Solving the Schrödinger Eq'n

We assume that PE is time-independent (no external forces, energy is conserved)

$V = V(x)$ (no t!)

$$+i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\cdot\Psi$$

Separation of Variables

We begin by seeking special sol'ns of form

$$\Psi(x,t) = \psi(x)\cdot\varphi(t) \Rightarrow \frac{\partial \Psi}{\partial t} = \psi(x)\frac{d\varphi}{dt}$$

(Notice full derivatives →) $\quad \frac{\partial^2 \Psi}{\partial x^2} = \varphi(t)\frac{d^2\psi}{dx^2}$

$$SE \Rightarrow \quad i\hbar\,\psi\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\varphi\frac{d^2\psi}{dx^2} + V\cdot\psi\cdot\varphi$$

$$\frac{1}{\varphi\cdot\psi}\times \Rightarrow \quad \underbrace{i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt}}_{f(t)} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V}_{g(x)} = \underbrace{E}_{\text{const!}}$$

The only way that a function of t, $f(t)$, can always equal a fcn of x, $g(x)$, is if both fcns are equal to the same const.

Note units: $[LHS] = [\hbar\omega]$, $[RHS] = \left[\frac{\hbar^2 k^2}{2m} + V\right]$

$\Rightarrow$ E has units of energy

Now have 2 ordinary (not partial) differential eq'ns:

(1) $i\hbar \dfrac{d\varphi}{dt} = E \cdot \varphi \quad \Rightarrow \quad \dot{\varphi} = \dfrac{-iE}{\hbar} \cdot \varphi$

(2) $-\dfrac{\hbar^2}{2m} \dfrac{d^2\psi}{dx^2} + V \cdot \psi = E \cdot \psi$

Sol'n of (1) is $\varphi(t) = \varphi_0 \, e^{-iEt/\hbar}$

φ_0 ← any const

(2) is called the "time-independent S.E." and it will occupy most of our attention for rest of semester. It has form:

$\hat{H}[\psi] = E \cdot \psi$ ← "eigenvalue eq'n"

$\hat{H}$ = Hamiltonian operator = $-\dfrac{\hbar^2}{2m} \dfrac{d^2}{dx^2} + V(x)$

$\hat{H}[\psi] = E \cdot \psi$ has sol'ns $\psi_1(x), \psi_2(x), \ldots \psi_n(x) \ldots$
corresponding to $E_1, E_2, \ldots E_n \ldots$

ψ: "eigenfunction" ; E: "eigenvalue"

Special Sol'ns: $\Psi_1(x,t) = \psi_1(x)\, e^{-iE_1 t/\hbar}$

$\Psi_2(x,t) = \psi_2(x)\, e^{-iE_2 t/\hbar}$

$\vdots$

(Have absorbed const φ_0 into ψ)

These special sol'ns are called "stationary states" or energy eigenstates

Notice $|\Psi_n(x,t)|^2 = |\psi_n(x)|^2$ ← time-independent "stationary"

(since $e^{+i\omega_n t} e^{-i\omega_n t} = 1$)

Ψ_n has a definite (single, well-defined) frequency

$$\omega_n = E_n/\hbar$$

de Broglie ⇒ $E_n = \hbar\omega_n$ = energy of state n

S.E. $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$ is a linear D.E. (contains only linear operators)

⇒ if Ψ_1 and Ψ_2 are sol'ns, so is $a\Psi_1 + b\Psi_2$

⇒ Most general sol'n of S.E. is

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

c_n's are any (complex or real) constants

Each Ψ_n has definite energy $E_n = \hbar\omega_n$ but general state $\Psi = \sum c_n \Psi_n$ does not have definite energy; it is a mixture of energy states.

Operators

Postulate 2 of QM (which we are not ready yet to state precisely) says that corresponding to every physically-observable quantity such as position x, momentum p, energy E there corresponds a linear operator $\hat{O}$ and sol'ns of the eigenvalue eq'n

$$\hat{O}[\Psi_n] = o_n \cdot \Psi_n$$ are states Ψ_n with a

definite value ($= o_n$) of that observable quantity.

The momentum operator is $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$

The position operator is $\hat{x} = x$

We can argue that the momentum operator has this form in 2 ways:

I. According to deBroglie, free particle

$\Psi = A e^{i(kx - \omega t)}$ has momentum $p = \hbar k$

Notice $\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi = \frac{\hbar}{i}(ik)\Psi = \hbar k \Psi$

$\hat{p}\,\Psi = \hbar k \Psi \Rightarrow \Psi = A e^{i(kx - \omega t)}$ is "eigenfcn

of momentum operator w/ eigenvalue $+\hbar k$"

II. Before, we showed that Postulate 3 $\Rightarrow$

$$\langle x \rangle = \int x\, |\Psi|^2\, dx = \int \Psi^* x\, \Psi\, dx$$

(Griffith's argues...) Assume that

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt}$$ (Makes sense, since QM should agree w/ classical mech)

$$\Rightarrow \langle p \rangle = m \int x \frac{\partial}{\partial t} |\Psi|^2 \, dx$$ = (algebra! S.E. + integ by parts)

$$= \frac{\hbar}{i} \int \Psi^* \frac{\partial \Psi}{\partial x} \, dx = \int \Psi^* \hat{p} \, \Psi \, dx$$

(see Griffiths, Ch1, for details)

In classical mechanics, every dynamical quantity Q is a function of x, p: $Q = Q(x, p)$

Examples: $KE = \frac{p^2}{2m}$, $\vec{L} = \vec{r} \times \vec{p}$, $E = \frac{p^2}{2m} + V(x)$

Later, we will show that Postulates $\Rightarrow$

QM operator corresponding to classical $Q(x, p)$ is

$\hat{Q}\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)$ and

$$\langle \hat{Q} \rangle = \int \Psi^* \hat{Q} \, \Psi \, dx$$

Example: hamiltonian = energy operator =

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

If Ψ_n is energy eigenstate $\Rightarrow \hat{H}\,\Psi_n = E_n \Psi$, then

$$\langle \hat{H} \rangle = \int \Psi_n^* \underbrace{\hat{H}\,\Psi_n}_{E_n \Psi_n} dx = E_n \int |\Psi|^2 dx = E_n$$

Furthermore, can show standard dev σ_E of energy measurement is zero:

$$\langle \hat{H}^2 \rangle = \int \Psi_n^* \underbrace{\hat{H}(\hat{H}\,\Psi_n)}_{E_n^2 \Psi_n} dx = E_n^2 \underbrace{\int |\Psi_n|^2 dx}_{1}$$

$$\sigma_E = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} = \sqrt{E_n^2 - E_n^2} = 0 \quad \checkmark$$

So, if system is in state Ψ_n = eigenstate of energy operator w/ eigenvalue E_n, and you measure energy, then you are <u>certain</u> to get result E_n. We can therefore say that Ψ_n is a state of <u>definite</u> energy.

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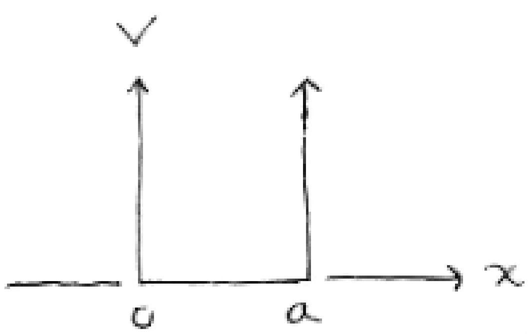
Infinite Square Well

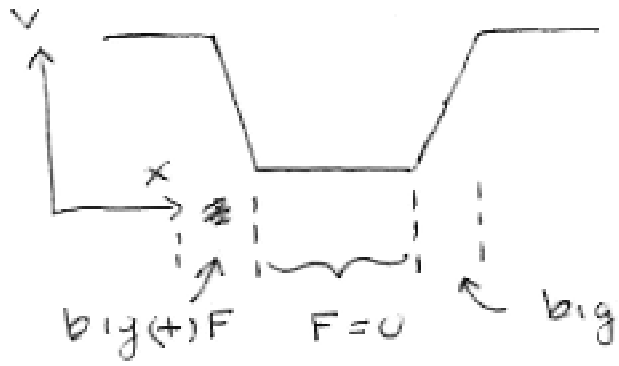
$$PE = V(x) = \begin{cases} 0, & 0 < x < a \\ \infty; & \text{elsewhere} \end{cases}$$



Somewhat artificial, but very instructive

← "square" edges in well

∞-square well is limit of steep-walled finite well ⇒



force $F = -\frac{dV}{dx}$

particle is confined to well but free to move about inside

Particle trapped in ∞-square well $\Rightarrow \Psi(x) = 0$ outside

Inside well: $$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \underbrace{V}_{0}\cdot\Psi = E\,\Psi$$

$$\frac{d^2\Psi}{dx^2} = \Psi'' = \frac{-2mE}{\hbar^2}\Psi = -k^2\cdot\Psi$$

where $k \equiv \frac{\sqrt{2mE}}{\hbar}$, $E = \frac{\hbar^2 k^2}{2m} > 0$

(can't have $E < V_{min} = 0$)

$\Psi'' = -k^2\cdot\Psi \Rightarrow$

$\Psi(x) = A\sin kx + B\cos kx$ or $\alpha e^{ikx} + \beta e^{-ikx}$

Postulate I says $\Psi(x)$ is continuous. Since $\Psi = 0$ outside well, must have (boundary conditions)

$\Psi(x=0) = 0 \Rightarrow A\cdot 0 + B\cdot 1 = 0 \Rightarrow B = 0$

$\Psi(a=0) = 0 \Rightarrow A\cdot\sin(ka) = 0 \Rightarrow$

$k\cdot a = 0, \pi, 2\pi, 3\pi \ldots = n\cdot\pi$

$k_n = n\cdot\pi/a$, $n = 1, 2, 3, \ldots$

We can exclude $n = 0$ case, since this yields

$$k = 0 \Rightarrow \Psi(x) \sim \sin(0 \cdot x) = 0 \Rightarrow \text{No } \Psi(x)!$$

Also can exclude negative values of n, k, since $(-)\,k$ gives <u>same</u> sol'n as $(+)\,k$ because

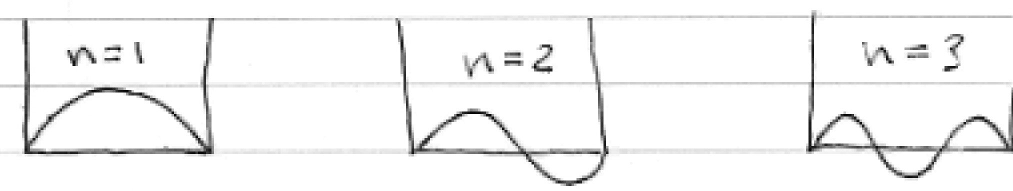
$$\sin(-k \cdot x) = -\sin(+kx) \Rightarrow \text{same } |\Psi|^2$$

same physical state

$\Rightarrow$ energy eigenstates are $\Psi_n(x) = A \sin(k_n \cdot x)$

where $k_n = n\dfrac{\pi}{a} = \dfrac{2\pi}{\lambda_n} \Rightarrow n \cdot \dfrac{\lambda_n}{2} = a$

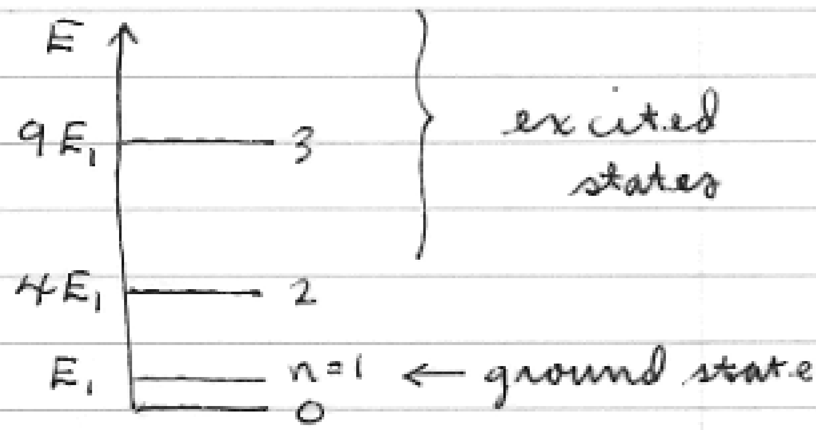
$\Rightarrow$ n half-wavelengths fill the well width a



etc.

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2ma^2} \cdot n^2 = E_1 \cdot n^2$$

Allowed energies:



Note quantization of energy arises from boundary conditions

Normalization:

$$\int |\Psi|^2 dx = A^2 \underbrace{\int_0^a \sin^2(k_n \cdot x)\, dx}_{a \cdot (1/2)} = 1$$

$\leftarrow$ avg of $\sin^2 = 1/2$

$\Rightarrow \quad A^2 = 2/a \;, \qquad A = \sqrt{2/a}$

Key features of energy eigenstate Ψ_n's

- They are <u>orthogonal</u> $\Rightarrow$

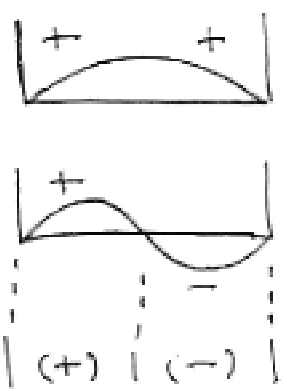
$$\int \Psi_m^* \Psi_n \, dx = \delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}$$

Example:

$\Psi_{m=1}$

$\Psi_{n=2}$

$\Psi_m \cdot \Psi_n$



$\Rightarrow \int \Psi_m^* \Psi_n \, dx = 0$

(See Griffiths for general proof)

- They form a <u>complete set</u>

$\Rightarrow$ <u>any</u> function $f(x) = \sum_{n=1}^{\infty} c_n \Psi_n(x)$

(since Ψ_n's are terms in Fourier series.)

How do you find the c_n's, given $f(x)$?

Fourier's Trick:

$$\int \Psi_m^* \cdot f(x) \, dx = \sum_n c_n \underbrace{\int \Psi_m^* \Psi_n \, dx}_{\delta_{mn}} = c_m$$

$$\Rightarrow \quad c_n = \int \Psi_n^* f(x) \, dx$$

In conclusion, stationary states of ∞ square well are

$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_nt/\hbar} = \sqrt{\frac{2}{a}}\,\sin(k_n x)\, e^{-i\omega_n t}$$

where $k_n = n\cdot\frac{\pi}{a}$, $E_n = \hbar\omega_n = n^2\cdot\frac{\hbar^2\pi^2}{2ma^2}$

Most general sol'n is

$$\Psi(x,t) = \sum_n c_n\, \psi_n(x)\, e^{-iE_nt/\hbar}$$

where c_n's are <u>any</u> constants (can be complex!)

c_n's determined from initial state:

$$\Psi(x,0) = \sum_n c_n \cdot \psi_n(x) \qquad (\text{since } e^{-i0} = 1)$$

$$\Rightarrow \quad c_n = \int \psi_n^* \cdot \Psi(x,0)\, dx$$

These results generalize. Will show later that for any isolated system (V independent of time), the eigenstates of the hamiltonian form a complete, orthonormal ~~state~~ set:

$$\hat{H}\psi_n = E_n\psi_n\,, \qquad \int \psi_m^*\,\psi_n\, dx = \delta_{mn}$$

<u>Any</u> state $\Psi(x,t) = \sum_n c_n\, \psi_n \cdot e^{-iE_nt/\hbar}$