

### Chapter 3 – The Schrödinger Equation and Particle in a Box

**Background:** We are finally able to introduce the Schrödinger equation and the first quantum mechanical model particle in a box. This equation is the basis of quantum mechanics and as we will learn in chapter 4 is a postulate rather than a derivable expression.

\* The Time-Independent Schrödinger equation

- we begin with the classical 1D wave equation

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \text{ with } u(x,t) = \psi(x) \cos(\omega t) \text{ and } \psi(x) \text{ is the spatial amplitude } u(x,t)$$

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \rightarrow \frac{d}{dx^2} \psi(x) + \frac{\omega^2}{v^2} \psi(x) = 0 \text{ with } \omega = 2\pi\nu \text{ \& } v\lambda = v$$

$$\frac{d}{dx^2} \psi(x) + \frac{(2\pi\nu)^2}{(v\lambda)^2} \psi(x) = \frac{d}{dx^2} \psi(x) + \frac{4\pi^2}{\lambda^2} \psi(x) = 0$$

- If we use de Broglie's relation  $\lambda = h/p$  and  $E = \text{K.E.} + \text{P.E.}$

$$E = \frac{p^2}{2m} + V(x) \rightarrow p = \sqrt{2m(E - V(x))} \therefore \lambda = \frac{h}{\sqrt{2m(E - V(x))}}$$

- Using  $\hbar = h/2\pi$  and substituting  $\lambda$  back into our equation:

$$\frac{d}{dx^2} \psi(x) + \frac{4\pi^2}{\lambda^2} \psi(x) = \frac{d}{dx^2} \psi(x) + 2m(E - V(x)) \frac{(2\pi)^2}{h^2} \psi(x) = \frac{d}{dx^2} \psi(x) + \frac{2m(E - V(x))}{\hbar^2} \psi(x) = 0$$

$$\frac{d}{dx^2} \psi(x) + \frac{2m(E - V(x))}{\hbar^2} \psi(x) = 0 \rightarrow \frac{\hbar^2}{2m} \frac{d}{dx^2} \psi(x) + (E - V(x)) \psi(x) = 0 \rightarrow$$

$$\frac{\hbar^2}{2m} \frac{d}{dx^2} \psi(x) + E\psi(x) - V(x)\psi(x) = 0$$

$$\therefore \boxed{\frac{\hbar^2}{2m} \frac{d}{dx^2} \psi(x) - V(x)\psi(x) = E\psi(x)}$$

The last equation is the time-independent Schrödinger equation.

\* Linear Operators,  $\hat{A}$  "A hat"

- In general, a linear operator  $\hat{A}$  is defined as

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) \text{ where } c_1 \text{ and } c_2 \text{ are constants}$$

- Examples:

$$\text{linear} : \hat{A} = \frac{d}{dx}, \frac{d}{dx} [c_1 f_1(x) + c_2 f_2(x)] = c_1 \frac{d}{dx} f_1(x) + c_2 \frac{d}{dx} f_2(x)$$

$$\text{non-linear} : \hat{A} = ^2, [c_1 f_1(x) + c_2 f_2(x)]^2 = c_1^2 f_1(x)^2 + \underbrace{2c_1 c_2 f_1(x) f_2(x)}_{\text{extra term}} + c_2^2 f_2(x)^2$$

\* Eigenvalue equations and Schrödinger

- definition of an eigenvalue equation:  $\hat{A}\psi = a\psi$  where  $a = \text{constant}$

- Examples:

-- linear momentum operator  $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$$\hat{p}_x \psi(x) \text{ where } \psi(x) = e^{ikx} \rightarrow -i\hbar \frac{\partial}{\partial x} e^{ikx} = -i\hbar \cdot ike^{ikx} = -\hbar k e^{ikx} = - \underbrace{\hbar k}_{\text{constant}} \psi(x)$$

-- direction operator  $\hat{x}$

$$\hat{x}\psi(x) = xe^{ikx} \neq \text{constant} \cdot \psi(x) \therefore \psi(x) \text{ is not an eigenfunction of operator } \hat{x}$$

- Back to Schrödinger

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x) \text{ or } \boxed{\hat{H}\psi(x) = E\psi(x)}$$

where  $\hat{H}$  is called the Hamiltonian operator

$E$  is the energy of our wavefunction,  $\psi(x)$ , which describes the state of the system

$$K.E. = \frac{\hat{p}_x^2}{2m} = \frac{1}{2m} \left( -i\hbar \frac{d}{dx} \right) \left( -i\hbar \frac{d}{dx} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \text{ and P. E.} = V(x)$$

\* Probability applied to wavefunctions

- as we will later point out wavefunctions are often thought of as vectors

- the intensity of the a wave is the square of the amplitude or magnitude of the Wavefunction,  $I = |\psi(x)| = \psi(x)^* \psi(x)$

- today,  $\psi(x)^* \psi(x)$  is the probability of finding a particle located btwn  $x$  and  $x + dx$

\* Our first quantum mechanical model – Particle in a Box

- this will become the model that UV-vis spectroscopy is based on

- 1D case: a particle is confined to move along one coordinate,  $x$

-- boundary conditions:  $\psi(0) = 0$  and  $\psi(a) = 0$

--- physically we are saying that the potential at the ends of our box is  $\infty$

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \leq x \leq a \\ \infty & x > a \end{cases}$$

--- the particle is thereby restricted to be located btwn 0 &  $a$  or  $0 \leq x \leq a$

-- How does this effect the Schrödinger equation?

Given our conditions for the potential,  $V(x)$

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

$$\text{Or, } \frac{d^2}{dx^2} \psi(x) + \frac{2mE}{\hbar^2} \psi(x) = 0$$

-- Now, let's look at  $\psi(x)$

--- from Chapter 2 that a possible “eigen” solution to our Schrödinger equation is

$$\psi(x) = e^{\beta x} \rightarrow \frac{d^2}{dx^2} \psi(x) = \beta^2 e^{\beta x} = \beta^2 \psi(x)$$

--- plugging this back into the equation:

$$\frac{d^2}{dx^2} \psi(x) + \frac{2mE}{\hbar^2} \psi(x) = 0 \rightarrow \beta^2 \psi(x) - \frac{2mE}{\hbar^2} \psi(x) = 0$$

$$\text{or } \left[ \beta^2 + \frac{2mE}{\hbar^2} \right] \psi(x) = 0 \rightarrow \beta^2 = -\frac{2mE}{\hbar^2} \text{ so } \beta = \pm i \sqrt{\frac{2mE}{\hbar^2}}$$

-- if we let  $k = \sqrt{\frac{2mE}{\hbar^2}}$  then  $\psi(x) = c_1 e^{ikx} + c_2 e^{-ikx}$

Or using Euler’s equations:  $\psi(x) = A \cos(kx) + B \sin(kx)$

-- Now let’s apply the boundary conditions,  $\psi(0) = 0$  and  $\psi(a) = 0$

$$\psi(0) = 0 \rightarrow A = 0$$

$$\psi(a) = 0 \rightarrow B \sin(ka) = 0 \text{ so } \sin(ka) = 0$$

So,  $ka = n\pi$  where  $n = 1, 2, 3, \dots$

Plugging k back in:  $ka = n\pi$  gives

$$ka = \sqrt{\frac{2mE}{\hbar^2}} a = n\pi \rightarrow \frac{2mE}{\hbar^2} a^2 = n^2 \pi^2 \rightarrow \frac{2mEa^2}{\left(\frac{\hbar}{2\pi}\right)^2} = n^2 \pi^2 \rightarrow \frac{8\pi^2 mEa^2}{\hbar^2} = n^2 \pi^2$$

$$\therefore E_n = \frac{n^2 \hbar^2}{8ma^2} \text{ and } \psi_n(x) = B \sin\left(\frac{n\pi x}{a}\right) \text{ where } n = 1, 2, 3, \dots$$

-- Great so what does all this mean?

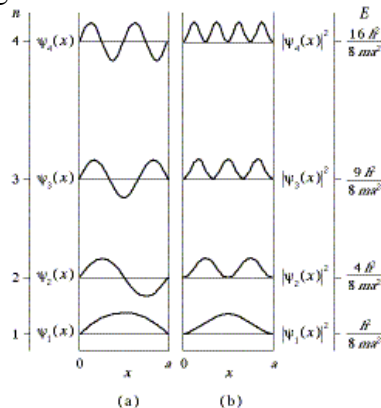
--- first, energy is quantized given our integer n dependence

--- n is a quantum number such that n describes the state of our system

---- for any n we will have an  $E_n$  and  $\psi_n$  for that state

---- also the smaller the n the closer our system is to ground state (g.s.)

--- see figure 3.2 from text



--- We can determine how much energy is required to promote an

e- from 1 state to the next  
 e.g. to go from  $n = 2$  to  $n = 4$ ,

$$\Delta E = E_4 - E_2 = \frac{16h^2}{8ma^2} - \frac{4h^2}{8ma^2} = \frac{12h^2}{8ma^2}$$

Since electronic transitions often occur in the visible, then  
 let  $\lambda_{\max} = 500 \text{ nm}$  which means  $a = 500.0 \times 10^{-9} \text{ m}$

$$\text{so } \Delta E_{2 \rightarrow 4} = \frac{12h^2}{8ma^2} = \frac{12(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2}{8 \cdot 9.109 \times 10^{-31} \text{ kg} \cdot (500.0 \times 10^{-9} \text{ m})^2} = \boxed{2.892 \times 10^{-19} \text{ J}}$$

\* Our wavefunction must be normalized

- remember we are doing a probabilistic approach here as such the probability of finding a particle inside our 1D box must be no greater than unity

- A normalized wavefunction,  $\psi(x)$ , will adhere to  $\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = 1$

- In our case we are talking about a particle which is confined to the limits of our box

So, to normalize our wavefunction,  $\psi_n(x) = B \sin\left(\frac{n\pi x}{a}\right)$ , the limits of integration

$$\text{Are } 0 \text{ and } a: \int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = |B|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx = 1 \rightarrow |B|^2 \cdot \frac{a}{2} = 1 \text{ or } B = \sqrt{\frac{2}{a}}$$

$$\therefore \text{the normalized 1D particle in a box wavefunction is: } \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

\* Average, variance, and standard deviation of our model

- Average/Mean

-- We can determine the average value of any operator,  $\hat{O}$ , which is applied to our

$$\text{system } \langle \hat{O} \rangle = \int_{-\infty}^{\infty} \psi^*(x)\hat{O}\psi(x)dx \text{ this is a postulate from Ch-4}$$

-- the average or mean position of a particle in constrained to our box is:

$$\langle x \rangle = \int_0^a \psi^*(x)\hat{x}\psi(x)dx = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right)x \sin\left(\frac{n\pi x}{a}\right)dx = \frac{2}{a} \frac{a^2}{4} = \frac{a}{2} \text{ for all } n$$

This is the midpoint of the box.

- Variance

-- Like the mean, the variance of any operator applied to the system is defined as

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

-- Since we have  $\langle x \rangle$ , we just need  $\langle x^2 \rangle$ :

$$\langle x^2 \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) x^2 \sin\left(\frac{n\pi x}{a}\right) dx = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{4} = \left(\frac{a}{2n\pi}\right)^2 \left(\frac{n^2\pi^2}{3} - 2\right)$$

- Standard Deviation,  $\sigma_x$

-- as we know the standard deviation is the  $\sqrt{\sigma_x^2}$  or  $\sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

-- for our model,  $\sigma_x = \left(\frac{a}{2n\pi}\right) \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2}$

- We know what the average position, let's see about momentum

$$\langle p_x \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{n\pi x}{a}\right) dx = -\frac{2i\hbar}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) dx = 0$$

Which means that the particle is moving in either directions equally

$$\langle p_x^2 \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \left(-\hbar \frac{d^2}{dx^2}\right) \sin\left(\frac{n\pi x}{a}\right) dx = \frac{2n^2\pi^2\hbar^2}{a^3} \frac{a}{2} = \frac{n^2\pi^2\hbar^2}{a^2}$$

\* Revisiting Heisenberg and his uncertainty

$$\sigma_p = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} = \sqrt{\frac{n^2\pi^2\hbar^2}{a^2} - 0} = \frac{n\pi\hbar}{a}$$

-- from this we see that  $\sigma_p \propto 1/a$  which means the more we try to localize (or make the box smaller) the more deviation we have in p

-- a free particle has no box limiting it, in this case we will have no uncertainty in the momentum

$$\sigma_x = \left(\frac{a}{2n\pi}\right) \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2}$$

-- from this we see that  $\sigma_x \propto a$  which means the smaller the box the smaller our deviation in position

-- for a free particle the uncertainty in position is infinity

- once again, if we have certainty in position we have uncertainty in momentum and vice-versa

$$\text{mathematically: } \sigma_x \sigma_p = \left(\frac{a}{2n\pi}\right) \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} \frac{n\pi\hbar}{a} = \frac{\hbar}{2} \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2}$$

$$\text{since } n \geq 1, \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} > 1 \text{ we can say that } \sigma_x \sigma_p > \frac{\hbar}{2}$$

\* Unto a real box – 3D time

- boundary conditions:

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ 0 & 0 \leq y \leq b \\ 0 & 0 \leq z \leq c \\ \infty & \text{elsewhere} \end{cases} \quad \psi(x, y, z) = \begin{cases} \psi(0, y, z) = \psi(a, y, z) & \text{for all } y \text{ \& } z \\ \psi(x, 0, z) = \psi(x, b, z) & \text{for all } x \text{ \& } z \\ \psi(x, y, 0) = \psi(x, y, c) & \text{for all } x \text{ \& } y \end{cases}$$

Once again the particle is restricted in all three directions

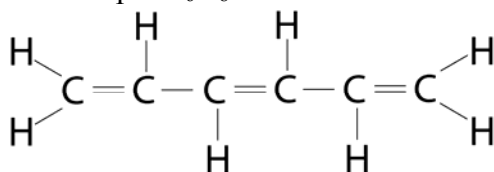
- the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \underbrace{\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}_{\text{Laplacian or } \nabla^2} \psi(x, y, z) = E\psi(x, y, z)$$

-- using separation of variables again we can derive the solution for the wavefunction and the energy description – see the text.

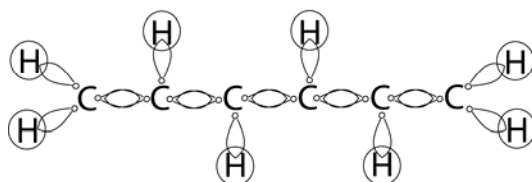
\* Application to particle in a box – conjugated polymers

- For example  $C_6H_8$ :

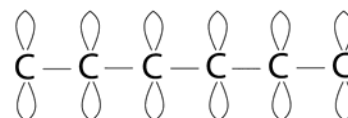


-- each carbon atom has 3  $sp^2$  orbitals and 1  $\pi$

**Sigma-bonding system**



**Pi - System**



-- it turns out that  $\pi \rightarrow \pi^*$  transitions for these conjugated systems are UV-Vis active

--- the average C – C bond length is  $1.4 \text{ \AA}$  this translates to  $5 \times 1.4 \text{ \AA} = 7 \text{ \AA}$  for the length of our box

--- the first excited state is from  $E_3 \rightarrow E_4$ , so

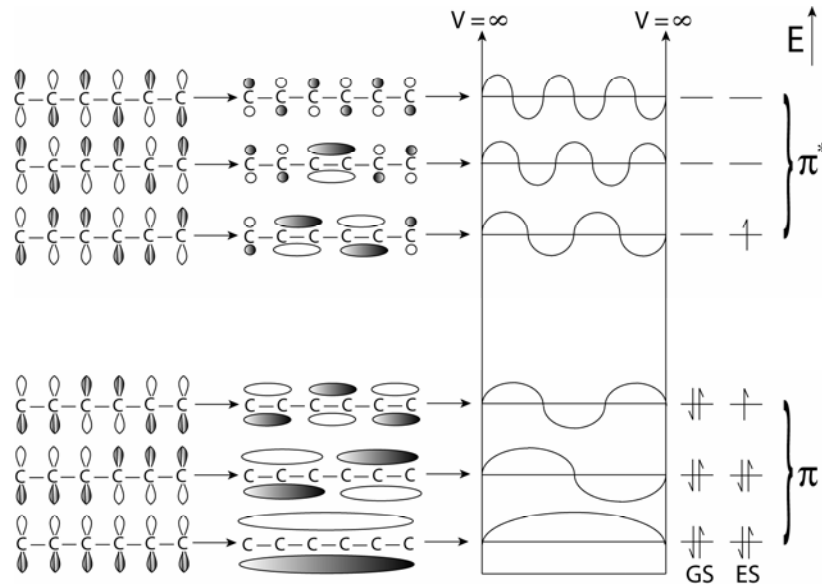
$$\Delta E_{3 \rightarrow 4} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2}{8 \cdot 9.109 \times 10^{-31} \text{ kg} \cdot (7 \times 10^{-10} \text{ m})^2} (16 - 9) = 7.38 \times 10^{-19} \text{ J}$$

-- this translates to a wavelength of:

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times 3 \times 10^8 \text{ m/s}}{7.38 \times 10^{-19} \text{ J}} = 2.69 \times 10^{-7} \text{ m} \quad \text{or} \quad 269 \text{ nm}$$

which is in the UV range

-- let's talk about the states



- HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied MO)
  - for the ground state the HOMO is  $\psi_3$  and the LUMO is  $\psi_4$
  - for the first excited state HOMO is  $\psi_4$  and the LUMO is  $\psi_5$
- the gap between the  $\pi$  and  $\pi^*$  band is called the band gap
  - the smaller the band gap the more conducting the system is
  - $\pi$ -band is also referred to as the valence band
  - $\pi^*$  band is also referred to as the conduction band

\* Dirac Notation – “bra” and “ket”

- this is a shorthand form of spatial integration which is commonly used by chemists & physicists

$$- \int \psi_n^* \psi_{n'} d\tau = \langle \psi_n | \psi_{n'} \rangle = \langle n | n' \rangle$$

--  $\langle n |$  is the “bra” and is the conjugate of  $\psi_n$

--  $\langle n' |$  is the “ket”

$$- \text{Kronecker Delta, } \delta_{n'n} = \begin{cases} 1 & n = n' \\ 0 & n \neq n' \end{cases}$$

-- this works for normalized wavefunctions

-- the  $n \neq n'$  implies that all the states are orthogonal to each other

-- these two stipulations combined lead to a set of wavefunctions which are orthonormal, normalized and orthogonal wavefunctions