Quantum Mechanics

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Lesson VI
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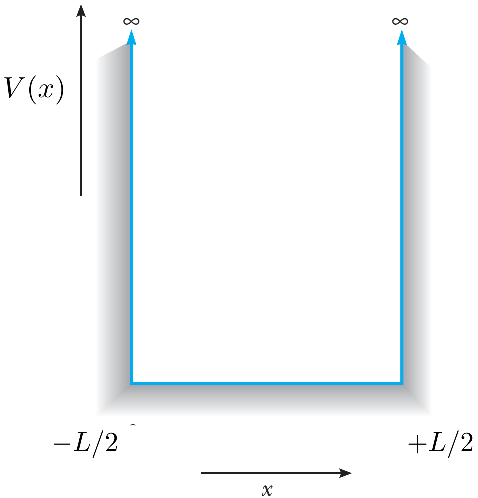
1. Bound states in one dimension
   - Particle in a box
   - Finite square well
   - Superposition and time dependence
   - Harmonic oscillator


ERWIN SCHRÖDINGER 1887–1961
NOBELPREISTRÄGER FÜR PHYSIK
S 5
REPUBLIK ÖSTERREICH

$$V(x) = \begin{cases} \infty & \text{for } x < L/2 \\ V_0 & \text{for } -L/2 \leq x \leq L/2 \\ \infty & \text{for } x > L/2 \end{cases} \tag{1}$$



- wave function outside box

$$\psi(x) = 0 \qquad x < -L/2 \wedge x > L/2 \tag{2}$$

- wave function inside box

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad -L/2 \leq x \leq L/2 \tag{3}$$

- energy and wave vector

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \Rightarrow k^2 = \frac{2m(E - V_0)}{\hbar^2} \tag{4}$$

- boundary conditions for wave function

$$\psi(-L/2) = Ae^{-ikL/2} + Be^{ikL/2} = 0 \tag{5}$$

$$\psi(+L/2) = Ae^{ikL/2} + Be^{-ikL/2} = 0 \tag{6}$$

- adding (5) to (6) gives

$$2(A+B)\cos(kL/2) = 0 \tag{7}$$

- while subtracting (5) from (6) gives

$$2i(A-B)\sin(kL/2) = 0 \tag{8}$$

- both conditions in (7) and (8) must be met
  - when $A = B$ (8) is met and to satisfy (7)

$$k = \frac{2\pi n_1}{L} + \frac{\pi}{L} \qquad n_1 = 0, 1, 2, 3, \cdots \tag{9}$$

  - when $A = -B$ in which (7) is met and to satisfy (8)

$$k = \frac{2\pi n_2}{L} \qquad n_2 = 1, 2, 3, \cdots \tag{10}$$

- Consolidate quantization conditions rewriting

$$k = \frac{\pi n}{L} \qquad n = 1, 2, 3 \cdots \tag{11}$$

and solution to time-independent Schrödinger equation

$$\psi_n(x) = A \begin{cases} \cos(n\pi x/L) & \text{for } n \text{ odd} \\ \sin(n\pi x/L) & \text{for } n \text{ even} \end{cases} = A \sin\left[\frac{n\pi}{L}\left(x + \frac{L}{2}\right)\right] \tag{12}$$

- Not only is the wave vector quantized ☞ but also

$$p = \hbar k = \hbar \pi n / L \tag{13}$$

and

$$E = V_0 + \frac{\hbar^2 k^2}{2m} = V_0 + \frac{\hbar^2 \pi^2 n^2}{2mL^2} \tag{14}$$

- Amplitude can be found by considering normalization condition

$$\int_{-\infty}^{+\infty} |\psi_n(x)|^2 dx = \int_{-L/2}^{+L/2} \left| A \sin\left[\frac{n\pi}{L}\left(x+\frac{L}{2}\right)\right]\right|^2 dx = |A|^2 \frac{L}{2}, \quad (15)$$

recall ☞

$$\int_{-L/2}^{+L/2} \left|\sin\left[\frac{n\pi}{L}\left(x+\frac{L}{2}\right)\right]\right|^2 dx = \frac{L}{2}. \quad (16)$$

- Since we require ☞ $|A|^2 L/2 = 1$

$$A = \sqrt{\frac{2}{L}} \Rightarrow \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left[\frac{n\pi}{L}\left(x+\frac{L}{2}\right)\right] \quad (17)$$

- Normalization can be met for a range of complex amplitudes

$$A = e^{i\phi}\sqrt{\frac{2}{L}} \quad (18)$$

in which phase ϕ is arbitrary

- This implies outcome of measurement about particle position (which is proportional to $|\psi(x)|^2$) is invariant under *global* phase factor

Hamiltonian operator

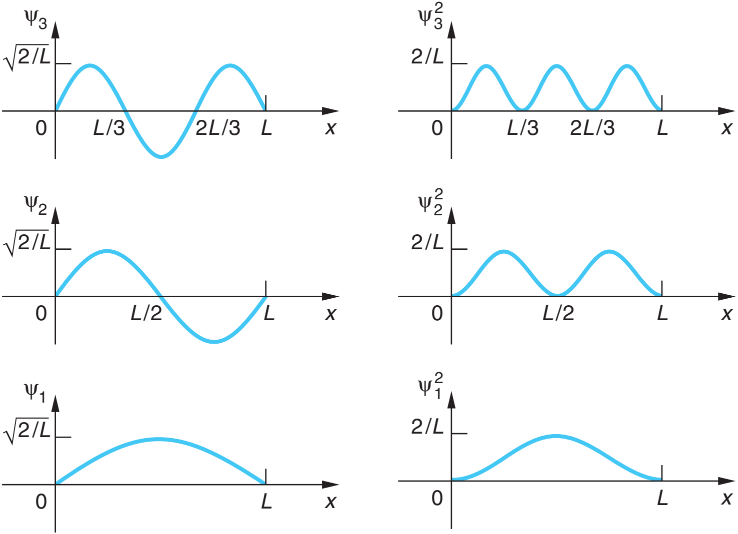
- Each solution $\psi_n(x)$ ☞ satisfies the eigenvalue problem

$$\hat{H}\psi_n(x) = E_n \psi_n(x) \qquad \hat{H} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right] \tag{19}$$

- Solutions are orthogonal to one another

$$\int_{-L/2}^{+L/2} \psi_m^*(x)\, \psi_n(x)\, dx = \delta_{mn} \tag{20}$$

$$\delta_{mn} \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases} \tag{21}$$


ψ_3
$\sqrt{2/L}$
0
$L/3$
$2L/3$
L
x
ψ_3^2
$2/L$
0
$L/3$
$2L/3$
L
x
ψ_2
$\sqrt{2/L}$
0
$L/2$
L
x
ψ_2^2
$2/L$
0
$L/2$
L
x
ψ_1
$\sqrt{2/L}$
0
L
x
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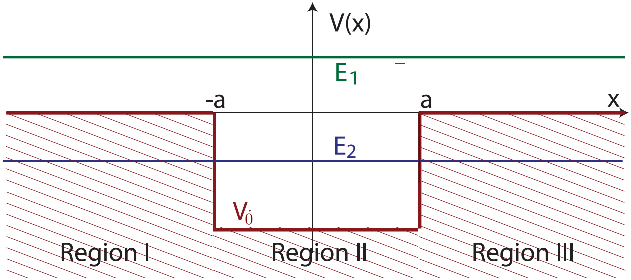
$2/L$
0
L
x



$$E_1 > V_0 \Rightarrow \begin{cases} -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx} = (E - V_0)\psi(x) & \text{in region I} \\ -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx} = E\psi(x) & \text{in region II} \\ -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx} = (E - V_0)\psi(x) & \text{in region III} \end{cases}$$

$$E_2 < V_0 \Rightarrow \begin{cases} -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx} = (V_0 - E)\psi(x) & \text{in region I} \\ -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx} = E\psi(x) & \text{in region II} \\ -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx} = (V_0 - E)\psi(x) & \text{in region III} \end{cases}$$

- E_1 ☛ Expect to find solution in terms of travelling waves
  Not so interesting ☞ describes case of unbound particle
- E_2 ☛ Expect waves inside the well and imaginary momentum
  (yielding exponentially decaying probability of finding particle)
  in outside regions
- More precisely
  - Region I: $k' = i\kappa \Rightarrow \kappa = \sqrt{\frac{2m(V_0 - E_2)}{\hbar^2}} = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$
  - Region II: $k = \sqrt{\frac{2mE_2}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}}$
  - Region III: $k' = i\kappa \Rightarrow \kappa = \sqrt{\frac{2m(V_0 - E_2)}{\hbar^2}} = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$
- And wave function is
  - Region I: $C'e^{-\kappa|x|}$
  - Region II: $A'e^{ikx} + B'e^{-ikx}$
  - Region III: $D'e^{-\kappa x}$

  In first region can write either $C'e^{-\kappa|x|}$ or $C'e^{\kappa x}$
  First notation makes it clear we have exponential decay

- Potential even function of x
- Differential operator also even function of x
- Solution has to be odd or even for equation to hold
- A and B must be chosen such that

$$\psi(x) = A'e^{ikx} + B'e^{-ikx}$$

is either even or odd

- Even solution ☛ $\psi(x) = A\cos(kx)$
- Odd solution ☛ $\psi(x) = A\sin(kx)$

Odd solution

- $\psi(-x) = -\psi(x)$ setting $C' = -D'$ ☛ rewrite $-C' = D' = C$
  - Region I $\psi(x) = -Ce^{\kappa x}$ and $\psi'(x) = -\kappa Ce^{\kappa x}$
  - Region II $\psi(x) = A\sin(kx)$ and $\psi'(x) = kA\cos(kx)$
  - Region III $\psi(x) = Ce^{-\kappa x}$ and $\psi'(x) = -\kappa Ce^{-\kappa x}$

- Since $\psi(-x) = -\psi(x)$ ☞ consider boundary condition @ $x = a$
- Two equations are

$$\begin{cases} A\sin(ka) = Ce^{-\kappa a} \\ Ak\cos(ka) = -\kappa Ce^{-\kappa a} \end{cases}$$

- Substituting first equation into second

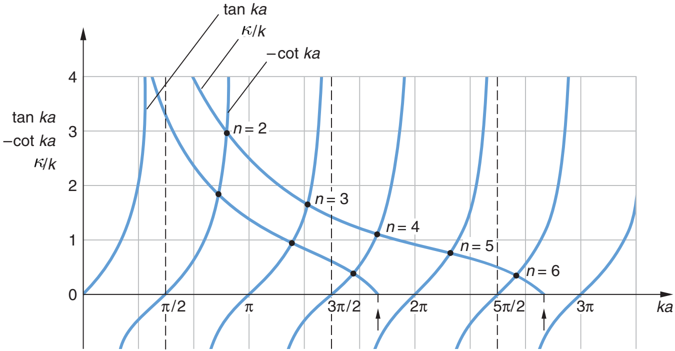
$$Ak\cos(ka) = -\kappa A\sin(ka)$$

- Constraint on eigenvalues k and κ ☞ $\kappa = -k\cot(ka)$

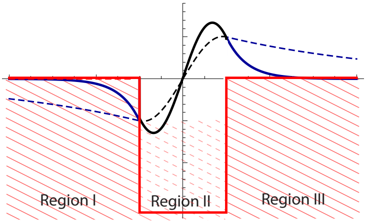
- For the even solution in the well ☞ $\psi(x) = A\cos(kx)$
  - For continuity of $\psi(x)$ ☞ $A\cos(ka) = Ce^{-\kappa a}$
  - For continuity of $\psi'(x)$ ☞ $-kA\sin(ka) = -C\kappa e^{-\kappa a}$
- Constraint on eigenvalues k and κ ☞ $\kappa = k\tan(ka)$

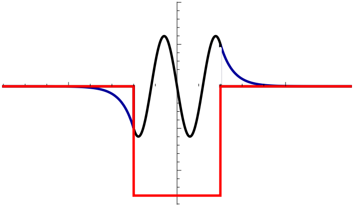
Graphical Solutions

- Two different curves of κ/k are shown
  each corresponding to different V_0 value
- V_0 given by value of ka where $\kappa/k = 0$☞ indicated by small arrows
- Top κ/k curve has $\kappa/k = 0$ for $ka = 2.75\pi$ or $\sqrt{2mV_0}\,a/h = 2.75\pi$
- Allowed values of E are given by values of ka at intersections of: κ/k and $\tan(ka)$ as well as κ/k and $-\cot(ka)$ curves

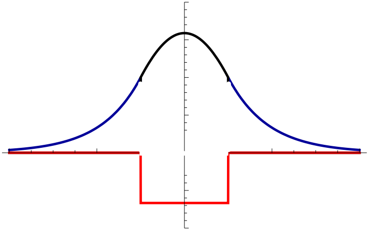


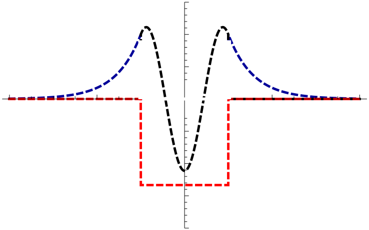
- Odd solutions





- Even solutions





Expansion in orthogonal eigenfunctions

- Time dependence of quantum states

$$\psi_n(x,t) = \psi_n e^{-iE_n t/\hbar} \tag{22}$$

- Solution for "particle in a box"
  can be expressed as a sum of different solutions

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x,t) \tag{23}$$

c_n must obey normalization condition ☞ $\sum_{n=1}^{\infty} |c_n|^2 = 1$

- Modulus squared of each coefficient
  gives probability to find particle in that state

$$P_n = |c_n|^2 \tag{24}$$

Example

- Particle initially prepared
  in symmetric superposition of ground and first excited states

$$\Psi^{(+)}(x, t=0) = \frac{1}{\sqrt{2}}\left[\psi_1(x) + \psi_2(x)\right] \tag{25}$$

- Probability to find particle in state 1 or 2 is 1/2
- State will then evolve in time according to

$$\begin{aligned} \Psi^{(+)}(x,t) &= \frac{1}{\sqrt{2}}\left[\psi_1(x)e^{-i\omega_1 t} + \psi_2(x)e^{-i\omega_2 t}\right] \\ &= e^{-i\omega_1 t}\frac{1}{\sqrt{2}}\left[\psi_1(x) + \psi_2(x)e^{-i\Delta\omega t}\right] \end{aligned} \tag{26}$$

- Probability to find particle in initial superposition state
  is not time independent

- H.O. characterized by quadratic potential ☞ $V(x) = \frac{kx^2}{2}$
- Schrödinger equation

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

- k ☞ spring constant which relates to restoring force
  of equivalent classical problem of mass m connected to spring

$$\omega = \sqrt{\frac{k}{m}} \quad \text{or} \quad k = m\omega^2$$

- Assume solution to be of the form

$$\psi(x) = f(x)\exp\left(-\frac{\gamma x^2}{2}\right) \quad \text{with} \quad \gamma^2 = mk/\hbar^2$$

  which reduces Schrödinger equation to

$$\frac{d^2 f(x)}{dx^2} - 2\gamma x\frac{df(x)}{dx} + f(x)\left[\frac{2mE}{\hbar^2} - \gamma\right] = 0$$

- Polynomial of order $n-1$ satisfies equation if

$$\frac{2mE_n}{\hbar^2\gamma}+1-2n=0 \quad \text{or} \quad E_n=\hbar\omega(n-1/2) \quad \text{with } n=1,2,3\cdots$$

- Minimal energy ☞ $E_1=\hbar\omega/2$
- All energy levels are separated from each other by an energy $\hbar\omega$
- Explicit form of normalized wave function

$$\psi_n(q)=\frac{\pi^{-1/4}}{\sqrt{2^{n-1}(n-1)!}}\,H_{n-1}(q)\,e^{-q^2/2} \quad \text{with} \quad q=\sqrt{\gamma}\,x$$

- nth order Hermite polynomial defined through relation

$$H_n(z)=e^{z^2/2}\left(z-\frac{d}{dz}\right)^n e^{-z^2/2}=(-1)^n e^z\frac{d^n}{dz^n}e^{-z}$$

(second expression obtained writing out powers in first expression inserting factors of the form $1=e^{-z^2/2}e^{z^2/2}$ between each factor and performing a little algebra)

First three harmonic oscillator wave functions are

- $n = 1$

$$\psi_1(q) = \pi^{-1/4}\, e^{-q^2/2}$$

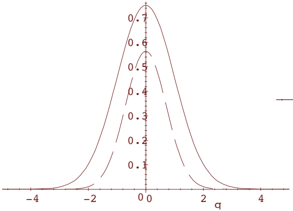
- $n = 2$

$$\psi_2(q) = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\left(q - \frac{d}{dq}\right)\left(\pi^{-1/4} e^{-q^2/2}\right) = \frac{\pi^{-1/4}}{\sqrt{2}}(2q)e^{-q^2/2}$$

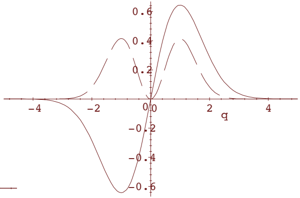
- $n = 3$

$$\psi_3(q) = \frac{1}{2}\left(q - \frac{d}{dq}\right)\left(\frac{\pi^{-1/4}}{\sqrt{2}}(2q)e^{-q^2/2}\right) = \frac{\pi^{-1/4}}{\sqrt{2}}\left(2q^2 - 1\right) e^{-q^2/2}$$

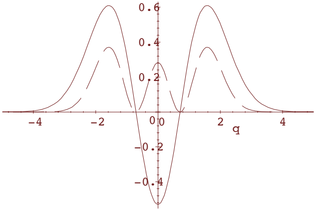
$\psi_n(q)$ wave functions graphed as solid lines
with associated probability densities $|\psi_n(q)|^2$ indicated as dashed lines



$n = 1$



$n = 2$



$n = 3$