Quantum Mechanics Note

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Contents

1 Foundamental Posulates

1.1 State Desription

Quantum state is a vector $|\psi\rangle$ in Hilbert space.

definition 1.1.1: Dirac Notation

The **ket** $|\psi\rangle$ is the $n \times 1$ column vector, and the **bra** $\langle\psi| = |\psi\rangle^\dagger$,

$$|\psi\rangle = [\psi_1 \ \cdots \ \psi_n]^\top, \qquad \langle\psi| = [\psi_1^* \ \cdots \ \psi_n^*].$$

The inner product of two vectors $|a\rangle$ and $|b\rangle$ is

$$\langle a|b\rangle := a_1^* b_1 + \cdots + a_n^* b_n = \sum_{i=1}^{n} a_i^* b_i.^{\mathrm{I}}$$

The quantum state should be **normalized**, i.e. $\langle\psi|\psi\rangle = 1$.

[I] I'll omit the upper and lower mark for simplicity.

theorem 1.1.1: Gram-Schmidt

Given a linearly independent bases $|v_1\rangle, \ldots, |v_n\rangle$, we can form linear combinations of the basis vectors to obtain an orthonormal basis.
Thus we could find a set of orthonormal bases $|a_i\rangle$, and

$$\langle a_i|a_j\rangle = \delta_{ij} \qquad \sum |a_i\rangle\langle a_i| = I.$$

In the $|a_i\rangle$ base, the representation of a vector is $|\psi\rangle = \sum \psi_i |a_i\rangle$.

$\langle x|\psi\rangle = \psi(x)$ is the wave function.

1.2 Measurable Physical Properties

Measurable physical properties can be represented by Hermite operator A.

theorem 1.2.1: Eigenvalues of Hermitian

The eigenvalues of Hermite A are **real**, because if $\mathsf{A}|a\rangle = a|a\rangle$,

$$\langle a|\mathsf{A}|a\rangle^\dagger = \langle a|\mathsf{A}|a\rangle,^{\mathrm{I}}$$
$$a^* \langle a|a\rangle = a\langle a|a\rangle,$$

thus $a \in \mathbb{R}$.

[I] Here the dagger symbol acts on the whole bracket $\langle a|\,\mathsf{A}\,|a\rangle$.

theorem 1.2.2: Eigenvectors of Hermitian

The eigenvectors corresponding to different eigenvalues are **orthogonal**, because if $\mathsf{A}\,|a_1\rangle = a_1\,|a_1\rangle\,, \mathsf{A}\,|a_2\rangle = a_2\,|a_2\rangle$

$$\begin{aligned}\langle a_2|\,\mathsf{A}\,|a_1\rangle^\dagger &= \langle a_1|\,\mathsf{A}\,|a_2\rangle\\ a_1^*\,\langle a_1|a_2\rangle &= a_2\,\langle a_1|a_2\rangle\,,\end{aligned}$$

for $a_1^* = a_1 \neq a_2$, $\langle a_1|a_2\rangle = 0$.

1.2.1 Position Operator X

Position operator X in $|x\rangle$ base satisfies: every position $|x\rangle$ is an eigenvector with its position x as the eigenvalue, thus

$$\mathsf{X}\,|x\rangle = x\,|x\rangle\,.$$

The base $|x\rangle$ is continuous, where $x \in \mathbb{R}$, and is orthonormal

$$\langle x'|x\rangle = \delta(x'-x), \qquad \int_{-\infty}^{+\infty} |x\rangle\langle x|\,\mathrm{d}x = I.$$

$\mathsf{X}\,|\psi\rangle$ is a new state, which could be represented as

$$\langle x|\,\mathsf{X}\,|\psi\rangle = x\,\langle x|\psi\rangle = x\psi(x).$$

example 1.2.1: Verifying the Hermitian

X is Hermite because

$$\begin{aligned}\langle\varphi|\,\mathsf{X}\,|\psi\rangle &= \int \langle\varphi|x\rangle\langle x|\,\mathsf{X}\,|\psi\rangle\,\mathrm{d}x\\ &= \int \langle x|\varphi\rangle\,x\,\langle x|\psi\rangle\,\mathrm{d}x = \int x\varphi^*(x)\psi(x)\mathrm{d}x;\\ \langle\psi|\,\mathsf{X}\,|\varphi\rangle &= \int x\psi^*(x)\varphi(x)\,\mathrm{d}x = \langle\varphi|\,\mathsf{X}\,|\psi\rangle^\dagger\,. \quad (x^* = x)\end{aligned}$$

1.2.2 Momentum Operator P

Momentum operator P in $|p\rangle$ base, similarily

$$\mathsf{P}\,|p\rangle = p\,|p\rangle\,.$$

We consider the state $|\psi\rangle$ in $|x\rangle$, $|k\rangle$ base, that $\langle x|\psi\rangle = \psi(x)$, $\langle k|\psi\rangle =: \hat{\psi}(k)$. Then by the **Fourier Transfromation**:

$$\psi(x) = \mathcal{F}^{-1}[\hat{\psi}(k)] = \frac{1}{\sqrt{2\pi}} \int \hat{\psi}(k) \exp(ikx)\, \mathrm{d}k.$$

According to the **de Broglie relation**: $p = \hbar k$, thus $\langle k|\psi\rangle \propto \langle p|\psi\rangle =: \varphi(p)$,

$$\begin{aligned} \psi(x) &\propto \int \varphi(p) \exp\left(i\frac{p}{\hbar}x\right) \mathrm{d}p, \\ \langle x|\psi\rangle &= \int \langle x|p\rangle\langle p|\psi\rangle\, \mathrm{d}p, \end{aligned}$$

the lower formula is the calculation of $\langle x|\psi\rangle$, comparing these two formulas, we could conclude that the eigenfunction $p(x)$ is

$$p(x) = \langle x|p\rangle \propto \exp\left(\frac{ip}{\hbar}x\right),$$

which meets the equation

$$\frac{\mathrm{d}\,\langle x|p\rangle}{\mathrm{d}x} = \frac{ip}{\hbar}\,\langle x|p\rangle\,,$$

From the definition $\mathsf{P}\,|p\rangle = p\,|p\rangle$, we have the eigenfunction $p(x)$ satisfies

$$\langle x|\,\mathsf{P}\,|p\rangle = p\,\langle x|p\rangle = -i\hbar\frac{\mathrm{d}\,\langle x|p\rangle}{\mathrm{d}x}.$$

Therefore, the momentum operator P in $|x\rangle$ base is $\mathsf{P} \to -i\hbar\,\mathrm{d}/\mathrm{d}x$,

$$\langle x|\,\mathsf{P}\,|\psi\rangle = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\,\langle x|\psi\rangle = -i\hbar\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}.$$

example 1.2.2: Verifying the Hermitian

P is Hermite because

$$\begin{aligned} \langle\varphi|\,\mathsf{P}\,|\psi\rangle &= \int \langle\varphi|x\rangle\langle x|\,\mathsf{P}\,|\psi\rangle\,\mathrm{d}x = -i\hbar\int \varphi^*(x)\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\mathrm{d}x \\ &= -i\hbar\left[\cancel{\varphi^*(x)\psi(x)\Big|_{-\infty}^{+\infty}} - \int \psi(x)\frac{\mathrm{d}\varphi^*(x)}{\mathrm{d}x}\mathrm{d}x\right] \\ &= i\hbar\int \psi(x)\frac{\mathrm{d}\varphi^*(x)}{\mathrm{d}x}\mathrm{d}x = \langle\psi|\,\mathsf{P}\,|\varphi\rangle^\dagger\,. \end{aligned}$$

Note: $x \to \infty, \quad \psi(x), \varphi(x) \to 0$

definition 1.2.1: Commutator

The commutator of two operators is

$$[\mathsf{A},\mathsf{B}] := \mathsf{AB}-\mathsf{BA}.$$

And anti-commutator $\{\mathsf{A},\mathsf{B}\} := \mathsf{AB}+\mathsf{BA}$, which is also useful later.

example 1.2.3: $[\mathsf{X},\mathsf{P}]$

$$\begin{aligned}\langle x|\,[\mathsf{X},\mathsf{P}]\,|\psi\rangle &= \langle x|\,\mathsf{XP}\,|\psi\rangle - \langle x|\,\mathsf{PX}\,|\psi\rangle = x\,\langle x|\,\mathsf{P}\,|\psi\rangle - \langle x|\,\mathsf{P}\,(\,\mathsf{X}\,|\psi\rangle\,) \\ &= -\,i\hbar\left(x\frac{\mathrm{d}\,\langle x|\psi\rangle}{\mathrm{d}x} - \frac{\mathrm{d}\,\langle x|\,\mathsf{X}\,|\psi\rangle}{\mathrm{d}x}\right) = -i\hbar\left(x\frac{\mathrm{d}\,\langle x|\psi\rangle}{\mathrm{d}x} - \frac{\mathrm{d}x\,\langle x|\psi\rangle}{\mathrm{d}x}\right) \\ &= -\,i\hbar\left[\cancel{x\frac{\mathrm{d}\,\langle x|\psi\rangle}{\mathrm{d}x}} - \left(\cancel{x\frac{\mathrm{d}\,\langle x|\psi\rangle}{\mathrm{d}x}} + \langle x|\psi\rangle\right)\right] = i\hbar\,\langle x|\psi\rangle\,,\end{aligned}$$

then we conclude that

$$[\mathsf{X},\mathsf{P}] = i\hbar.$$

3-D case $\mathsf{P}\to -i\hbar\nabla$,

$$\langle \boldsymbol{r}|\,\mathsf{P}\,|\psi\rangle = -i\hbar\nabla\psi(\boldsymbol{r}) = -i\hbar\left(\frac{\partial\psi}{\partial x}\hat{\boldsymbol{\imath}} + \frac{\partial\psi}{\partial y}\hat{\boldsymbol{\jmath}} + \frac{\partial\psi}{\partial z}\hat{\boldsymbol{k}}\right).$$

1.2.3 Angular Momentum Operator L

The classical angular momentum is

$$\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p}.$$

In the quantum, the momentum $\mathsf{P} = -i\hbar\nabla$, and

$$\begin{aligned}\mathsf{L} &= -i\hbar\,\boldsymbol{r}\times\nabla \\ &= -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\,,\, z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\,,\, x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]^{\top},\end{aligned}$$

$\mathsf{L}_x, \mathsf{L}_y, \mathsf{L}_z$ are three portions of L, and the angular momentum squared is

$$\mathsf{L}^2 = \mathsf{L}_x^2 + \mathsf{L}_y^2 + \mathsf{L}_z^2.$$

example 1.2.4: $[\mathsf{L}_x, \mathsf{L}_y]$ & $[\mathsf{L}^2, \mathsf{L}_x]$

$$\mathsf{L}_x\mathsf{L}_y = -\hbar^2\left(y\frac{\partial}{\partial x} + \cancel{yz\frac{\partial^2}{\partial z\partial x}} - \cancel{xy\frac{\partial^2}{\partial z^2}} - \cancel{z^2\frac{\partial^2}{\partial y\partial x}} + \cancel{xz\frac{\partial^2}{\partial y\partial z}}\right);$$

$$\mathsf{L}_y\mathsf{L}_x = -\hbar^2\left(\cancel{yz\frac{\partial^2}{\partial x\partial z}} - \cancel{z^2\frac{\partial^2}{\partial x\partial y}} - \cancel{xy\frac{\partial^2}{\partial z^2}} + x\frac{\partial}{\partial y} + \cancel{xz\frac{\partial^2}{\partial z\partial y}}\right),$$

$$[\mathsf{L}_x, \mathsf{L}_y] = -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) = i\hbar\,\mathsf{L}_z.$$

Similarly,

$$[\mathsf{L}_x, \mathsf{L}_y] = i\hbar\,\mathsf{L}_z \quad [\mathsf{L}_y, \mathsf{L}_z] = i\hbar\,\mathsf{L}_x, \quad [\mathsf{L}_z, \mathsf{L}_x] = i\hbar\,\mathsf{L}_y.$$

Then calculate $[\mathsf{L}^2, \mathsf{L}_x] = [\mathsf{L}_x^2, \mathsf{L}_x] + [\mathsf{L}_y^2, \mathsf{L}_x] + [\mathsf{L}_z^2, \mathsf{L}_x]$,

$$\begin{aligned}
[\mathsf{L}_x^2, \mathsf{L}_x] &= \mathsf{L}_x^3 - \mathsf{L}_x^3 = 0,\\
[\mathsf{L}_y^2, \mathsf{L}_x] &= \mathsf{L}_y[\mathsf{L}_y, \mathsf{L}_x] + [\mathsf{L}_y, \mathsf{L}_x]\mathsf{L}_y\\
&= -i\hbar\,\mathsf{L}_y\mathsf{L}_z - i\hbar\,\mathsf{L}_z\mathsf{L}_y = -i\hbar\,\{\mathsf{L}_y, \mathsf{L}_z\},\\
[\mathsf{L}_z^2, \mathsf{L}_x] &= \mathsf{L}_z[\mathsf{L}_z, \mathsf{L}_x] + [\mathsf{L}_z, \mathsf{L}_x]\mathsf{L}_z = i\hbar\,\{\mathsf{L}_z, \mathsf{L}_y\}.
\end{aligned}$$

Thus

$$[\mathsf{L}^2, \mathsf{L}_x] = 0 - i\hbar\,\{\mathsf{L}_y, \mathsf{L}_z\} + i\hbar\,\{\mathsf{L}_z, \mathsf{L}_y\} = 0.$$

Similarly,

$$[\mathsf{L}^2, \mathsf{L}_x] = [\mathsf{L}^2, \mathsf{L}_y] = [\mathsf{L}^2, \mathsf{L}_z] = 0.$$

definition 1.2.2: Ladder Operator

Define the useful ladder operator $\mathsf{L}_\pm := \mathsf{L}_x \pm i\,\mathsf{L}_y$.

example 1.2.5: Denote L^2 by $\mathsf{L}_\pm$ & L_z

$\mathsf{L}^2 = \mathsf{L}_\pm\mathsf{L}_\mp + \mathsf{L}_z^2 \mp \hbar\,\mathsf{L}_z$, because

$$\begin{aligned}
\mathsf{L}_\pm\mathsf{L}_\mp &= (\mathsf{L}_x \pm i\,\mathsf{L}_y)(\mathsf{L}_x \mp i\,\mathsf{L}_y)\\
&= \mathsf{L}_x^2 + \mathsf{L}_y^2 \mp i\,(\mathsf{L}_x\mathsf{L}_y - \mathsf{L}_y\mathsf{L}_x) = \mathsf{L}^2 - \mathsf{L}_z^2 \pm \hbar\,\mathsf{L}_z.
\end{aligned}$$

From the definition, its commutator with $\mathsf{L}_z, \mathsf{L}^2$ is

$$[\mathsf{L}_z, \mathsf{L}_\pm] = \pm\hbar\,\mathsf{L}_\pm, \quad [\mathsf{L}^2, \mathsf{L}_\pm] = 0.$$

As $[\mathsf{L}^2, \mathsf{L}_z] = 0$, $\mathsf{L}_2, \mathsf{L}_z$ have the same eigenfunction $|\psi\rangle$, i.e.

$$\mathsf{L}^2 |\psi\rangle = \lambda |\psi\rangle , \quad \mathsf{L}_z |\psi\rangle = \mu |\psi\rangle .$$

Considering $\mathsf{L}_\pm |\psi\rangle$,

$$\mathsf{L}^2 \mathsf{L}_\pm |\psi\rangle = \mathsf{L}_\pm \mathsf{L}^2 |\psi\rangle = \lambda \mathsf{L}_\pm |\psi\rangle ,$$

$|\psi\rangle$, $\mathsf{L}_\pm |\psi\rangle$ share the **same** eigenvalue of L^2.

$$\mathsf{L}_z \mathsf{L}_\pm |\psi\rangle = (\mathsf{L}_\pm \mathsf{L}_z \pm \hbar\, \mathsf{L}_\pm) |\psi\rangle = (\mu \pm \hbar) \mathsf{L}_\pm |\psi\rangle .$$

We call L_+ the **rasing operator**, as it increases the eigenvalue of L_z by $\hbar$, and L_- the **lowering operator**.

Simplify $|\psi_n\rangle := \mathsf{L}_+^n |\psi\rangle$, $(n \geqslant 0)$

$$\left\langle \mathsf{L}^2 \right\rangle = \langle \psi_n | \mathsf{L}^2 |\psi_n\rangle = \lambda.$$

$$\left\langle \mathsf{L}_z^2 \right\rangle = \langle \psi_n | \mathsf{L}_z^2 |\psi_n\rangle = (\mu + n\hbar)^2.$$

While

$$\left\langle \mathsf{L}^2 \right\rangle = \left\langle \mathsf{L}_x^2 \right\rangle + \left\langle \mathsf{L}_y^2 \right\rangle + \left\langle \mathsf{L}_z^2 \right\rangle \geqslant \left\langle \mathsf{L}_z^2 \right\rangle .$$

Hence, the rising progress can't go on forever, there must exist a **top** $|\psi_t\rangle$:

$$\mathsf{L}_+ |\psi_t\rangle = 0, \qquad \text{then } |\psi_n\rangle \equiv 0, \ \forall\, n > t.$$

Let $\ell\hbar$ be the eigenvalue of L_z at $|\psi_t\rangle$, i.e. $\mathsf{L}_z |\psi_t\rangle = \ell\, \hbar\, |\psi_t\rangle$.

$$\begin{aligned} \mathsf{L}^2 |\psi_t\rangle &= (\mathsf{L}_- \mathsf{L}_+ + \mathsf{L}_z^2 + \hbar\, \mathsf{L}_z) |\psi_t\rangle \\ &= (0 + \ell^2 \hbar^2 + \ell\, \hbar^2) |\psi_t\rangle = \ell(\ell+1)\hbar^2 |\psi_t\rangle . \end{aligned}$$

Also, there exists a **bottom** $|\psi_b\rangle$ that $\mathsf{L}_- |\psi_b\rangle = 0$, $\mathsf{L}_z |\psi_b\rangle = \jmath\, \hbar\, |\psi_b\rangle$

$$\begin{aligned} \mathsf{L}^2 |\psi_b\rangle &= (\mathsf{L}_+ \mathsf{L}_- + \mathsf{L}_z^2 - \hbar \mathsf{L}_z) |\psi_b\rangle \\ &= (0 + \jmath^2 \hbar^2 - \jmath\, \hbar^2) |\psi_b\rangle = \jmath(\jmath - 1)\hbar^2 |\psi_b\rangle . \end{aligned}$$

Because $\forall\, n, \mathsf{L}^2 |\psi_n\rangle \equiv \lambda |\psi_n\rangle$,

$$\lambda = \ell(\ell+1)\hbar^2 = \jmath(\jmath-1)\hbar^2 \quad \Rightarrow \quad \jmath = -\ell \text{ or } \cancel{\jmath = \ell + 1}.$$

While $\mathsf{L}_z |\psi\rangle = m\hbar |\psi\rangle$, where $m = -\ell, \ldots, \ell$ in N integer steps, hence, $2\ell \in \mathbb{N}$. $|\psi\rangle$ contains two numbers ℓ, m, using the notation $|\ell, m\rangle := |\psi\rangle$ is more clear for different $|\psi\rangle$,

$$\mathsf{L}^2 |\ell, m\rangle = \ell(\ell+1)\hbar^2 |\ell, m\rangle , \quad \mathsf{L}_z |\ell, m\rangle = m\hbar |\ell, m\rangle .$$

where $\ell = 0, 1/2, 1, 3/2, \ldots; m = -\ell, -\ell+1, \ldots, \ell$.

example 1.2.6: $\mathsf{L}_\pm$ changes m

$\mathsf{L}_\pm$ changes the value of m, i.e.

$$\mathsf{L}_+ \left|\ell, m\right\rangle = \alpha \left|\ell, m+1\right\rangle, \quad \mathsf{L}_- \left|\ell, m+1\right\rangle = \beta \left|\ell, m\right\rangle,$$

We set $\alpha, \beta \in \mathbb{R}_+$.

$$\left(\mathsf{L}_+ \left|\ell, m\right\rangle\right)^\dagger = \left\langle\ell, m\right| \mathsf{L}_- = \alpha \left\langle\ell, m+1\right|,$$

right multiply $\left|\ell, m+1\right\rangle$,

$$\begin{aligned}\left\langle\ell, m\right| \mathsf{L}_- \left|\ell, m+1\right\rangle = \beta \left\langle\ell, m|\ell, m\right\rangle &= \alpha \left\langle\ell, m+1|\ell, m+1\right\rangle, \\ \Rightarrow \quad \alpha &= \beta.\end{aligned}$$

$$\begin{aligned}\mathsf{L}_-\mathsf{L}_+ \left|\ell, m\right\rangle &= \left(\mathsf{L}^2 - \mathsf{L}_z^2 - \hbar\,\mathsf{L}_z\right)\left|\ell, m\right\rangle \\ \alpha^2 \left|\ell, m\right\rangle &= [\ell(\ell+1) - m(m+1)]\hbar^2 \left|\ell, m\right\rangle.\end{aligned}$$

$$\Rightarrow \quad \mathsf{L}_\pm \left|\ell, m\right\rangle = \sqrt{\ell(\ell+1) - m(m\pm1)}\hbar \left|\ell, m\pm1\right\rangle.$$

Spherical Expression The nabla in spherical coordinate,

$$\nabla = \frac{\partial}{\partial r}\hat{\boldsymbol{r}} + \frac{1}{r}\frac{\partial}{\partial\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat{\boldsymbol{\phi}}.$$

Because $\boldsymbol{r} = r\,\hat{\boldsymbol{r}}$, and $\hat{\boldsymbol{r}} \times \hat{\boldsymbol{r}} = \boldsymbol{0}, \hat{\boldsymbol{r}} \times \hat{\boldsymbol{\theta}} = \hat{\boldsymbol{\phi}}, \hat{\boldsymbol{r}} \times \hat{\boldsymbol{\phi}} = -\hat{\boldsymbol{\theta}}$,

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

Back to Cartesian components,

$$\begin{aligned}\hat{\boldsymbol{\theta}} &= \cos\theta\cos\phi\,\hat{\boldsymbol{i}} + \cos\theta\sin\phi\,\hat{\boldsymbol{j}} - \sin\theta\,\hat{\boldsymbol{k}}, \\ \hat{\boldsymbol{\phi}} &= -\sin\phi\,\hat{\boldsymbol{i}} + cos\phi\,\hat{\boldsymbol{j}}.\end{aligned}$$

Evidently,

$$\begin{aligned}\mathsf{L}_x &= +i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right), \\ \mathsf{L}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right),\end{aligned} \qquad \mathsf{L}_z = -i\hbar\frac{\partial}{\partial\phi}.$$

Then,

$$\mathsf{L}_\pm = \mathsf{L}_x \pm i\,\mathsf{L}_y = \hbar\,e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\phi\frac{\partial}{\partial\phi}\right).$$

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

$$\mathsf{L}^2 = \mathsf{L}_+\mathsf{L}_- + \mathsf{L}_z^2 - \hbar\,\mathsf{L}_z = -\hbar^2\Lambda^2,$$

where the Legendrian

$$\Lambda^2 := \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2},$$

the eigenfunction of L^2, i.e.

$$\mathsf{L}^2\psi = -\hbar^2\Lambda^2\psi = \lambda\psi,$$

is the Legendre function we'll solve in H-Atom.[I]

[I]Note, parenthetically, that eigenfunctions of L^2 have been known since the 19th century, long before quantum mechanics was born.

1.2.4 Function of Operator

Using the **Taylor Expansion**

$$f(x)=\sum_{k=0}^{\infty}\frac{f^{(k)}(0)}{k!}x^k=f(0)+f'(0)x+\frac{1}{2}f''(0)x^2+\cdots,$$

just replace x by A,

$$f(\mathsf{A})=\sum_{k=0}^{\infty}\frac{f^{(k)}(0)}{k!}\mathsf{A}^k=f(0)+f'(0)\mathsf{A}+\frac{1}{2}f''(0)\mathsf{A}^2+\cdots.$$

theorem 1.2.3: About eigenvectors

If $\mathsf{A}\,|a_i\rangle=a_i\,|a_i\rangle$, then

$$f(\mathsf{A})\,|a_i\rangle=f(a_i)\,|a_i\rangle\,.$$

Because $\mathsf{A}^n\,|a_i\rangle=a_i^n\,|a_i\rangle$ and $f(\mathsf{A})=\sum c_n\mathsf{A}^n$

$$f(\mathsf{A})\,|a_i\rangle=\sum c_n\mathsf{A}^n\,|a_i\rangle=f(a_i)\,|a_i\rangle\,.$$

thus $f(\mathsf{A})=\sum f(\mathsf{A})\,|a_i\rangle\langle a_i|=\sum f(a_i)\,|a_i\rangle\langle a_i|$.

example 1.2.7: K & $V(\mathsf{X})$

Kinetic energy $\mathsf{K}:=K(\mathsf{P})=\dfrac{\mathsf{P}^2}{2m}$, and potential energy function $V(\mathsf{X})$

$$\begin{aligned}\langle x|\,\mathsf{K}\,|\psi\rangle=&\frac{1}{2m}\,\langle x|\,\mathsf{P}^2\,|\psi\rangle=\frac{1}{2m}\,\langle x|\,\mathsf{P}(\mathsf{P}\,|\psi\rangle)\\=&\frac{\hbar}{2im}\frac{\mathrm{d}\,\langle x|\,\mathsf{P}\,|\psi\rangle}{\mathrm{d}x}=-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}.\\\langle x|\,V(\mathsf{X})\,|\psi\rangle=&\int\langle x|\,V(\mathsf{X})\,|x'\rangle\,\langle x'|\psi\rangle\,\mathrm{d}x'\\=&\int V(x')\,\langle x|x'\rangle\,\psi(x')\mathrm{d}x'=V(x)\psi(x).\end{aligned}$$

And the Hamiltonian $\mathsf{H}=\mathsf{K}+V(\mathsf{X})$.

theorem 1.2.4: About Commutator

Commutator is anti-Hermite, because

$$[\mathsf{A},\mathsf{B}]^\dagger=\mathsf{B}^\dagger\mathsf{A}^\dagger-\mathsf{A}^\dagger\mathsf{B}^\dagger=\mathsf{BA}-\mathsf{AB}=-[\mathsf{A},\mathsf{B}],$$

The first thing about commutator is that

$$[\mathsf{A}, \mathsf{A}^n] = 0, \qquad \forall\, n \in \mathbb{N}.$$

Therefore,

$$[\mathsf{A}, f(\mathsf{A})] = 0.$$

Commutator is much like cross product for they both satisfy the **inverse exchange law**:

$$[\mathsf{B}, \mathsf{A}] = -[\mathsf{A}, \mathsf{B}] \quad \leftrightarrow \quad \boldsymbol{b} \times \boldsymbol{a} = -\boldsymbol{a} \times \boldsymbol{b}.$$

In cross product, we have the Lagrange equation:

$$(\boldsymbol{a} \times \boldsymbol{b}) \times \boldsymbol{c} = (\boldsymbol{a} \cdot \boldsymbol{c})\, \boldsymbol{b} - \boldsymbol{a}\, (\boldsymbol{b} \cdot \boldsymbol{c});$$
$$\boldsymbol{a} \times (\boldsymbol{b} \times \boldsymbol{c}) = \boldsymbol{b}\, (\boldsymbol{a} \cdot \boldsymbol{c}) - (\boldsymbol{a} \cdot \boldsymbol{b})\, \boldsymbol{c}.$$

In the commutator, the relation is similar:

- $[\mathsf{AB}, \mathsf{C}] = [\mathsf{A}, \mathsf{C}]\mathsf{B} + \mathsf{A}[\mathsf{B}, \mathsf{C}]$

$$\begin{aligned} [\mathsf{AB}, \mathsf{C}] &= \mathsf{ABC} - \mathsf{CAB} \\ &= \mathsf{ABC} - \mathsf{ACB} + \mathsf{ACB} - \mathsf{CAB} = [\mathsf{A}, \mathsf{C}]\mathsf{B} + \mathsf{A}[\mathsf{B}, \mathsf{C}]. \end{aligned}$$

- $[\mathsf{A}, \mathsf{BC}] = \mathsf{B}[\mathsf{A}, \mathsf{C}] + [\mathsf{A}, \mathsf{B}]\mathsf{C}$

$$\begin{aligned} [\mathsf{A}, \mathsf{BC}] &= \mathsf{ABC} - \mathsf{BCA} \\ &= \mathsf{BAC} - \mathsf{BCA} + \mathsf{ABC} - \mathsf{BAC} = \mathsf{B}[\mathsf{A}, \mathsf{C}] + [\mathsf{A}, \mathsf{B}]\mathsf{C}. \end{aligned}$$

Let $\mathsf{B} = \mathsf{C}$, then

$$[\mathsf{A}, \mathsf{B}^2] = \mathsf{B}[\mathsf{A}, \mathsf{B}] + [\mathsf{A}, \mathsf{B}]\mathsf{B} = \{[\mathsf{A}, \mathsf{B}], \mathsf{B}\}.$$

Especially, when $\mathsf{B}[\mathsf{A}, \mathsf{B}] = [\mathsf{A}, \mathsf{B}]\mathsf{B}$,

- $\begin{aligned}[t] [\mathsf{A}, \mathsf{B}^n] =& [\mathsf{A}, \mathsf{B}^{n-1}]\mathsf{B} + [\mathsf{A}, \mathsf{B}]\mathsf{B}^{n-1} \\ =& [\mathsf{A}, \mathsf{B}^{n-2}]\mathsf{B}^2 + 2[\mathsf{A}, \mathsf{B}]\mathsf{B}^{n-1} = \cdots = n[\mathsf{A}, \mathsf{B}]\mathsf{B}^{n-1} \end{aligned}$
- $\begin{aligned}[t] [\mathsf{A}, f(\mathsf{B})] &= \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!}[\mathsf{A}, \mathsf{B}^n] = \sum_{n=1}^{\infty} \frac{f^{(n)}(0)}{n!}[\mathsf{A}, \mathsf{B}]n\mathsf{B}^{n-1} \\ &= \sum_{n=1}^{\infty} \frac{f^{(n)}(0)}{(n-1)!}\mathsf{B}^{n-1}[\mathsf{A}, \mathsf{B}] = f'(\mathsf{B})[\mathsf{A}, \mathsf{B}]. \end{aligned}$

1.3 Measurement

The system in a state $|\psi\rangle$ which is normalized, and A is any operator observable, then $|\psi\rangle$ can be represented as

$$|\psi\rangle = \sum |a_i\rangle\langle a_i|\psi\rangle = \sum c_i\, |a_i\rangle$$

where $c_i = \langle a_i|\psi\rangle$ is the probability amplitude of getting $|a_i\rangle$ if measuring A.

1.3.1 Probability and Expectation

The possibility of getting a_i is

$$P(a_i) = |c_i|^2 = |\langle a_i|\psi\rangle|^2 .$$

The expectation result when measuring A is

$$\langle \mathsf{A}\rangle = \sum P(a_i)a_i = \sum |c_i|^2 a_i.$$

theorem 1.3.1

$$\langle \mathsf{A}\rangle = \langle\psi|\, \mathsf{A}\, |\psi\rangle .$$

Proof: $$\begin{aligned}\langle\psi|\, \mathsf{A}\, |\psi\rangle &= \sum \langle\psi|\, \mathsf{A}\, |a_i\rangle\langle a_i|\psi\rangle = \sum \langle\psi|\, a_i\, |a_i\rangle\langle a_i|\psi\rangle \\ &= \sum a_i \,\langle\psi|a_i\rangle\, \langle a_i|\psi\rangle = \sum |c_i|^2 a_i,\end{aligned}$$

For continuous case, the **probability density** is

$$P(x) = |\langle x|\psi\rangle|^2 = |\psi(x)|^2,$$
$$\langle\psi|\psi\rangle = \int \langle\psi|x\rangle\langle x|\psi\rangle\, \mathrm{d}x = \int |\psi(x)|^2 \mathrm{d}x = \int P(x)\, \mathrm{d}x = 1.$$

$P(x)\, \mathrm{d}x$ is the probability between x and $x + \mathrm{d}x$.
And the average

$$\langle \mathsf{A}\rangle = \langle\psi|\, \mathsf{A}\, |\psi\rangle = \int \langle\psi|\, \mathsf{A}\, |x\rangle\langle x|\psi\rangle\, \mathrm{d}x$$

example 1.3.1

The average of x, p is

$$\langle \mathsf{X}\rangle = \int x|\psi(x)|^2 \mathrm{d}x, \quad \langle \mathsf{P}\rangle = -i\hbar \int \psi'(x)\psi^*(x)\mathrm{d}x$$

Warning: $\langle \mathsf{P}\rangle = \xcancel{\int p(x)|\psi(x)|^2 \mathrm{d}x}.$

1.3.2 Uncertainty

If the measurements result in many values, then the deviation is $\Delta\mathsf{A} = \mathsf{A} - \langle \mathsf{A} \rangle$

$$\left\langle \Delta\mathsf{A}^2 \right\rangle = \left\langle (\mathsf{A} - \langle \mathsf{A} \rangle)^2 \right\rangle = \left\langle \mathsf{A}^2 - 2\mathsf{A}\langle \mathsf{A} \rangle + \langle \mathsf{A} \rangle^2 \right\rangle$$
$$= \left\langle \mathsf{A}^2 \right\rangle - 2\langle \mathsf{A} \rangle\langle \mathsf{A} \rangle + \langle \mathsf{A} \rangle^2 = \left\langle \mathsf{A}^2 \right\rangle - \langle \mathsf{A} \rangle^2 .$$

Define the uncertainty $\sigma_{\mathsf{A}}^2 := \left\langle \Delta\mathsf{A}^2 \right\rangle$.[II]

theorem 1.3.2: Uncertainty Principle

lemma Schwarz

$$\langle \alpha|\alpha \rangle\langle \beta|\beta \rangle \geqslant |\langle \alpha|\beta \rangle|^2 . \tag{1}$$

Proof: $\forall\lambda \in \mathbb{R}$,

$$||\alpha\rangle + \lambda\,|\beta\rangle|^2 = (\langle \alpha| + \lambda\,\langle \beta|)(|\alpha\rangle + \lambda\,|\beta\rangle)$$
$$= \langle \alpha|\alpha \rangle + \lambda\,(\langle \alpha|\beta \rangle + \langle \beta|\alpha \rangle) + \lambda^2\,\langle \beta|\beta \rangle \geqslant 0,$$

for λ, it is a quadratic inequality, so

$$\Delta = (2\,\mathrm{Re}\langle \alpha|\beta \rangle)^2 - 4\,\langle \alpha|\alpha \rangle\langle \beta|\beta \rangle$$
$$= 4\,|\langle \alpha|\beta \rangle|^2 - 4\,\langle \alpha|\alpha \rangle\langle \beta|\beta \rangle \leqslant 0,$$

that is what we need to proof. lemma If $\mathsf{A}^\dagger = \mathsf{A}$ Hermitian, $\langle \mathsf{A} \rangle \in \mathbb{R}$ for

$$\langle \psi|\,\mathsf{A}\,|\psi\rangle^\dagger = \langle \psi|\,\mathsf{A}^\dagger\,|\psi\rangle = \langle \psi|\,\mathsf{A}\,|\psi\rangle .$$

If $\mathsf{A}^\dagger = -\mathsf{A}$ anti-Hermitian, $\langle \mathsf{A} \rangle \in i\,\mathbb{R}$ for

$$\langle \psi|\,\mathsf{A}\,|\psi\rangle^\dagger = \langle \psi|\,\mathsf{A}^\dagger\,|\psi\rangle = -\,\langle \psi|\,\mathsf{A}\,|\psi\rangle .$$

We take $|\alpha\rangle \to \Delta\mathsf{A}\,|\psi\rangle\,, |\beta\rangle \to \Delta\mathsf{B}\,|\psi\rangle$, from the Schwarz Lemma,

$$\sigma_{\mathsf{A}}^2\sigma_{\mathsf{B}}^2 = \left\langle \Delta\mathsf{A}^2 \right\rangle\left\langle \Delta\mathsf{B}^2 \right\rangle \geqslant |\langle \Delta\mathsf{A}\Delta\mathsf{B} \rangle|^2 .$$

Noticing that

$$\langle \Delta\mathsf{A}\Delta\mathsf{B} \rangle = \langle (\mathsf{A} - \langle \mathsf{A} \rangle)(\mathsf{B} - \langle \mathsf{B} \rangle) \rangle = \langle \mathsf{AB} \rangle - \langle \mathsf{A} \rangle\langle \mathsf{B} \rangle .$$

Decompose AB,

$$\mathsf{AB} = \tfrac{1}{2}[\mathsf{A}, \mathsf{B}] + \tfrac{1}{2}\{\mathsf{A}, \mathsf{B}\},$$

$[\mathsf{A}, \mathsf{B}] = \mathsf{AB} - \mathsf{BA}$ is anti-Hermitian, and $\{\mathsf{A}, \mathsf{B}\} = \mathsf{AB} + \mathsf{BA}$ is Hermitian,

$$\langle \Delta\mathsf{A}\Delta\mathsf{B} \rangle = \langle \mathsf{AB} \rangle + \langle \mathsf{A} \rangle\langle \mathsf{B} \rangle = \underbrace{\tfrac{1}{2}\,\langle [\mathsf{A}, \mathsf{B}] \rangle}_{\text{Im-part}} + \underbrace{\tfrac{1}{2}\,\langle \{\mathsf{A}, \mathsf{B}\} \rangle - \langle \mathsf{A} \rangle\langle \mathsf{B} \rangle}_{\text{Re-part}}.$$

[II] Textbooks tend to confuse $\Delta\mathsf{A}$ and σ_{A}, it's understandable because $\Delta\mathsf{A}$'s original definition in a single experiment doesn't matter.

Then

$$\sigma_{\mathsf{A}}\sigma_{\mathsf{B}} \geqslant |\langle \Delta\mathsf{A}\Delta\mathsf{B}\rangle| \geqslant |\mathrm{Im}\langle \Delta\mathsf{A}\Delta\mathsf{B}\rangle| = \tfrac{1}{2}\,|\langle[\mathsf{A},\mathsf{B}]\rangle|\,.$$

For $[\mathsf{X},\mathsf{P}] = i\hbar$, we conduct the **Uncertainty Principle**

$$\sigma_{\mathsf{X}}\sigma_{\mathsf{P}} \geqslant \frac{\hbar}{2},$$

which means we can't precisely measure X and P simultaneously.

1.4 Schrödinger Equation

The Schrödinger Equation is

$$i\hbar\frac{\mathrm{d}\,|\psi\rangle}{\mathrm{d}t} = \mathsf{H}\,|\psi\rangle\,, \tag{2}$$

where Hamiltonian $\mathsf{H} = \mathsf{K} + V(\mathsf{X})$.

1.4.1 Time Dependent Schrödinger Equation

Left multiply Eqn.(2) by $\langle x|$, we get

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t), \tag{3}$$

definition 1.4.1: Probability Current

Let's review the calculation of

$$P(a \leqslant x \leqslant b) = \int_a^b |\psi(x)|^2\mathrm{d}x.$$

From Sch-Eqn.(3): $\dfrac{\partial\psi}{\partial t} = \dfrac{i\hbar}{2m}\dfrac{\partial^2\psi}{\partial x^2} + \dfrac{1}{i\hbar}V\psi,$

$$\begin{aligned}
\frac{\mathrm{d}P}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\int_a^b \psi^*\psi\mathrm{d}x = \int_a^b \left(\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t}\right)\mathrm{d}x \\
&= \int_a^b \left[\left(-\frac{i\hbar}{2m}\frac{\partial^2\psi^*}{\partial x^2} - \cancel{\frac{1}{i\hbar}V\psi^*}\right)\psi + \psi^*\left(\frac{i\hbar}{2m}\frac{\partial^2\psi}{\partial x^2} + \cancel{\frac{1}{i\hbar}V\psi}\right)\right]\mathrm{d}x \\
&= \frac{i\hbar}{2m}\int_a^b \left(\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right)\mathrm{d}x = \frac{i\hbar}{2m}\int_a^b \frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)\mathrm{d}x \\
&= \frac{i\hbar}{2m}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]_a^b =: j(a,t) - j(b,t),
\end{aligned}$$

where $j := \dfrac{i\hbar}{2m}\left(\psi\dfrac{\partial\psi^*}{\partial x} - \psi^*\dfrac{\partial\psi}{\partial x}\right)$ is the **probability current**.

Directly solving Eqn.(3) is difficult, we need the eigenfunctions.

1.4.2 Time Independent Schrödinger Equation

If we use $|E\rangle$ base, which is the eigenvector of H, i.e.

$$\mathsf{H}\,|E\rangle = E\,|E\rangle\,, \tag{4}$$

and left multiply Eqn.(2) by $\langle E|$,

$$\langle E|\,\mathsf{H}\,|\psi\rangle = i\hbar\frac{\mathrm{d}\,\langle E|\psi\rangle}{\mathrm{d}t} = E\,\langle E|\psi\rangle\,.$$

Define $\zeta(t) := \langle E|\psi\rangle$ as a function of t, then

$$i\hbar\frac{\mathrm{d}\zeta(t)}{\mathrm{d}t} = E\zeta(t),$$

which is easy to solve and the solution is

$$\zeta(t) = \zeta(0)e^{E/i\hbar\,t}.$$

Because $|\psi\rangle = \sum |E_n\rangle\langle E_n|\psi\rangle = \sum \zeta_n(t)\,|E_n\rangle$,

$$|\psi\rangle = \sum \zeta_n(0)e^{-i\omega_n t}\,|E_n\rangle\,,\quad \omega_n = \frac{E_n}{\hbar},$$

Define $\psi(x) := \langle x|E\rangle$, left multiply Eqn.(4) by $\langle x|$,

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x). \tag{5}$$

Clarify Here $\psi(x)$ is **different** from $\psi(x,t)$ in Eqn.(3). $\psi(x,t)$ is the wave function; $\psi(x)$ is the eigenfunction of Eqn.(5), and it's independent of t.

Link Taking different E_n, we get a series of $\psi_n(x)$ by sloving Eqn.(5), $|E_n\rangle$ is the base in space so

$$\psi(x,0) = \sum c_n\psi_n(x),$$

then as t evolves,

$$\psi(x,t) = \sum c_n e^{-i\omega_n t}\psi_n(x),\quad \omega_n = \frac{E_n}{\hbar}.$$

1.4.3 Ehrenfest Theorem

theorem 1.4.1: Ehrenfest

$$\frac{\mathrm{d}\langle \mathsf{A}\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\langle [\mathsf{A},\mathsf{H}]\rangle .$$

Proof: $\frac{\mathrm{d}\langle \mathsf{A}\rangle}{\mathrm{d}t} = \frac{\mathrm{d}\langle\psi|\mathsf{A}|\psi\rangle}{\mathrm{d}t} = \frac{\mathrm{d}\langle\psi|}{\mathrm{d}t}\mathsf{A}|\psi\rangle + \langle\psi|\mathsf{A}\frac{\mathrm{d}|\psi\rangle}{\mathrm{d}t}$.[I]

From Sch-Eqn.(2): $\frac{\mathrm{d}|\psi\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\mathsf{H}|\psi\rangle$, $\frac{\mathrm{d}\langle\psi|}{\mathrm{d}t} = -\frac{1}{i\hbar}\langle\psi|\mathsf{H}$, hence,

$$\frac{\mathrm{d}\langle \mathsf{A}\rangle}{\mathrm{d}t} = \left(-\frac{1}{i\hbar}\langle\psi|\mathsf{H}\right)\mathsf{A}|\psi\rangle + \langle\psi|\mathsf{A}\left(\frac{1}{i\hbar}\mathsf{H}|\psi\rangle\right) = \frac{1}{i\hbar}\langle [\mathsf{A},\mathsf{H}]\rangle .$$

[I] Most operators are independent of time, i.e. $\partial\mathsf{A}/\partial t \equiv 0$.

example 1.4.1: $\mathsf{A} = \mathsf{X}$

$$\frac{\mathrm{d}\langle \mathsf{X}\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\langle [\mathsf{X},\mathsf{H}]\rangle = \frac{\langle \mathsf{P}\rangle}{m}.$$

For

$$[\mathsf{X},\mathsf{H}] = \frac{1}{2m}[\mathsf{X},\mathsf{P}^2] + [\mathsf{X},V(\mathsf{X})] = \frac{\mathsf{P}}{m}[\mathsf{X},\mathsf{P}] + 0 = \frac{i\hbar}{m}\mathsf{P}.$$

This makes perfect sense because in classic

$$v = \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{p}{m}.$$

example 1.4.2: $\mathsf{A} = \mathsf{P}$

$$\frac{\mathrm{d}\langle \mathsf{P}\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\langle [\mathsf{P},\mathsf{H}]\rangle = -\langle V'(\mathsf{X})\rangle .$$

For

$$[\mathsf{P},\mathsf{H}] = \frac{1}{2m}[\mathsf{P},\mathsf{P}^2] + [\mathsf{P},V(\mathsf{X})] = 0 + V'(\mathsf{X})[\mathsf{P},\mathsf{X}] = -i\hbar V'(\mathsf{X}).$$

This alse makes sense,

$$F = \frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\mathrm{d}V(x)}{\mathrm{d}x}.$$

In 3-D space,

$$\frac{\mathrm{d}\langle \mathsf{P}\rangle}{\mathrm{d}t} = -\langle \nabla V\rangle ,$$

and for the angular momentum, like $\boldsymbol{\tau} = \frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}t} = \boldsymbol{r} \times \boldsymbol{F}$,

$$\frac{\mathrm{d}\langle \mathsf{L} \rangle}{\mathrm{d}t} = \langle -\boldsymbol{r} \times \nabla V(\boldsymbol{r}) \rangle$$

theorem 1.4.2: Time-Energy Uncertainty Principle

Let's go back to the Uncertainty Principle

$$\sigma_{\mathsf{A}} \sigma_{\mathsf{B}} \geqslant \frac{1}{2} \left| \langle [\mathsf{A}, \mathsf{B}] \rangle \right|,$$

when $\mathsf{B} \equiv \mathsf{H}$, from Ehrenfest Theorem: $\langle [\mathsf{A}, \mathsf{H}] \rangle = i\hbar \, \mathrm{d}\langle \mathsf{A} \rangle / \mathrm{d}t$

$$\sigma_{\mathsf{A}} \sigma_{\mathsf{H}} \geqslant \frac{1}{2} \left| \langle [\mathsf{A}, \mathsf{H}] \rangle \right| = \frac{\hbar}{2} \left| \frac{\mathrm{d}\langle \mathsf{A} \rangle}{\mathrm{d}t} \right|,$$

when $\mathsf{A} \equiv \mathsf{T}$, which is the time operator

$$\sigma_{\mathsf{T}} \sigma_{\mathsf{H}} \geqslant \frac{\hbar}{2}.$$

1.5 Conclusion

General strategy working on Quantum.

- Predict measurement result.

$$\mathsf{A} \left| a_i \right\rangle = a_i \left| a_i \right\rangle, \quad \left| \psi \right\rangle = \sum \langle a_i | \psi \rangle | a_i \rangle .$$

- Transfromation between bases.

$$\mathsf{B} \left| b_j \right\rangle = b_j \left| b_j \right\rangle, \quad \left| \psi \right\rangle = \sum \langle b_j | \psi \rangle | b_j \rangle .$$
$$\langle b_j | \psi \rangle = \sum \langle b_j | a_i \rangle \langle a_i | \psi \rangle .$$

- Time evolution - Expand as components of $|\psi_{E_a}\rangle$.

1.5.1 Example: Spin-1/2 System

There is another type of angular momentum, called **spin angular momentum**, represented by the spin operator

$$\mathsf{S} = \mathsf{S}_x\hat{\boldsymbol{i}} + \mathsf{S}_y\hat{\boldsymbol{j}} + \mathsf{S}_z\hat{\boldsymbol{k}},$$

and the eigenvalue is just the same as the orbit angular momentum,[III]

$$\mathsf{S}^2 |s, s_z\rangle = s(s+1)\hbar^2 |s, s_z\rangle, \quad \mathsf{S}_z |s, s_z\rangle = s_z\hbar |s, s_z\rangle.$$

where $s = 0, 1/2, 1, 3/2, \dots; s_z = -s, -s+1, \dots, s$.

example 1.5.1: Stern–Gerlach Experiment

In classic, the magnetic dipole $\boldsymbol{\mu}$ of an electron rotating in a circle is

$$\boldsymbol{\mu} := I\boldsymbol{S} = \frac{ev}{2\pi r} \cdot \pi r^2\,\hat{\boldsymbol{n}} = \frac{evr}{2}\hat{\boldsymbol{n}}.$$

While the angular momentum of electron is $\boldsymbol{L} = -mvr\hat{\boldsymbol{n}}$,

$$\boldsymbol{\mu} = g_L\boldsymbol{L}, \qquad g_L = -\frac{e}{2m}.$$

In quantum,

$$\boldsymbol{\mu} = g_s\mathsf{S}, \qquad g_s = g_0 g_L,$$

interestingly, $g_0 = 2.00\cdots$ is not a integer.
When magnetic pole $\boldsymbol{\mu}$ interacts with magnetic feild $\boldsymbol{B}$, the torque

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \boldsymbol{B}.$$

Then the energy

$$U = \int \mu B \sin\theta \,\mathrm{d}\theta = -\mu B\cos\theta = -\boldsymbol{\mu}\cdot\boldsymbol{B}.$$

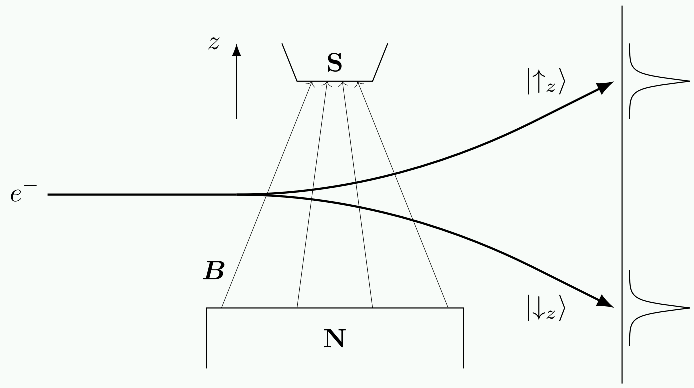
In the experiment, $\boldsymbol{B} = B_z\hat{\boldsymbol{k}}$, thus

$$\mathsf{H} = -g_s\mathsf{S}_z B_z.$$

Shoot electrons into a magnetic field $\boldsymbol{B}$ whose z-axis direction field strength B_z is not a const, then the electrons will be deflected

$$F = -\frac{\partial H_{\text{int}}}{\partial z} = g_z S_z \frac{\mathrm{d}B_z}{\mathrm{d}z},$$

[III] Spin is often depicted as a particle literally spinning around an axis, but this is only a metaphor: spin is an intrinsic property of a particle, unrelated to any sort of (yet experimentally observable) motion in space. All elementary particles have a characteristic spin, which is usually nonzero. For example, electrons always have spin-1/2 while photons always have spin-1.



Stern–Gerlach Experiment Setup

Eventually there are two bands shown on the screen, indicating that there are only two values for the spin S_z of the electron, i.e.

$$\begin{aligned} s_z &= \pm\tfrac{1}{2}, &\quad \mathsf{S}_z &\to \pm\tfrac{1}{2}\hbar, \\ s &= \tfrac{1}{2}, &\quad |\mathsf{S}| &\to \tfrac{\sqrt{3}}{2}\hbar, \end{aligned}$$

which is the **spin-1/2 system**.

Define the spin notation:

$$|\uparrow_z\rangle := \left|s = \tfrac{1}{2}, s_z = \tfrac{1}{2}\right\rangle, \quad |\downarrow_z\rangle := \left|s = \tfrac{1}{2}, s_z = -\tfrac{1}{2}\right\rangle.$$

In the $|\uparrow_z\rangle, |\downarrow_z\rangle$ base,

$$|\uparrow_z\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |\downarrow_z\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

As

$$\mathsf{S}_z |\uparrow_z\rangle = \frac{\hbar}{2} |\uparrow_z\rangle, \quad \mathsf{S}_z |\downarrow_z\rangle = -\frac{\hbar}{2} |\downarrow_z\rangle.$$

Thus

$$\mathsf{S}_z = \frac{\hbar}{2} |\uparrow_z\rangle\langle\uparrow_z| - \frac{\hbar}{2} |\downarrow_z\rangle\langle\downarrow_z| = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

Transformation between bases After the S-G experimental setup, $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$ are separated, and the percent is 50%-50%, then shoot the $|\uparrow_z\rangle$ part into another S-G setup, however, this time along x-axis, the outcome is that $|\uparrow_x\rangle$ and $|\downarrow_x\rangle$ are separated, and the percent is also 50%-50%, i.e.

$$|\langle\uparrow_x|\uparrow_z\rangle|^2 = \frac{1}{2}, \quad |\langle\downarrow_x|\uparrow_z\rangle|^2 = \frac{1}{2}.$$

Then we can let

$$\begin{aligned}|\uparrow_x\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle + \frac{1}{\sqrt{2}}e^{i\theta_+}|\downarrow_z\rangle,\\ |\downarrow_x\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle + \frac{1}{\sqrt{2}}e^{i\theta_-}|\downarrow_z\rangle,\end{aligned}$$

where $e^{i\theta_+}, e^{i\theta_-}$ are just the phase difference,

$$|\langle\downarrow_x|\uparrow_x\rangle|^2 = \frac{1}{2} + \frac{1}{2}\cos(\theta_+ - \theta_-) = 0,$$

thus $e^{i\theta_-} = -e^{i\theta_+}$. For y-axis, similarily,

$$\begin{aligned}|\uparrow_x\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle + \frac{1}{\sqrt{2}}e^{i\theta_+}|\downarrow_z\rangle, &\quad |\uparrow_y\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle + \frac{1}{\sqrt{2}}e^{i\theta'_+}|\downarrow_z\rangle,\\ |\downarrow_x\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle - \frac{1}{\sqrt{2}}e^{i\theta_+}|\downarrow_z\rangle, &\quad |\downarrow_y\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle - \frac{1}{\sqrt{2}}e^{i\theta'_+}|\downarrow_z\rangle,\end{aligned}$$

while

$$|\langle\uparrow_x|\uparrow_y\rangle|^2 = \frac{1}{2} + \frac{1}{2}\cos(\theta'_+ - \theta_+) = \frac{1}{2},$$

the convention is to set $\theta_+ = 0, \theta'_+ = \pi/2$, i.e.

$$\begin{aligned}|\uparrow_x\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle + \frac{1}{\sqrt{2}}|\downarrow_z\rangle, &\quad |\uparrow_y\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle + \frac{i}{\sqrt{2}}|\downarrow_z\rangle,\\ |\downarrow_x\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle - \frac{1}{\sqrt{2}}|\downarrow_z\rangle, &\quad |\downarrow_y\rangle &= \frac{1}{\sqrt{2}}|\uparrow_z\rangle - \frac{i}{\sqrt{2}}|\downarrow_z\rangle,\end{aligned}$$

thus,

$$\mathsf{S}_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}, \quad \mathsf{S}_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix},$$

$\mathsf{S}_x, \mathsf{S}_y, \mathsf{S}_z$ contains the Pauli spin matrixes

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

For any a normalized vector

$$\hat{\boldsymbol{u}} = [\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta]^\top,$$

the spin operator along this direction is

$$\begin{aligned}\mathsf{S}_u = \hat{\boldsymbol{u}}\cdot\mathsf{S} &= \frac{\hbar}{2}(\sin\theta\cos\phi\ \sigma_x + \sin\theta\sin\phi\ \sigma_y + \cos\theta\ \sigma_z)\\ &= \frac{\hbar}{2}\begin{bmatrix}\cos\theta & \sin\theta e^{-i\phi}\\ \sin\theta e^{i\phi} & -\cos\theta\end{bmatrix}.\end{aligned}$$

The eigenvalues are still $\pm\hbar/2$ and the eigenvectors

$$\begin{aligned}
\mathsf{S}_u \left|\uparrow_u\right\rangle &= \frac{\hbar}{2}\left|\uparrow_u\right\rangle, \quad \mathsf{S}_u \left|\downarrow_u\right\rangle = -\frac{\hbar}{2}\left|\downarrow_u\right\rangle, \\
\left|\uparrow_u\right\rangle &= +\cos\frac{\theta}{2}e^{-i\phi/2}\left|\uparrow_z\right\rangle + \sin\frac{\theta}{2}e^{i\phi/2}\left|\downarrow_z\right\rangle, \\
\left|\downarrow_u\right\rangle &= -\sin\frac{\theta}{2}e^{-i\phi/2}\left|\uparrow_z\right\rangle + \cos\frac{\theta}{2}e^{i\phi/2}\left|\downarrow_z\right\rangle,
\end{aligned}$$

Predict the measurements

$$\begin{aligned}
P(s_z = \tfrac{1}{2}) &= \left|\langle\uparrow_z|\uparrow_u\rangle\right|^2 = \cos^2\frac{\theta}{2}; \\
P(s_x = \tfrac{1}{2}) &= \left|\langle\uparrow_x|\uparrow_u\rangle\right|^2 = \frac{1}{2}\left|\cos\frac{\theta}{2}e^{-i\phi/2} + \sin\frac{\theta}{2}e^{i\phi/2}\right|^2 \\
&= \frac{1}{2}\left(1 + \sin\theta\cos\phi\right); \\
P(s_y = \tfrac{1}{2}) &= \left|\langle\uparrow_y|\uparrow_u\rangle\right|^2 = \frac{1}{2}\left|\cos\frac{\theta}{2}e^{-i\phi/2} + i\sin\frac{\theta}{2}e^{i\phi/2}\right|^2 \\
&= \frac{1}{2}\left(1 + \sin\theta\sin\phi\right).
\end{aligned}$$

Evolution in a const B_0

$$\mathsf{H} = -g_s\mathsf{S}_z B_0 = \Omega\,\mathsf{S}_z, \quad \Omega := -g_s B_0,$$

then $\left|\uparrow_z\right\rangle, \left|\downarrow_z\right\rangle$ are the eigenvectors of H

$$\mathsf{H}\left|\uparrow_z\right\rangle = \frac{\hbar\Omega}{2}\left|\uparrow_z\right\rangle, \qquad \mathsf{H}\left|\downarrow_z\right\rangle = -\frac{\hbar\Omega}{2}\left|\downarrow_z\right\rangle,$$

then time evolution for $|\psi\rangle = \left|\uparrow_u\right\rangle$

$$|\psi(t)\rangle = \cos\frac{\theta}{2}e^{-i(\phi+\Omega t)/2}\left|\uparrow_z\right\rangle + \sin\frac{\theta}{2}e^{i(\phi+\Omega t)/2}\left|\downarrow_z\right\rangle$$

The probability evolving with time is

$$\begin{aligned}
P(s_z = \tfrac{1}{2}) &= \cos^2\frac{\theta}{2}, \\
P(s_x = \tfrac{1}{2}) &= \frac{1}{2}[1 + \sin\theta\cos(\phi + \Omega t)].
\end{aligned}$$

S_z is a well state because it commute with H

$$\langle\mathsf{S}_z\rangle = \cos^2\frac{\theta}{2}\cdot\frac{\hbar}{2} + \sin^2\frac{\theta}{2}\left(-\frac{\hbar}{2}\right) = \frac{\hbar\cos\theta}{2}, \qquad \frac{\mathrm{d}\langle\mathsf{S}_z\rangle}{\mathrm{d}t} = 0.$$

2 Simple Systems

2.1 Free Particle

Free means $V(x) \equiv 0$, then $|p\rangle$ is the eigenvector of H because

$$\mathsf{H}|p\rangle = \frac{\mathsf{P}^2}{2m}|p\rangle = \frac{p^2}{2m}|p\rangle,$$
$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad \omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}.$$

Knowing $\psi(x,0)$, we could know $\hat{\psi}(k)$,

$$\hat{\psi}(k) = \mathcal{F}[\psi(x,0)] = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\psi(x,0)e^{-ikx}\mathrm{d}x,$$

then we will know

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\hat{\psi}(k)e^{ikx}e^{-i\frac{\hbar k^2}{2m}t}\mathrm{d}k$$

example 2.1.1: Trivial

$$|\psi_0\rangle = |p_0\rangle, \psi(x,0) = \frac{1}{\sqrt{2\pi\hbar}}e^{ik_0 x}, \quad k_0 := \frac{p_0}{\hbar}.$$

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}e^{i(k_0 x - \omega t)}, \quad \omega = \frac{\hbar k_0^2}{2m}.$$

Phase speed $v_\varphi = \frac{\omega}{k_0} = \frac{\hbar k_0}{2m}$; and group speed $v_g = \frac{\mathrm{d}\omega}{\mathrm{d}k} = \frac{\hbar k_0}{m} = \frac{p_0}{m}$.

example 2.1.2: Gaussian Wavepacket

The Gaussian wavepacket is

$$\psi(x,0) = Ae^{-x^2/\sigma^2}e^{ik_0 x},$$

A is the normalization coefficient

$$\int_{-\infty}^{+\infty} e^{-2x^2/\sigma^2}\mathrm{d}x = \sqrt{\frac{\pi}{2}}\sigma, \qquad A = \sqrt[4]{\frac{2}{\pi\sigma^2}}.$$

Work out $\hat{\psi}(k) = \mathcal{F}[\psi(x,0)]$

$$\hat{\psi}(k) = \sqrt[4]{\frac{\sigma^2}{2\pi}}e^{-\sigma^2(k-k_0)^2/4}.$$

Then

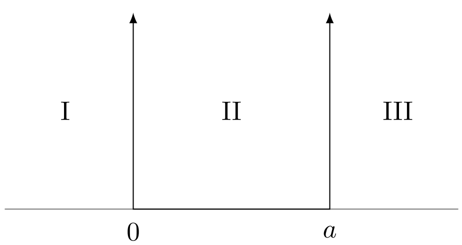
$$\begin{aligned}\psi(x,t) &= \frac{1}{\sqrt{2\pi}}\sqrt[4]{\frac{\sigma^2}{2\pi}}\int_{-\infty}^{+\infty} e^{-\frac{\sigma^2(k-k_0)^2}{4}} e^{ikx} e^{-i\frac{\hbar k^2}{2m}t}\mathrm{d}k \\ &= \sqrt[4]{\frac{\sigma^2}{2\pi}}\frac{e^{i(k_0x-\varphi_0)}}{\sqrt[4]{\sigma^4+\frac{4\hbar^2t^2}{m^2}}}\exp\left[-\frac{\left(x-\frac{\hbar k_0}{m}t\right)^2}{\sigma^2+\frac{2i\hbar t}{m}}\right].\end{aligned}$$

where $\varphi_0 = \dfrac{1}{2}\arctan\dfrac{2\hbar t}{m\sigma^2} + \dfrac{\hbar k_0^2}{2m}t$.[I]

$$|\psi(x,t)|^2 = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{\sigma^2+\frac{4\hbar^2t^2}{m^2\sigma^2}}}\exp\left[-\frac{2\left(x-\frac{\hbar k_0}{m}t\right)^2}{\sigma^2+\frac{4\hbar^2t^2}{m^2\sigma^2}}\right].$$

[I] Everyone should calculate it once in their lifetime. - Shuo Jiang.

2.2 Infinite Potential Well



$$V(x) = \begin{cases} 0\ , & 0 \leqslant x \leqslant a \\ \infty, & \text{elsewhere} \end{cases}.$$

In region I and III, $\psi \equiv 0$, in region II, use Eqn.(5)

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi, \qquad k^2 := \frac{2mE}{\hbar^2}$$

then

$$\psi = Ae^{ikx} + Be^{-ikx} = C\cos kx + D\sin kx.$$

Boundary condition:

$$\begin{cases} \psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0), \\ \psi_{\mathrm{II}}(a) = \psi_{\mathrm{III}}(a), \end{cases} \quad \Rightarrow \quad \begin{cases} C = 0, \\ D\sin ka = 0, \end{cases}$$

thus $ka = n\pi$, after normalized,

$$\psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right), \quad E_n = \frac{\hbar^2k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

If we shift the rigion II to the center $-a/2 \leqslant x \leqslant a/2$, then

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x + \frac{n\pi}{2}\right) = \begin{cases} (-1)^k \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), & n = 2k+1, \\ (-1)^k \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi}{a}x\right), & n = 2k. \end{cases}$$

which is either odd or even.

example 2.2.1: Verifying the Uncertainty Principle

ψ_n^2 is even, $x\psi_n^2$ and $\psi_n^* \psi_n'$ is always odd.

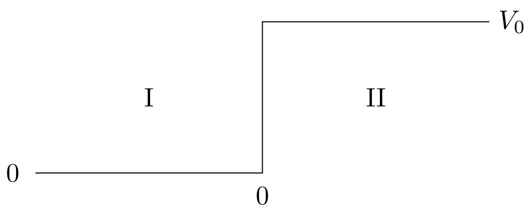
$$\langle \mathsf{X} \rangle = \int_{-a/2}^{a/2} x\psi_n^2 \mathrm{d}x = 0. \qquad \langle \mathsf{P} \rangle = -i\hbar \int_{-a/2}^{a/2} \psi_n^* \psi_n' \mathrm{d}x = 0.$$

$$\begin{aligned} \left\langle \mathsf{X}^2 \right\rangle &= \int_{-a/2}^{a/2} x^2 \psi_n^2 \mathrm{d}x = \frac{2}{a} \int_{-a/2}^{a/2} \frac{x^2}{2} \left[1 - \cos\left(\frac{2n\pi}{a}x + n\pi\right)\right] \mathrm{d}x \\ &= \left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right) a^2. \\ \left\langle \mathsf{P}^2 \right\rangle &= -\hbar^2 \int_{-a/2}^{a/2} \psi_n^* \psi_n'' \mathrm{d}x = \frac{n^2\pi^2\hbar^2}{a^2} \int_{-a/2}^{a/2} \psi_n^2 \mathrm{d}x = \frac{n^2\pi^2\hbar^2}{a^2}. \end{aligned}$$

Thus

$$\sigma_{\mathsf{X}} \sigma_{\mathsf{P}} = \frac{\hbar}{2} \sqrt{\frac{n^2\pi^2}{3} - 2} \geqslant \frac{\hbar}{2} \sqrt{\frac{\pi^2}{3} - 2} \doteq 1.1357 \times \frac{\hbar}{2} > \frac{\hbar}{2}.$$

2.3 Potential Step



$$V(x) = \begin{cases} 0\ , x \leqslant 0 \\ V_0, x > 0 \end{cases}.$$

1. $E > V_0$

$$\begin{aligned} &\mathrm{I}: \quad \frac{\mathrm{d}^2\psi_{\mathrm{I}}}{\mathrm{d}x^2} + \frac{2mE}{\hbar^2}\psi_{\mathrm{I}} = 0, && k_1^2 := \frac{2mE}{\hbar^2}, \\ &\mathrm{II}: \quad \frac{\mathrm{d}^2\psi_{\mathrm{II}}}{\mathrm{d}x^2} + \frac{2m(E - V_0)}{\hbar^2}\psi_{\mathrm{II}} = 0, && k_2^2 := \frac{2m(E - V_0)}{\hbar^2}. \end{aligned}$$

$$\Rightarrow \quad \psi_{\mathrm{I}} = Ae^{ik_1x} + Be^{-ik_1x}, \quad \psi_{\mathrm{II}} = Ce^{ik_2x} + De^{-ik_2x}.$$

Boundary condition at $x = 0$:

$$\begin{cases} \psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0) \\ \psi'_{\mathrm{I}}(0) = \psi'_{\mathrm{II}}(0) \end{cases} \Rightarrow \begin{cases} A + B = C + D \\ k_1 A - k_1 B = k_2 C - k_2 D \end{cases}$$

$$\Rightarrow \begin{bmatrix} 1 & 1 \\ k_1 & -k_1 \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ k_2 & -k_2 \end{bmatrix} \begin{bmatrix} C \\ D \end{bmatrix}.$$

We have the transfromation

$$\begin{bmatrix} A \\ B \end{bmatrix} = \mathsf{M} \begin{bmatrix} C \\ D \end{bmatrix}, \quad \begin{bmatrix} B \\ C \end{bmatrix} = \mathsf{S} \begin{bmatrix} A \\ D \end{bmatrix},$$

where M is the transfer matrix, S is the reflect matrix,

$$\mathsf{M} = \frac{1}{2k_2} \begin{bmatrix} k_1 + k_2 & k_2 - k_1 \\ k_2 - k_1 & k_1 + k_2 \end{bmatrix}, \quad \mathsf{S} = \frac{1}{k_1 + k_2} \begin{bmatrix} k_2 - k_1 & 2k_2 \\ 2k_1 & k_2 - k_1 \end{bmatrix}.$$

Suppose incident wave only from left ($D = 0$):

$$\frac{B}{A} = \mathsf{S}_{11} = \frac{k_1 - k_2}{k_1 + k_2}, \qquad \frac{C}{A} = \mathsf{S}_{21} = \frac{2k_2}{k_1 + k_2}.$$

For a wave $\psi = Ae^{-ikx}$, its pribability current

$$j = \frac{i\hbar}{2m} \left(\psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right) = |A|^2 \frac{\hbar k}{m},$$

then the Reflection Probability R and the Transmission Probability T is

$$R = \frac{j_r}{j_i} = \left| \frac{B}{A} \right|^2 \frac{k_1}{k_1} = \left(\frac{k_1 - k_2}{k_1 + k_2} \right)^2,$$

$$T = \frac{j_t}{j_i} = \left| \frac{C}{A} \right|^2 \frac{k_2}{k_1} = \frac{4k_1 k_2}{(k_1 + k_2)^2}.$$

thus $R + T = 1$.

2. $0 < E < V_0$ **Evanescent Wave**

$$k_1^2 = \frac{2mE}{\hbar^2}, \qquad \psi_{\mathrm{I}} = Ae^{ik_1 x} + Be^{-ik_1 x},$$

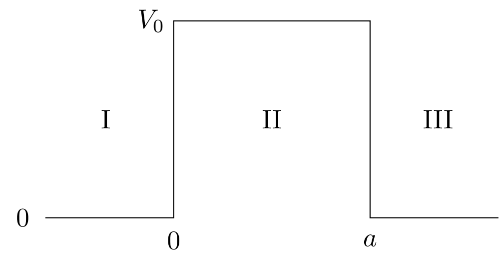
$$\kappa_2^2 = \frac{2m(V_0 - E)}{\hbar^2}, \qquad \psi_{\mathrm{II}} = Ce^{-\kappa_2 x}. \ (De^{\kappa_2 x} \text{ diverges})$$

Then the boundary condition is

$$\begin{cases} A + B = C \\ ik_1 A - ik_1 B = \kappa_2 C \end{cases} \Rightarrow \qquad \frac{B}{A} = \frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}, \quad \frac{C}{A} = \frac{2k_1}{k_1 + i\kappa_2},$$

you'll notice that $R = 1$, actually it makes sense because ψ_{II} contains no wave, it dosen't spread energy, thus $T = 0$.

2.4 Potential Barrier



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

1. $E > V_0$ **Transmission**

$$k_1^2 = \frac{2mE}{\hbar^2}, \qquad \psi_{\mathrm{I}} = Ae^{ik_1x} + Be^{-ik_1x},$$
$$\psi_{\mathrm{II}} = Ce^{ik_2x} + De^{-ik_2x},$$
$$k_2^2 = \frac{2m(E-V_0)}{\hbar^2}, \qquad \psi_{\mathrm{III}} = Fe^{ik_1x} + Ge^{-ik_1x}.$$

Boundary condition:

$$\begin{aligned} A + B &= C + D \\ k_1A - k_1B &= k_2C - k_2D \\ Ce^{ik_2a} + De^{-ik_2a} &= Fe^{ik_1a} + Ge^{-ik_2a} \\ k_2Ce^{ik_2a} - k_2De^{-ik_2a} &= k_1Fe^{ik_1a} - k_1Ge^{-ik_2a}. \end{aligned}$$

Let $G = 0$,

$$\begin{bmatrix} C \\ D \end{bmatrix} = \mathsf{M}_{\mathrm{I}} \begin{bmatrix} A \\ B \end{bmatrix}, \quad \begin{bmatrix} F \\ G \end{bmatrix} = \mathsf{M}_{\mathrm{II}} \begin{bmatrix} C \\ D \end{bmatrix} = \mathsf{M} \begin{bmatrix} A \\ B \end{bmatrix}, \quad \begin{bmatrix} B \\ F \end{bmatrix} = \mathsf{S} \begin{bmatrix} A \\ G \end{bmatrix}.$$

The transmission probability is

$$T = \left[1 + \frac{1}{4}\left(\frac{k_1^2 - k_2^2}{k_1k_2}\right)^2 \sin^2 k_2a\right]^{-1} = \left[1 + \frac{\sin^2 k_2a}{4\varepsilon(\varepsilon-1)}\right]^{-1}, \varepsilon := \frac{E}{V_0} > 1,$$

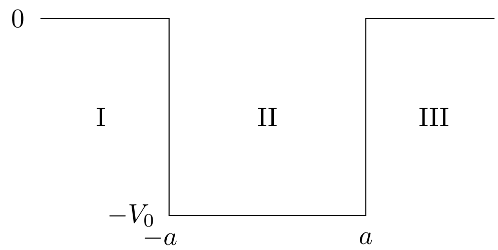
when $k_2a = m\pi$, $T_{\max} = 1$.

2. $0 < E < V_0$ **Tunneling**

$$T = \left[1 + \frac{1}{4}\left(\frac{k_1^2 + \kappa_2^2}{k_1\kappa_2}\right)^2 \sinh^2 \kappa_2a\right]^{-1} = \left[1 + \frac{\sinh^2 \kappa_2a}{4\varepsilon(1-\varepsilon)}\right]^{-1} \doteq 16\varepsilon(1-\varepsilon)e^{-2\kappa_2a},$$

where $\kappa_2^2 = \dfrac{2m(V_0-E)}{\hbar^2}$, thus there exists the poprability of tunneling the barrier.

2.5 Finite Potential Well



$$V(x) = \begin{cases} -V_0, & -a \leqslant x \leqslant a \\ 0\ , & \text{elsewhere} \end{cases}.$$

1. $-V_0 < E < 0$

$$k_1^2 = -\frac{2mE}{\hbar^2}, \qquad \psi_{\mathrm{I}} = Ae^{k_1 x}, \ (Be^{-k_1 x} \text{ diverges})$$
$$\psi_{\mathrm{II}} = C\cos k_2 x + D \sin k_2 x,$$
$$k_2^2 = \frac{2m(E+V_0)}{\hbar^2}, \qquad \psi_{\mathrm{III}} = Ge^{-k_1 x}. \ (Fe^{k_1 x} \text{ diverges})$$

theorem 2.5.1: Even Potential

If $V(x)$ is even, ψ can have either even or odd solution.

For even ψ, $D = 0, G = A$. Boundary condition at $x = a$,

$$\begin{cases} Ae^{-k_1 a} = C\cos k_2 a \\ k_1 Ae^{-k_1 a} = k_2 C \sin k_2 a \end{cases} \Rightarrow \quad \tan k_2 a = \frac{k_1}{k_2} = \sqrt{\frac{2mV_0}{\hbar^2 k_2^2} - 1}.$$

Define $z := k_2 a, z_0^2 := \dfrac{2mV_0 a^2}{\hbar^2}$ (z_0 is the potnetial parameter),

$$\tan z = \sqrt{\frac{z_0^2}{z^2} - 1}.$$

For odd ψ, the equation is

$$-\cot z = \sqrt{\frac{z_0^2}{z^2} - 1}.$$

When $V_0 \to \infty$, $z = \dfrac{\pi}{2}, \pi, \dfrac{3\pi}{2}, \ldots$, with is exactly the infinite well condition. The number of the bound state is fixed by z_0:

$$\frac{n}{2}\pi < z_0 < \frac{n+1}{2}\pi, \quad \to \quad (n+1) \text{ states}.$$

2. $E > 0$ The condition is the same as 2.4 Barrier $E > V_0$.

2.6 Harmonic Oscillator

$V(x) = \frac{1}{2}kx^2$, the Time Independent Schrödinger Equation is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}kx^2\psi = E\psi.$$

$\omega^2 := \frac{k}{m}, \xi := \sqrt{\frac{m\omega}{\hbar}}x, K := \frac{2E}{\hbar\omega}$, the equation becomes

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} + (K - \xi^2)\psi = 0, \tag{6}$$

which is Hermite Equation.
Considering the asymptote behavior: when $\xi \to \infty$, Eqn.(6) approach

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} - \xi^2\psi = 0,$$

thus when $\xi \to \infty$, $\psi \to Ae^{-\xi^2/2}$ ($Be^{\xi^2/2}$ diverges unless $B \equiv 0$).
Guess $A = h(\xi)$, expand it

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{i=0}^{\infty} a_i\xi^i,$$

because $V(x)$ is even, $h(\xi)$ can be either odd or even, i.e.

$$h(\xi) = \sum_{m=0}^{\infty} a_j\xi^j, \quad j \equiv 2m \text{ xor } j \equiv 2m+1.$$ [IV]

Substitute into the original Eqn.(6),

$$\begin{aligned}
\frac{\mathrm{d}\psi}{\mathrm{d}\xi} &= (h' - \xi h)\, e^{-\xi^2/2},\\
\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} &= [h'' - 2\xi h' + (\xi^2 - 1)h]e^{-\xi^2/2},\\
\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} + (K - \xi^2)\psi &= [h'' - 2\xi h' + (K-1)h]e^{-\xi^2/2}.
\end{aligned}$$

Thus $h'' - 2\xi h' + (K-1)h = 0$:

$$\begin{gathered}
\sum_{m=0}^{\infty} j(j-1)a_j\xi^{j-2} - 2\sum_{m=0}^{\infty} ja_j\xi^j + (K-1)\sum_{m=0}^{\infty} a_j\xi^j = 0,\\
\Rightarrow \quad a_{j+2} = \frac{2j+1-K}{(j+2)(j+1)}a_j.
\end{gathered}$$

[IV] The xor (exclusive or) means either one, but not both. Its symbol $\oplus$ is too ugly to use.

When $j \to \infty$,

$$\frac{a_{j+2}\xi^{j+2}}{a_j \xi^j} \to \frac{\xi^2}{m}.$$

While $e^{\xi^2} = \sum_{m=0}^{\infty} \frac{\xi^{2m}}{m!}$, i.e.

$$h(\xi) \to e^{\xi^2}, \quad \psi \to e^{\xi^2/2} \text{ (diverges)}.$$

The only way out of the dilemma is $a_j = 0$ when $j \geqslant n$, i.e. $K = 2n+1$,

$$E_n = \frac{\hbar\omega}{2}K = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots.$$

For the certain n, $\psi_n = h_n(\xi)e^{-\xi^2/2}$, then work out the coefficients through the recursion

$$a_{j-2} = \frac{j(j-1)}{2(j-n-2)}a_j, \quad j = n, n-2, \ldots,$$

and the normalization $\langle \psi_n | \psi_n \rangle = 1$.

example 2.6.1: $n = 0$

$h(\xi) = a_0$, $\psi_0 = a_0 e^{-\xi^2/2}$,

$$\int_{-\infty}^{+\infty} \psi_0^2 \mathrm{d}x = a_0^2 \int_{-\infty}^{+\infty} e^{-m\omega x^2/\hbar}\mathrm{d}x = a_0^2 \sqrt{\frac{\pi\hbar}{m\omega}} = 1.$$

Thus $\psi_0 = \sqrt[4]{\frac{m\omega}{\pi\hbar}} e^{-\xi^2/2}$.

The general wave function is

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

where the Hermite Polynomial

$$H_n(x) = (-1)^n e^{x^2} \frac{\mathrm{d}^n}{\mathrm{d}x^n} e^{-x^2}.$$

example 2.6.2: Table of Hermite

The first few items are

$$\begin{aligned} &H_0 = 1, && H_2 = 4x^2 - 2, && H_4 = 16x^4 - 48x^2 + 12, \\ &H_1 = 2x, && H_3 = 8x^3 - 12x, && H_5 = 32x^5 - 160x^3 + 120x. \end{aligned}$$

2.7 Hydrogen Atom

For a system consists of a proton p and a electron e, the distance between is r. The Hamiltonian in $|x\rangle$ base is

$$\mathsf{H} = -\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r),$$

Decompose H into the free-particle motion of the total mass, and relative motion of reduced mass.

For the center of mass part, $M = m_p + m_e$, $R_{CM} = \dfrac{m_p R_p + m_e R_e}{m_p + m_e}$; for the reduced mass part, $m = \dfrac{m_p m_e}{m_p + m_e}$, $r = R_p - R_e$.

$$\mathsf{H}_{CM} = -\frac{\hbar^2}{2M}\nabla_{CM}^2, \qquad \mathsf{H}_m = -\frac{\hbar^2}{2m}\nabla_r^2 + V(r).$$

We know how to solve the free particle and here we shall only concentrate on the relative motion $\psi(r,\theta,\phi)$:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi. \tag{7}$$

Separation of Variables Since the potential $V(r)$ only depends on distance, not on direction. It has the spherical symmetry, in spherical coordinate

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

Because the three variables r,θ,ϕ are independent, the wave function can be decomposed, i.e.

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi),$$

where the $R(r)$ is the radial part, and $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ is the angular part. Then substitute into the Eqn.(7),

$$-\frac{\hbar^2}{2mr^2}\left[\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + (V-E)RY = 0,$$
$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2mr^2}{\hbar^2}(V-E) = -\frac{1}{Y}\Lambda^2 Y,$$

Thus $LHS(r) = RHS(\theta,\phi) = J$ (constant).

The Legendrian Λ^2 have been mentioned in angular momentum, and Y is the eigenfunction of L^2

$$\mathsf{L}^2 Y = -\hbar^2\Lambda^2 Y = J\hbar^2 Y.$$

2.7.1 Solution of Legendrian

$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$, separate variables,

$$-\frac{1}{\Theta\Phi}\left[\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\frac{1}{\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}\right] = J,$$
$$\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+J\sin^2\theta = -\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}.$$

$\Rightarrow \quad LHS(\theta) = RHS(\phi) = m^2$ (constant).

Solving Φ in the RHS

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+m^2\Phi = 0, \quad \Rightarrow \quad \Phi(\phi) = e^{im\phi}.$$

As $\Phi(\phi+2\pi) = \Phi(\phi)$, $m = 0, \pm1, \pm2, \ldots; \Phi$ is the eigenfunction of L_z

$$\mathsf{L}_z\Phi = -i\hbar\frac{\partial\Phi}{\partial\phi} = m\hbar\Phi.$$

Solving Θ in the LHS [V]

$$\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+J\sin^2\theta = m^2.$$

Let $x = \cos\theta, y = \Theta(\theta)$, then

$$\left(1-x^2\right)\frac{\mathrm{d}^2y}{\mathrm{d}x^2}-2x\frac{\mathrm{d}y}{\mathrm{d}x}+\left(J-\frac{m^2}{1-x^2}\right)y = 0.$$

Guess $y = \left(1-x^2\right)^{m/2}v$,

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \left(1-x^2\right)^{m/2}\left(v'-\frac{mx}{1-x^2}v\right),$$
$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} = \left(1-x^2\right)^{m/2}\left[v''-\frac{2mx}{1-x^2}v'+\frac{m(m-1)x^2-m}{\left(1-x^2\right)^2}v\right].$$

Thus $\left(1-x^2\right)v''-2(m+1)xv'+\left[J-m(m+1)\right]v = 0$.

$$\sum t(t-1)c_tx^{t-2}-\sum t(t-1)c_tx^t$$
$$-2(m+1)\sum tc_tx^t+\left[J-m(m+1)\right]\sum c_tx^t = 0,$$
$$\Rightarrow \quad c_{t+2} = \frac{(t+m+1)(t+m)-J}{t(t+1)}c_t.$$

[V] In the LHS, m's sign dosen't really matter, thus we take m positive.

To converge, $J = \ell(\ell+1)$, and $\ell = t_0 + m = 0, 1, 2, 3, \ldots$, (s, p, d, f, ...)

$$\Theta(\theta) = AP_\ell^m(\cos\theta),$$

where Legendre Function $P_\ell^m(x)$

$$P_\ell^m(x) = \frac{\left(1-x^2\right)^{m/2}}{2^\ell \ell!}\frac{\mathrm{d}^{\ell+m}}{\mathrm{d}x^{\ell+m}}(x^2-1)^\ell,$$

$$Y_\ell^m = \pm\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}P_\ell^m(\cos\theta)e^{im\phi},$$

where $-$ is taken only when $m = 1, 3, 5, \ldots$.

example 2.7.1: Table of Legendre

Legendre Polynomial P_l and associated Legendre Function $P_l^m(\cos\theta)$

$P_0 = 1$	$P_0^0 = 1.$	
$P_1 = x$	$P_1^0 = \cos\theta$	$P_1^1 = \sin\theta.$
$P_2 = \frac{1}{2}(3x^2-1)$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$	$P_2^1 = 3\sin\theta\cos\theta$
	$P_2^2 = 3\sin^2\theta.$	
$P_3 = \frac{1}{2}(5x^3-3x)$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
	$P_3^2 = 15\sin^2\theta\cos\theta$	$P_3^3 = 15\sin^3\theta.$

example 2.7.2: Tbale of Y_l^m

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}, \qquad Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm2i\phi},$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad Y_3^0 = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta - 3\cos\theta),$$

$$Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}, \qquad Y_3^{\pm1} = \mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi},$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \qquad Y_3^{\pm2} = \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{\pm2i\phi},$$

$$Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}, \qquad Y_3^{\pm3} = \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta e^{\pm3i\phi}.$$

2.7.2 Solution of Radial Part

$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)-\frac{2mr^2}{\hbar^2}(V-E)=\ell(\ell+1),$$

where $V=-\dfrac{e^2}{4\pi\varepsilon_0 r}$.

Noticing

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)=2r\frac{\mathrm{d}R}{\mathrm{d}r}+r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2}=r\frac{\mathrm{d}^2rR}{\mathrm{d}r^2}.$$

To simplify, define $u:=rR$, $k=\sqrt{-\dfrac{2mE}{\hbar^2}}$, $\xi:=kr$, $N=\dfrac{me^2}{2\pi\varepsilon_0\hbar^2 k}$,

$$\frac{\mathrm{d}^2u}{\mathrm{d}\xi^2}=\left[1-\frac{N}{\xi}+\frac{\ell(\ell+1)}{\xi^2}\right]u. \tag{8}$$

Asymptote behavior

$$\begin{aligned}
&\xi\to+\infty, && \frac{\mathrm{d}^2u}{\mathrm{d}\xi^2}=u && \Rightarrow\quad u\to Ae^{-\xi},(Be^{\xi}\text{ diverges})\\
&\xi\to 0, && \frac{\mathrm{d}^2u}{\mathrm{d}\xi^2}=\frac{\ell(\ell+1)}{\xi^2}u && \Rightarrow\quad u\to C\xi^{\ell+1},(D\xi^{-\ell}\text{ diverges})
\end{aligned}$$

therefore, $u=v(\xi)\xi^{\ell+1}e^{-\xi}$.

$$\frac{\mathrm{d}u}{\mathrm{d}\xi}=[v'\xi+v(\ell+1)-v\xi]\xi^{\ell}e^{-\xi},$$

$$\frac{\mathrm{d}^2u}{\mathrm{d}\xi^2}=[v''\xi^2+2v'(\ell+1)\xi-2v'\xi^2+v(\ell+1)\ell-2v(\ell+1)\xi+v\xi^2]\xi^{\ell-1}e^{-\xi}$$

$$\left[1-\frac{N}{\xi}+\frac{\ell(\ell+1)}{\xi^2}\right]u=[\xi^2-N\xi+\ell(\ell+1)]v\xi^{\ell-1}e^{-\xi}.$$

Then $\xi v''+2(\ell+1-\xi)v'+[N-2(\ell+1)]v=0$.

$$\begin{aligned}
&\sum t(t-1)c_t\xi^{t-1}+2(\ell+1)\sum tc_t\xi^{t-1}\\
&\quad -2\sum tc_t\xi^t+[N-2(\ell+1)]\sum c_t\xi^t=0.\\
&\quad\Rightarrow\quad c_{t+1}=\frac{2(t+\ell+1)-N}{(t+1)(t+2\ell+2)}c_t.
\end{aligned}$$

To converge, $N=2n$, and $n=t_0+\ell+1$.

$$N=2n=\frac{me^2}{2\pi\varepsilon_0\hbar^2}\frac{1}{k},\quad k=\frac{1}{n}\frac{me^2}{4\pi\varepsilon_0\hbar^2},$$

$$E=-\frac{\hbar^2k^2}{2m}=-\frac{1}{n^2}\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2.$$

Define the reduced Bohr radius[VI]

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.53 \times 10^{-10}\,\text{m},$$

and the ground energy at $n = 1$,

$$E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -13.6\ \text{eV}.$$

For the certain $n, \ell, k = \dfrac{1}{na}$, $\xi = kr$

$$R = \frac{u}{r} = v(\xi)\xi^\ell e^{-\xi},\ (k \text{ in the } v)$$

then work out the coefficients through the recursion

$$c_{j+1} = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)}c_j, \quad j = 0, 1, \ldots, n-\ell-2,$$

and the normalization.

example 2.7.3: 1s orbit

$n = 1, \ell = 0, m = 0, R = c_0 e^{-\xi} = c_0 e^{-r/a}$,

$$\int_0^{+\infty} R^2 r^2 \mathrm{d}r = c_0^2 \int_0^{+\infty} r^2 e^{-2r/a} dr = \frac{a^3 c_0^2}{4} = 1.$$

Thus

$$R_{10} = \frac{2}{\sqrt{a^3}} e^{-r/a},$$

While $Y_0^0 = \dfrac{1}{2\sqrt{\pi}}$, $\psi_{100} = R_{10}Y_0^0 = \dfrac{1}{\sqrt{\pi a^3}} e^{r/a}$.

Define $\rho = 2\xi = \dfrac{2r}{na}, p = 2\ell + 1, q = n - \ell - 1$, then

$$\rho v'' + (p + 1 - \rho)v' + qv = 0, \quad \Rightarrow \quad v \propto L_q^p(\rho).$$

$$R_{n\ell} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+l)!}}\,\rho^\ell e^{-\rho/2} L_q^p(\rho),$$

where the Laguerre Function $L_q^p(x)$

$$L_q^p(x) = (-1)^p L_{p+q}^{(p)}(x),$$

and the Laguerre Polynomial $L_q(x)$

$$L_q(x) = \frac{e^x}{q!}\frac{\mathrm{d}^q}{\mathrm{d}x^q}\frac{x^q}{e^x}.$$

[VI] The original Bohr radius uses m_e in the mass part, the reduced mass m (or μ) $\doteq 0.999\,m_e$.

example 2.7.4: Table of R_{nl}

$$\begin{aligned}
R_{10} &= 2a^{-3/2}e^{-\xi}, \\
R_{20} &= \frac{a^{-3/2}}{\sqrt{2}}(1-\xi)e^{-\xi}, \\
R_{21} &= \frac{a^{-3/2}}{\sqrt{6}}\xi e^{-\xi}, \\
R_{30} &= \frac{2a^{-3/2}}{3\sqrt{3}}(2-6\xi+3\xi^2)e^{-\xi}, \\
R_{31} &= \frac{a^{-3/2}}{3\sqrt{6}}(4\xi-3\xi^2)e^{-\xi}, \\
R_{32} &= \frac{a^{-3/2}}{\sqrt{30}}\xi^2 e^{-\xi}, \\
R_{40} &= \frac{a^{-3/2}}{12}(3-9\xi+6\xi^2-\xi^3)e^{-\xi}, \\
R_{41} &= \frac{a^{-3/2}}{8\sqrt{15}}(5\xi-5\xi^2+\xi^3)e^{-\xi}, \\
R_{42} &= \frac{a^{-3/2}}{12\sqrt{5}}(3\xi^2-\xi^3)e^{-\xi}, \\
R_{43} &= \frac{a^{-3/2}}{12\sqrt{35}}\xi^3 e^{-\xi}.
\end{aligned}$$

$$\psi_{m\ell n} = R_{n\ell}(r)Y_\ell^m(\theta,\phi).$$

The meaning of *n*,*l*,*m*

- n is the Principle Quantum Number: $\mathsf{H}\,|\psi\rangle = E_1 n^{-2}\,|\psi\rangle$.
- ℓ is the Azzimuthal Quantum Number: $\mathsf{L}^2\,|\psi\rangle = \ell(\ell+1)\hbar^2\,|\psi\rangle$.
- m is the Magnetic Quantum Number: $\mathsf{L}_z\,|\psi\rangle = m\hbar\,|\psi\rangle$.

The values are quantized: $n = 1,2,3,\ldots;\ell = 0,1,\ldots,n-1; m = 0,\pm1,\ldots,\pm\ell$.

More n,ℓ,m is still not enough, the spin S should also be taken into account, i.e.

$$|\psi\rangle = |n,\ell,m\rangle \otimes |s,s_z\rangle \,.$$

$\otimes$ is the tensor product, meaning the value of s, s_z is independent of n,ℓ,m.

3 Appendix

3.1 Nabla

3.1.1 Definition

Introduction We could use linear function to approximate a function near a certain point, that is

$$\begin{aligned}
f(x) \sim & f(x_0) + f'(x_0)(x - x_0) \\
= & f(x_0) + f'(x_0)\Delta x, \\
f(x,y) \sim & f(x_0, y_0) + f'_x(x_0, y_0)(x - x_0) + f'_y(x_0, y_0)(y - y_0) \\
= & f(x_0, y_0) + \left[\frac{\partial f}{\partial x}(x_0, y_0), \frac{\partial f}{\partial y}(x_0, y_0)\right] \cdot [\Delta x, \Delta y],
\end{aligned}$$

then $f(x, y, z)$ at $P_0(x_0, y_0, z_0)$

$$\nabla f(P_0) := \left[\frac{\partial f}{\partial x}(P_0), \frac{\partial f}{\partial y}(P_0), \frac{\partial f}{\partial z}(P_0)\right] = \left[\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z}\right]_{P_0}$$

$$f(P) \sim f(P_0) + \nabla f(P_0) \cdot \Delta P.$$

Gradient In Cartesian coordinates,

$$\nabla f = \frac{\partial f}{\partial x}\,\hat{\boldsymbol{i}} + \frac{\partial f}{\partial y}\,\hat{\boldsymbol{j}} + \frac{\partial f}{\partial z}\,\hat{\boldsymbol{k}}.$$

We take the notation nabla ∇

$$\nabla = \frac{\partial}{\partial x}\,\hat{\boldsymbol{i}} + \frac{\partial}{\partial y}\,\hat{\boldsymbol{j}} + \frac{\partial}{\partial z}\,\hat{\boldsymbol{k}},$$

which is very useful later.

Divergence The flux Φ of $\boldsymbol{F}$ through a surface S.

$$\Phi = \int_S \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S}.$$

If closed surface $S = \partial V$,

$$\Phi = \oint_{\partial V} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S} = \sum_{i=1}^{N} \frac{1}{V_i} \oint_{\partial V_i} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S}\, V_i.$$

Define divergence

$$\mathrm{div}\boldsymbol{F} := \lim_{V \to 0} \frac{1}{V} \oint_{\partial V} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S},$$

then we conduct the Gauss's law

$$\Phi = \oint_{\partial V} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S} = \int_V \mathrm{div}\boldsymbol{F} \, \mathrm{d}V.$$

Take V as a cube origin at (x, y, z) with a delta $(\Delta x, \Delta y, \Delta z)$, thus

$$\Delta V = \Delta x \, \Delta y \, \Delta z$$

In the z direction,

$$\begin{aligned} \int F_z \, \mathrm{d}S_z &= F_z(x, y, z + \Delta z)\Delta x \Delta y - F_z(x, y, z)\Delta x \Delta y \\ &= \frac{F_z(x, y, z + \Delta z) - F_z(x, y, z)}{\Delta z} \Delta x \Delta y \Delta z. \end{aligned}$$

Therefore,

$$\mathrm{div}\boldsymbol{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}.$$

Noticing that this formally fit

$$\nabla \cdot \boldsymbol{F} = \left[\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right] \cdot [F_x, F_y, F_z] = \frac{\partial}{\partial x} F_x + \frac{\partial}{\partial y} F_y + \frac{\partial}{\partial z} F_z,$$

we can use the notation:

$$\nabla \cdot \boldsymbol{F} = \mathrm{div}\boldsymbol{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}.$$

Curl Path integral

$$\oint_{\partial S} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} = \sum_{i=1}^{N} \frac{1}{S_i} \oint_{\partial S_i} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} \, S_i.$$

Define curl, whose projection along the unit vector $\hat{\boldsymbol{n}}$ direction is

$$\mathrm{curl}\boldsymbol{F} \cdot \hat{\boldsymbol{n}} := \lim_{S \to 0} \frac{1}{S} \oint_{\partial S} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell},$$

then we conduct the Stokes's law

$$\oint_{\partial S} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} = \int_S \mathrm{curl}\boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S}.$$

As $\hat{\boldsymbol{n}} = \hat{\boldsymbol{k}}$, take S_k as a square origin at (x, y, z) with a delta $(\Delta x, \Delta y, 0)$, thus

$$\Delta S_k = \Delta x \Delta y.$$

$$\begin{aligned} &F_x(x, y, z)\Delta x + F_y(x + \Delta x, y, z)\Delta y - F_x(x, y + \Delta y, z)\Delta x - F_y(x, y, z)\Delta y \\ &= \left[\frac{F_x(x, y, z) - F_x(x, y + \Delta y, z)}{\Delta y} + \frac{F_y(x + \Delta x, y, z) - F_y(x, y, z)}{\Delta x}\right] \Delta x \Delta y. \end{aligned}$$

Therefore,

$$(\mathrm{curl}\boldsymbol{F})_z = \frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}.$$

That is,

$$\mathrm{curl}\boldsymbol{F} = \left[\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z}, \frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x}, \frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}\right].$$

Noticing that this formally fit

$$\nabla \times \boldsymbol{F} = \begin{vmatrix} \hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ F_x & F_y & F_z \end{vmatrix}.$$

we can use the notation:

$$\nabla \times \boldsymbol{F} = \mathrm{curl}\boldsymbol{F}.$$

Laplacian In the Possion equation

$$\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} + \frac{\mathrm{d}^2\varphi}{\mathrm{d}y^2} + \frac{\mathrm{d}^2\varphi}{\mathrm{d}z^2} = \frac{\rho}{\varepsilon_0}.$$

The Laplacian can be written as the divergence of the nabla:

$$\nabla^2 = \nabla \cdot \nabla = \frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{\mathrm{d}^2}{\mathrm{d}y^2} + \frac{\mathrm{d}^2}{\mathrm{d}z^2}.$$

3.1.2 Nabla Notation in Coordinate Transformation

In Cartesian coordinates, bases $\{\hat{\boldsymbol{i}}, \hat{\boldsymbol{j}}, \hat{\boldsymbol{k}}\}$,

$$\boldsymbol{r} = x_1\,\hat{\boldsymbol{i}} + x_2\,\hat{\boldsymbol{j}} + x_3\,\hat{\boldsymbol{k}}.$$

In another orthogonal normalized bases $\{\hat{\boldsymbol{e}}_1, \hat{\boldsymbol{e}}_2, \hat{\boldsymbol{e}}_3\}$,

$$\boldsymbol{r} = \xi_1\,\hat{\boldsymbol{e}}_1 + \xi_2\,\hat{\boldsymbol{e}}_2 + \xi_3\,\hat{\boldsymbol{e}}_3,$$

We have the mapping $\mathcal{T}$:

$$\mathcal{T} : (\xi_1, \xi_2, \xi_3) \to (x_1, x_2, x_3),$$

i.e. $x_i = x_i(\xi_1, \xi_2, \xi_3)$, and

$$\mathrm{d}x_i = \frac{\partial x_i}{\partial \xi_1}\mathrm{d}\xi_1 + \frac{\partial x_i}{\partial \xi_2}\mathrm{d}\xi_2 + \frac{\partial x_i}{\partial \xi_3}\mathrm{d}\xi_3,$$

compose as $\mathrm{d}\boldsymbol{r} = \mathrm{d}x_1\,\hat{\boldsymbol{i}} + \mathrm{d}x_2\,\hat{\boldsymbol{j}} + \mathrm{d}x_3\,\hat{\boldsymbol{k}}$,[VII]

$$\mathrm{d}\boldsymbol{r} = \frac{\partial \boldsymbol{r}}{\partial \xi_1}\mathrm{d}\xi_1 + \frac{\partial \boldsymbol{r}}{\partial \xi_2}\mathrm{d}\xi_2 + \frac{\partial \boldsymbol{r}}{\partial \xi_3}\mathrm{d}\xi_3.$$

[VII] Warning: $\partial\boldsymbol{r}/\partial\xi_i \neq \partial r/\partial\xi_i\,\hat{\boldsymbol{r}}$, i.e. $\partial\boldsymbol{r}/\partial\xi_i$ isn't along $\hat{\boldsymbol{r}}$.

Decompose the small displacement $\mathrm{d}\boldsymbol{r}$ along $\hat{\boldsymbol{e}}_1, \hat{\boldsymbol{e}}_2, \hat{\boldsymbol{e}}_3$ directions:

$$\mathrm{d}\boldsymbol{r} = \mathrm{d}\boldsymbol{\ell}_1 + \mathrm{d}\boldsymbol{\ell}_2 + \mathrm{d}\boldsymbol{\ell}_3.$$

Noticing that $\mathrm{d}\ell_i \neq \mathrm{d}\xi_i$[VIII], we use the Lame coefficient: $\mathrm{d}\boldsymbol{\ell}_i = H_i\,\mathrm{d}\xi_i\,\hat{\boldsymbol{e}}_i$.

$$\mathrm{d}\boldsymbol{r} = H_1\mathrm{d}\xi_1\,\hat{\boldsymbol{e}}_1 + H_2\mathrm{d}\xi_2\,\hat{\boldsymbol{e}}_2 + H_3\mathrm{d}\xi_3\,\hat{\boldsymbol{e}}_3.$$

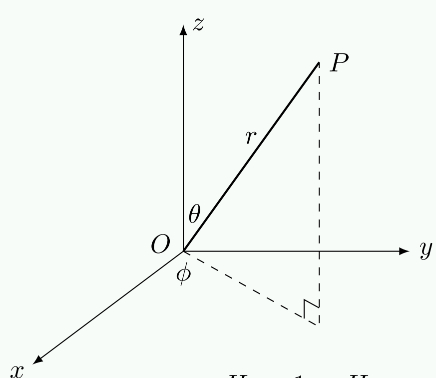
Thus

$$\frac{\partial \boldsymbol{r}}{\partial \xi_i} = \frac{\partial x_1}{\partial \xi_i}\,\hat{\boldsymbol{i}} + \frac{\partial x_2}{\partial \xi_i}\,\hat{\boldsymbol{j}} + \frac{\partial x_3}{\partial \xi_i}\,\hat{\boldsymbol{k}} = H_i\,\hat{\boldsymbol{e}}_i,$$

we can calculate H_i

$$H_i = \left|\frac{\partial \boldsymbol{r}}{\partial \xi_i}\right| = \sqrt{\left(\frac{\partial x_1}{\partial \xi_i}\right)^2 + \left(\frac{\partial x_2}{\partial \xi_i}\right)^2 + \left(\frac{\partial x_3}{\partial \xi_i}\right)^2}$$

example 3.1.1: Lame Coefficient in Spherical Coordinate



$$\begin{cases} x = r\sin\theta\cos\phi, \\ y = r\sin\theta\sin\phi, \\ z = r\cos\theta. \end{cases}$$

$$H_r = 1, \quad H_\theta = r, \quad H_\phi = r\sin\theta.$$
$$\mathrm{d}\boldsymbol{r} = \mathrm{d}r\,\hat{\boldsymbol{r}} + r\,\mathrm{d}\theta\,\hat{\boldsymbol{\theta}} + r\sin\theta\,\mathrm{d}\phi\,\hat{\boldsymbol{\phi}}.$$

Gradient Follow the definition

$$\nabla f := \sum_{i=1}^{3} \frac{\partial f}{\partial \boldsymbol{\ell}_i} = \sum_{i=1}^{3} \hat{\boldsymbol{e}}_i \frac{\partial f}{H_i\,\partial \xi_i}.$$

We take the notation:

$$\nabla \equiv \sum_{i=1}^{3} \hat{\boldsymbol{e}}_i \frac{\partial}{H_i \partial \xi_i}.$$

[VIII] If so, $\mathrm{d}\boldsymbol{r} = \mathrm{d}\xi_1\,\hat{\boldsymbol{e}}_1 + \mathrm{d}\xi_2\,\hat{\boldsymbol{e}}_2 + \mathrm{d}\xi_3\,\hat{\boldsymbol{e}}_3$, the new coordinate is just a rotated Cartesian, the form won't change.

Divergence Follow the definition

$$\nabla \cdot \boldsymbol{F} := \lim_{V\to 0} \frac{1}{V} \oint_{\partial V} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S}.$$

Taking V as a cube origin at (ξ_1, ξ_2, ξ_3) with a delta $(\mathrm{d}\ell_1, \mathrm{d}\ell_2, \mathrm{d}\ell_3)$, thus

$$\begin{gathered} \mathrm{d}V = \mathrm{d}\ell_1 \wedge \mathrm{d}\ell_2 \wedge \mathrm{d}\ell_3 = H_1 H_2 H_3 \, \mathrm{d}\xi_1 \mathrm{d}\xi_2 \mathrm{d}\xi_3, \\ \mathrm{d}S_i = \mathrm{d}\ell_j \wedge \mathrm{d}\ell_k = H_j H_k \, \mathrm{d}\xi_j \mathrm{d}\xi_k, \quad (ijk) = (123) \end{gathered}$$

In the $\boldsymbol{e}_k$ direction,

$$\begin{aligned} \int F_i \, \mathrm{d}S_i &= \frac{\partial F_i H_j H_k}{\partial \ell_i} \mathrm{d}\ell_i \, \mathrm{d}\xi_j \mathrm{d}\xi_k, \\ \Rightarrow \quad \oint_{\partial V} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{S} &= \sum_{ijk} \frac{\partial F_i H_j H_k}{\partial \xi_i} \mathrm{d}\xi_i \mathrm{d}\xi_j \mathrm{d}\xi_k. \end{aligned}$$

Then,

$$\nabla \cdot \boldsymbol{F} = \frac{1}{H_1 H_2 H_3} \sum_{ijk} \frac{\partial}{\partial \xi_i} F_i H_j H_k.$$

Curl Follow the definition

$$(\nabla \times \boldsymbol{F}) \cdot \hat{\boldsymbol{n}} := \lim_{S\to 0} \frac{1}{S} \oint_{\partial S} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell}.$$

Take $\hat{\boldsymbol{n}} = \hat{\boldsymbol{e}}_i$, S_i as square origin at (ξ_j, ξ_k) with a delta $(\mathrm{d}\ell_j, \mathrm{d}\ell_k)$, thus

$$\begin{gathered} \mathrm{d}S_i = \mathrm{d}\ell_j \wedge \mathrm{d}\ell_k = H_j H_k \, \mathrm{d}\xi_j \mathrm{d}\xi_k. \\ \oint_{\partial S_i} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} = \frac{\partial F_k H_k}{\partial \ell_j} \mathrm{d}\ell_j \, \mathrm{d}\xi_k - \frac{\partial F_j H_j}{\partial \ell_k} \mathrm{d}\ell_k \, \mathrm{d}\xi_j. \end{gathered}$$

By using antisymmetric tensor ε_{ijk}

$$\varepsilon_{ijk} = \begin{cases} 1, & (ijk) = (123); \\ -1, & (ijk) = (321); \\ 0, & \text{otherwise}. \end{cases}$$

We can simplify the formula

$$\begin{aligned} \nabla \times \boldsymbol{F} &= \sum_{ijk} \varepsilon_{ijk} \, \hat{\boldsymbol{e}}_i \frac{\partial}{H_j H_k \partial \xi_j} F_k H_k \\ &= \frac{1}{H_1 H_2 H_3} \begin{vmatrix} H_1 \boldsymbol{e}_1 & H_2 \boldsymbol{e}_2 & H_3 \boldsymbol{e}_3 \\ \partial/\partial\xi_1 & \partial/\partial\xi_2 & \partial/\partial\xi_3 \\ H_1 F_1 & H_2 F_2 & H_3 F_3 \end{vmatrix} \end{aligned}$$

Laplacian Follow the definition

$$
\begin{aligned}
\nabla^2 :=& \nabla\cdot\nabla = \nabla\cdot\sum_{i=1}^{3}\boldsymbol{e}_i\frac{\partial}{H_i\partial\xi_i}\\
=& \frac{1}{H_1H_2H_3}\sum_{ijk}\frac{\partial}{\partial\xi_i}H_jH_k\frac{\partial}{H_i\partial\xi_i}
\end{aligned}
$$

example 3.1.2: Nabla in Spherical Coordinate

$H_r = 1,\ H_\theta = r,\ H_\phi = r\sin\theta,$

Gradient

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{1}{r}\frac{\partial}{\partial\theta}, \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right];$$

Divergence

$$
\begin{aligned}
\nabla\cdot\boldsymbol{F} =& \frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial r}\left(r^2\sin\theta\,F_r\right) + \frac{\partial}{\partial\theta}\left(r\sin\theta\,F_\theta\right) + \frac{\partial}{\partial\phi}\left(rF_\phi\right)\right]\\
=& \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2F_r\right) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,F_\theta\right) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}F_\phi;
\end{aligned}
$$

Warning:

$$\cancel{\nabla\cdot\boldsymbol{F} = \frac{\partial F_r}{\partial r} + \frac{1}{r}\frac{\partial F_\theta}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial F_\phi}{\partial\phi}}.$$

actually,

$$\nabla\cdot\boldsymbol{F} = \underline{\frac{2}{r}F_r} + \frac{\partial F_r}{\partial r} + \underline{\frac{\cos\theta}{r\sin\theta}F_\theta} + \frac{1}{r}\frac{\partial F_\theta}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial F_\phi}{\partial\phi}$$

Curl

$$
\begin{aligned}
\nabla\times\boldsymbol{F} =& \frac{1}{r^2\sin\theta}\begin{vmatrix}\hat{\boldsymbol{r}} & r\,\hat{\boldsymbol{\theta}} & r\sin\theta\,\hat{\boldsymbol{\phi}}\\ \partial/\partial r & \partial/\partial\theta & \partial/\partial\phi\\ F_r & rF_\theta & r\sin\theta\,F_\phi\end{vmatrix}\\
=& \left[\frac{1}{r\sin\theta}\left(\frac{\partial}{\partial\theta}(F_\phi\sin\theta) - \frac{\partial}{\partial\phi}F_\theta\right),\right.\\
&\left.\frac{1}{r}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}F_r - \frac{\partial}{\partial r}(rF_\phi)\right), \frac{1}{r}\left(\frac{\partial}{\partial r}(rF_\theta) - \frac{\partial}{\partial\theta}F_r\right)\right];
\end{aligned}
$$

Laplacian

$$
\begin{aligned}
\nabla^2 =& \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\
=& \underline{\frac{2}{r}\frac{\partial}{\partial r}} + \frac{\partial^2}{\partial r^2} + \underline{\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}
\end{aligned}
$$

3.2 Functions and Integrals

There are some important and useful functions to have a look.[IX]

3.2.0 Fourier Transformation

We shall define the **inner product** in $[-\pi,\pi]$ of real functions $f(x)$ and $g(x)$:

$$\langle f|g\rangle := \int_{-\pi}^{\pi} f(x)g(x)\,\mathrm{d}x.$$

Omit math proofs[X], we take it for granted the definition is **complete** in physics. On the other hand:

$$\int_{-\pi}^{\pi} \sin nx\,\mathrm{d}x = \int_{-\pi}^{\pi} \cos nx\,\mathrm{d}x = 0.$$

$$\int_{-\pi}^{\pi} \sin nx \sin mx\,\mathrm{d}x = \frac{1}{2}\int_{-\pi}^{\pi} \cos(n-m)x - \cos(n+m)x\,\mathrm{d}x = \pi\delta_{nm};$$

$$\int_{-\pi}^{\pi} \sin nx \cos mx\,\mathrm{d}x = \frac{1}{2}\int_{-\pi}^{\pi} \sin(n+m)x + \sin(n-m)x\,\mathrm{d}x = 0;$$

$$\int_{-\pi}^{\pi} \cos nx \cos mx\,\mathrm{d}x = \frac{1}{2}\int_{-\pi}^{\pi} \cos(n-m)x + \cos(n+m)x\,\mathrm{d}x = \pi\delta_{nm}.$$

Therefore, The set

$$\{1, \sin nx, \cos nx \,|\, n \in \mathbb{N}_+\} = \{1, \sin x, \cos x, \sin 2x, \dots\}$$

consists a set of bases in $[-\pi,\pi]$. Normalize it:

$$\left\{\frac{1}{\sqrt{2\pi}}, \frac{\sin x}{\sqrt{\pi}}, \frac{\cos x}{\sqrt{\pi}}, \frac{\sin 2x}{\sqrt{\pi}}, \dots\right\}$$

Then, for $f(x)$ with period 2π can be expand

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos nx + b_n \sin nx\right),$$

which is the **Fourier Expansion**, where

$$a_n = \frac{1}{\pi}\langle f|\cos nx\rangle = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\cos nx\,\mathrm{d}x,$$

$$b_n = \frac{1}{\pi}\langle f|\sin nx\rangle = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\sin nx\,\mathrm{d}x.$$

[IX] Sorry, I haven't yet learned *Mathematical Physics Equations and Special Functions*.
[X] In math, something may not be strictly valid, but they're indeed useful **in physics**.

Use $e^{ix} = \cos x + i \sin x$, we can write

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n e^{inx}, \quad c_n = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) e^{-inx} \mathrm{d}x.$$

For any period $T = \lambda, k_0 = 2\pi/\lambda$ function $f(x)$

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n e^{ink_0 x}, \quad c_n = \frac{1}{\lambda} \int_{-\lambda/2}^{\lambda/2} f(x) e^{-ink_0 x} \mathrm{d}x.$$

When $f(x)$ is non-period, Fourier Expansion can't be taken into use.
However, we could take very LARGE $\lambda = 2N, \Delta k = \dfrac{2\pi}{\lambda}, k := n\Delta k$,

$$f(x) = \sum_k \left[\frac{\Delta k}{2\pi} \int_{-N}^{N} f(x) e^{-ikx} \mathrm{d}x \right] e^{ikx}.$$

When $N \to \infty, \Delta k \to 0$, define

$$\hat{f}(k) := \int_{-\infty}^{\infty} f(x) e^{-ikx} \, \mathrm{d}x,$$

then,

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{f}(k) e^{ikx} \, \mathrm{d}k,$$

which is the Fourier Transformation. In Shou's Note, for symmetrization,

$$\hat{f}(k) = \mathcal{F}[f(x)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, \mathrm{d}x,$$
$$f(x) = \mathcal{F}^{-1}[\hat{f}(k)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{f}(k) e^{ikx} \, \mathrm{d}k.$$

3.2.1 Gaussian Function

The Gaussian is

$$f(x) = e^{-x^2/\sigma^2}.$$

The integral is

$$\int_{-\infty}^{+\infty} e^{-x^2/\sigma^2} \mathrm{d}x = \sqrt{\pi}\sigma.$$

The Fourier Transformation is

$$\mathcal{F}\left(e^{-x^2/\sigma^2}\right) = \frac{\sigma}{\sqrt{2}} e^{-\sigma^2 k^2/4}.$$

3.2.2 Hermite Polynomial

The conventional solution of

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} + (K - \xi^2)\psi = 0,$$

is $K = 2n + 1$, and

$$\psi_n = AH_n(\xi)e^{-\xi^2/2}, \quad n = 0, 1, 2, \ldots,$$

where the Hermite Polynomial

$$H_n(x) = (-1)^n e^{x^2} \frac{\mathrm{d}^n}{\mathrm{d}x^n} e^{-x^2},$$

which is the solution of

$$y'' - 2xy' + 2ny = 0.$$

The integral is

$$\int_{-\infty}^{+\infty} H_n H_{n'} e^{-x^2} \mathrm{d}x = 2^n n! \sqrt{\pi}\delta_{nn'},$$

3.2.3 Legendre Function

The solution of

$$\left(1 - x^2\right) \frac{\mathrm{d}^2 y}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}y}{\mathrm{d}x} + \left[J - \frac{m^2}{1 - x^2}\right] y = 0,$$

is $J = \ell(\ell + 1)$ and $\ell = 0, 1, 2, \ldots; m = 0, \pm 1, \ldots, \pm \ell$,[XI]

$$y = AP_\ell^m(x),$$

where the Legendre Function $P_n^m(x)$

$$P_n^m(x) = P_n^{-m}(x) = (1 - x^2)^{m/2} \frac{\mathrm{d}^m}{\mathrm{d}x^m} P_n(x),$$

and the Legendre Polynomial $P_n(x)$

$$P_n(x) = \frac{1}{2^n n!} \frac{\mathrm{d}^n}{\mathrm{d}x^n} (x^2 - 1)^n.$$

Which is the solution of

$$(1 - x^2)y'' - 2xy' + n(n + 1)y = 0.$$

The integral

$$\int_{-1}^{1} P_n P_{n'} \mathrm{d}x = \frac{2}{2n + 1}\delta_{nn'},$$

$$\int_{-1}^{1} P_n^m P_{n'}^{m'} \mathrm{d}x = \frac{2}{2n + 1} \frac{(n + m)!}{(n - m)!}\delta_{nn'}\delta_{mm'}.$$

[XI] In the calculation, we neglect m's sign, i.e. in the formula, $m = |m|$.

3.2.4 Laguerre Function

The solution of
$$\frac{\mathrm{d}^2 u}{\mathrm{d}\xi^2} = \left[1 - \frac{N}{\xi} + \frac{\ell(\ell+1)}{\xi^2}\right] u,$$
is $N = 2n$ and $n = 1, 2, \ldots; \ell = 1, 2, \ldots, n-1$,
$$R = A\rho^\ell e^{-\rho/2} L_q^p(\rho),$$
where the Laguerre Function $L_q^p(x)$
$$L_q^p(x) = (-1)^p \frac{\mathrm{d}^p}{\mathrm{d}x^p} L_{p+q}(x),$$
and the Lagrange Polynomial $L_q(x)$
$$L_q(x) = \frac{e^x}{q!} \frac{\mathrm{d}^q}{\mathrm{d}x^q} \frac{x^q}{e^x}.$$
Which is the solution of
$$xy'' + (1-x)y' + qy = 0.$$
The integral
$$\int_0^{+\infty} L_q L_{q'} e^{-x} \mathrm{d}x = \delta_{qq'},$$
$$\int_0^{+\infty} L_q^p L_{q'}^{p'} x^p e^{-x} \mathrm{d}x = \frac{(p+q)!}{q!} \delta_{pp'} \delta_{qq'},$$
$$\int_0^{+\infty} L_q^p L_{q'}^{p'} x^{p+1} e^{-x} \mathrm{d}x = (2q+p+1) \frac{(p+q)!}{q!} \delta_{pp'} \delta_{qq'}.$$

3.2.5 Bessel Function

$$x^2 y'' + xy' + (x^2 - p^2)y = 0.$$
$$J_p(x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{\Gamma(n+1)\Gamma(n+1+p)} \left(\frac{x}{2}\right)^{2n+p}.$$

Postscript

About the Note *This is a biref note taken by me after finishing the General Physics II taught by Shuo Jiang. Shuo is a nice teacher and I strongly recommend you to have a listen. Much of the note is taken from what Shuo wrote on the blackboard and I simply copied them. Hope that this note is helpful for you.*

If you find any mistakes in this note, please let me know. My WeChat is Dait_Pef. *Dait*

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