Week 10 - Time evolution

→ Systems over time

- $|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle$ gives Schrödinger's $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$

This comes from our previous discussion on unitary operators:

1. The generator of time translations is $\hat{H}$
2. Stone's theorem says that for every self-adjoint operator $\hat{A} = \hat{A}^{+}$ we have a unitary group $\hat{U}(t)$. So:

   $\hat{U}(t) = e^{-i\hat{A}t}$ or, in our case, the $\hat{U}(t)$ that governs evolution over time of a system has some corresponding $\hat{A}$.

   I guess experimentally, $\hat{A} = \hat{H}/\hbar$, similar to last class...?
3. So:

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle, \text{ which means}$$

$$|\psi(t+dt)\rangle = e^{-i\hat{H}dt/\hbar}|\psi(t)\rangle$$ to which we can apply the expansion we've been using:

$$|\psi(t+dt)\rangle = |\psi(t)\rangle + dt\frac{\partial}{\partial t}|\psi(t)\rangle$$

$$= |\psi(t)\rangle + dt\frac{\partial}{\partial t}\left(e^{-i\hat{H}t/\hbar}|\psi(0)\rangle\right)$$

$$= |\psi(t)\rangle - i\hat{H}\frac{dt}{\hbar}|\psi(t)\rangle$$

4. $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$

This is how a system evolves over time (if isolated) - deterministically! Very different from the stochastic change as a result of measurement.

→ Spectral Properties of the Hamiltonian

- For eigenstates of $\hat{H}$, $|\varphi_i\rangle$:

$$\hat{H}|\varphi_i\rangle = E_i|\varphi_i\rangle$$

so, if our initial state $|\psi(t=0)\rangle = |\varphi_i\rangle$, we know:

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle = e^{-i\hat{H}t/\hbar}|\varphi_i\rangle$$

$$= e^{-iE_it/\hbar}|\varphi_i\rangle$$ because $|\varphi_i\rangle$ is an eigenstate of $\hat{H}$.

This tells us that the state changes by a global phase factor $e^{-iE_it/\hbar}$, and a state is a <u>ray</u>, so global phase factors don't actually matter (they change the length but not direction) — State does <u>not</u> change.

- We can see this another way:

$$\langle \hat{A} \rangle_{\psi(t)} = \langle \psi(t) | \hat{A} | \psi(t) \rangle = e^{iE_it/\hbar} \langle \varphi_i | \hat{A} | \varphi_i \rangle e^{-iE_it/\hbar}$$
$$= \langle \varphi_i | \hat{A} | \varphi_i \rangle$$
$$= \langle \hat{A} \rangle_{\psi(0)}$$

The expectation value of the isolated system does not change with time.

- The final state after measurement also does not change:

$|\psi\rangle \mapsto \hat{P}|\psi\rangle$ after measurement

so, after time t (of a system with initial state $|\varphi_i\rangle$...) we measure:

$\hat{P} e^{-iE_it/\hbar} |\varphi_i\rangle = e^{-iE_it/\hbar} \hat{P} |\varphi_i\rangle$

which to us, where states are rays, is the same as state $\hat{P}|\varphi_i\rangle$, where we measure at $t=0$.

- For this reason, eigenstates of $\hat{H}$ are called <u>stationary states</u>.

- If our initial state is <u>not</u> a stationary state $|\varphi_i\rangle$, this is different:

$$|\psi(t)\rangle = \sum_i |\varphi_i\rangle\langle \varphi_i | \psi(t)\rangle = \sum_i |\varphi_i\rangle c_i(t) \text{ and,}$$

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\psi(t=0)\rangle = e^{-i\hat{H}t/\hbar} \sum_i |\varphi_i\rangle c_i(t=0)$$
$$= \sum_i e^{-i\hat{H}t/\hbar} |\varphi_i\rangle c_i(t=0) = \sum_i e^{-iE_it/\hbar} |\varphi_i\rangle c_i(0)$$
$$= \sum_i |\varphi_i\rangle c_i(t), \text{ where } c_i(t) = e^{-iE_it/\hbar} c_i(0)$$

We see that each expansion coefficient $c_i(t)$ for each corresponding eigenbasis vector of $\hat{H}$, $|\varphi_i\rangle$ <u>changes over time</u> at the rate $E_i/\hbar$.

Because E_i is <u>different</u> for each $|\varphi_i\rangle$, $|\psi(t)\rangle$ is <u>not</u> the same state as $|\psi(0)\rangle$. Each <u>component</u> of $|\psi(t)\rangle$ changes differently over time. (if all E_i eigenvalues were the same, we could pull out a <u>global</u> phase factor. But clearly that is not the case!)

- The expectation value is also not constant:

$$\langle \hat{A} \rangle_{\psi(t)} = \langle \psi(t) | \hat{A} | \psi(t) \rangle$$
$$= \sum_{ij} \underbrace{e^{iE_it/\hbar} c_i^*(0)}_{c_i^*(t)} \langle \varphi_i | \hat{A} | \varphi_j \rangle \underbrace{e^{-iE_jt/\hbar} c_j(0)}_{c_j(t)}$$

If our basis is the eigenstates of $\hat{H}$, an element in $\hat{A}$'s matrix, A_{ij} is

$A_{ij} = \langle \varphi_i | \hat{A} | \varphi_j \rangle$

Also, $\omega_{ji} = E_j - E_i / \hbar$ is what we call a Bohr angular frequency.

We can then rewrite:

$$\langle \hat{A} \rangle_{\Psi(t)} = \sum_{ij} A_{ij} \, c_i^*(0) \, c_j(0) \, e^{-i\omega_{ji}t}$$ which must be a real value.

We can break this down further:

$$\langle \hat{A} \rangle_{\Psi(t)} = \sum_{j=i} A_{ii} |c_i(0)|^2 + \sum_{j>i} A_{ij} \, c_i^*(0) \, c_j(0) \, e^{-i\omega_{ji}t}$$
$$+ \sum_{j<i} A_{ij} \, c_i^*(0) \, c_j(0) \, e^{-i\omega_{ji}t}$$

since they are just indices, we can flip all i's & j's in the last term:

$$\sum_{i<j} A_{ji} \, c_j^*(0) \, c_i(0) \, e^{-i\omega_{ij}t}$$

we know $A_{ji} = A_{ij}^*$ and $\omega_{ji} = E_j - E_i / \hbar$, so $\omega_{ij} = -\omega_{ji}$ and $e^{-i\omega_{ij}t} = e^{i\omega_{ji}t}$, so this whole term is actually the complex conjugate of the second term!

By definition, $z + z^* = 2\mathrm{Re}(z)$, so:

$$\langle \hat{A} \rangle_{\Psi(t)} = \sum_i A_{ii} |c_i(0)|^2 + 2\mathrm{Re} \sum_{j>i} A_{ij} \, c_i^*(0) \, c_j(0) \, e^{-i\omega_{ji}t}$$

We can also write any complex z as $|z| e^{i\phi}$ for some ϕ, so we can rewrite $A_{ij} \, c_i^*(0) c_j(0)$ as $|A_{ij} \, c_i^*(0) c_j(0)| \, e^{i\phi_{ij}}$.

$$\langle \hat{A} \rangle_{\Psi(t)} = \sum_i A_{ii} |c_i(0)|^2 + 2 \sum_{j>i} |A_{ij} \, c_i^*(0) \, c_j(0)| \, \mathrm{Re}\{e^{-i(\omega_{ji}t - \phi_{ij})}\}$$
$$= \sum_i A_{ii} |c_i(0)|^2 + 2 \sum_{j>i} |A_{ij} \, c_i^*(0) \, c_j(0)| \cos(\omega_{ji}t - \phi_{ij})$$

Evidently, this first term does not vary with time (it is static) and the second is a sinusoid with period $T = 2\pi / \omega_{ji}$ and is offset a distance $\tau = \phi_{ij} / \omega_{ji}$ from the origin.

∴ The expectation value wrt a system with arbitrary initial state $|\Psi(0)\rangle$ <u>oscillates with time</u>

For an arbitrary $|\Psi(0)\rangle$, the expectation value is static only if $|\Psi(0)\rangle = |\varphi_i\rangle$ as we saw earlier, or $\hat{A}$ commutes with $\hat{H}$:

- We want the "t" term to be 0. Since ω_{ji} can't be 0 for all j and i, and not all $c_i(0)$, $c_j(0)$ can be 0 (for arbitrary $|\psi(0)\rangle$), we need $A_{ij} = 0$.
- For A_{ij} (which recall is in $\hat{H}$'s eigenbasis), $A_{ij} = \langle \varphi_i | \hat{A} | \varphi_j \rangle$ which is guaranteed if $[\hat{A}, \hat{H}] = 0$

$$\langle \varphi_i | [\hat{A}, \hat{H}] | \varphi_j \rangle = \langle \varphi_i | 0 | \varphi_j \rangle = 0$$
$$= \langle \varphi_i | \hat{A}\hat{H} - \hat{H}\hat{A} | \varphi_j \rangle$$
$$= \langle \varphi_i | \hat{A}\hat{H} | \varphi_j \rangle - \langle \varphi_i | \hat{H}\hat{A} | \varphi_j \rangle$$
$$= E_j \langle \varphi_i | \hat{A} | \varphi_j \rangle - E_i \langle \varphi_i | \hat{A} | \varphi_j \rangle$$
$$= (E_j - E_i) \langle \varphi_i | \hat{A} | \varphi_j \rangle$$

So for $j \neq i$, $A_{ij} = 0$, so the matrix of A is diagonal in $\hat{H}$'s eigenbasis $\Longrightarrow$ $\hat{A}$ and $\hat{H}$ commute.

$\therefore [\hat{A}, \hat{H}] = 0 \Longrightarrow \langle \hat{A} \rangle_{\psi(t)}$ is constant over t.

- In other words:

$$\langle \hat{A} \rangle_{\psi(t)} = \langle \psi(t) | \hat{A} | \psi(t) \rangle$$
$$= \langle \psi(0) | e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} | \psi(0) \rangle$$

if $[\hat{H}, \hat{A}] = 0$ we can rearrange these operators

$$\langle \hat{A} \rangle_{\psi(t)} = \langle \psi(0) | \hat{A} e^{i\hat{H}t/\hbar} e^{-i\hat{H}t/\hbar} | \psi(0) \rangle = \langle \hat{A} \rangle_{\psi(0)}$$

- More about expectation values... Assuming $\frac{\partial A}{\partial t} = 0$ and we know (or expect) $\frac{d}{dt} \langle \hat{A} \rangle_{\psi(t)} \neq 0$ unless $\hat{A}$ and $\hat{H}$ commute. We can obtain this relationship as:

$$\frac{d}{dt} \langle \hat{A} \rangle_{\psi(t)} = \frac{d}{dt} \langle \psi(0) | e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} | \psi(0) \rangle$$

$$= \langle \psi(0) | \frac{d}{dt} e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar} \hat{A} \frac{d}{dt} e^{-i\hat{H}t/\hbar} | \psi(0) \rangle$$

$$= \frac{i}{\hbar} \langle \psi(0) | e^{i\hat{H}t/\hbar} \hat{H}\hat{A} - \hat{A}\hat{H} e^{-i\hat{H}t/\hbar} | \psi(0) \rangle$$

$$= \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle_{\psi(t)}$$

We can apply this to get N2L / Ehrenfest's theorem. Say we have a free particle in 1D with $\hat{H} = \hat{p}^2/2m + V(\hat{x})$. If our $\hat{A}$ is $\hat{p}$:

$$\langle x | [\hat{H}, \hat{A}] = \langle x | [\frac{\hat{p}^2}{2m} + V(\hat{x}), \hat{p}] = \langle x | [V(\hat{x}), \hat{p}]$$

$$= \langle x | V(\hat{x}) \hat{p} - \langle x | \hat{p} V(\hat{x})$$

$$\langle x|V(\hat{x})\hat{p} - \langle x|\hat{p}V(\hat{x}) = V(x)\langle x|\hat{p} - \langle x|\hat{p}V(\hat{x})$$
$$= V(x)(-i\hbar\tfrac{d}{dx})\langle x| + i\hbar\tfrac{d}{dx}(\langle x|V(\hat{x}))$$
$$= -i\hbar V(x)\tfrac{d}{dx}\langle x| + i\hbar\tfrac{d}{dx}(V(x)\langle x|)$$
$$= \underline{-i\hbar V(x)d/dx\langle x|} + i\hbar\, dV/dx\langle x| + \underline{i\hbar V(x)\tfrac{d}{dx}\langle x|}$$

$$= i\hbar\frac{dV}{dx}\langle x| = i\hbar\langle x|\frac{dV}{dx}(\hat{x})$$

so, $[\hat{H},\hat{p}]$ in this case is $i\hbar\frac{dV}{dx}(\hat{x})$

We can use our earlier result to do:

$$\frac{d\langle\hat{p}\rangle_{\psi(t)}}{dt} = \frac{i}{\hbar}\langle[\hat{H},\hat{p}]\rangle_{\psi(t)} = \frac{i}{\hbar}\langle i\hbar\frac{dV}{dx}\rangle_{\psi(t)}$$
$$= -\langle\frac{dV}{dx}\rangle_{\psi(t)} \quad \text{(Ehrenfest's theorem)}$$

Note how this mirrors $\frac{dp}{dt} = ma = F = -\frac{dV}{dx}$ in classical mechanics!

→ Momentum and the Hamiltonian

- Momentum-space wave function $\langle p|\psi\rangle = \phi(p)$

For a free particle in 1D with mass m:

$\hat{H} = \hat{p}^2/2m$, so $[\hat{H},\hat{p}] = 0$ and eigenstates of $\hat{p}$ are eigenstates of $\hat{H}$. We also have generalized eigenstates so that

$\hat{p}|p\rangle = p|p\rangle$, $p \in \sigma(\hat{p}) = \mathbb{R}$ (momentums are real valued)

$\langle p|p'\rangle = \delta(p-p')$

and, $\hat{H}|p\rangle = p^2/2m\,|p\rangle$, so $\sigma(\hat{H}) = \mathbb{R}_0^+$ (p^2 is 0 or $\mathbb{R}^+$)

What does $\hat{p}|p\rangle$ look like in position space?

$\langle x|\hat{p}|p\rangle = p\langle x|p\rangle$

$-i\hbar\frac{d}{dx}\phi_p(x) = p\,\phi_p(x) \rightarrow (-i\hbar\frac{d}{dx} - p)\phi_p(x) = 0$ which is a linear ODE (1st order) with a known solution:

$$\frac{d\phi_p}{dx}\left(\frac{1}{\phi_p}\right) = \frac{ip}{\hbar} \Rightarrow \frac{d(\ln\phi_p)}{dx} = \frac{ip}{\hbar} \quad \text{(which is a constant!)}$$

$$\ln\phi_p(x) = \frac{ip}{\hbar}x + C_p \rightarrow e^{C_p}e^{ipx/\hbar} = \phi_p(x)$$

call e^{C_p} some normalization constant N_p.

We can determine N_p by enforcing $\langle p|p'\rangle = \delta(p-p')$

Insert the identity $\int dx\,|x\rangle\langle x|$:

$$\langle p|p'\rangle = \int dx\,\langle p|x\rangle\langle x|p'\rangle = \int dx\,\phi_p^*(x)\phi_{p'}(x)$$

$$= N_p^* N_{p'} \int_{-\infty}^{\infty} e^{i(p'-p)x/\hbar} dx = \hbar N_p^* N_{p'} \int_{-\infty}^{\infty} e^{-i(p'-p)x/\hbar} dx/\hbar$$

(say $u = x/\hbar$)

$$= \hbar N_p^* N_p' \int_{-\infty}^{\infty} du\, e^{-i(p'-p)u}$$

$$= 2\pi\hbar N_p^* N_{p'} \delta(p'-p) \quad \left(\text{using } \int_{-\infty}^{\infty} e^{ikx} dx = 2\pi\delta(k)\ldots\right)$$

since we want $\langle p|p'\rangle = \delta(p-p')$, and $\delta(p-p') = \delta(p'-p)$,

$$2\pi\hbar N_p^* N_{p'} \delta(p'-p) = 2\pi\hbar N_p^* N_p \delta(p'-p) = \delta(p'-p)$$

$$|N_p|^2 = \frac{1}{2\pi\hbar}$$

$$|N_p| = \frac{1}{\sqrt{2\pi\hbar}}, \text{ so } N_p = \frac{1}{\sqrt{2\pi\hbar}} e^{i\theta_p}$$

so, $\phi_p(x) = \langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{i\theta_p} e^{ipx/\hbar}$

Finally, to enforce the action of $\hat{B}_{\Delta p}|p\rangle = |p+\Delta p\rangle$, we can set θ_p:

$$\langle x|\hat{B}_{\Delta p}|p\rangle = \langle x|p+\Delta p\rangle$$

LHS, since $\hat{B}_{\Delta p} = e^{i\Delta p\hat{X}/\hbar}$ is $e^{i\Delta px/\hbar} \frac{1}{\sqrt{2\pi\hbar}} e^{i\theta_p} e^{ipx/\hbar}$

RHS, using $\phi_{p+\Delta p}(x)$ is $\frac{1}{\sqrt{2\pi\hbar}} e^{i\theta_{p+\Delta p}} e^{i(p+\Delta p)x/\hbar}$

so clearly $\theta_p = \theta_{p+\Delta p}$ for any Δp, so θ_p is the same for all p. For convenience we can even set it to 0. Now:

$$\phi_p(x) = \langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

- We can see what $\hat{T}_{\Delta x}$ and $\hat{B}_{\Delta p}$ applied to $\phi_p(x)$ looks like (where, of course, $\langle x|p\rangle$ is the position-space wave function of a momentum eigenstate)

$$\langle x|\hat{T}_{\Delta x}|p\rangle = \langle \hat{T}_{-\Delta x} x|p\rangle = \langle x-\Delta x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ip(x-\Delta x)/\hbar}$$

$$\langle x|\hat{B}_{\Delta p}|p\rangle = \langle x|p+\Delta p\rangle = e^{i\Delta px/\hbar} \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} = \frac{1}{\sqrt{2\pi\hbar}} e^{i(p+\Delta p)x/\hbar}$$

- Because $p \to |p\rangle$ (each eigenvalue p corresponds to a unique eigenvector $|p\rangle$, $\hat{p}$ is non-degenerate), $\{\hat{p}\}$ is a CSCO.

But because $\hat{H}|p\rangle = \frac{p^2}{2m}|p\rangle$, where eigenvalue $E = p^2/2m$, a single E corresponds to two eigenvectors, $|p\rangle = |\sqrt{2mE}\rangle$ and $|p\rangle = |-\sqrt{2mE}\rangle$ (in other words, $\hat{H}|p\rangle = E|p\rangle$ and $\hat{H}|-p\rangle = E|-p\rangle \ldots$)

How can we create a CSCO with $\hat{H}$? We start by re-defining the set of eigenstates we're working with:

$$|\psi\pm\rangle = |p\rangle \pm |-p\rangle$$

We can guarantee that states $|\psi\pm\rangle$ are still eigenvectors because $|p\rangle$ and $|-p\rangle$ have the same eigenvalue wrt $\hat{H}$:

$$\hat{H}(|p\rangle \pm |-p\rangle) = \hat{H}|p\rangle \pm \hat{H}|-p\rangle = E|p\rangle \pm E|-p\rangle$$

$$= E(|p\rangle \pm |-p\rangle)$$

it follows that $|\psi\pm\rangle$ are not eigenstates of $\hat{p}$ since $|p\rangle$ and $|-p\rangle$ do <u>not</u> have the same eigenvalue wrt $\hat{p}$!

$$\hat{p}|\psi\pm\rangle = p|p\rangle \pm (-p)|-p\rangle = p|\psi\mp\rangle$$

As a position-space wavefunction, we now have:

$$\langle x|\psi\pm\rangle = \langle x|p\rangle \pm \langle x|-p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\left(e^{ipx/\hbar} \pm e^{-ipx/\hbar}\right)$$

and if we choose to add, we get $\frac{2}{\sqrt{2\pi\hbar}}\cos\left(\frac{px}{\hbar}\right) = \sqrt{\frac{2}{\pi\hbar}}\cos\left(\frac{px}{\hbar}\right)$

to subtract, we get $i\sqrt{\frac{2}{\pi\hbar}}\sin\left(\frac{px}{\hbar}\right)$

This alone does not make $\hat{H}$ a CSCO, though. We need the parity operator $\hat{\pi}$:

$$\hat{\pi}|x\rangle = |-x\rangle \to \hat{\pi}|\psi\pm\rangle = |-p\rangle \pm |p\rangle = \pm|\psi\pm\rangle$$

$\hookrightarrow |-p\rangle + |p\rangle = +|\psi+\rangle$

$\hookrightarrow |-p\rangle - |p\rangle = -|\psi-\rangle$

Clearly $\hat{\pi}$ is self-adjoint:

$$\langle \phi | \hat{\pi} \psi \rangle = \int_{-\infty}^{\infty} \phi^*(x)\, \hat{\pi}\, \psi(x)\, dx = \int_{-\infty}^{\infty} \phi^*(x)\, \psi(-x)\, dx$$, if $u = -x$ and $du = -dx$:

$$\langle \phi | \hat{\pi} \psi \rangle = -\int_{\infty}^{-\infty} \phi^*(-u)\, \psi(u)\, du = \int_{-\infty}^{\infty} \phi^*(-u)\, \psi(u)\, du$$

$$= \int_{-\infty}^{\infty} (\hat{\pi}\, \phi(u))^* \, \psi(u)\, du = \langle \hat{\pi} \phi | \psi \rangle$$

and it commutes with $\hat{H}$:

$$\hat{H} \hat{\pi} |\psi \pm \rangle = \hat{H} (\pm |\psi \pm \rangle) = \pm E |\psi \pm \rangle$$

$$\hat{\pi} \hat{H} |\psi \pm \rangle = \hat{\pi} (E |\psi \pm \rangle) = E(\pm |\psi \pm \rangle) = \pm E |\psi \pm \rangle$$

We also see that where $\hat{H}$ is degenerate, $\hat{\pi}$ is not:

$\hat{H} |\psi \pm \rangle = E |\psi \pm \rangle$ but $\hat{\pi} |\psi \pm \rangle = \pm |\psi \pm \rangle$ (for both $|\psi + \rangle$ and $|\psi - \rangle$, $\hat{H}$ gives eigenvalue E, but $\hat{\pi}$ gives $+1$ and -1 respectively.)

So, $\{\hat{H}, \hat{\pi}\}$ is a CSCO.