use Columb gauge[4]: $\vec{\nabla} \cdot \vec{A} = 0$, then $\hat{\vec{p}} \cdot \vec{A} = \vec{A} \cdot \hat{\vec{p}}$. And radiation gauge: $\phi = 0$, consider $\left|\frac{q^2}{c^2}\vec{A}^2\right| \ll \left|\frac{q}{c}\vec{A} \cdot \vec{p}\right|$ then expand $\hat{H}$,

$$\hat{H} = \frac{1}{2m}\left(\hat{\vec{p}}^2 - \frac{q}{c}\hat{\vec{p}} \cdot \vec{A} - \frac{q}{c}\vec{A} \cdot \hat{\vec{p}} + \frac{q^2}{c^2}\hat{\vec{A}}^2\right) + q\phi = \frac{\hat{\vec{p}}^2}{2m} - \frac{q}{mc}\hat{\vec{A}} \cdot \hat{\vec{p}}$$

[3] Einstein convention is used.

[4] Gauge can be chose for convenience: $\vec{A} \to \vec{A}' = \vec{A} + \vec{\nabla}\chi$, $\phi \to \phi' = \phi - \frac{1}{c}\partial_t\partial_t\chi \quad \Rightarrow \quad \vec{E}' = \vec{E}$, $\vec{B}' = \vec{B}$

Assume $\vec{B} = \mathrm{const}$, and $\vec{A} = \frac{1}{2}\vec{B} \times \vec{x}$, then

$$\begin{aligned}
\vec{\nabla} \times \vec{A} &= \frac{1}{2}\varepsilon_{ijk}\partial_j\varepsilon_{klm}B_l x_m = \frac{1}{2}[\partial_j(B_i x_j) - \partial_j(B_j x_i)] = \frac{1}{2}(B_i\delta_{jj} - B_j\delta_{ij}) = B_i \\
\vec{\nabla} \cdot \vec{A} &= \frac{1}{2}\partial_i\varepsilon_{ijk}B_j x_k = \frac{1}{2}\varepsilon_{ijk}B_j\delta_{ik} = \frac{1}{2}\varepsilon_{iji}B_j \equiv 0 \quad \text{(satisfy Columb gauge)} \\
\hat{H}_M &= -\frac{q}{mc}\vec{A} \cdot \hat{\vec{p}} = -\frac{q}{mc}\frac{1}{2}\left(\vec{B} \times \hat{\vec{x}}\right) \cdot \hat{\vec{p}} = -\frac{q}{mc}\left(\hat{\vec{x}} \times \hat{\vec{p}}\right) \cdot \vec{B} = -\frac{q}{2mc}\hat{\vec{L}} \times \vec{B} = -\vec{\mu}_L
\end{aligned}$$

- Orbital magnetic moment: $\vec{\mu}_L = \frac{q}{2mc}\vec{L} = \frac{e}{2mc}\vec{L} = \mu_B\left(\frac{\vec{L}}{\hbar}\right), \qquad q = -e$
- Bohr magetom: $\mu_B = \frac{e\hbar}{2mc}$

Magnetic Harmiltonian of charged partical without spin in magnetic field and its z-direction:

$$\hat{H}_M = -\frac{q}{2mc}\hat{\vec{L}} \times \vec{B} = -\vec{\mu}_L \cdot \vec{B}, \qquad \hat{H}_{M_z} = \mu_B B\left(\frac{L_z}{\hbar}\right)$$

Order of magnitude analysis:

1. $\hat{H}_E = -q\vec{d} \cdot \vec{E} = ezE$, $\hat{H}_M = \mu_B B(L_z/\hbar) \sim \mu_B B$,
   So, if $|E| \sim |B|$, $\frac{|H_M|}{|H_E|} \sim \frac{\mu_B}{ea_0} = \frac{e\hbar}{2mc} \cdot \frac{1}{ea_0} \sim \frac{\hbar}{mc}\frac{1}{a_0} \sim \frac{\lambda}{a_0} = \alpha = \frac{1}{137}$
   - Comptom wavelength: $\lambda = \hbar/mc$; α fince structure constant
2. $\frac{q^2}{c^2}\vec{A}^2 \sim \frac{q^2}{c^2}\left(\vec{B} \times \vec{x}\right)^2 \sim \frac{q^2}{c^2}B^2 r^2 = \frac{e^2}{c^2}B^2 a_0^2$
   $\frac{\left|\frac{q^2}{c^2}\vec{A}^2\right|}{\frac{q}{mc}\vec{A} \cdot \vec{p}} \sim \left(\frac{e^2}{\hbar c}\right)\frac{Ba_0^2}{4e} \sim \alpha\left(\frac{B}{e/a_0^2}\right) = \frac{1}{137} \cdot \delta$
   - even if $B < 10^5\mathrm{Gs}$ very big, it is $\sim 10^{-4}$
3. $\vec{\mu}_L = \frac{q}{2mc}\vec{L} \cong g_L\mu_B\frac{\vec{L}}{\hbar} \Leftrightarrow \vec{\mu}_L = \frac{q}{mc}\vec{S} \cong g_S\mu_B\frac{\vec{S}}{\hbar}$ (intrinsic magnetic moment)
   - $g_L \cong 1$, $g_S \cong 2$

Relativistic QM (SPIN)

From scalor to spinor, then $\hat{H} = \frac{\hat{\vec{p}}^2}{2m} \cdot \mathbb{1} = \frac{1}{2m}\left(\hat{\vec{\sigma}} \cdot \hat{\vec{p}}\right)^2$, in Magnetic field $(\phi = 0)$

$$\hat{H} = \frac{1}{2m}\left[\hat{\vec{\sigma}} \cdot \left(\hat{\vec{p}} - \frac{q}{c}\vec{A}\right)\right]^2 = \frac{1}{\pi}\left(\hat{\vec{\sigma}} \cdot \hat{\vec{\pi}}\right)^2, \qquad \hat{\vec{\pi}} = \hat{\vec{p}} - \frac{q}{c}\vec{A}$$

Since Pauli matrix $\left(\vec{\sigma} \cdot \vec{A}\right)\left(\vec{\sigma} \cdot \vec{B}\right) = \left(\vec{A} \cdot \vec{B}\right)\mathbb{1}_2 + i\vec{\sigma}\left(\vec{A} \cdot \vec{B}\right)$ and $\vec{S}\frac{\hbar}{2}\vec{\sigma}$, then

$$\hat{H} = \frac{1}{2m}\left[\hat{\vec{\pi}}^2 + i\hat{\vec{\sigma}} \cdot \left(\hat{\vec{\pi}} \times \hat{\vec{\pi}}\right)\right] = \frac{\hat{\vec{p}}^2}{2m} - \frac{q}{2mc}\hat{\vec{L}} \cdot \vec{B} - \frac{q}{mc}\hat{\vec{S}} \cdot \vec{B}$$

Proof. $\left(\hat{\vec{\pi}} \times \hat{\vec{\pi}}\right)_i = \varepsilon_{ijk}\hat{\vec{\pi}}_j\hat{\vec{\pi}}_k = \frac{1}{2}\varepsilon_{ijk}[\hat{\vec{\pi}}_j, \hat{\vec{\pi}}_k] = -\frac{1}{2}\varepsilon_{ijk}\frac{q}{c}\left([\hat{p}_j, \hat{A}_k] + [\hat{A}_j, \hat{p}_k]\right) = \frac{i\hbar q}{2c}\varepsilon_{ijk}(\partial_j A_k - \partial_k A_j) = \frac{i\hbar q}{c}\vec{B}$ □

Introduce

- $\vec{\mu}_L = \frac{q}{2mc}\hat{\vec{L}} = \frac{-e}{2mc}\hat{\vec{L}} = -\mu_B\left(\frac{\hat{\vec{L}}}{\hbar}\right)$
- $\vec{\mu}_S = \frac{q}{mc}\hat{\vec{S}} = \frac{-e}{2mc}\hat{\vec{L}} = -2\mu_B\left(\frac{\hat{\vec{S}}}{\hbar}\right)$

Magnetic Harmiltonian of charged partical with spin in magnetic field and its z-direction:

$$\hat{H}_M = -\left(\hat{\vec{\mu}}_L + \hat{\vec{\mu}}_S\right) \cdot \vec{B}, \qquad \hat{H}_{M_z} = \mu_B B \left(\frac{\hat{L}_z + 2\hat{S}_z}{\hbar}\right)$$

Note:

- μ_B is energy dimension; $\left(\hat{L}_z + 2\hat{S}_z\right)/\hbar$ is dimensionless
- $[\hat{\pi}_i, \hat{\pi}_j] = \frac{iq\hbar}{c}(\partial_i - \partial_j A_i) = \frac{iq\hbar}{c}\varepsilon_{ijk}B_k \quad \Leftrightarrow \quad \vec{\pi} \times \vec{\pi} = \frac{iq\hbar}{c}\vec{B}$
- $\hat{v}_i = \frac{\hat{\pi}}{m} \quad \Rightarrow \quad \hat{\vec{v}} \times \hat{\vec{v}} = \frac{iq\hbar}{m^2 c}\vec{B} \quad \Leftrightarrow \quad [\hat{v}_i, \hat{v}_j] = \frac{iq\hbar}{m^2 c}\varepsilon_{ijk}B_k$
- $[\hat{v}_i, \hat{\vec{v}}^2] = \frac{iq\hbar}{m^2 c}\varepsilon_{ijk}(\hat{v}_j B_k - B_j \hat{v}_k) \quad \Leftrightarrow \quad [\vec{v}, \hat{\vec{v}}^2] = \frac{iq\hbar}{m^2 c}\left(\hat{\vec{v}} \times \vec{B} - \vec{B} \times \hat{\vec{v}}\right)$

7.4.3 Zeeman Effect

1. Phenomenon: 1896
2. QM interpretation:
   (a) Normal Zeeman: Classical Mechanics; Non-relativistic QM
   (b) Anormalous Zeeman: Relativistic QM; Spin: fine structure

Theoretical analysis of normal Zeeman effect

Consider $\vec{B} = B\vec{e}_z$, $\hat{H}_M = \frac{\mu_B B L_z}{\hbar}$, and use perturbation theory
$\hat{H}^{(0)} = \frac{\hat{\vec{p}}^2}{2m} - \frac{e^2}{r} \rightarrow$ eigenstate is $|nlm_l\rangle$, satisfy $\hat{H}_M \ll E_n^{(0)}$
since CSCO of $\left(\hat{H}^{(0)}, \hat{\vec{L}}^2, \hat{L}_z\right)$, then

$$\langle nlm_l|\hat{H}_M|nlm_l\rangle = \frac{\mu_B B}{\hbar}\langle nlm_l|\hat{L}_z|nlm_l\rangle = \mu_B B m_l \quad \Rightarrow \quad E_{nlm_l} = E_n^{(0)} + \mu_B B m_l$$

Theoretical analysis of anormalous Zeeman effect

Review Hydrogen atom, eigen state is $|nlm_l s_l\rangle$, CSSO $\left(\hat{H}^{(0)}, \hat{\vec{L}}^2, \hat{\vec{L}}, \hat{L}_z, \hat{\vec{S}}^2, \hat{S}_z\right)$, good quantum number (n, l, m_l, s, m_s)
For fine structure analysis:

$$\hat{H}^{(0)} = \frac{\hat{\vec{p}}^2}{2m} - \frac{e^2}{r} + a_r\hat{\vec{p}}^4 + a_{L-S}\xi(r)\hat{\vec{S}} \cdot \hat{\vec{L}} + \cancel{\delta\hat{H}}$$

* $a_r\hat{\vec{p}}^4$: relativistic revise
* $l = 0 \quad \Rightarrow \quad \delta\hat{H} = 0$

- Eigen state $|nljm_j\rangle$, CSSO $\left(\hat{H}^{(0)}, \hat{\vec{L}}^2, \hat{\vec{S}}^2, \hat{\vec{J}}^2, \hat{J}_z\right)$, good quantum number (n, l, s, j, m_j)

  Proof. $[\hat{L}_i, V(r)] = 0 \quad \Rightarrow \quad [\hat{L}_z, \xi(r)] = 0, \qquad [\hat{L}_i, \hat{\vec{L}} \cdot \hat{\vec{S}}] = [\hat{L}_i, \hat{L}_j]\hat{S}_j = i\hbar\varepsilon_{ijk}\hat{L}_k\hat{S}_j \neq 0$
  $[\hat{\vec{L}}^2, \hat{\vec{L}} \cdot \hat{\vec{S}}] = [\hat{\vec{L}}^2, \hat{L}_z]\hat{S}_z = 0, \ [\hat{\vec{S}}^2, \hat{\vec{L}} \cdot \hat{\vec{S}}] = [\hat{\vec{S}}^2, \hat{S}_z]\hat{L}_z = 0$
  $[\hat{J}_i, \hat{\vec{L}} \cdot \hat{\vec{S}}] = [\hat{L}_i, \hat{L}_j\hat{S}_j] + [\hat{S}_i, \hat{L}_j\hat{S}_j] = i\hbar\varepsilon_{ijk}(\hat{L}_k\hat{S}_j + \hat{L}_j\hat{S}_k) = 0$ □

$$|jm\rangle = \sum_{m_1+m_2=m}|j_1m_1j_2m_2\rangle\langle j_1m_1j_2m_2|jm\rangle = \sum_{m_1+m_2=m}|lm_lsm_s\rangle\langle lm_lsm_s|jm\rangle$$

- $m = -j, \cdots, j, \qquad j = |l-s|, \cdots, |l+s|$

Then eigen state $|nljm_j\rangle \to \left(\hat{\vec{J}}^2, \hat{J}_z\right)$ for $\hat{H}_M = \mu_B B\left(\hat{J}_z + \hat{S}_z\right)/\hbar$

$$\langle nljm_j|\hat{H}_M|nljm_j\rangle = \mu_B B\hbar m_j + \langle nljm_j|\hat{S}_z|nljm_j\rangle$$

From projection theorem (Eq: 7.3), $\forall \vec{v}$ in arbitary vector, let $\vec{v} = \vec{S}$,
dot product $\hat{\boldsymbol{e}}_z$ in both sides, yields $\vec{v}\cdot\hat{\boldsymbol{e}}_z = \hat{S}_z$, $\vec{J}\cdot\hat{\boldsymbol{e}}_z = \hat{J}_z$

$$\langle jm|\hat{S}_z|jm\rangle = \frac{\langle jm|\left(\vec{S}\cdot\vec{J}\right)\vec{J}|jm\rangle}{\hbar^2 j(j+1)} = \frac{m_j\langle jm|\hat{\vec{S}}\cdot\vec{J}|jm\rangle}{\hbar j(j+1)}$$

Since $[\hat{J}_i, \hat{S}_i] = [\hat{S}_i, \hat{S}_i] = 0$, $\hat{\vec{L}}^2 = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2\hat{\vec{S}}\cdot\hat{\vec{L}} \quad \Rightarrow \quad \hat{\vec{S}}\cdot\hat{\vec{L}} = \frac{1}{2}\left(\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2\right)$, then

$$\langle jm|\hat{\vec{S}}\cdot\vec{J}|jm\rangle = \frac{\hbar^2}{2}[j(j+1) + s(s+1) + l(l+1)] = \frac{\hbar^2}{2}\left[j(j+1) + \frac{3}{4} + l(l+1)\right]$$

The energy is

$$\Delta E = \langle nljm_j|\hat{H}_M|nljm_j\rangle = m_j\left[1 + \frac{j(j+1) + \frac{3}{4} + l(l+1)}{2j(j+1)}\right]\mu_B B = \mu_B B m_j g_j$$

Landé g factor of an atomic level:

$$g_j = 1 + \frac{j(j+1) + l(l+1) + \frac{3}{4}}{2j(j+1)} \tag{7.2}$$

Projection Theorem:

$$\langle jm|\vec{v}|jm\rangle = \frac{\langle jm|\left(\vec{v}\cdot\vec{J}\right)\vec{J}|jm\rangle}{\langle jm|\vec{J}^2|jm\rangle} = \frac{\langle jm|\left(\vec{v}\cdot\vec{J}\right)\vec{J}|jm\rangle}{\hbar^2 j(j+1)} \tag{7.3}$$

Proof. Since $[\hat{J}_i, \hat{v}_j] = i\hbar\varepsilon_{ijk} \Leftrightarrow \vec{J}\times\vec{v} + \vec{v}\times\vec{J} = 2i\hbar\vec{v} \quad \Rightarrow \quad [\hat{\vec{J}^2}, \vec{v}] = 2i\hbar\left(\vec{v}\times\vec{J} - i\hbar\vec{v}\right) \quad \Rightarrow$
$\frac{1}{(2i\hbar)^2}\left[\hat{\vec{J}}^2, [\hat{\vec{J}}^2, \hat{\vec{v}}]\right] = \left((\hat{\vec{v}}\times\hat{\vec{J}})\cdot\hat{\vec{J}} - \frac{1}{2}(\hat{\vec{v}}\hat{\vec{J}}^2 + \hat{\vec{J}}^2\hat{\vec{v}})\right)$; $\qquad \langle jm|\,\hat{\vec{J}}^2 = \hbar^2 j(j+1)\langle jm|$
$\langle jm|\left[\hat{\vec{J}}^2, [\hat{\vec{J}}^2, \hat{\vec{v}}]\right]|jm\rangle = \langle jm|\hat{\vec{J}}^2[\hat{\vec{J}}^2, \hat{\vec{v}}] - [\hat{\vec{J}}^2, \hat{\vec{v}}]\hat{\vec{J}}^2|jm\rangle \equiv 0 \quad \Rightarrow \quad \left[\hat{\vec{J}}^2, [\hat{\vec{J}}^2, \hat{\vec{v}}]\right] \equiv 0$, therefore
$\langle jm|(\hat{\vec{v}}\cdot\hat{\vec{J}})\vec{J}|jm\rangle = \frac{1}{2}\langle jm|\hat{\vec{J}}^2 + \hat{\vec{v}}\hat{\vec{J}}^2|jm\rangle = \frac{1}{2}\cdot 2\langle jm|\vec{v}|jm\rangle j(j+1)$ □

????

$$\langle nlm_l m_s|\hat{H}_M|nlm_l m_s\rangle = \mu_B B(m_l + 2m_s)$$

- $m_l + 2m_s$ overlap

—————-
Thanks for warching. You are your best!