MODEL SYSTEM: PARTICLE IN A BOX

Important because:

It illustrates quantum mechanical principals

It illustrates the use of differential eqns. & boundary conditions to solve for ψ

It shows how discrete energy levels arise when a small particle is confined to a region of space

It can predict the absorption spectrum of some linear conjugated molecules by treating the π electrons as free particles in a 1-dimensional box with infinite walls

Ordinary Differential Eq.:

Involves only 1 independent variable

x - independent variable
y(x) - dependent variable

$y'(x) = dy/dx$, $y''(x) = d^2y/dx^2$, ... $y^{(n)}(x) = d^ny/dx^n$

A differential eqn. expresses a functional relationship between x & the derivatives of y with respect to x:

$f(x, y'(x), y''(x), \ldots y^{(n)}(x)) = 0$

The *order* of the eq. is the order of the highest derivative of y with respect to x.

An n-th order differential eq. has n independent solutions (i.e. solutions that are not multiples of each other)

Examples: $y^{(4)} + (y')^2 + \sin x \cos y = 3 e^x$, order = 4

$x (y')^2 + \sin x \cos y = 3 e^x$, order = 1

Linear Differential Eq.:

$$A_n(x) y^{(n)} + A_{n-1}(x) y^{(n-1)} + ... + A_0(x) y = g(x)$$

g(x) = 0: homogeneous
g(x) not =0: inhomogeneous

Example: Schrödinger Eq.

$$d^2\psi(x)/dx^2 + (2m/\underline{h}^2) (E - V(x)) \psi(x) = 0$$

is a 2nd order homogeneous linear differential eq. with

$$A_0(x) = (2m/\underline{h}^2) (E - V(x))$$

$$A_1(x) = 0$$

$$A_2(x) = 1$$

To solve a 2nd order homogeneous linear differential eq.,

$$A_2(x) y'' + A_1(x) y' + A_0(x) y = 0,$$

divide by $A_2(x)$ to give:

$$y'' + P(x) y' + Q(x) y = 0, \qquad (1)$$

where $P(x) = A_1(x)/A_2(x)$ and $Q(x) = A_0(x)/A_2(x)$.

If there are two independent solutions y_1 and y_2 (where y_1 is not a constant x y_2) such that

$$y_1'' + P(x)\, y_1' + Q(x)\, y_1 = 0$$

and

$$y_2'' + P(x)\, y_2' + Q(x)\, y_2 = 0,$$

then the general solution is

$$y = c_1\, y_1 + c_2\, y_2$$

(Prove this yourself by plugging the general solution into Eq. (1).)

In order to solve for c_1 & c_2, must have two eqs. for y. Get the 2nd Eq. by using *boundary conditions* &/or *normalization conditions*. This will be illustrated by the Particle in a Box.

But first, consider a special case--a 2nd order linear differential eq. with constant coefficients:

$$P(x) = p,\ Q(x) = q,\ p \,\&\, q \text{ are constants}$$

Then,

$$y'' + p\, y' + q\, y = 0$$

and the solution must be a function which has the same functional form for the 1st & 2nd derivatives as the function itself, i.e.

$$y = e^{sx}.$$

Then $\quad y' = s\, e^{sx} = s\, y$

and $\quad y'' = s^2\, e^{sx} = s^2\, y$

So that $\quad s^2\, e^{sx} + ps\, e^{sx} + q\, e^{sx} = 0$

and the auxiliary eq. is

$$s^2 + ps + q = 0$$

or $$s = -p/2 \pm (1/2) \sqrt{(p^2 - 4q)} = s_1, s_2$$

and $$y = c_1 e^{s1x} + c_2 e^{s2x}$$

Now we will use this knowledge of 2nd order linear differential eqs. to solve the Schrödinger Eq. for a model problem--

The Particle in a 1-DimensionalBox

The particle is constrained to move on the x-axis & is subject to an infinite potential outside the box & a zero potential inside. The box stretches from x = 0 to x = L (see Fig. 2.1)

Must solve the Schrödinger Eq.

$$d^2\psi(x)/dx^2 + (2m/\underline{h}^2)(E - V(x))\,\psi(x) = 0$$

in three regions:

I & III: $V=\infty$, (E-V) blows up, so $\psi(x)$ must be taken as 0.

II: $V = 0$, $d^2\psi(x)/dx^2 + (2m/\underline{h}^2) E \psi(x) = 0$

This is a 2nd order homogeneous linear differential eq. with constant coefficients: $p = 0$, $q = (2m/\underline{h}^2)E$

So the auxiliary eq. is: $s^2 + q = 0$,

or $s = \pm \sqrt{(-q)} = \pm \sqrt{-(2m/\underline{h}^2)E}$

E = kinetic energy + potential energy

kinetic energy is always > 0

here, potenial energy = $V(x) = 0$

so $E > 0$ and $s = \pm i\sqrt{(2m/\underline{h}^2)E} = s_1, s_2$

So $\psi_{II} = c_1 e^{s1x} + c_2 e^{s2x} = c_1 e^{i\theta} + c_2 e^{-i\theta}$

where $\theta = x \sqrt{(2mE/\underline{h}^2)}$

$\psi_{II} = c_1(\cos\theta + i\sin\theta) + c_2(\cos\theta - i\sin\theta)$

$= (c_1 + c_2)\cos\theta + i(c_1 - c_2)\sin\theta$

$= A\cos\theta + B\sin\theta$, where $A = (c_1 + c_2)$ & $B = i(c_1 - c_2)$

Solve for A & B by applying the *Boundary Condition:* ψ must be continuous at the boundaries of the different regions:

Define A from the boundary condition at x = 0:

$$\lim_{x\to 0} \psi_I = \lim_{x\to 0} \psi_{II}$$

$$0 = \lim_{x\to 0} (A \cos\theta + B \sin\theta)$$

As $x\to 0$, $\theta\to 0$, $\cos\theta\to 1$, & $\sin\theta\to 0$

To make $A \cos\theta = 0$ at $x = 0$, must choose $A = 0$.

Then $\psi_{II} = B \sin\theta$

<u>Define B from the boundary condition at x = L:</u>

$$\lim_{x\to L} \psi_{II} = \lim_{x\to L} \psi_{III}$$

$B \sin\theta = 0$

B can't be zero because then ψ would be zero everywhere & the box would be *empty.* So must have

$\sin\theta = 0$, or $\theta = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \ldots$

At $x=L$, $\theta = L\sqrt{(2mE/\hbar^2)} = \pm n\pi$, $n = 0, 1, 2, \ldots$

This leads to a *quantum condition* on the energy:

$E = n^2\pi^2\hbar^2/(L^2 2m) = n^2h^2/(L^2 8m)$, $n = 1,2,3, \ldots$

Then $\psi_{II} = B \sin\theta = B \sin[x\sqrt{(2mE/\hbar^2)}]$

$\quad = B \sin(\pm n\pi x/L)$

Since $\sin x = \sin(-x)$, $+n\pi x/L$ gives the same solution as $-n\pi x/L$. So

$\psi_{II} = B \sin(n\pi x/L)$

Determine B from the *Normalization Condition:*

$$\int_{-\infty}^{\infty} |\psi|^2 \, dx = 1$$

$$= \int_{-\infty}^{0} |\psi_I|^2 \, dx + \int_0^L |\psi_{II}|^2 \, dx + \int_L^{\infty} |\psi_{III}|^2 \, dx$$

$$= \int_0^L |\psi_{II}|^2 \, dx$$

$$= |B|^2 \int_0^L \sin^2(n\pi x/L) \, dx$$

$$= |B|^2 \int_0^L [1/2 - 1/2 \cos(2n\pi x/L)] \, dx$$

$$= |B|^2 \, [L/2 - 0]$$

$$B = \sqrt{(2/L)}$$

$$\psi_{II} = \sqrt{(2/L)} \; \sin(n\pi x/L), \; n = 1, 2, 3, \ldots$$

where n is called the quantum number. A node is a point at which the wavefunction equals zero. For each increment in n, the number of nodes inceases by 1 (see Fig. 2.3) so that there are (n+1) nodes.

Note that at n=2, there is zero probability for the particle to be in the center of the box. But how does it get from one side to another? The situation is different than that of a classical particle. A classical particle of constant energy would have an equal probability of being found anywhere in the box since constant energy means constant speed. A quantum mechanical particle of constant energy would have a maximum probability of being found in the center for n=1. But as n increases, the number of maxima & number of nodes increase and the quantum mechanical behavior approaches the classical limit, i.e. the particle would have equal probability of being found anywhere in the box. This is an example of the *Bohr Correspondence Principle:* In the limit of large quantum number, quantum mechanics approaches classical mechanics.

Variations on a Particle in a 1-Dimensional Box:

What happens if the walls are removed?
Free Particle in 1-Dimension

"Free" means not subject to any force, so V is a constant (independent of x). Arbirarily set V = 0. Then region II is spread out over the whole x-axis; no regions I & III.

$$d^2\psi(x)/dx^2 + (2m/\hbar^2)\, E\, \psi(x) = 0$$

$$\psi = c_1\, e^{iAx} + c_2\, e^{-iAx}, \text{ where } A = (1/\hbar)\sqrt{(2mE)}$$

But how can one solve for the constants in ψ? Previously they were determined by the boundary conditions between regions.

Since $|\psi|^2$ is the probability density, ψ must be finite as $x \rightarrow \infty$.

For E>0, $\psi = c_1 e^{iAx} + c_2 e^{-iAx}$

As $x \rightarrow \infty$, e^{iAx} & e^{-iAx} oscillate as sin (Ax) & cos (Ax), so ψ is finite

For E<0, $\psi = c_1 e^{iAx} + c_2 e^{-iAx}$

Let $A' = (1/\underline{h})\sqrt{(2m|E|)}$

Then $e^{iAx} = e^{-iA'x}$, which $\rightarrow 0$ as $x \rightarrow \infty$.

And $e^{-iAx} = e^{A'x}$, which $\rightarrow \infty$ as $x \rightarrow \infty$.

So $\psi \rightarrow \infty$ as $x \rightarrow \infty$.

So, in order to have a well-behaved wavefunction, one must choose E>0. There is no quantum condition on the energy. It can take on a continuous range of values.

But note, for E>0, ψ can't be normalized because

$\int_{-\infty}^{\infty} |\psi|^2 \, dx$ is not finite.

A free particle is an unphysical situation because there is no partcle in the physical world that is not acted on by any forces.

<u>What happens if finite walls are used?</u>
Particle in a 1-Dimensional Well (See Fig. 2.5a)

$$
\begin{aligned}
V(x) &= V_0 && \text{for } x \leq 0 \\
&= 0 && 0 \leq x \leq L \\
&= V_0 && \text{for } x \geq L
\end{aligned}
$$

<u>Case 1: $E < V_0$</u>

In Regions I & III, have

$$d^2\psi(x)/dx^2 + (2m/\hbar^2)\,(E - V_0)\,\psi(x) = 0$$

This has the form of a homogeneous linear 2nd order differential eq. with constant coefficients

$$p = 0, \qquad q = (2m/\hbar^2)\,(E - V_0)$$

Setting $\psi = e^{sx}$ leads to the auxiliary eq.

$$s^2 + ps + q = 0 = s^2 + q$$

Or $\quad s = \pm\sqrt{(-q)} = \pm\sqrt{(2m/\hbar^2)\,(V_0 - E)}$

Therefore, the general form of ψ for Regions I & III is

$$\psi_{I,III} = c_1\, e^{s1x} + c_2\, e^{s2x}$$

with $s_1 = +\sqrt{(-q)} = \sqrt{(2m/\hbar^2)\,(V_0 - E)}$

and $s_2 = -\sqrt{(-q)} = \sqrt{(2m/\hbar^2)\,(E - V_0)}$

In Region II, have the same form of the solution as in the case with infinite walls:

$$\psi_{II} = c_1 e^{ix\sqrt{q'}} + c_2 e^{-ix\sqrt{q'}}$$

But c_1 & c_2 will be different for the regions I, II, & III. They are determined, as before, by choosing them so that the wavefunction is well-behaved as $x \rightarrow \pm\infty$ (For Regions I & III), by matching the solutions at the boundaries, and by normalization. Since the wavefunction is not zero in Regions I & III, this is more difficult to solve mathematically. Matching Regions I & II results in the relationship

$$\tan \sqrt{(2mE/\underline{h}^2)} = 2/(2E - V_0)\sqrt{(V_0 - E)E}$$

By graphing the left & right sides of the eq., it can be seen that only for certain values of E will the two sides be equal. This means that the energy of the system is quantized. The points of intersection are the quantized energy values.

It is possible to show that there are n energy levels with $E < V_0$ such that

$$n\text{-}1 < (L/h)\sqrt{(8mV_0)} \leq n$$

Choose a sample value of V_0: $\qquad V_0 = h^2/(mL^2)$

Then $\qquad (L/h) \sqrt{(8mV_0)} = \sqrt{8} = 2.83 \leq n$, so n = 3

The values of n determine the number of bound states of the system. See Fig. 2.5 b & c for a plot of the ground & first excited states of the system. (What would a plot of $|\psi|^2$ look like?) The wavefunction oscillates inside the box & drops off asymptotically outside the box. The number of nodes increases by one for each higher level. States with $E < V_0$ are called *bound states*.

<u>Case 2: $E > V_0$</u>

This means that $\sqrt{(V_0 - E)}$ is imaginary and that ψ_I & ψ_{III} oscillate. E is not restricted to take on certain values, so all energies $> V_0$ are allowed. These are called *unbound states.*

Tunneling

Since $|\psi|^2$ is not equal to 0 in Regions I & III outside the box, there is a finite probability of finding the particle there even though E, the total energy is $< V_0$, the potential energy.

This is called the *classically forbidden region* because in classical mechanics

$$E = T + V \qquad \& \; T > 0 \quad \text{so E is never} < V.$$

Tunneling occurs when a particle passes through a classically forbidden region. The particle can pass through a barrier even if it doesn’t have enugh energy to go over the barrier. Tunneling occurs for particles of small mass, such as the electron or H atom.

Examples:

Emission of α particles from a radioactive nucleus. The α particles "tunnel through" the potential energy barrier of attractive nuclear & Coulombic forces.

Ammonia inversion. The barrier to inversion (from one "umbrella" shaped conformation to another) of NH_3 is due to the high energy conformation in which all four atoms are planar. H atoms tunnel through this barrier.