P423, Lecture 2: Review of P323

In the previous Class we argued that in the classical limit ($\hbar \to 0$) the wave fnc should be

$$\psi_{\text{Class}}(\vec{r},t) \approx a\, e^{\frac{i}{\hbar} S(\vec{r},t)}$$

$$\Rightarrow \begin{cases} \dfrac{\partial \psi_{\text{class}}}{\partial t} = \dfrac{i}{\hbar}\dfrac{\partial S}{\partial t}\psi_{\text{class}} = \dfrac{1}{i\hbar} H \psi_{\text{class}}, & \text{motivates Schrödinger's eqn: } i\hbar \dfrac{\partial|\psi\rangle}{\partial t} = \hat{H}|\psi\rangle \\ \vec{p}\,\psi_{\text{class}} = (\vec{\nabla}_r S)\,\psi_{\text{class}} = \left(\dfrac{\hbar}{i}\vec{\nabla}\right)\psi_{\text{class}} & \text{so } \vec{p} \to \dfrac{\hbar}{i}\vec{\nabla} \end{cases}$$

If we define $\psi(\vec{r},t) = \langle \vec{r}\,|\,\psi(t)\rangle$ as the wave fnc, then we may rewrite Schrödinger's eqn as

$$i\hbar \frac{\partial \psi}{\partial t}(\vec{r},t) = \hat{H}\,\psi(\vec{r},t),$$

where $\hat{H} = H(\hat{\vec{r}}_i, \hat{\vec{p}}_i)$ is the Hamiltonian fnc with $\vec{p}_i \to \frac{\hbar}{i}\vec{\nabla}_{r_i}$ and $\vec{r}_i \to \hat{\vec{r}}_i$.

For example, particle in $d=3$ subject to a potential $V(\vec{r})$: $H = \dfrac{\vec{p}^{\,2}}{2m} + V(\vec{r}) = \dfrac{1}{2m}\left(\dfrac{\hbar}{i}\vec{\nabla}\right)^2 + V(\vec{r})$

$$= -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}).$$

Furthermore, if H does not depend explicitly in time, we can solve for the time evolution of any state at $t = t_0$:

$$\boxed{\psi(\vec{r},t) = \underbrace{e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}}_{\hat{U}(t,t_0),\ \text{Time evolution operator}}\,\psi(\vec{r},t_0)}$$

Check: $i\hbar \dfrac{\partial \psi}{\partial t} = i\hbar \dfrac{\partial}{\partial t}\left[e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}\right]\psi(\vec{r},t_0) = i\hbar\left(-\dfrac{i}{\hbar}\right)\dfrac{\partial}{\partial t}(t-t_0)\hat{H}\,\underbrace{e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}\psi(\vec{r},t_0)}_{\psi(\vec{r},t)}$

$$= \hat{H}\,\psi(\vec{r},t).$$

If we focus on initial states that are eigenstates of $\hat{H}$:

$$\hat{H}\,\varphi_E(\vec{r}) = E\,\varphi_E(\vec{r})$$

Their time evolution is quite simple:

$$\varphi_E(\vec{r},t) = e^{-\frac{i}{\hbar}\hat{H}t}\varphi_E(\vec{r}) = e^{-\frac{i}{\hbar}Et}\varphi_E(\vec{r}).$$ Note that $|\varphi_E(\vec{r},t)|^2$ does not change in time.

That is why the $\varphi_E(\vec{r})$ are often called "stationary states".

In ket notation, a superposition of energy eigenstates such as

$$|\psi(t_0)\rangle = \sum_i a_i\,|E_i\rangle \qquad \left(\text{here } \varphi_{E_i}(\vec{r}) = \langle \vec{r}\,|E_i\rangle\right)$$

evolves like

$$|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle = \sum_i a_i\, e^{-\frac{i}{\hbar}E_i t}\,|E_i\rangle.$$ Any state can be written in this way, because $\sum_i |E_i\rangle\langle E_i| = \mathbb{1}$ (completeness).

Note: $|\psi\rangle = \underbrace{\sum |E_i\rangle\langle E_i|}_{\mathbb{1}}\,|\psi\rangle = \sum_i \underbrace{\langle E_i|\psi\rangle}_{a_i}|E_i\rangle$

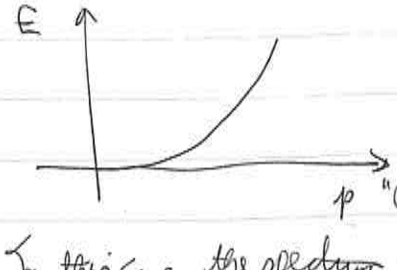
<u>Example 1</u>: Free particle

$$H = \frac{(\vec{p})^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2.$$ In this case the energy eigenstates are also eigenstates of momentum.

The eigenstates of momentum are just plane waves: $\psi_{\vec{p}}(\vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}}e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$

$$\vec{p}\,\psi_{\vec{p}}(\vec{r}) = \frac{\hbar}{i}\vec{\nabla}\left[\frac{1}{(2\pi)^{3/2}}e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\right] = \frac{\hbar}{i}\frac{i}{\hbar}\vec{\nabla}(\vec{p}\cdot\vec{r})\,\psi_p = \vec{p}\,\psi_p(\vec{r}),$$ hence

$$\hat{H}\psi_{\vec{p}} = \frac{(\hat{\vec{p}})^2}{2m}\psi_p = \underbrace{\left(\frac{p^2}{2m}\right)}_{E}\psi_{\vec{p}}$$



p "Quantum number": labels the energy eigenstates

In this case the spectrum is continuous (propagation mode).

Plane waves do not go to zero at $|\vec{r}| \to \infty$. How do we normalize? Using the $\frac{1}{(2\pi\hbar)^{3/2}}$ prefactor.

Consider

$$\langle \vec{r} | \vec{r}' \rangle = \int d^3p \, \underbrace{\langle \vec{r} | \vec{p} \rangle}_{= \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}} \underbrace{\langle \vec{p} | \vec{r}' \rangle}_{\frac{1}{(2\pi\hbar)^{3/2}} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}'}} = \frac{1}{(2\pi\hbar)^3} \int d^3p \, e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}')} = \delta(\vec{r}-\vec{r}')$$

"Delta fnc normalization".

where we used completeness of the vector space spanned by $\psi_{\vec{p}}$: $\{|\vec{p}\rangle\}$ forms a complete basis of Hilbert space : $\int d^3p \, |\vec{p}\rangle\langle\vec{p}| = \mathbb{1}$.

Note how propagating modes (with a continuous energy spectra) cannot satisfy $\int d^3r \, |\psi|^2 = 1$.

We can write any quantum state in terms of the complete basis $\{|\vec{p}\rangle\}$:

$$|\psi\rangle = \underbrace{\int d^3p \, |\vec{p}\rangle\langle\vec{p}|}_{= \mathbb{1}} \psi\rangle ,$$

So any state can be written as

$$\psi(\vec{r}) = \langle \vec{r} | \psi \rangle = \int d^3p \, \langle \vec{r} | \vec{p} \rangle \underbrace{\langle \vec{p} | \psi \rangle}_{\varphi(\vec{p})} = \int d^3p \, \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}} \varphi(\vec{p}) ,$$

wave fnc in momentum representation

and the inverse relation is

$$\boxed{\varphi(\vec{p}) = \int d^3r \, \frac{1}{(2\pi\hbar)^{3/2}} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}} \psi(\vec{r})} .$$

Based on postulate IV $|\varphi(\vec{p}_0)|^2 d^3p$ gives the probability for measuring $\vec{p}$ within d^3p of $\vec{p}_0$.

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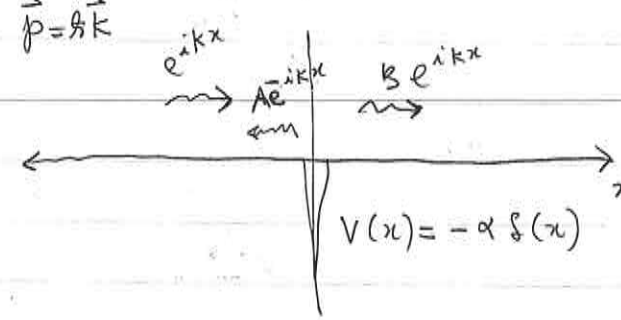
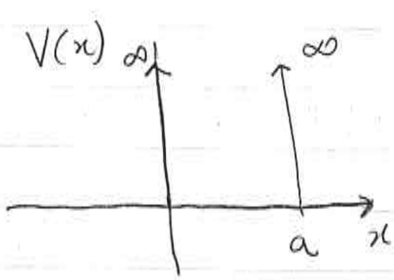
Propagating modes are usually represented as sum of plane waves, see e.g. problem 4 in A1.



<u>Example 2</u>: Particle in $d=1$ box. $V(x) = \begin{cases} 0 & \text{for } 0<x<a \\ \infty & \text{for } x \leq 0 \text{ and } x \geq a \end{cases}$



Find energy eigenstates, $\hat{H}\psi = E\psi$.

Since $V(x) = \infty$ outside the box we must have $\psi = 0$ this region. This requirement <u>quantizes</u> the energy in discrete amounts.

The eigenstates of $\hat{H}$ are still plane waves, $e^{\pm ikx}$. But we need to combine them so that

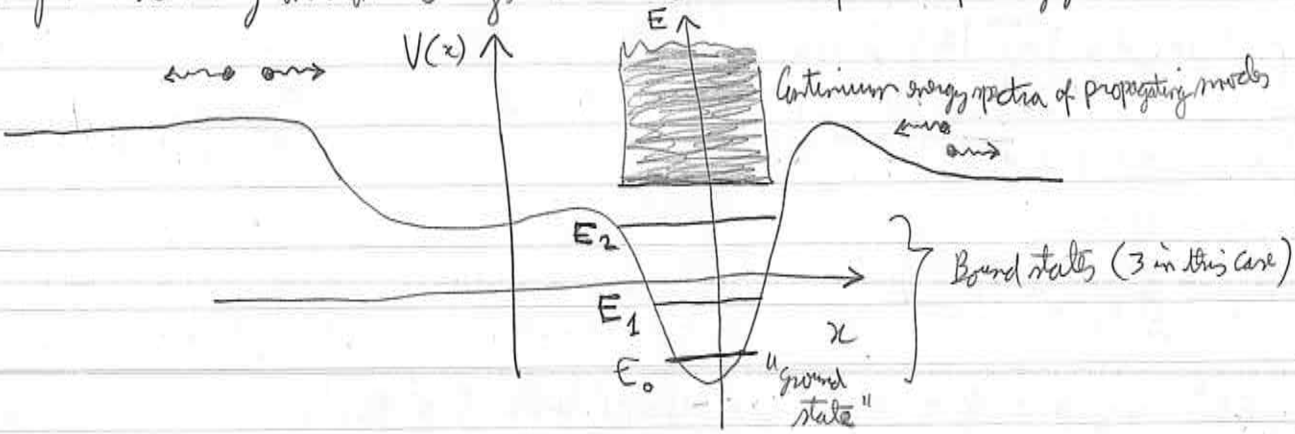
$\psi(0) = \psi(a) = 0$. The solution is:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right) \qquad n = 1, 2, 3, \ldots$$

Check that $\hat{H}\psi_n = -\frac{\hbar^2}{2m}D^2\psi_n = \underbrace{+\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2}_{E_n}\psi_n \Rightarrow E_n = \frac{\hbar^2\pi^2}{2ma^2}n^2$ //

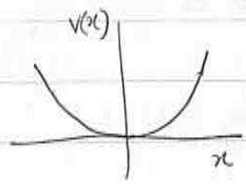
Also check that $\int dx\, |\psi|^2 = 1$.

An energy eigenstate will be a "bound state" when $\psi(\vec{r}) \to 0$ when $|\vec{r}| \to \infty$. We can show that imposing this boundary condition always leads to a discrete spectra of energy.



In problem 3 of A1 you will be asked to calculate the bound states of $V(x) = -\alpha\,\delta(x)$.

Example 3: Harmonic oscillator in $d=1$.
(reasonable approximation for the ground state of any potential well).



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

There are always two methods to find eigenstates: Operator method and differential eqn method.

Operator: Define
$$\begin{cases} \hat{a} = \dfrac{1}{\sqrt{2}}\left(\dfrac{\hat{x}}{x_0} + i\dfrac{x_0}{\hbar}\hat{p}\right) \\[2ex] \hat{a}^\dagger = \dfrac{1}{\sqrt{2}}\left(\dfrac{\hat{x}}{x_0} - i\dfrac{x_0}{\hbar}\hat{p}\right) \end{cases}$$
where $x_0 = \sqrt{\dfrac{\hbar}{m\omega}}$ is a length scale.

(Note: $\hat{a}$ is not Hermitian!)

We can show that using $[x,p] = i\hbar \Rightarrow [a, a^\dagger] = 1$, and that

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

Moreover, we can prove that the set of eigenstates of $a^\dagger a$ are $a^\dagger a|n\rangle = n|n\rangle$ with $n = 0, 1, 2, \ldots$

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So the energy eigenstates are $|n\rangle$ with energy $E_n = \left(n+\frac{1}{2}\right)\hbar\omega \quad n=0,1,2,\dots$

Also, $\begin{cases} \hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle \\ \hat{a}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle \end{cases}$

and using $\begin{cases} \hat{x} = \dfrac{x_0}{\sqrt{2}}\left(\hat{a}+a^\dagger\right) \\ \hat{p} = -\dfrac{i\hbar}{\sqrt{2}\,x_0}\left(\hat{a}-a^\dagger\right) \end{cases}$

we can calculate any property of the Harmonic oscillator (Problem 5 in A1).

<u>Differential eqn method:</u>

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

Introduce $\xi = \frac{x}{x_0}$ and divide by $\hbar\omega$:

$$\underbrace{-\frac{\hbar^2}{2m}\frac{1}{x_0^2\hbar\omega}}_{=\frac{1}{2}}\frac{d^2\psi}{d\xi^2} + \frac{1}{2}\underbrace{\frac{m\omega^2x_0^2}{\hbar\omega}}_{=1}\xi^2\psi = \frac{E}{\hbar\omega}\psi.$$

$$\Rightarrow\left(-\frac{d^2}{d\xi^2}+\xi^2\right)\psi = \underbrace{\left(\frac{2E}{\hbar\omega}\right)}_{=2\nu+1}\psi\,,\qquad \text{Define } \nu \text{ so that } \frac{2E}{\hbar\omega} = 2\nu+1$$

and plug $\psi = H(\xi)e^{-\frac{1}{2}\xi^2}$:

$$\Rightarrow \boxed{H'' - 2\xi H' + 2\nu H = 0}$$

Solve with Frobenius: $H(\xi) = \sum_{j=0}^{\infty} a_j\,\xi^j$

$$\Rightarrow \sum_j\left[j(j-1)a_j\xi^{j-2} - 2ja_j\xi^j + 2\nu a_j\xi^j\right] = 0 \Rightarrow (j+2)(j+1)a_{j+2} - 2ja_j + 2\nu = 0$$

or $$\boxed{a_{j+2} = \frac{2(j-\nu)}{(j+2)(j+1)}\, a_j}.$$

Now, $\dfrac{a_{j+2}}{a_j} = \dfrac{2(j-\nu)}{(j+2)(j+1)} \longrightarrow \dfrac{2}{j}$ when $j \to \infty$.

This is shows that $H(\xi) \approx e^{+\xi^2} = \sum_{j=0}^{\infty} \underbrace{\frac{1}{j!}}\, \xi^{2j}$

Because $a_{2j} = \dfrac{1}{j!} \Rightarrow \dfrac{a_{2j+2}}{a_{2j}} = \dfrac{j!}{(j+1)!} = \dfrac{1}{j+1}$

or $\dfrac{a_{j+2}}{a_j} = \dfrac{1}{\frac{j}{2}+1} \to \dfrac{2}{j}$ when $j \to \infty$

Thus, if the series does not terminate at finite power the wave function

$$\psi(\xi) = H(\xi)e^{-\frac{1}{2}\xi^2} \approx e^{\frac{1}{2}\xi^2} \to \infty \text{ when } \xi \to \infty$$

will not be normalizable.

The only way the series can terminate is for $\nu =$ integer $= 0, 1, 2, \dots$, with $a_1 = 0$ if ν is even and $a_0 = 0$ if ν is odd.

The $H(\xi) = H_\nu(\xi)$ are the Hermite polynomials.

$$\hat{H}\psi_\nu(x) = E_\nu \psi_\nu(x)$$

$$E_\nu = \hbar\omega\left(\nu + \tfrac{1}{2}\right), \quad \nu = 0, 1, 2, \dots$$

$$\psi_\nu(x) = \frac{1}{\sqrt{\sqrt{\pi}\, x_0 2^\nu \nu!}} H_\nu\!\left(\frac{x}{x_0}\right) e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)^2},$$

$H_0(\xi) = 1$

$H_1(\xi) = 2\xi$

$H_2(\xi) = 4\xi^2 - 2$

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

$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12, \dots$

Note: What we are showing here is that while there exists eigenstates with non-integer or negative ν, these behave like

$$\psi_\nu(x) \sim e^{+\frac{1}{2}\left(\frac{x}{x_0}\right)^2} \text{ when } |x| >> x_0 .$$

These states are unphysical because

they blow up in the forbidden classical region, where $E < V(x)$.

Therefore, they can not be propagating or bound quantum states. Only $\nu = 0, 1, 2, 3, \ldots$ leads to physical quantum states. All of them are bound states since $\psi_\nu(x) \to 0$ when $x \to \infty$ $(x >> x_0)$.