The 1D Schrodinger Eq is an example of a second-order linear homogeneous differential eq. (DE)

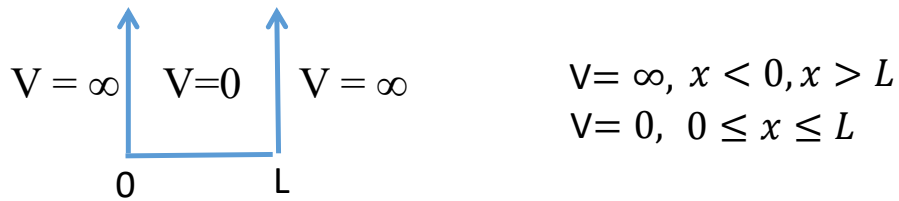General solution of a 2nd order linear homogeneous DE

$y''+P(x)y'+Q(x)y=0$

is $y = c_1 y_1(x)+c_2 y_2(x)$, where y_1 and y_2 obey the DE

There are two constants consistent with the need to integrate y'' twice to solve the eq.

$$c_1 y_1'' + c_2 y''_2 + P(c_1 y_1' + c_2 y'_2) + Q(c_1 y_1 + c_2 y_2) = 0$$

$$c_1[y_1'' + Py_1' + Qy_1] + c_2[y_2'' + Py_2' + Qy_2] = 0$$

The particle in a box problem

$V = \infty$ | $V=0$ | $V = \infty$ $V= \infty,\ x < 0, x > L$
                                                $V= 0,\ \ 0 \leq x \leq L$

0   L

For this potential, the particle can only be in the box where V= 0

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=E\psi \qquad \text{inside the box}$$

$-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$ Is the kinetic energy operator

Possible solutions are: $\sin(ax)$ and $\cos(ax)$ where a is some constant

$$\frac{d^2}{dx^2}\cos(ax) = -a^2\cos(ax)$$

$$\frac{d^2}{dx^2}\sin(ax) = -a^2\sin(ax)$$

So a general solution is: $\psi = c_1\sin(ax) + c_2\cos(ax)$

Now lets apply the boundary conditions

$\psi(x) = 0$ at $x = 0, L$

Using the boundary condition at x = 0

$\psi(0) = 0 \implies c_2 = 0$, since $\cos(0) = 1$

$\psi = c_1 \sin(ax)$

Using the boundary condition at x = L

$\psi(L) = c_1 \sin(aL)$

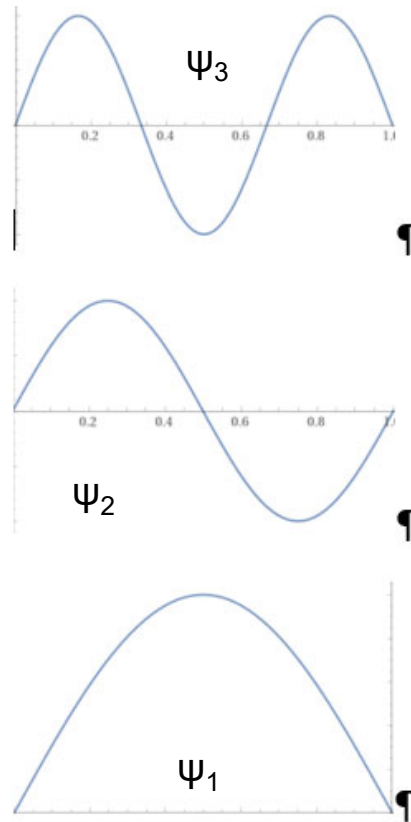$c_1 = 0$ would imply no particle

Nontrivial case: $c_1 \neq 0$

$\implies aL = n\pi, n = 1,2,3\ldots$

$\psi(x) = c_1 \sin\left(\dfrac{n\pi x}{L}\right)$

c_1 is just a normalization constant

Normalize the wave function

$$\psi_n = \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right)$$

Ψ₃

Ψ₂

Ψ₁

Suppose Ψ(x,0) = Ψ₁+Ψ₂

Ψ(x,t) = a₁exp(-iE₁t/ħ)Ψ₁ + a₂exp(-iE₂t/ħ)Ψ₂

For 1D systems, the energy increases with the number of nodes.

Now plug ψ into SE

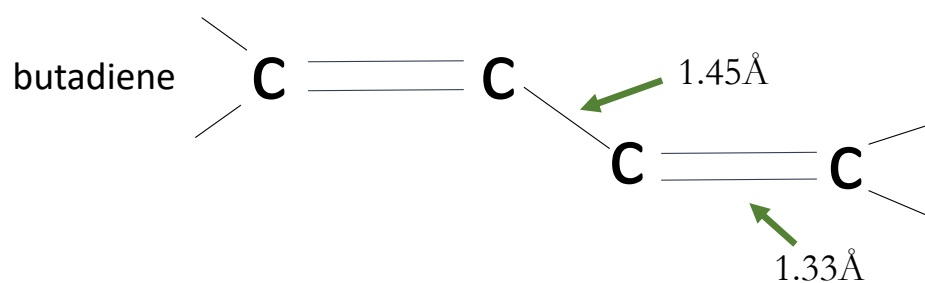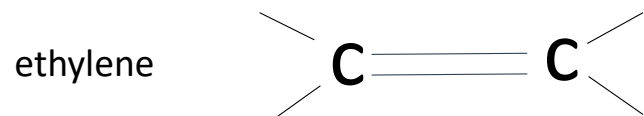$$\frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{L^2}\right) = E \qquad\bigg| \qquad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

Things to note:

- energy levels are quantized

- $E \neq 0$. Why?

- Levels get closer as m >, L >, or h $\rightarrow$ 0

    I.e., as the system approaches classical behavior

Can use to model π electrons of polyenes

ethylene   butadiene

Lets take all bond lengths to be 1.4Å

Since the orbitals extend beyond the C atoms we should add ~0.5 Å to each end

	box size	# π electrons
Ethylene	1.4+1.0=2.4Å	2
Butadiene	3(1.4)+1.0=5.2Å	4
Hexatriene	5(1.4)+1.0=8Å	6

Node count

ψ_1	0
ψ_2	1
ψ_3	2

Same # of nodes as the "real" π orbitals of polyenes (not counting the sign change due to reflecting in the plane of the atoms)

From past experience we know that there can be at most 2 electrons per orbital.

What is the energy of the lowest optical absorption?

Ethylene $\Delta n = 1 \rightarrow 2$

Butadiene $\Delta n = 2 \rightarrow 3$

Hexatriene $\Delta n = 3 \rightarrow 4$

Introduction of atomic units (a.u.)

In atomic units $\hbar$, c, m_e all = 1

Atomic unit of distance	= 1Bohr = 0.529 Å
Atomic unit of energy	= 27.211 eV = 2x the energy of the 1s orbital of the H atom

What would you guess to be the atomic unit of time?

Butadiene absorption

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2\pi^2}{2(10)^2} \sim \frac{n^2\pi^2}{200} \sim \frac{n^2}{20} = 0.049n^2$$

Switch to atomic units

n=1   1.33 eV

n=2   5.33 eV

n=3   12.0 eV   red~1.8eV, blue~3.1eV

Thus $\Delta E(n = 2 \rightarrow 3) = 6.67$ eV

As the chain length increases, the transition moves from the UV to the visible and then into the infrared.

Recall that the dot product between two vectors is

$$\vec{r} \cdot \vec{s} = r_x s_x + r_y s_y + r_z s_z$$

The dot product is 0 if the vectors are orthogonal

The integral $\displaystyle\int_{-\infty}^{\infty} \psi_i{}^* \psi_j dx$ is the continuous function

analog of the dot product of vectors in Cartesian space

In Dirac notation $\displaystyle\int_{-\infty}^{\infty} \psi_i{}^* \psi_j dx = \langle \psi_i | \psi_j \rangle$

For the particle in the box problem

$$\int_0^L \psi_i \psi_j dx = \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases}$$

The functions $\{\psi_i\}$ form an orthonormal (both orthogonal and normalized) set.

The integration runs from 0 to L for the particle in the box problem

They also form a basis set in which any other function on (0,L) can be represented

Free particle and momentum

Free particle $\psi = e^{ikx}$ travelling to right

e^{-ikx} travelling to left

momentum operator (for motion in the x direction)

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

$$p_x e^{ikx} = \hbar k e^{ikx}$$

$$p_x e^{-ikx} = -\hbar k e^{-ikx}$$

For a free particle k can take on any real value

For a free particle

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

$A\phi = a\,\phi$ is an example of an eigenvalue problem
with A being some operator, a being the eigenvalue,
and ϕ an eigenfunction

Note $\sin(kx)$ and $\cos(kx)$ are not eigenfunctions of the momentum
operator

Euler's relations

$e^{ix} = \cos(x) + i \sin(x)$

$e^{-ix} = \cos(x) - i \sin(x)$

$\cos(x) = (e^{ix} + e^{-ix})/2$

$\sin(x) = (e^{ix} - e^{-ix})/2i$

Note: $\exp(i\pi) = -1$