Lecture 6

Particle in a Box and the Real World

Study Goal of This Lecture

- π-conjugated systems.
- Particle in a finite depth well.
- Tunneling.

6.1 Application of particle in a box model.

"Particle-in-a-box" is more that an idealized simple model. It explains qualitatively many important quantum phenomenon in the real world. e.g. color of quantum dots, quantum cofinement effects $\cdots$.

When apply it to the real world, we get at best a qualitative description. However, many concepts that are already exhibits in the model are quite general and useful in chemistry. In this chapter, we will quickly cover two examples, naming the "absorption spectrum of conjugated polyenes" and "tunneling". More applications can be found in the book *"Quantum Chemistry and Spectroscopy", Thomas Engel, Ch.5, Prentice Hall.*

Recall the ideal gas model. Although it contains lots of approximations, it is still a good model in dealing with various problem.

6.1.1 Recall a particle in a box model

Recall some important results of particles in a box. The Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2},\ 0 \le x \le a. \tag{6.1}$$

Eigenfunctions and energy:

$$\hat{H}\psi_n(x) = E_n\psi_n(x), \tag{6.2}$$

$$E_n = \frac{p_n^2}{2m} = \frac{n^2h^2}{8ma^2},\ \psi_n(x) = \sqrt{\frac{2}{a}}\sin\Big(\frac{n\pi x}{a}\Big). \tag{6.3}$$

$\{\psi_n\}$ form an orthornormal set.

Some useful relationship:

$$\lambda_n = \frac{2a}{n},\ p_n = \frac{n}{\lambda_n} = \frac{nh}{2a}. \tag{6.4}$$

It is no need to memorize these.

6.1.2 π-electron in conjugated polyenes

UV-Vis spectrum of molecules are often dependent of the π-conjugated systems in the molecule. Molecules that exhibit absorption of light in the UV/Vis regime, called dyes or chromphores, are often π-conjugated system. The prototype is the π-conjugated polyene: for example, today we consider molecules have this general skeleton: π-electrons delocalized on the backbone and determine the main UV/Vis

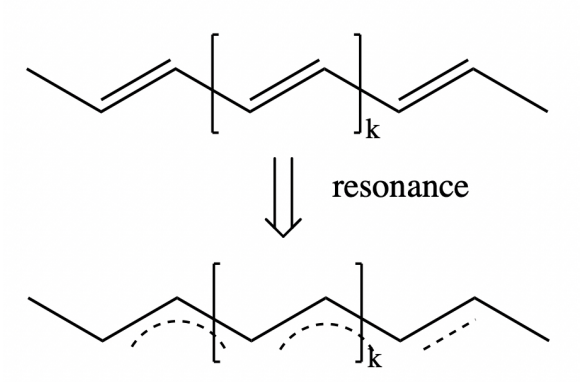

Figure 6.1: Polyene

absorption of these materials. $\Rightarrow$ It's just alike free electrons confined on a 1-D box.

Energy of particle in a box: $E_n = \frac{h^2 m^2}{8ma^2}$. Lets consider $k = 2$ case (2,4,6-dectetraene) , where 8 carbon atoms in the conjugated system $\Rightarrow 8\pi$-electrons and 7 bonds. Note

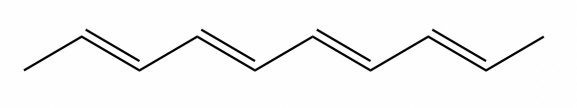

Figure 6.2: 2,4,6-dectetraene

that this is not a single particle problem. Sum all the above conditions, we need to consider:

1. More than one electron
2. Size of the box

1. More than one electron

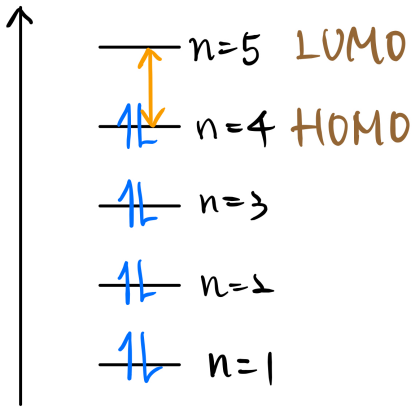

Figure 6.3: Filling the electron into the states.

Electron are fermions and they have to obey Pauli's exclusion principle, i.e. each state can accommondate up to two electrons(independent electrons). The lowest energy absorption maxima corresponding to HOMO $\rightarrow$ LUMO transition, thus, in this case:

$$\Delta E = \frac{h^2}{8ma^2}(n^2_{LUMO} - n^2_{HOMO}) = \frac{h^2}{8ma^2} \times 9 = h\nu_{abs} = \frac{hc}{\lambda_{abs}}, \tag{6.5}$$

$$\lambda_{abs} = \frac{hc}{\Delta E} = \frac{8ma^2 c}{9h}. \tag{6.6}$$

2. Size of the box

Average bond length is 1.35 Å. Therefore, the box size is:

Exact numbers are not important.

$$7 \times 1.35 = 9.45\text{Å} \tag{6.7}$$

Plug in other parameter:

$$m_e = 9.109 \times 10^{-31} kg$$
$$h = 6.626 \times 10^{-34} J \cdot s = 6.626 \times 10^{-34} kg \cdot m^2 \cdot s^{-1}$$
$$c = 3 \times 10^8 m \cdot s^{-1}$$

We obtain $\lambda_{abs} = 328nm$. Compare to experimental value:

	Aborption wavelength	
	Particle in a Box	Experiment
$k = 1$	215	275
$k = 2$	328	310
$k = 3$	443	341

The numbers are bad, but the trend is correct. The general concept which stated that "the bigger the box, the lower the absorption maxima (hence more red)" is correct and useful in chemistry.

6.2 Particle in a Finite Depth Well

Let's consider a particle in a finite depth well. (We consider only total energy $E < V_0$) The potential is:

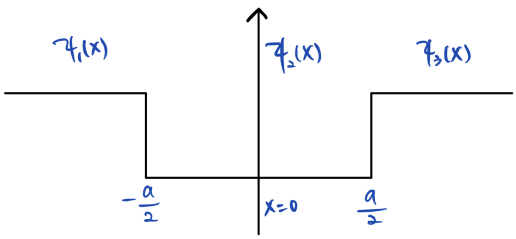

Figure 6.4: Particle in a finite depth well.

$$\begin{cases} V(x) = 0 & \text{for } -\frac{a}{2} < x < \frac{a}{2}, \\ V(x) = V_0 & \text{for } x \geq \frac{a}{2},\ x \leq -\frac{a}{2}. \end{cases} \tag{6.8}$$

Because the potential $V_0 < \infty$, the wavefunction in no longer zero at the edge of the well, we need to consider wavefunction outside the well. The Schrödinger equation is then:

but still $\psi(x) \to 0$ at $x = \pm\infty$.

$$\begin{cases} \frac{d^2}{dx^2}\psi(x) = \frac{-2mE}{\hbar^2}\psi(x) & \text{for } -\frac{a}{2} < x < \frac{a}{2}, \\ \frac{d^2}{dx^2}\psi(x) = \frac{2m(V_0-E)}{\hbar^2}\psi(x) & \text{for } x \geq \frac{a}{2}\ x \leq -\frac{a}{2}. \end{cases} \tag{6.9}$$

and the general solutions will be:

$$\begin{aligned} \psi_2(x) = A\cos(kx) + B\sin(kx) \quad & \text{for } -\frac{a}{2} < x < \frac{a}{2}, \\ \psi_3(x) = Ce^{-\kappa x} + De^{\kappa x} \quad & \text{for } x \geq \frac{a}{2}, \\ \psi_1(x) = C'e^{-\kappa x} + D'e^{\kappa x} \quad & \text{for } x \leq -\frac{a}{2}. \end{aligned} \tag{6.10}$$

Now we turn to find the boundary conditions. Because the wavefunction have to be continuous, smooth and normalizable $\Rightarrow \psi_1(-\infty) = \psi_2(\infty) = 0$, so $C' = D = 0$. The values and first derivative of eigenfunction must match at the edge $x = \pm\frac{a}{2}$.

$$\begin{aligned} \psi_1(-\frac{a}{2}) &= \psi_2(-\frac{a}{2}), \\ \frac{d}{dx}\psi_1(x)\Big|_{x=-\frac{a}{2}} &= \frac{d}{dx}\psi_2(x)\Big|_{x=-\frac{a}{2}}, \\ \psi_2(\frac{a}{2}) &= \psi_3(\frac{a}{2}), \\ \frac{d}{dx}\psi_2(x)\Big|_{x=\frac{a}{2}} &= \frac{d}{dx}\psi_3(x)\Big|_{x=\frac{a}{2}}. \end{aligned} \tag{6.11}$$

This allow us to firstly find conditions for E, i.e. possible energies and then the coefficient A, B, C, D', but it requires numerical solution and is beyond the scope of the class.

Nevertheless, an example result is:

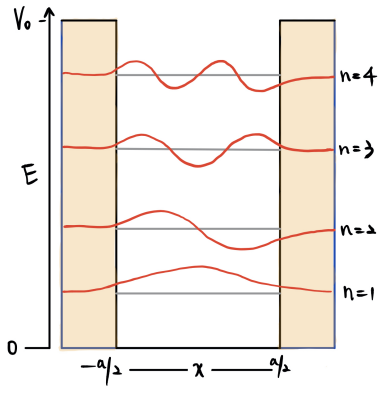

Figure 6.5: Wavefunctions of particle in a finite well.

The above is the plot of wavefunctions of particle in a finite well, on the tail outside the edge. The wavefunction outside the edge is in the form: $e^{-\kappa(x-\frac{a}{2})}$ where $\kappa = \sqrt{\frac{2m(V_0-E)}{\hbar}}$.

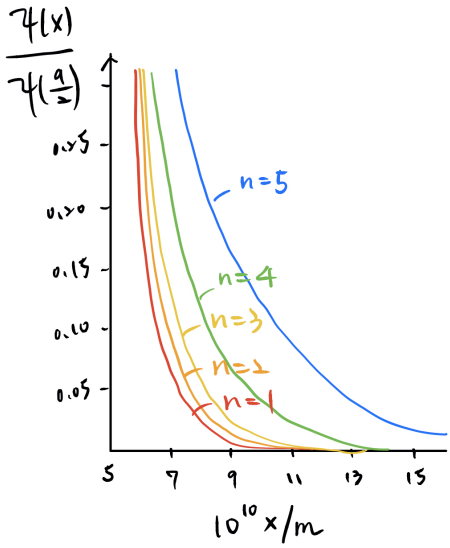

Figure 6.6: Different eigenfunctions and its tunneling .

Here we list some key points for a particle in a finite well.

1. $|\psi(x)|^2 \neq 0$ at $|x| \geq \frac{a}{2}$ even when $E < V_0$ which is the classical forbidden region.

2. The probability density decays exponentailly and the penetration depth $\delta = \frac{1}{\kappa}$. Therefore, high energy state extends more.

3. The source of tunneling $\Rightarrow$ put two wells together, the overlap is "tunneling current." (Important in STM experiment.)

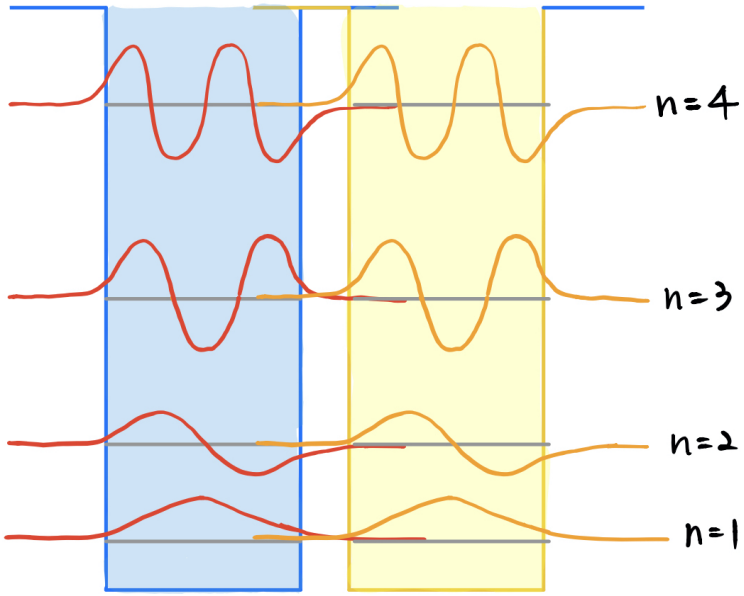

Figure 6.7: Two finite wells overlap. It is important in STM experiment.

6.3 Quantum Tunneling

The exponential tail of the wave function in the region $E < V_0$ is a general quantum phenomena found in many system. Let's focus on this region.

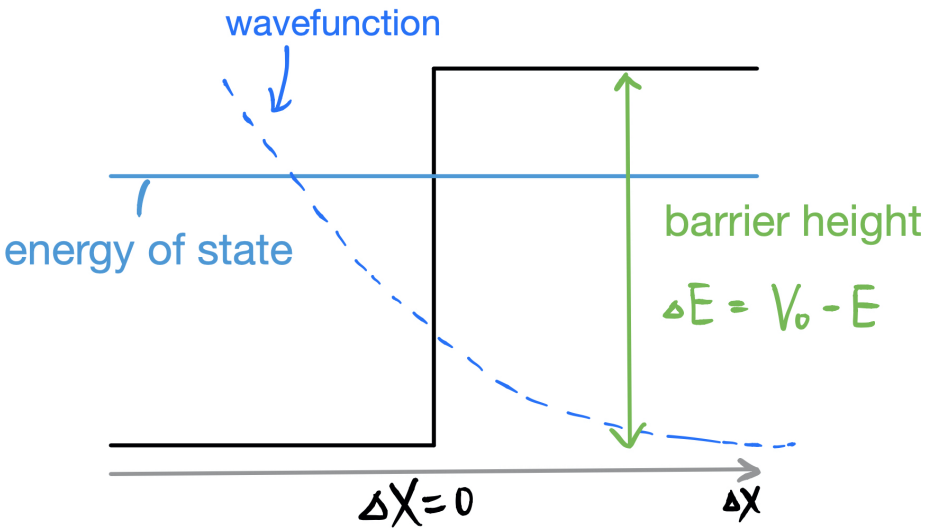

Figure 6.8: Tunneling.

In this tunneling region,

$$\psi(x) \propto e^{\frac{\sqrt{2m(V_0-E)}\hbar}{\Delta}x}. \tag{6.12}$$

Equ(6.12) show us that tunneling depends on the height of the barrier and the width of the barrier!! Experimentally, the tunneling is very sensitive, so STM(Scanning Tunneling Microscope) has atomoic level resolution.

Thinking:

Does tunneling violate the conservation of energy? (Hint: total energy = $\langle E \rangle$, what does $\langle \quad \rangle$ means?)