Chapter 3 – Formalism

This chapter is an extended excursion into the math of quantum mechanics. One of the useful analogies is to linear algebra.

wave functions $\rightarrow$ vectors

operators $\rightarrow$ matrices

$$|\alpha\rangle \rightarrow \vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \qquad \hat{Q} \rightarrow \underline{\underline{Q}} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} & \cdots \\ Q_{21} & Q_{22} & Q_{23} & \cdots \\ Q_{31} & Q_{32} & Q_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Inner product $\quad \overbrace{\langle\alpha|}^{\text{bra}}\overbrace{|\beta\rangle}^{\text{ket}} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}^{\dagger} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ \vdots \end{pmatrix} = (a_1^* \ a_2^* \ a_3^* \ \ldots) \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ \vdots \end{pmatrix}$

$$= a_1^* b_1 + a_2^* b_2 + a_3^* b_3 + \ldots$$

$$\hat{Q}|\alpha\rangle = |\beta\rangle \rightarrow \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} & \cdots \\ Q_{21} & Q_{22} & Q_{23} & \cdots \\ Q_{31} & Q_{32} & Q_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ \vdots \end{pmatrix}$$

$$b_1 = Q_{11} a_1 + Q_{12} a_2 + Q_{13} a_3 + \ldots$$
$$b_2 = Q_{21} a_1 + Q_{22} a_2 + Q_{23} a_3 + \ldots$$

$$b_j = \sum_i Q_{ji} a_i$$

In quantum mechanics, the dimension is often ∞.

An important point: there are many different <u>representations</u> of the states $|\Psi(t)\rangle$ and the operators $\hat{Q}$

Example: Infinite square well, state $5 = |\psi_5\rangle$, $\hat{x}$, $\hat{p}$

Representation $\quad \langle x|\psi_5\rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{5\pi x}{a}\right)$

$$\hat{x} = x \qquad \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$\langle x|\psi_n\rangle$ = inner product of $|x\rangle$ and $|\psi_n\rangle$ Interpret??

Our wave functions exist in Hilbert space.

The inner product of two functions $\langle f | g \rangle \equiv \int_a^b f^*(x)\, g(x)\, dx$

Same thing: $\langle f | g \rangle = \int_a^b \langle f | x \rangle \langle x | g \rangle\, dx$

This can only be true if $\hat{1} = \int_a^b |x\rangle\langle x|\, dx$

Because $\langle f | g \rangle = \langle f | \hat{1} g \rangle = \langle f | \hat{1} | g \rangle$

Schwartz inequality is obvious for vectors

$$\langle f | g \rangle \langle g | f \rangle \leq \langle f | f \rangle \langle g | g \rangle$$

Vector form
$$(\vec{a} \cdot \vec{b})^2 \leq (\vec{a} \cdot \vec{a})(\vec{b} \cdot \vec{b})$$
$$a^2 b^2 \cos^2\theta_{ab} \leq a^2 b^2$$

An orthonormal set of states $\langle f_n | f_m \rangle = \int f_n^*(x)\, f_m(x)\, dx = \delta_{nm}$

Completeness: $|f\rangle = \sum_n |f_n\rangle c_n \Rightarrow c_n = \langle f_n | f \rangle$

Interpret??

Hermitian Operators $\langle Q \rangle (t) = \langle Q \rangle^* (t)$ for all states $|\Psi(t)\rangle$

Different ways of writing

$$\langle Q \rangle (t) \equiv \langle \Psi(t) | \hat{Q} | \Psi(t) \rangle = \langle \Psi(t) | \hat{Q} \Psi(t) \rangle \overset{\text{Hermitian}}{=} \langle \hat{Q} \Psi(t) | \Psi(t) \rangle$$

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

Show $\langle \Psi | \hat{Q} | \Psi \rangle = \langle \Psi | \hat{Q} | \Psi \rangle^*$ for any $|\Psi\rangle$ implies

$$\langle \Psi_1 | \hat{Q} | \Psi_2 \rangle = \langle \Psi_2 | \hat{Q} | \Psi_1 \rangle^*$$

(Put $|\Psi\rangle = |\Psi_1\rangle + |\Psi_2\rangle$ in original expression.)

Important: Observables are represented by Hermitian operators.

The matrix representation of $\hat{Q}$ has property $Q_{ij} = Q_{ji}^*$

Common notation $\underline{\underline{Q}} = \underline{\underline{Q}}^{\dagger}$ ← Hermitian conjugate or
" adjoint

An important implication of $\langle \hat{Q} \rangle(t) = \langle \hat{Q} \rangle^*(t)$: All eigenvalues are real

The only states that have $\sigma_Q = 0$ are eigenstates. Determinate states are eigenstates of $\hat{Q}$.

$$\sigma_Q^2 = \langle \Psi | (\hat{Q} - \langle \hat{Q} \rangle)(\hat{Q} - \langle \hat{Q} \rangle) | \Psi \rangle = \langle (\hat{Q} - \langle \hat{Q} \rangle)\Psi | (\hat{Q} - \langle \hat{Q} \rangle)\Psi \rangle = 0$$

The only way this can be 0 is if $\hat{Q}|\Psi\rangle = \langle \hat{Q} \rangle |\Psi\rangle$ which is the definition of eigenstate.

The collection of all eigenvalues is called the spectrum. If 2 or more states have same eigenvalue, those states are degenerate.

Example: Hermitian operator $\hat{H}$

$$\langle \hat{H} \rangle(t) = \int \Psi^*(x,t) \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} \right] + \Psi^*(x,t) V(x,t) \Psi(x,t) \, dx$$

integrate by parts twice

$$= \int -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} \Psi + \Psi^* V \Psi \, dx$$

$$= \int (\hat{H} \Psi(x,t))^* \Psi(x,t) \, dx = \langle \hat{H} \Psi | \Psi \rangle = \langle \Psi | \hat{H} \Psi \rangle^*$$

Example: Non Hermitian operator $\hat{x}\hat{p}$

$$\langle \Psi | \hat{x}\hat{p}\Psi \rangle \stackrel{?}{=} \langle \hat{x}\hat{p}\Psi | \Psi \rangle$$

notice $\langle px\Psi | \Psi \rangle$

$$= \int \Psi^*(x,t)\, x \frac{\hbar}{i}\frac{\partial \Psi(x,t)}{\partial x} dx \stackrel{\text{int. by parts}}{=} \int \left(-\frac{\hbar}{i}\frac{\partial}{\partial x}\left(x\Psi^*(x,t)\right)\right)\Psi(x,t)\, dx$$

$$= \int i\hbar\, \Psi^*(x,t)\Psi(x,t) dx + \int x\left(-\frac{\hbar}{i}\frac{\partial \Psi^*(x,t)}{\partial x}\right)\Psi(x,t)\, dx$$

$$= i\hbar + \int \left(x\frac{\hbar}{i}\frac{\partial \Psi}{\partial x}\right)^* \Psi\, dx = \underline{i\hbar + \langle \hat{x}\hat{p}\Psi | \Psi \rangle}$$

Example: Hermitian conjugate of products of operators

$$(\hat{A}\hat{B})^+ = ?$$

First need definition $\langle \Psi_1 | \hat{Q}^+ | \Psi_2 \rangle \equiv \langle \Psi_2 | \hat{Q} | \Psi_1 \rangle^*$

$$= \langle \hat{Q}\Psi_1 | \Psi_2 \rangle$$

$$\langle \Psi_1 | (\hat{A}\hat{B})^+ | \Psi_2 \rangle = \langle \hat{A}\hat{B}\Psi_1 | \Psi_2 \rangle = \langle \hat{B}\Psi_1 | \hat{A}^+\Psi_2 \rangle = \langle \Psi_1 | \hat{B}^+\hat{A}^+ | \Psi_2 \rangle$$

Apply to $\hat{x}\hat{p}$: $(\hat{x}\hat{p})^+ = \hat{p}^+\hat{x}^+ \stackrel{\text{because } \hat{x} + \hat{p} \text{ herm.}}{=} \hat{p}\hat{x} = \hat{x}\hat{p} + (\hat{p}\hat{x} - \hat{x}\hat{p})$

$$= \hat{x}\hat{p} - i\hbar$$

Since $(\hat{x}\hat{p})^+ \neq \hat{x}\hat{p}$, $\hat{x}\hat{p}$ is not Hermitian

Example: Commutator of 2 Hermitian operators

$$\hat{Q}^+ = (\hat{A}\hat{B} - \hat{B}\hat{A})^+ = \hat{B}^+\hat{A}^+ - \hat{A}^+\hat{B}^+ = \hat{B}\hat{A} - \hat{A}\hat{B} = -\hat{Q}$$

Whenever $\hat{Q}^+ = -\hat{Q}$, then $\hat{Q} =$ <u>i times Hermitian operator</u>

Example: Sum of product of 2 Hermitian operators

$$\hat{Q}^+ = (\hat{A}\hat{B} + \hat{B}\hat{A})^+ = \hat{B}^+\hat{A}^+ + \hat{A}^+\hat{B}^+ = \hat{B}\hat{A} + \hat{A}\hat{B} = \hat{Q}$$ Hermitian

When can two operators can simultaneously have eigenstates for all states?

$\hat{A}|\Psi_{\alpha,\gamma}\rangle = \alpha|\Psi_{\alpha,\gamma}\rangle$ and $\hat{G}|\Psi_{\alpha,\gamma}\rangle = \gamma|\Psi_{\alpha,\gamma}\rangle$

The condition is found by finding $\hat{A}\hat{G}|\Psi_{\alpha,\gamma}\rangle$ and $\hat{G}\hat{A}|\Psi_{\alpha,\gamma}\rangle$

$$\hat{A}\hat{G}|\Psi_{\alpha,\gamma}\rangle = \gamma\hat{A}|\Psi_{\alpha,\gamma}\rangle = \alpha\gamma|\Psi_{\alpha,\gamma}\rangle$$
$$\hat{G}\hat{A}|\Psi_{\alpha,\gamma}\rangle = \alpha\hat{G}|\Psi_{\alpha,\gamma}\rangle = \alpha\gamma|\Psi_{\alpha,\gamma}\rangle$$

This implies $(\hat{A}\hat{G}-\hat{G}\hat{A})|\Psi\rangle = 0$ for all states.

$$\boxed{\hat{A}\hat{G}-\hat{G}\hat{A}=0}$$

We showed this for $\hat{H}$. Generally true that eigenstates of Hermitian operators with distinct eigenvalues are orthogonal.

$\hat{A}|\psi_\alpha\rangle = \alpha|\psi_\alpha\rangle$ and $\hat{A}|\psi_{\alpha'}\rangle = \alpha'|\psi_{\alpha'}\rangle$

$$\langle\psi_{\alpha'}|\hat{A}\psi_\alpha\rangle = \alpha\langle\psi_{\alpha'}|\psi_\alpha\rangle$$

if $\alpha \neq \alpha'$, then $\langle\psi_{\alpha'}|\psi_\alpha\rangle = 0$

$$\overset{\text{Hermitian}}{=} \langle\hat{A}\psi_{\alpha'}|\psi_\alpha\rangle = \alpha'\langle\psi_{\alpha'}|\psi_\alpha\rangle$$

What to do if $\alpha = \alpha'$? Crude method is Gramm-Schmidt orthogonalization.

1) Start with $|\psi_1\rangle$ where $\langle\psi_1|\psi_1\rangle = 1$
2) Construct $|\bar{\psi}_2\rangle = |\psi_2\rangle - |\psi_1\rangle\langle\psi_1|\psi_2\rangle$ Show orthogonal + eigenstate
3) Normalize $|\bar{\psi}_2\rangle \rightarrow |\bar{\psi}_2\rangle / \langle\bar{\psi}_2|\bar{\psi}_2\rangle^{1/2}$
4) Construct $|\bar{\psi}_3\rangle = |\psi_3\rangle - |\psi_1\rangle\langle\psi_1|\psi_3\rangle - |\bar{\psi}_2\rangle\langle\bar{\psi}_2|\psi_3\rangle$

etc

More typical (better) method is to find other operator that commutes with $\hat{A}$ and make eigenstates of both.

Example: Free particle $\rightarrow$ doubly degenerate states

2 states with energy $E = \frac{\hbar^2 k^2}{2m}$

Also make eigenstates of $\hat{p}$ $\quad e^{ikx}$ and e^{-ikx}

Also make eigenstate of symmetry operator $\hat{S}\psi(x) = \pm\psi(-x)$

$\cos(kx)$ eig val of $\hat{S}$ is 1
$\sin(kx)$ " " " " -1

Review: If the spectrum of an operator is discrete, apply the results of Chap 2

$$\hat{Q}|\psi_n\rangle = q_n|\psi_n\rangle \quad \text{and} \quad \langle\psi_n|\psi_{n'}\rangle = \delta_{nn'}$$

If the spectrum of an operator is continuous, the generalization is

$$\hat{Q}|\psi_q\rangle = q|\psi_q\rangle \quad \text{and} \quad \langle\psi_q|\psi_{q'}\rangle = \delta(q-q')$$

Dirac orthonormality

We will <u>assume</u> the eigenstates of an observable operator are <u>complete</u>. Has been proved in many cases.

My heuristic guiding principle is that I can represent any physical operators <u>and</u> states for a finite time using approximate methods whose errors can be controlled. For any finite error can solve on computer. $\Rightarrow$ Always OK.

Example $\hat{x}$ operator: $\hat{x}|\psi_y\rangle = y|\psi_y\rangle$

A representation $\langle x|\psi_y\rangle = \delta(x-y)$

Check $\langle\psi_y|\psi_{y'}\rangle = \int \delta(x-y)\,\delta(x-y')\,dx \overset{\checkmark}{=} \delta(y-y')$

Another representation $\langle p|\psi_y\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{-ipy/\hbar}$

Check $\langle\psi_y|\psi_{y'}\rangle = \frac{1}{2\pi\hbar}\int e^{ip(y'-y)/\hbar}\,dp = \frac{1}{2\pi}\int e^{ik(y'-y)}\,dk \overset{\checkmark}{=} \delta(y-y')$

A cool thing: since $\hat{x}|\psi_y\rangle = y|\psi_y\rangle$, the representation $\hat{x} = i\hbar\frac{\partial}{\partial p}$ OK

Example $\hat{p}$ operator: $\hat{p}|\psi_{p'}\rangle = p'|\psi_{p'}\rangle$

A representation $\langle p|\psi_{p'}\rangle = \delta(p-p')$

Another representation $\langle x|\psi_{p'}\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ip'x/\hbar}$

Follow same steps as above for $\hat{x}$ to show reasonable and the representation $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ OK

A typical way of writing the states $|\psi_y\rangle = |y\rangle$, $|\psi_p\rangle = |p\rangle$

<u>Statistical interpretation</u>: We want to specify the probability for measuring the value q_n for operator $\hat{Q}$.

$\hat{Q}|f_n\rangle = q_n|f_n\rangle$ then $|\langle f_n|\Psi\rangle|^2$ = prob to measure q_n

This is for discrete states and assumes $\langle f_n|f_{n'}\rangle = \delta_{nn'}$

$\hat{Q}|f_q\rangle = q|f_q\rangle$ then $|\langle f_q|\Psi\rangle|^2 dq$ = prob to measure between q and $q+dq$

This is for continuum states and assumes $\langle f_q|f_{q'}\rangle = \delta(q-q')$

There are many interesting ways to explore these definitions.

$C_n \equiv \langle f_n | \Psi \rangle$ Normalization $\sum_n C_n^* C_n = 1 = \sum_n \langle \Psi | f_n \rangle \langle f_n | \Psi \rangle$
$= \langle \Psi | \Psi \rangle$

$\sum_n |f_n\rangle \langle f_n| = \hat{1}$

Operator $\hat{Q}|f_n\rangle = q_n |f_n\rangle \implies \hat{Q} = \sum_n |f_n\rangle q_n \langle f_n|$ Show!

The continuum versions

$\hat{1} = \int |f_q\rangle \langle f_q| \, dq$ and $\hat{Q} = \int |f_q\rangle q \langle f_q| \, dq$

We can apply this to momentum and position.

$\langle x | \Psi(t) \rangle = \Psi(x,t)$ $\langle p | \Psi(t) \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x,t) \, dx$
$= \int_{-\infty}^{\infty} \langle p | x \rangle \langle x | \Psi(t) \rangle dx$

This means $\langle p | x \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar}$] how to interpret??
What about $\langle x | p \rangle = ?$

We could have done this with the tools of Chap 2 but now it is easy to derive the uncertainty relations.

$$\sigma_A^2 = \langle \Psi | (\hat{A} - \langle \hat{A} \rangle)(\hat{A} - \langle \hat{A} \rangle) | \Psi \rangle = \langle (\hat{A} - \langle \hat{A} \rangle)\Psi | (\hat{A} - \langle \hat{A} \rangle)\Psi \rangle \equiv \langle f | f \rangle$$

$$\sigma_B^2 = \langle g | g \rangle \qquad |g\rangle = (\hat{B} - \langle \hat{B} \rangle)|\Psi\rangle$$

The Schwartz inequality gives $\sigma_A^2 \sigma_B^2 = \langle f|f\rangle \langle g|g\rangle \geq \langle f|g\rangle \langle g|f\rangle$

So I don't need to carry so many terms $\hat{A}' = \hat{A} - \langle \hat{A} \rangle$; $\hat{B}' = \hat{B} - \langle \hat{B} \rangle$

$$\langle f|g\rangle \langle g|f\rangle = \langle \Psi | \hat{A}'\hat{B}' | \Psi \rangle \langle \Psi | \hat{B}'\hat{A}' | \Psi \rangle$$

Now use $z z^* \geq \mathrm{Im}(z)^2 = \left(\frac{z - z^*}{2i}\right)^2$

$$\langle f|g\rangle \langle g|f\rangle \geq \left(\frac{\langle \Psi | \hat{A}'\hat{B}' | \Psi \rangle - \langle \Psi | \hat{B}'\hat{A}' | \Psi \rangle}{2i} \right)^2 = \left(\frac{\langle \Psi | [\hat{A}', \hat{B}'] | \Psi \rangle}{2i} \right)^2$$

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

Can drop the prime because $[\hat{A}', \hat{B}'] = [\hat{A}, \hat{B}]$

Because $\hat{A}\hat{B} - \hat{B}\hat{A}$ is antihermitian the expectation value is <u>pure imaginary</u>.

Example $\sigma_x^2 \sigma_p^2 \geq \hbar^2/4$?

$$[\hat{x}, \hat{p}] = i\hbar \qquad \sigma_x^2 \sigma_p^2 \geq \left(\frac{\langle i\hbar \rangle}{2i} \right)^2 = \left(\frac{\hbar}{2} \right)^2 \checkmark$$

Griffiths is correct that the energy-time uncertainty relation is different.

$$\Delta E \, \Delta t \geq \hbar/2$$

People have used this to argue that energy is not conserved for small times. This is wrong

$\langle H \rangle(t) = \langle H \rangle(0)$ for any time independent H

You can use this expression for estimating the energy width of states made under time dependent situations.

Example: you use a laser pulse with a duration Δt and central energy E_{ph}. An atom that absorbs one photon will have an energy $E = E_{init} + E_{ph}$ with an energy spread $\Delta E \geq \frac{\hbar}{2\Delta t}$

This section is interesting derivation of $\frac{d}{dt}\langle Q\rangle(t)$. In Chap 1 we found $\frac{d\langle x\rangle(t)}{dt} = \frac{\langle p\rangle(t)}{m}$ and $\frac{d\langle p\rangle(t)}{dt} = -\langle \frac{\partial V}{\partial x}\rangle(t)$

General derivation

$$\frac{d}{dt}\langle Q\rangle(t) = \frac{d}{dt}\langle \Psi(t)|\,\hat{Q}(t)\,|\Psi(t)\rangle$$

$$= \langle \frac{\partial \Psi}{\partial t}|\,\hat{Q}(t)\,|\Psi(t)\rangle + \langle \Psi|\,\hat{Q}(t)\,|\frac{\partial \Psi}{\partial t}\rangle + \langle \Psi(t)|\,\frac{\partial \hat{Q}(t)}{\partial t}\,|\Psi(t)\rangle$$

$$= \langle \frac{1}{i\hbar}\hat{H}\Psi|\hat{Q}|\Psi\rangle + \langle \Psi|\,\hat{Q}\,|\frac{1}{i\hbar}\hat{H}\Psi\rangle + \langle \frac{\partial \hat{Q}}{\partial t}\rangle$$

$$= -\frac{1}{i\hbar}\langle \Psi|\,\hat{H}\hat{Q}\,|\Psi\rangle + \frac{1}{i\hbar}\langle \Psi|\,\hat{Q}\hat{H}\,|\Psi\rangle + \langle \frac{\partial \hat{Q}}{\partial t}\rangle$$

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

Example: $\frac{d\langle \hat{x}\rangle}{dt} = ?$

$$\frac{\partial \hat{x}}{\partial t} = 0 \qquad [\hat{H},\hat{x}] = [\frac{\hat{p}^2}{2m},\hat{x}] + \cancel{[V(\hat{x}),\hat{x}]}^{0}$$

$$= \frac{1}{2m}\left(\hat{p}\,[\hat{p},\hat{x}] + [\hat{p},\hat{x}]\,\hat{p}\right) = -\frac{i\hbar}{m}\hat{p}$$

$$\frac{d\langle \hat{x}\rangle(t)}{dt} = \frac{i}{\hbar}\,\frac{-i\hbar}{m}\langle \hat{p}\rangle(t) = \frac{1}{m}\langle \hat{p}\rangle(t) \ \checkmark$$

Example: $\frac{d}{dt}\langle \hat{H}\rangle(t) = ?$ for time independent $\hat{H}$

$$\frac{\partial \hat{H}}{\partial t} = 0 \qquad [\hat{H},\hat{H}] = 0 \implies \frac{d}{dt}\langle \hat{H}\rangle(t) = 0 \ \checkmark$$

Dirac Notation: I don't know why Griffiths uses $|\mathcal{S}(t)\rangle$ for $|\Psi(t)\rangle$. Note the change from book notation.

Distinguish vector $\vec{A}$ from representation (A_x, A_y, A_z)

$|\Psi(t)\rangle$ is the actual state vector

Three representations

$$\underbrace{\langle x|}_{\text{bra}}\underbrace{\Psi(t)\rangle}_{\text{ket}} = \Psi(x,t) \qquad \langle p|\Psi(t)\rangle = \Phi(p,t) \qquad \langle f_n|\Psi(t)\rangle = c_n(t)$$

This gives

$$|\Psi(t)\rangle = \int |x\rangle\, \Psi(x,t)\,dx = \int |p\rangle\, \Phi(p,t)\,dp = \sum_n |f_n\rangle c_n(t)$$

If you specify the underlying unit vector, then the coefficients are sufficient.

States are like vectors. Operators are like matrices. Operators in quantum mechanics are linear transformations of one state (vector) into another.

$$\hat{Q}|\alpha\rangle = |\beta\rangle$$

To see how this works use a representation. (I use a discrete representation, but continuous works as well.)

$$|\alpha\rangle = \sum_n |f_n\rangle \overbrace{\langle f_n|\alpha\rangle}^{\alpha_n} \quad \text{and} \quad |\beta\rangle = \sum_n |f_n\rangle \overbrace{\langle f_n|\beta\rangle}^{\beta_n}$$

The representation of $\hat{Q}$ in <u>this</u> basis

$$\hat{Q} = \sum_{nn'} |f_n\rangle Q_{nn'} \langle f_{n'}| \quad \Rightarrow \quad Q_{nn'} = \langle f_n|\hat{Q}|f_{n'}\rangle$$

Substitute the representation

$$\hat{Q}|\alpha\rangle = \sum_{nn'n''} |f_n\rangle Q_{nn'} \langle f_{n'}|f_{n''}\rangle\langle f_{n''}|\alpha\rangle = \sum_n \sum_{n'} |f_n\rangle Q_{nn'}\alpha_{n'}$$

$$= \sum_n |f_n\rangle \sum_{n'} Q_{nn'}\alpha_{n'} = \sum_n |f_n\rangle \beta_n \Rightarrow \beta_n = \sum_{n'} Q_{nn'}\alpha_{n'}$$

In many cases this is written as $\vec{\beta} = \underline{\underline{Q}}\,\vec{\alpha}$

The matrix representation of a Hermitian operator has property
$(Q^\dagger)_{nn'} = Q^*_{n'n}$ for any representation

Example: Find the representation of $\hat{a}_\pm$ using harmonic oscillator eigenstates.

$$(a_+)_{nn'} = \langle \psi_n | a_+ | \psi_{n'} \rangle = \sqrt{n'+1}\,\langle \psi_n | \psi_{n'+1} \rangle = \sqrt{n'+1}\;\delta_{n,n'+1}$$

$$(a_-)_{nn'} = \langle \psi_n | a_- | \psi_{n'} \rangle = \sqrt{n'}\,\langle \psi_n | \psi_{n'-1} \rangle = \sqrt{n'}\;\delta_{n,n'-1} = \sqrt{n+1}\;\delta_{n,n'-1}$$

I once said $a_- = a_+^\dagger$ Is $(a_-)_{nn'} = (a_+^\dagger)_{nn'} = (a_+)^*_{n'n}$

$(a_-)_{nn'} = \sqrt{n+1}\;\delta_{n+1,n'}$ $\quad (a_+)^*_{n'n} = \sqrt{n+1}\;\delta_{n',n+1}$ ✓ same

From Eq 2.55 $\hat{a}_-\hat{a}_+ - \hat{a}_+\hat{a}_- = \hat{1}$

$$\underline{\underline{a}}_- = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & & \end{pmatrix} \qquad \underline{\underline{a}}_+ = \underline{\underline{a}}_-^\dagger = \begin{pmatrix} 0 & 0 & 0 & \cdots & \cdots \\ \sqrt{1} & 0 & 0 & \cdots & \cdots \\ 0 & \sqrt{2} & 0 & \cdots & \cdots \end{pmatrix}$$

$$\underline{\underline{a}}_-\underline{\underline{a}}_+ = \begin{pmatrix} 1 & 0 & 0 & 0 & \cdots \\ 0 & 2 & 0 & 0 & \cdots \\ 0 & 0 & 3 & 0 & \cdots \end{pmatrix} \qquad \underline{\underline{a}}_+\underline{\underline{a}}_- = \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 2 & \cdots \\ \ddots & \ddots & \ddots & \end{pmatrix}$$

$$\underline{\underline{a}}_-\underline{\underline{a}}_+ - \underline{\underline{a}}_+\underline{\underline{a}}_- = \begin{pmatrix} 1-0 & 0 & 0 & \cdots \\ 0 & 2-1 & 0 & 0 & \cdots \\ 0 & 0 & 3-2 & 0 & \cdots \end{pmatrix} = \underline{\underline{1}} = \begin{pmatrix} 1 & 0 & 0 & 0 & \ddots \\ 0 & 1 & 0 & 0 & \ddots \\ 0 & 0 & 1 & 0 & \ddots \\ & \ddots & \ddots & \ddots & \end{pmatrix}$$

The representation of the product of 2 operators is the matrix product of the representations.

$$\hat{Q} = \hat{A}\hat{B} \to \hat{Q} = \sum_{nn'} |f_n\rangle Q_{nn'} \langle f_{n'}| = \sum_{nn''} |f_n\rangle A_{nn''} \langle f_{n''}| \sum_{n'''n'} |f_{n'''}\rangle B_{n'''n'} \langle f_{n'}|$$

$$= \sum_{nn'} |f_n\rangle \Big(\sum_{n''n'''} A_{nn''}\,\delta_{n'',n'''}\,B_{n''',n'} \Big) \langle f_{n'}|$$

$$= \sum_{nn'} |f_n\rangle \Big(\sum_{n''} A_{nn''}\,B_{n'',n'} \Big) \langle f_{n'}|$$

This means $\underline{\underline{Q}} = \underline{\underline{A}}\;\underline{\underline{B}}$

In many (most?) cases, it is easier to work with matrices for operators and vectors for states. (Approximately all of my calculations use matrices and vectors.)

Derive the time dependent Schrodinger Eq. from a vector/matrix representation.

1) Choose a representation $|f_n\rangle$ with $\langle f_n | f_{n'}\rangle = \delta_{nn'}$

2) Compute $H_{nn'} = \langle f_n | \hat{H} | f_{n'}\rangle$ in that representation.

3) $|\Psi(t)\rangle = \sum_{n'} |f_{n'}\rangle C_{n'}(t)$

$$\langle f_n | i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \langle f_n | \sum_{n'} |f_{n'}\rangle \left(i\hbar \frac{dC_{n'}(t)}{dt}\right) = i\hbar \frac{dC_n(t)}{dt}$$

$$\langle f_n | \hat{H} | \Psi(t)\rangle = \sum_{n'} \langle f_n | \hat{H} | f_{n'}\rangle C_{n'}(t) = \sum_{n'} H_{nn'}^{(t)} C_{n'}(t)$$

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle \longrightarrow i\hbar \frac{dC_n(t)}{dt} = \sum_{n'} H_{nn'}^{(t)} C_{n'}(t)$$

If $\underline{\underline{H}}$ is a time independent matrix of size $N \times N$, then there are N orthogonal eigenstates. The time independent Schrodinger eq is derived as

$$C_{n,\alpha}(t) = C_{n,\alpha}\, e^{-iE_\alpha t/\hbar} \rightarrow \qquad C_{n,\alpha} E_\alpha = \sum_{n'} H_{n,n'} C_{n',\alpha}$$

Orthonormality properties of the $C_{n,\alpha}$

$$\sum_n H_{n,n'} C^*_{n,\alpha'} = \sum_n H^*_{n',n} C^*_{n,\alpha'} = C^*_{n',\alpha'} E^*_{\alpha'} = C^*_{n'\alpha'} E_{\alpha'}$$

Take the original eq., mult. by $C^*_{n,\alpha'}$ and sum over n
" " next " " $C_{n',\alpha}$ " " " n'
subtract these

$$\left(\sum_n C_{n,\alpha} C^*_{n,\alpha'}\right)(E_\alpha - E_{\alpha'}) = 0 \Rightarrow \sum_n \left(C^\dagger\right)_{\alpha';n} C_{n,\alpha} = \delta_{\alpha\alpha'}$$

This is the definition of unitary matrix $\underline{\underline{C}}^\dagger \underline{\underline{C}} = \underline{\underline{1}}$

Important implications of unitary matrix:

$$\underline{\underline{C}}^{\dagger} = \underline{\underline{C}}^{-1} \Rightarrow \underline{\underline{C}}\,\underline{\underline{C}}^{-1} = \underline{\underline{C}}\,\underline{\underline{C}}^{\dagger} = \underline{\underline{1}} \longrightarrow \sum_{\alpha} C_{n,\alpha} C^{*}_{n',\alpha} = \delta_{nn'}$$

Example $\underline{\underline{H}} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$, write Sch. eq. + find eigenstates and eigenvalues

S. eq: $i\hbar \frac{dC_1}{dt} = H_{11}C_1 + H_{12}C_2 \qquad i\hbar \frac{dC_2}{dt} = H_{21}C_1 + H_{22}C_2$

Find eig vals + vecs $\qquad C_{1\alpha}E_\alpha = H_{11}C_{1\alpha} + H_{12}C_{2\alpha} \qquad C_{2\alpha}E_\alpha = H_{21}C_{1\alpha} + H_{22}C_{2\alpha}$

$$\left.\begin{aligned} 0 &= (H_{11}-E_\alpha)C_{1\alpha} + H_{12}C_{2\alpha} \\ 0 &= H_{21}C_{1\alpha} + (H_{22}-E_\alpha)C_{2\alpha} \end{aligned}\right] \rightarrow (E_\alpha - H_{11})(E_\alpha - H_{22}) = H_{12}H_{21} = |H_{12}|^2$$

There are 2 solutions

$$E_\pm = \frac{H_{11}+H_{22}}{2} \pm \left(\left(\frac{H_{11}-H_{22}}{2}\right)^2 + |H_{12}|^2 \right)^{1/2} = \bar{E} \pm \sqrt{\Delta^2 + |H_{12}|^2}$$

$$\bar{E} = \frac{H_{11}+H_{22}}{2} \qquad \Delta = \frac{H_{22}-H_{11}}{2} = \bar{E} - H_{11} = H_{22} - \bar{E}$$

Now find the eigenvectors (Do for $\alpha = +$)

$$C_{1\pm} = H_{12}C_{2\pm}/(E_\pm - H_{11})$$

Normalize $|C_{1\pm}|^2 + |C_{2\pm}|^2 = |C_{2\pm}|^2 \left[\frac{|H_{12}|^2}{(E_\pm - H_{11})^2} + 1 \right] = 1$

$$C_{2\pm} = \frac{E_\pm - H_{11}}{\left[(E_\pm - H_{11})^2 + |H_{12}|^2\right]^{1/2}} \qquad C_{1\pm} = \frac{H_{12}}{\left[(E_\pm - H_{11})^2 + |H_{12}|^2\right]^{1/2}}$$

Note $(E_\pm - H_{11})^2 + |H_{12}|^2 = \left(\Delta \pm \sqrt{\Delta^2 + |H_{12}|^2}\right)^2 + |H_{12}|^2$

$$= \Delta^2 \pm 2\Delta\sqrt{\Delta^2+|H_{12}|^2} + \Delta^2 + |H_{12}|^2 + |H_{12}|^2$$

$$= 2\sqrt{\Delta^2+|H_{12}|^2}\left(\sqrt{\Delta^2+|H_{12}|^2} \pm \Delta\right)$$

Be careful when using these expressions for $H_{12} = 0$

In this case $C_{2+} = 1 \quad C_{1+} = 0$; $C_{2-} = 0, C_{1-} = 1$ if $H_{22} > H_{11}$

Example $H_{11} = H_{22} = h$ and $H_{12} = H_{21} = g > 0$

$\Delta = 0 \qquad \bar{E} = h \qquad E_+ = h + g \qquad E_- = h - g$

$C_{2+} = g/\sqrt{g^2+g^2} = 1/\sqrt{2} \qquad C_{1+} = g/\sqrt{g^2+g^2} = 1/\sqrt{2}$

$C_{2-} = -g/\sqrt{g^2+g^2} = -1/\sqrt{2} \qquad C_{1-} = g/\sqrt{g^2+g^2} = 1/\sqrt{2}$

For the previous $\underline{\underline{H}}$, what is $\Psi(t)$ if $|\Psi(0)\rangle = |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$?

$$|+\rangle = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \qquad |-\rangle = \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$$

$$C_+(0) = \langle + | 1 \rangle = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1/\sqrt{2}$$

$$C_-(0) = \langle - | 1 \rangle = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1/\sqrt{2})$$

$$|\Psi(t)\rangle = |+\rangle C_+(0) e^{-iE_+t/\hbar} + |-\rangle C_-(0) e^{-iE_-t/\hbar}$$

$$= \left(|+\rangle \frac{1}{\sqrt{2}} e^{-igt/\hbar} + |-\rangle \frac{1}{\sqrt{2}} e^{igt/\hbar} \right) e^{-iht/\hbar}$$

$$= \begin{pmatrix} \frac{1}{2} e^{-igt/\hbar} + \frac{1}{2} e^{igt/\hbar} \\ \frac{1}{2} e^{-igt/\hbar} - \frac{1}{2} e^{igt/\hbar} \end{pmatrix} e^{-iht/\hbar} = e^{-iht/\hbar} \begin{pmatrix} \cos(gt/\hbar) \\ -i\sin(gt/\hbar) \end{pmatrix}$$