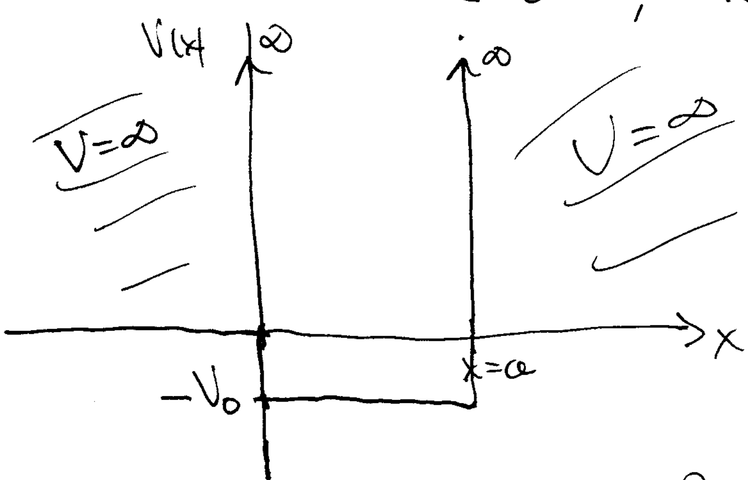
III) Examples in One Dimension

II A) The Infinite Square Well

$$V(x) = \begin{cases} \infty \,, & x<0 \\ -V_0 \,, & 0 \le x \le a \\ \infty \,, & x>a \end{cases}$$



The particle is confined to the region $0 \le x \le a$.

Recall BC: $\psi(x) = 0$ wherever $V(x) \to \infty$

ψ is finite and continuous, $\frac{d\psi}{dx}$ is not continuous, it jumps at the walls.

So $\boxed{\psi(x=0) = 0 = \psi(x=a) \text{ are the BC}}$

Hence we only need to solve the Sch. eq. inside the well – then match up to $\psi = 0$ at the walls since $\psi = 0$ for $x \le 0$ & $x \ge a$

The Sch. Eq. inside the well is

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi \,, \text{ for } 0 \le x \le a \quad \text{with } \psi(0) = 0 = \psi(a)}$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E+V_0)\psi = 0}$$ $\boxed{E > -V_0}$ Prob. 2.2

-II A) Let $k \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar} > 0 \Rightarrow$

$$\boxed{\frac{d^2}{dx^2}\psi + k^2\psi = 0}$$ Sch. Eq. $0 \le x \le a$

The solution to this (classical) "SHO" equation is

$$\psi(x) = A\sin kx + B\cos kx$$

with A, B arb. constants.

B.C. 1) $\psi(0) = 0 = B$

2) $\psi(a) = 0 = A\sin ka$

If $B=0$ then we have unphysical trivial solution of $\psi = 0$ everywhere, but the particle must be somewhere! Hence we require $\sin ka = 0$

$\Rightarrow$ k can only have discrete allowed values k_n

$$\boxed{k_n = \frac{n\pi}{a} \quad \text{with } n = 1, 2, 3, \ldots}$$

$\Rightarrow \sin k_n a = \sin n\pi = 0$ ✓

II A) Thus we find

$$\boxed{\psi_n(x) = A_n \sin k_n x} \qquad 0 \leq x \leq a$$

$(\psi_n(x) = 0$ outside well$)$

i.e.

$$\boxed{\psi_n(x) = \begin{cases} 0 & x \leq 0 \\ A_n \sin k_n x & 0 \leq x \leq a \\ 0 & x \geq a\,. \end{cases}}$$

~~Hence~~ We normalize the wavefunction

$$1 = \int_{-\infty}^{+\infty} dx\, |\psi_n(x)|^2$$

$$= |A_n|^2 \int_0^a dx\, \sin^2 \frac{n\pi x}{a}$$

let $\theta = \frac{n\pi x}{a}$; $\frac{a}{n\pi}\, d\theta = dx$

$$\Rightarrow 1 = |A_n|^2 \frac{a}{n\pi} \underbrace{\int_0^{n\pi} d\theta \sin^2\theta}$$

$$= n \int_0^{\pi} d\theta \sin^2\theta \qquad \sin^2\theta = \frac{(1-\cos 2\theta)}{2}$$

$$= \frac{n}{2}\left[\theta - \frac{1}{2}\sin 2\theta\right]\Big|_0^{\pi}$$

$$= \frac{n\pi}{2}$$

II A) $1 = |A_n|^2 \frac{a}{n\pi} \frac{n\pi}{2} = |A_n|^2 \frac{a}{2}$

$\Rightarrow |A_n|^2 = \frac{2}{a}$ Choose A_n to be real and positive $\Rightarrow$

$$\boxed{A_n = \sqrt{\frac{2}{a}}}$$

Hence

$$\boxed{\psi_n(x) = \begin{cases} 0 & , \quad x \leq 0 \\ \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} & , \quad 0 \leq x \leq a \\ 0 & , \quad x \geq a \end{cases}}$$

$$\boxed{n = 1, 2, 3, \ldots}$$

These are the energy eigenfunctions for the infinite square well potential

The <u>bound state</u> energies are

$$E_n = \frac{\hbar^2}{2m} k_n^2 - V_0$$
$$= \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2 - V_0$$
$$\boxed{E_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2 - V_0} \quad n = 1, 2, \ldots$$

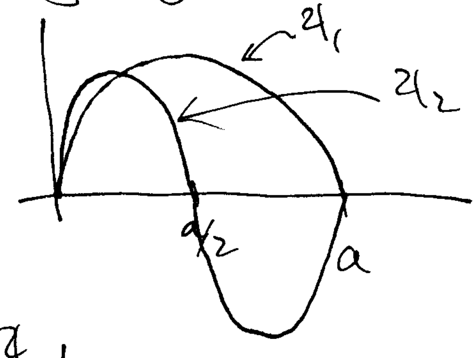
II A) The energy of the particle cannot be any value but must take on only the above **allowed** values — The energy is said to be *quantized*.

The lowest energy state is called the **ground state** it corresponds to

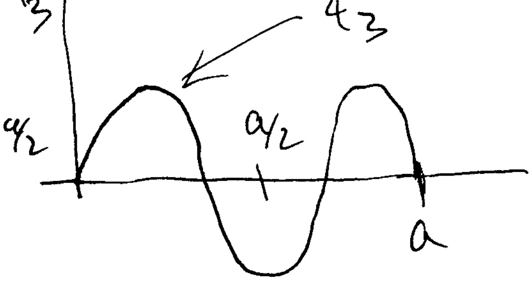
$$n = 1 \qquad \psi_1 = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \quad , \quad 0 \le x \le a.$$

For $n > 1$, the states are called **excited** states.

Properties of the energy eigenfunctions



1) The wavefunctions alternate as **even** or **odd** functions of x about $x = a/2$ as n increases



i.e. $0 \le x \le \frac{a}{2}$

$$\sin \frac{n\pi}{a}(a - x) = \cancel{\sin n\pi}^{\,0} \cos \frac{n\pi}{a} x - \underbrace{\cos n\pi}_{(-1)^n} \sin \frac{n\pi}{a} x$$

II A) 1) So

$$\sin \frac{n\pi}{a}(a-x) = -(-1)^n \sin \frac{n\pi}{a} x$$

$$\Rightarrow \boxed{\begin{array}{ll} n = \text{odd} & \psi_n \text{ is even} \\ n = \text{even} & \psi_n \text{ is odd} \end{array}}$$

2) As energy increases each successive state has <u>one</u> more <u>node</u> ← zero <u>crossing</u>

<u>i.e.</u>

ψ_1 has no nodes
ψ_2 has 1 node
ψ_3 has 2 nodes
⋮

(This is in <u>general</u> the case, for arbitrary shaped potential!)

$$\boxed{\psi_n \text{ has } (n-1)\text{-nodes}}$$

---

3) The eigenfunctions are <u>orthonormal</u>

a) $\displaystyle\int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\psi_n(x) = 1$

b) $\displaystyle\int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\psi_n(x) = 0 \qquad m \neq n$

Direct calculation:

II A) 3b) $\displaystyle\int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\, \psi_n(x) = \frac{2}{a}\int_0^a dx \sin\frac{m\pi x}{a}\sin\frac{n\pi x}{a}$

Recall

$$\cos(A+B) = cAcB - sAsB$$
$$\cos(A-B) = cAcB + sAsB$$

Subtract

$$\frac{1}{2}\left[\cos(A-B) - \cos(A+B)\right] = \sin A \sin B$$

$\Rightarrow$

$$= \frac{1}{a}\int_0^a dx\left[\cos\left(\frac{(m-n)\pi x}{a}\right) - \cos\left(\frac{(m+n)\pi x}{a}\right)\right]$$

(Note if $m=n$ here stop and do integrals)

$$= \left\{\frac{1}{(m-n)\pi}\sin\left(\frac{(m-n)\pi x}{a}\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{(m+n)\pi x}{a}\right)\right\}\Bigg|_{x=0}^{a}$$

$m \neq n$ here!

$$= \frac{1}{\pi}\left\{\frac{\sin\underbrace{(m-n)}_{=\text{integer}}\pi}{(m-n)} - \frac{\sin\underbrace{(m+n)}_{=\text{integer}}\pi}{(m+n)}\right\}$$

$$= 0.$$

$$\Rightarrow \boxed{\int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\, \psi_n(x) = \delta_{mn}}$$

– A) 3) Recall our general proof in this context

1) $$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\right]\psi_n(x) = E_n\,\psi_n(x)$$

take c.c. & call $n \to m$

2) $$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\right]\psi_m^*(x) = E_m^*\,\psi_m^*(x)$$

Mult. (1) on left by ψ_m^*
(2) on Right by ψ_n

1') $$\psi_m^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\right]\psi_n(x) = E_n\,\psi_m^*(x)\psi_n(x)$$

2') $$\left(\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\right]\psi_m^*(x)\right)\psi_n(x) = E_m^*\,\psi_m^*(x)\psi_n(x)$$

Subtract

$$-\frac{\hbar^2}{2m}\left[\psi_m^*\frac{d^2}{dx^2}\psi_n - \left(\frac{d^2}{dx^2}\psi_m^*\right)\psi_n\right] = (E_n - E_m^*)\psi_m^*\psi_n$$

Integrate

$$-\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} dx\left[\psi_m^*\frac{d^2}{dx^2}\psi_n - \left(\frac{d^2}{dx^2}\psi_m^*\right)\psi_n\right] = (E_n - E_m^*)\int_{-\infty}^{+\infty} dx\,\psi_m^*\psi_n$$

$$\parallel$$

$$-\frac{\hbar^2}{2m}\int_0^a dx\left[\psi_m^*\frac{d^2}{dx^2}\psi_n - \frac{d}{dx}\left(\left(\frac{d}{dx}\psi_m^*\right)\psi_n\right) + \frac{d}{dx}\psi_m^*\frac{d}{dx}\psi_n\right]$$

$$= -\frac{\hbar^2}{2m}\int_0^a dx\left[\cancel{\psi_m^*\frac{d^2}{dx^2}\psi_n} - \frac{d}{dx}\left(\left(\frac{d}{dx}\psi_m^*\right)\psi_n\right) + \frac{d}{dx}\left(\psi_m^*\frac{d}{dx}\psi_n\right) - \cancel{\psi_m^*\frac{d^2}{dx^2}\psi_n}\right]$$

in A) 3) $\Rightarrow$

$$-\frac{\hbar^2}{2m}\Big[\underbrace{\psi_m^* \frac{d}{dx}\psi_n - \left(\frac{d}{dx}\psi_m^*\right)\psi_n}_{=0 \text{ at walls of well } \psi_n=0.}\Big]\Big|_{x=0}^{a}$$

$$= (E_n - E_m^*)\int_{-\infty}^{+\infty} dx\, \psi_m^* \psi_n$$

$$\Rightarrow \boxed{(E_n - E_m^*)\int_{-\infty}^{+\infty} dx\, \psi_m^* \psi_n = 0}$$

1) $m = n \Rightarrow E_n = E_n^* = \text{real}$

as we found

$$E_n = \frac{\hbar^2 \pi^2}{2ma} n^2 - U_0$$

2) $m \neq n \quad E_m \neq E_n$

$$\Rightarrow \int_{-\infty}^{+\infty} dx\, \psi_m^* \psi_n = 0$$

as found directly above.

So & $\boxed{\begin{array}{l} E_n \text{ real} \\ \int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\,\psi_n(x) = \delta_{mn} \end{array}}$

II A) 4) The $\{\psi_n(x)\}$ are <u>complete</u>: any other function ~~fkt~~ $\psi(x)$ (vanishing at walls) can be expressed as a linear combo. of ψ_n

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

$$= \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right)$$

This is Fourier series for $\psi(x)$.

The closure relation looks a little different here since $\{\psi_n\}$ are complete for functions that vanish at $x = 0, a$ and are for $0 \le x \le a$ so we will not bother to write it out here — or prove it — suffice it to say we may expand any $\psi(x)$ ~~between~~ $0 \le x \le a$ with $\psi(0) = 0 = \psi(a)$ in terms of $\{\psi_n(x)\}$ as above.

A4) Since the $\{\psi_n\}$ are orthonormal,

$$\int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\, \psi_n(x) = \delta_{mn},$$

we may use that property to invert the expansion — mult. by ψ_m^* and integrate

$$\int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\, \psi(x) = \sum_{n=1}^{\infty} c_n \underbrace{\int_{-\infty}^{+\infty} dx\, \psi_m^*(x)\, \psi_n(x)}_{=\delta_{mn}}$$

$$= \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

$\Rightarrow$

$$\boxed{c_n = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\, \psi(x)}$$

as we had found more generally previously, for any potential!

Given the energy eigenfunctions $\{\psi_n(x)\}$ recall the stationary states of the infinite square well are

$$\psi_n(x,t) = \psi_n(x)\, e^{-i\frac{E_n t}{\hbar}}$$

$$= \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\, e^{-i\frac{n^2\pi^2\hbar}{2ma^2}t} \, \underbrace{e^{+i\frac{V_0}{\hbar}t}}_{\text{overall phase as discussed earlier.}}$$

that satisfies the BC at the wall

- II A) Then the most general solution to the <u>time-dependent</u> Sch. equation is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n t}{\hbar}}$$

It is a solution to the Sch. Eq since each $\Psi_n(x,t)$ is a solution

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \underbrace{\left(i\hbar\frac{\partial}{\partial t} e^{-i\frac{E_n t}{\hbar}}\right)}_{= E_n e^{-i\frac{E_n t}{\hbar}}}$$

$$= \sum_{n=1}^{\infty} c_n E_n \psi_n(x) e^{-i\frac{E_n t}{\hbar}}$$

But ψ_n are eigenfunctions of H with eigenvalue E_n ; $H\psi_n = E_n \psi_n$

So

$$= \sum_{n=1}^{\infty} c_n H \psi_n(x) e^{-iE_n t/\hbar}$$

$$= H \sum_{n=1}^{\infty} c_n \cdot \psi_n(x) e^{-iE_n t/\hbar}$$

$$= H\Psi(x,t). \checkmark$$

A) And as in general we have the <u>initial</u> wavefunction

$$\psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x),$$

and its form determines the expansion coefficients

$$c_n = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\, \psi(x,0)$$ from the orthonormality relations.

Thus we have exhibited our general procedure explicitly for the ∞ potential well. But we will follow the same steps in other cases, given $V(x)$ we will find the BC, the stationary states, the eigenvalues of the energy, the eigenfunctions and then expand the most (any) general solution in terms of them. Then we will use that expansion to calculate physical observables like expectation values of $\langle x \rangle \langle p \rangle$ etc.