Phys. 2b 2025, Lecture Notes (Lect. 3 & 4) (1/14-16/2025)

Key Concepts

1. **Solving Schrödinger's Eq & Stationary States**
2. **Solutions to Infinite Well Potential**

Recall:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

Since $\hat{p} = i\hbar\frac{\partial}{\partial x}$, we get $\hat{p}^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$, and the first term on the right becomes $\frac{\hat{p}^2}{2m}\psi = \hat{T}\psi$, where $\hat{T}$ is the kinetic energy operator. Thus Schrodinger's Eq becomes:

$i\hbar\frac{\partial\psi}{\partial t} = \left(\hat{T} + \hat{V}\right)\psi = \hat{H}\psi$

Where $\hat{H}$ is called the Hamiltonian or total energy operator.

How to solve it?

Can solve the full Schrödinger Equation ($i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$) easily for a special case:

if $\hat{H}$ is *not an explicit function of time* - i.e. $\hat{V} \neq V(t)$.

To do this, we assume separable solns exist, namely $\Psi_n(x,t) = \psi_n(x)\phi_n(t)$ (see text). Plugging this in Schrödinger Eq. leads to two separate differential equations (one time-dependent and one x-dependent. Thus both must be equal to a constant ($\equiv E_n$).

$$\rightarrow i\hbar\frac{1}{\phi_n}\frac{\partial\phi_n}{\partial t} = E_n, \text{ and } \frac{1}{\psi_n}\hat{H}\psi_n = E_n$$

First equation clearly has exponential soln:

$$\phi_n(t) = e^{-\frac{iE_nt}{\hbar}}$$

and second equation is the called the Time-Independent Schrödinger Equation and is also an Eigenvalue Equation:

$$\hat{H}\psi_n = E_n\psi_n$$

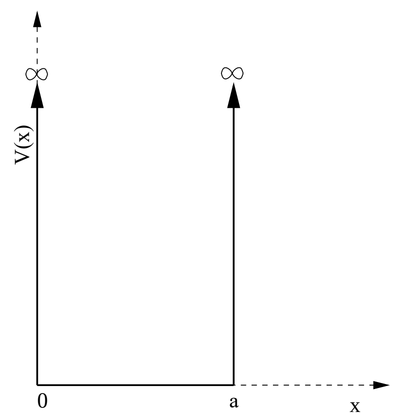
where ψ_n is an eigenfunction on eigenstate and E_n is an eigenvalue or eigenenergy.

Note:

1. In some cases E_n are discrete due to Boundary Conditions
2. In other cases E_n are continuous if no Boundary Conditions
3. These solutions $\Psi_n(x,t)$ are called stationary states since $\Psi^*\Psi = f(x) \neq g(t)$.
4. These solns form a "complete set" (see Ch3) i.e. any arbitrary soln is a superposition of $\psi_n\phi_n$ via $\Psi(x,t) = \sum_1^\infty c_n\psi_n(x)e^{-\frac{iE_nt}{\hbar}}$, where c_n are constants.

EXAMPLE I: Infinite Square Well

Particle of mass m confined in an infinite 1-d potential



$V(x) = 0;\ 0 < x < a$
$V(x) = \infty;\ x \leq 0,\ x \geq a$

Find: $E_n, \psi_n(x)$ by solving $\hat{H}\psi_n = E_n\psi_n$, with

$\hat{H} = \frac{\hat{p}_x^2}{2m} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$ for $0 < x < a$
$\hat{H} = \infty$ for $x \leq 0,\ x \geq a$

For a particle with finite energy, we must have $\psi_n = 0$ for $x \geq a$ and for $x \leq 0$.
In addition, for $0 < x < a$ we need to solve a simple diff. eq.:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = E_n\psi_n$$

$$\Rightarrow \frac{d^2\psi_n}{dx^2} = \left(\frac{-2mE_n}{\hbar^2}\right)\psi_n = -k_n^2\psi_n \text{ with } k_n^2 = \frac{2mE_n}{\hbar^2}$$

$\therefore$ the general solution is $\psi_n(x) = A\sin(k_n x) + B\cos(k_n x)$

$\Rightarrow$ but we must also satisfy the "Boundary Conditions": $\psi_n(0) = \psi_n(a) = 0$.

This implies that $B = 0$ and $A\sin(k_n a) = 0$ which leads to
$k_n a = n\pi,\ n = 1, 2, \ldots$. Note: $n = 0$ not useful since then $\psi^*\psi = 0$ so no particle in the box.

Thus we find:

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \text{ for } n = 1, 2, 3, \ldots}$$

These are the energies of the eigenstates for a particle in a box.
Substituting this form for $k_n = \sqrt{\frac{2mE_n}{\hbar^2}}$ in the general solution we get for the eigenstates:

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right)$$

Note: minimum energy for particle has $E > 0$ (mmm... interesting = zero-point energy).

What about the value of A? $\rightarrow$ can use **Normalization** of probability:
This requires that $\int_{-\infty}^{\infty}\psi^*\psi dx = 1$. Thus

$$1 = \int_0^a |A|^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = |A|^2\left(\frac{a}{2}\right)$$

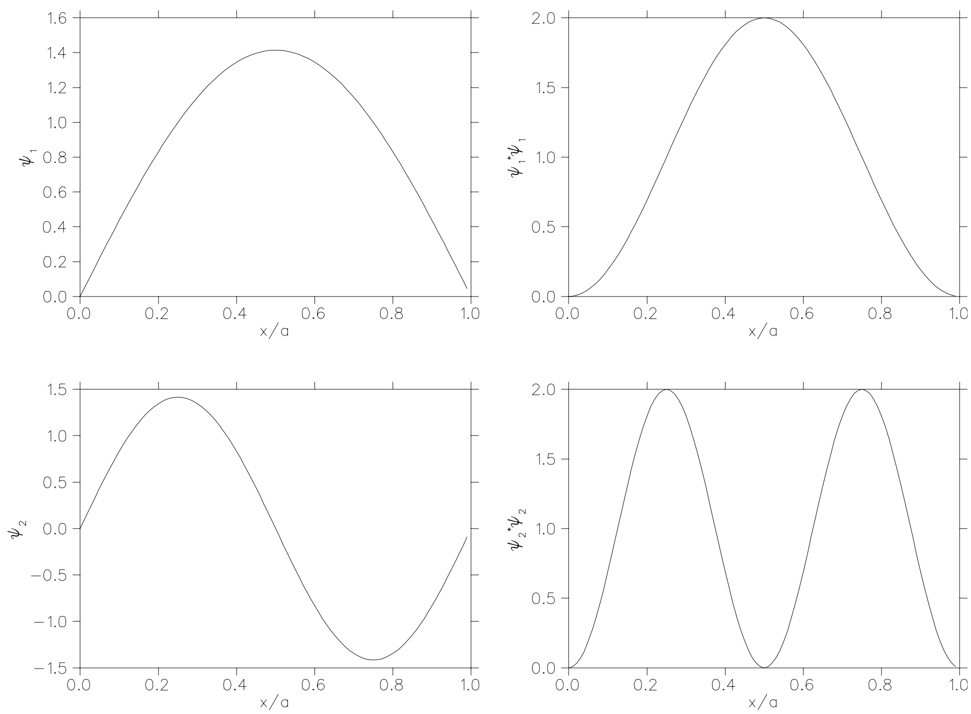
since

$$\int_0^{n\pi} \sin^2(u)du = \frac{n\pi}{2}$$

$\therefore A = \sqrt{\frac{2}{a}}$; "up to an overall phase" $\Rightarrow$ i.e., $A = \sqrt{\frac{2}{a}}e^{i\alpha}$ is also OK since $A^*A = \frac{2}{a}$, but this *overall* phase α can't make any difference to what we measure (i.e. the probability density) so for "convenience" we choose $\alpha = 0$. (Note: Relative phases in a superpostion are VERY important - see later).
Thus

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

These are the eigenstates (aka stationary states or energy eigenfunctions) for a particle in box
Some pictures of these states:



We can define average values (aka "expectation values") for observables like average position $<x>$ and average momentum $<p_x>$ via e.g.

$$<p_x> = \int_{-\infty}^{\infty} \psi^* \hat{p_x} \psi dx$$

then for these stationary states we have:

$\langle x \rangle = \frac{a}{2}$ for all n. Is this obvious?

$\langle p \rangle = 0$ for all n since $\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi x}{a}\right)dx = 0$

Key Concepts

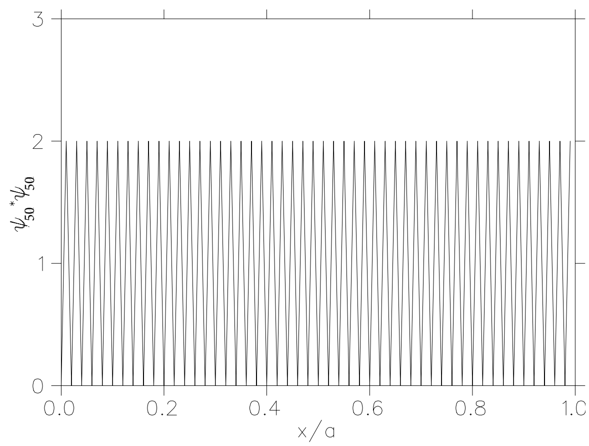
1. **Overview of Schrödinger Eq Solns when $\hat{H} \neq f(t)$**
2. **Quantum Simple Harmonic Oscillator (QSHO)**

Last time we solved Infinite Square Well

Note:

1. For eigenstates of infinte well what about $n >>> 1$? In general $\psi_n^*(x)\psi_n(x)$ will have n maxima and probability of finding the particle is $\simeq$ uniform inside the box, $\simeq$ classical

   E.g. $n = 50$:



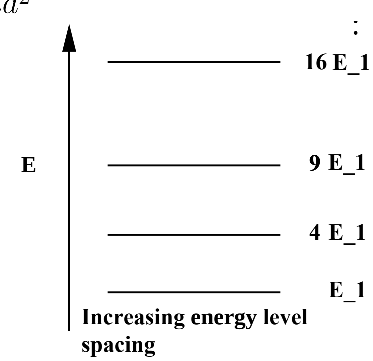
   This is example of *Bohr's Correspondence Principle* = Bohr's C.P.

   | Quantum systems behave like classical systems when $n >> 1$ and $\hbar$ is unimportant or absent |

   Consider 10 gram mass in 7 cm box with $v \sim 10$ cm/s

$$E = \frac{1}{2}mv^2 \simeq 5 \cdot 10^{-5}\,\text{joules} \simeq \frac{n^2\pi^2\hbar^2}{2ma^2} \Rightarrow n \simeq 10^{29}$$

2. The energy spectrum for the infinite square well:



   Now if $n >>> 1$, the energies should be nearly continuous (classical) according to Bohr's Correspondence Principle.

   But apparently the level spacing is increasing as n increases:

$$\Rightarrow \Delta E_n = E_{n+1} - E_n = [(n+1)^2 - n^2]E_1 = (2n+1)E_1$$

   What's up?... Actually fractional energy spacing: $\frac{\Delta E_n}{E_n} = \left(\frac{2}{n} + \frac{1}{n^2}\right) \Rightarrow 0$ if $n >> 1$

   Thus the level spacing is a tiny tiny fraction of the energy value - way below the ability to resolve discrete lines experimentally.

3. ψ_n are discrete, infinite set of functions $\rightarrow$ can be used to represent any function that satisfies $f(0) = f(a) = 0 \Rightarrow$ Fourier's Theorem.

4. Superposition state is **not** a stationary state:

   Let's look at time evolution $[\Psi^*(x,t)\Psi(x,t)]$ for a state that is a superposition of the first three eigenstates of the infinite square well. In particular:

$$\Psi(x,t) = c_1\psi_1 e^{\frac{-itE_1}{\hbar}} + c_2\psi_2 e^{\frac{-itE_2}{\hbar}} + c_3\psi_3 e^{\frac{-itE_3}{\hbar}}$$

   with $c_1 = 0.648, c_2 = 0.648, c_3 = 0.40$. See video demo on webpage link.

Where does this weird behavior come from?? $\rightarrow$ consider simple superposition of ψ_1 & ψ_2: with $x_1 = \frac{\pi x}{a}$, $x_2 = \frac{2\pi x}{a}$ and $\Psi(x,t) = sin(x_1)e^{-iE_1 t/\hbar} + sin(x_2)e^{-iE_2 t/\hbar}$.
Then probability distribution of finding particle at x (prob. density) is given by:

$$\Psi^*\Psi = sin^2(x_1) + sin^2(x_2) + sin(x_1)sin(x_2)e^{-i(E_2-E_1)t/\hbar} + sin(x_1)sin(x_2)e^{i(E_2-E_1)t/\hbar}$$

$$= sin^2(x_1) + sin^2(x_2) + 2sin(x_1)sin(x_2)cos[(E_2 - E_1)t/\hbar]$$

and we get an extra time-dependent term [since $2cos(u) = e^{iu} + e^{-iu}$]. Of course this time-dependent term vanishes when we integrate over x because $sin(x_1)$ and $sin(x_2)$ are orthogonal.

Summary of stationary state solns. for $\hat{H}$

For $\hat{H} \neq H(t)$, eigenstates of $\hat{H}$ are stationary states and can form a complete set of *orthonormal* functions. "Normal" means normalized, "ortho" means orthogonal (see below).

Now recalling that an arbitrary solution of Schrödinger's Eq can be written:

$$\Psi(x,t) = \sum_1^\infty c_n\psi_n(x)e^{-\frac{iE_n t}{\hbar}}$$

we can show that $\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)dx = 1$:

This is a product of sums, each with ∞ # of terms $\cdots$
Picking some specific terms to calculate:

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)dx = \int_{-\infty}^{\infty} \left[c_1^*\psi_1^* e^{iE_1 t/\hbar}\ c_1\psi_1 e^{-iE_1 t/\hbar} + \cdots + c_1^*\psi_1^* e^{iE_1 t/\hbar}\ c_2\psi_2 e^{-iE_2 t/\hbar} + \cdots\right] dx$$

$$= \int_{-\infty}^{\infty} |c_1|^2\psi_1^*\psi_1 dx + \int_{-\infty}^{\infty} |c_2|^2\psi_2^*\psi_2 dx + \cdots + \int_{-\infty}^{\infty} c_1^* c_2\psi_1^*\psi_2 e^{i(E_1-E_2)t/\hbar}dx + \cdots$$

But normalization gives $\int_{-\infty}^{\infty} \psi_1^*\psi_1 dx = 1$ while orthogonality gives $\int_{-\infty}^{\infty} \psi_1^*\psi_2 dx = 0$

Thus **all** of the cross terms vanish leaving us with:

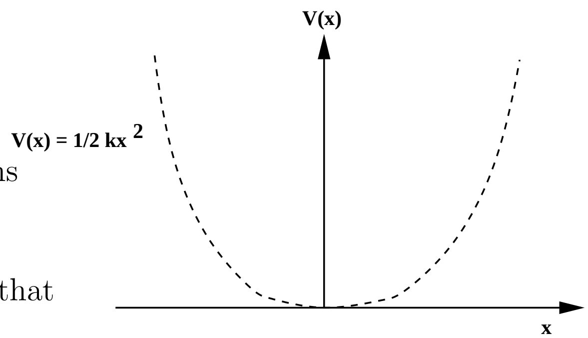
$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)dx = \sum_{n}^{\infty} |c_n|^2 = 1$$

Overall we have developed a general path to solving Quantum Problems:

1. Solve $\hat{H}\psi_n = E_n\psi_n$ (i.e. find the eigenstates ψ_n and associated eigenenergies E_n of $\hat{H}$)
2. Given arbitrary initial state $\Psi(x,0)$, express this in terms of a superposition of eigenstates ψ_n, e.g. $\Psi(x,0) = \sum a_n\psi_n(x)$ → we'll see how this is always possible next week
3. Use $\psi(x,t) = e^{\frac{-it\hat{H}}{\hbar}}\Psi(x,0)$ to evolve wavefunction in time. Thus: $\Psi(x,t) = \sum c_n\psi_n(x)e^{-iE_nt/\hbar}$

1D Quantum Simple Harmonic Oscillator (QSHO):

- Any $V(x)$ with a minimum looks like a SHO, at least near the minimum
- It's a useful 1st guess for bound systems (e.g., p, n in nucleus, quarks in p, n)
- It almost looks like square well except that $V \to \infty$ only when $x \to \pm\infty$
  ∴ particle in SHO can have finite probability all the way to $x \to \pm\infty$



For Quantum Mechanics Solution ⇒ find Energy eigenvalues and eigenfunctions!
Given the Hamiltonian:

$$\hat{H}_{SHO} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}k\hat{x}^2$$

then the Eigenvalue Equation is:

$$\hat{H}_{SHO}\psi_n(x) = \frac{-\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} + \frac{k}{2}x^2\psi_n(x) = E_n\psi_n(x)$$

The E_n are discrete because the solutions must be bounded (since $V \to \infty$ as $x \to \pm\infty$).
Now let $\omega_0 = \sqrt{\frac{k}{m}}$ and $\xi = \sqrt{\frac{m\omega_0}{\hbar}}x$, then $(dx)^2 = \frac{\hbar}{m\omega_0}(d\xi)^2$ and the Differential Equation becomes:

$$\frac{-\hbar^2}{2m}\left(\frac{m\omega_0}{\hbar}\right)\frac{d^2\psi_n(\xi)}{d\xi^2} + \frac{m\omega_o^2}{2}\left(\frac{\hbar}{m\omega_0}\right)\xi^2\psi_n(\xi) = E_n\psi_n(\xi)$$

simplifying:

$$-\hbar\omega_0 \frac{d^2\psi_n(\xi)}{d\xi^2} + \hbar\omega_0 \xi^2 \psi_n(\xi) = 2E_n \psi_n(\xi)$$

rewriting gives our final, simple, Diff. Eq:

$$\frac{d^2\psi_n}{d\xi^2} = \left(\xi^2 - \frac{2E_n}{\hbar\omega_0}\right)\psi_n$$

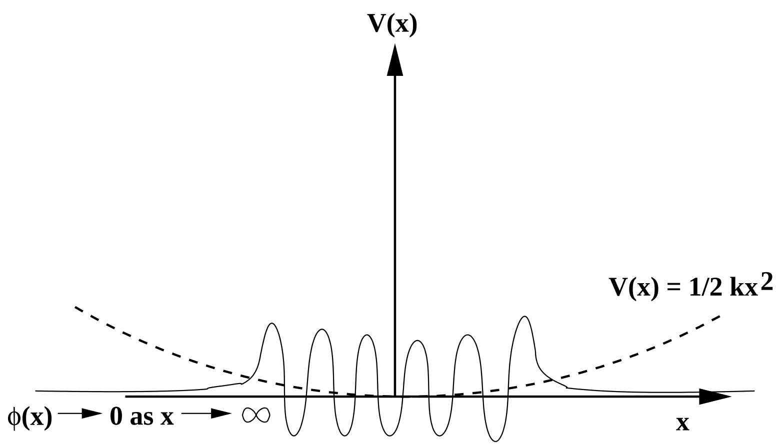
⇒ Likewise we can "guess" an approximate solution if $x \to 0$ (e.g. $\xi \to 0$)
which simplifies the Diff Eq to: $\frac{d^2\psi_n}{d\xi^2} = -K^2\psi_n(\xi)$
which has the soln., for K = constant: $\psi_n = \sin(K\xi)$ or $\cos(K\xi)$.
⇒ Likewise we can "guess" an approximate solution if $x \to \infty$
which simplifies the Diff Eq to: $\frac{d^2\psi_n}{d\xi^2} = \xi^2\psi_n(\xi)$
which has the soln.: $\psi_n = e^{-\xi^2/2}$.

How do we know this works? ⇒ Check it! $\cdots$

$$\frac{d}{dx}\left(\frac{d}{dx}\left(e^{-\xi^2/2}\right)\right) = \frac{d}{dx}\left(-(2\xi/2)e^{-\xi^2/2}\right) = \frac{d}{dx}\left(-\xi e^{-\xi^2/2}\right) = -\xi(-2\xi/2)e^{-\xi^2/2} - e^{-\xi^2/2}$$

$$= \left(\xi^2 - 1\right)e^{-\xi^2/2} \simeq \xi^2 e^{-\xi^2/2} = \xi^2\psi_n \text{ since } \xi \to \infty \text{ Q.E.D.}$$

Thus we can guess that the stationary states (energy eigenstates) are standing waves (e.g. sin/cos) near the origin that vanish as $|x| \to \infty$:



Now, from the text which does all of the Math, we can write the exact solns for both the eigenstates and energy eigenvalues:

$$\psi_n(\xi) = \left(\frac{m\omega_0}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{\frac{-\xi^2}{2}} \quad \text{, with} \quad n = 0, 1, 2, ...$$

where $H_n(\xi)$ are the so-called Hermite Polynomials (see text) with e.g.
$H_0 = 1, H_1 = 2\xi, H_2 = 4\xi^2 - 2, ...$

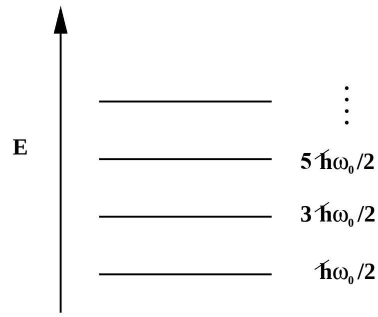
$\hookrightarrow$ They are a complete set of orthogonal functions well-known to mathematicians.

And finally the energy eigenvalues are

$E_n = (n + \frac{1}{2})\hbar\omega_0, \quad n = 0, 1, 2, \ldots$

and the spectrum of energies is uniform
(e.g. energy spacing is equal) - see Figure ⇒

with $\Delta E_n \equiv E_{n+1} - E_n = \hbar\omega_0$!



Equally spaced energy levels