

Self check: Consider a particle of mass m in a box of length a with the wavefunction $x(x-a)$. What is the energy of the particle? What is the probability that an energy measurement returns the value $h^2/8ma^2$?

$$\Psi = A x (x-a)$$

$$\Psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

a) Normalize the wavefunction.

$$\int_0^a A x (x-a) \times A x (x-a) dx$$

1) Estimate the energy

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad \hat{H} \psi_n = E_n \psi_n$$

Note that $\psi = A x(x-a)$ is not an eigenfunction of \hat{H} .

$$\hat{H} \psi \neq E \psi$$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} A x(x-a) = \mathcal{L} \times \left(-\frac{\hbar^2}{2m} \right)$$

$\neq \text{const} \times A x(x-a)$

Thus to evaluate the energy of the particle in this state,

$$\langle \mathcal{H} \rangle = \bar{E} = \int \Psi^* \mathcal{H} \Psi dx = \int \Psi^* \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \Psi dx$$

$$= -\frac{\hbar^2 A^2}{2m} \int x(x-a) \times 2 dx$$

o

o

o

Note that ψ for the particle does not necessarily be an eigenfunction of \hat{x} .

Operator for the total energy $\hat{H} = \hat{T} + V(x) = \frac{\hat{p}_x^2}{2m} + 0$

$$\hat{p}_x = -i\hbar \frac{d}{dx}$$
$$\hat{p}_x^2 = \hat{p}_x \times \hat{p}_x = \left(-i\hbar \frac{d}{dx}\right) \left(-i\hbar \frac{d}{dx}\right) = -\hbar^2 \frac{d^2}{dx^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) = g(x)$$

$$V(x) = A x (x-a) = g(x)$$

$$\hat{H} \psi = \text{constant} \times \psi \rightarrow \left. \begin{array}{l} \text{Not} \\ \text{eigen value} \\ \text{equation} \end{array} \right\}$$

Measurement postulate says that when you measure the energy you get $E_1, E_2, E_3, E_4, \dots, E_\infty$,

where
$$E_n = \frac{n^2 \hbar^2}{8ma^2}$$

b) What is the probability that you get energy $E_1 = \frac{h^2}{8ma^2}$?

$$\Psi = C_1 \Psi_1 + C_2 \Psi_2 + C_3 \Psi_3 + \dots$$

See the analogy with position vector in Cartesian coordinates

$$\vec{r} = 3\hat{i} + 4\hat{j} + 5\hat{k}$$

$$\Psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

Expand Ψ in the basis of energy eigenstates

$$\Psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

For a different state say

$$\Psi' = A x^2 (x-a)^2$$

$$\Psi' = C_1' \Psi_1 + C_2' \Psi_2 + C_3' \Psi_3 + \dots$$

The expansion coefficients are different

$$\hat{H} \Psi_1 = E_1 \Psi_1$$

$$C = \int \psi_i^* (C_1 \psi_1 + C_2 \psi_2 + C_3 \psi_3 + \dots) dx$$



$$\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

Analogy

$$i \cdot i = j \cdot j = k \cdot k = 1$$

$$i \cdot j = 0$$

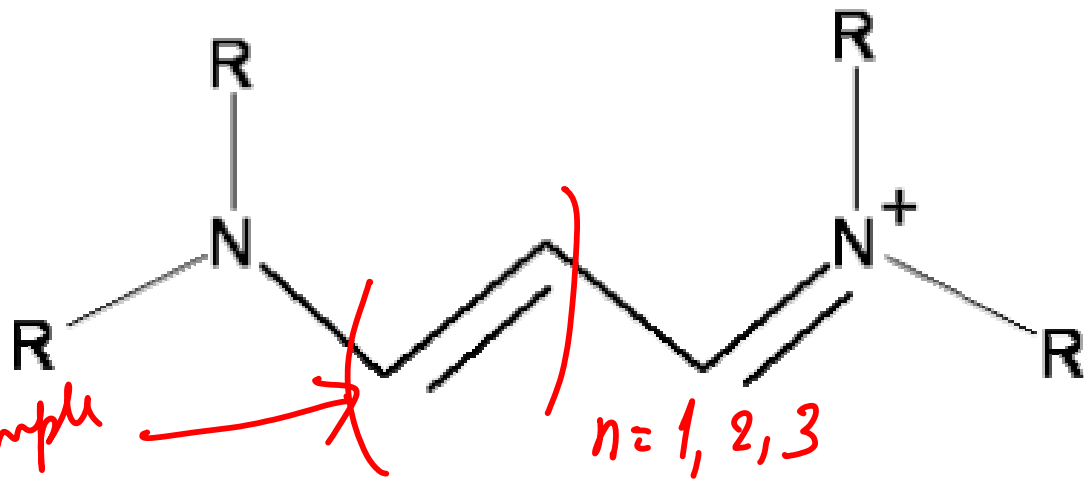
$$\int \psi_i^* \psi_j dx = \delta_{ij}$$

$|C_i|^2$ gives the prob of measuring energy E_i

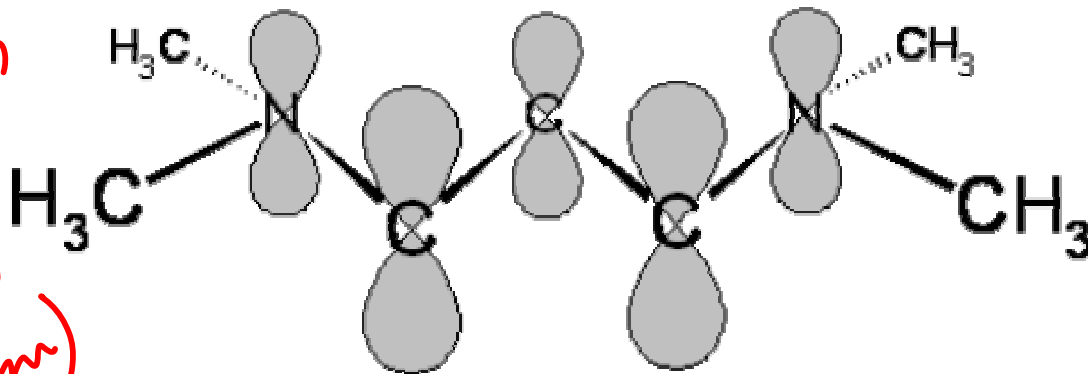
See www.falstad.com for some QM
(and other physics) animations

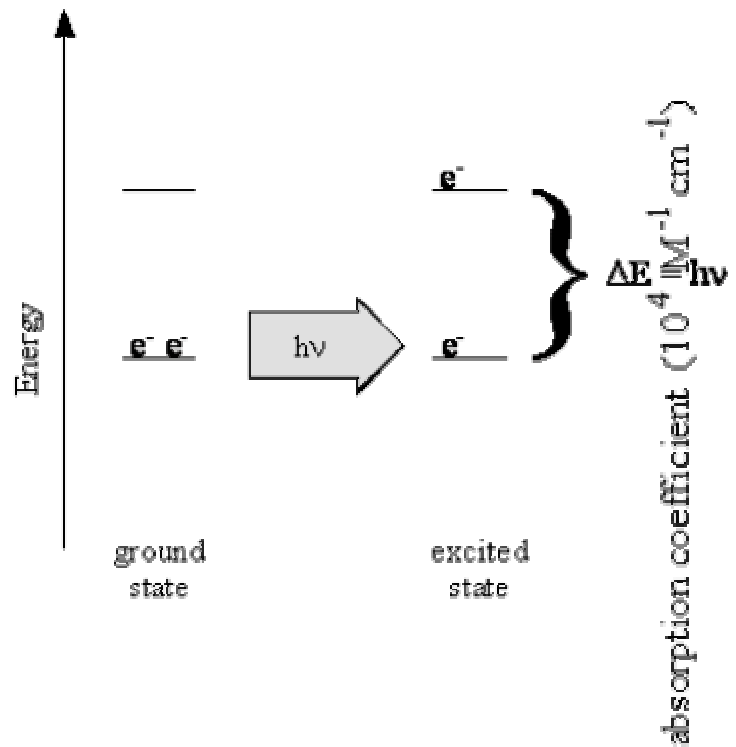
Particle in a box: chemical application

Electronic Spectra and color of cyanine dyes
one example

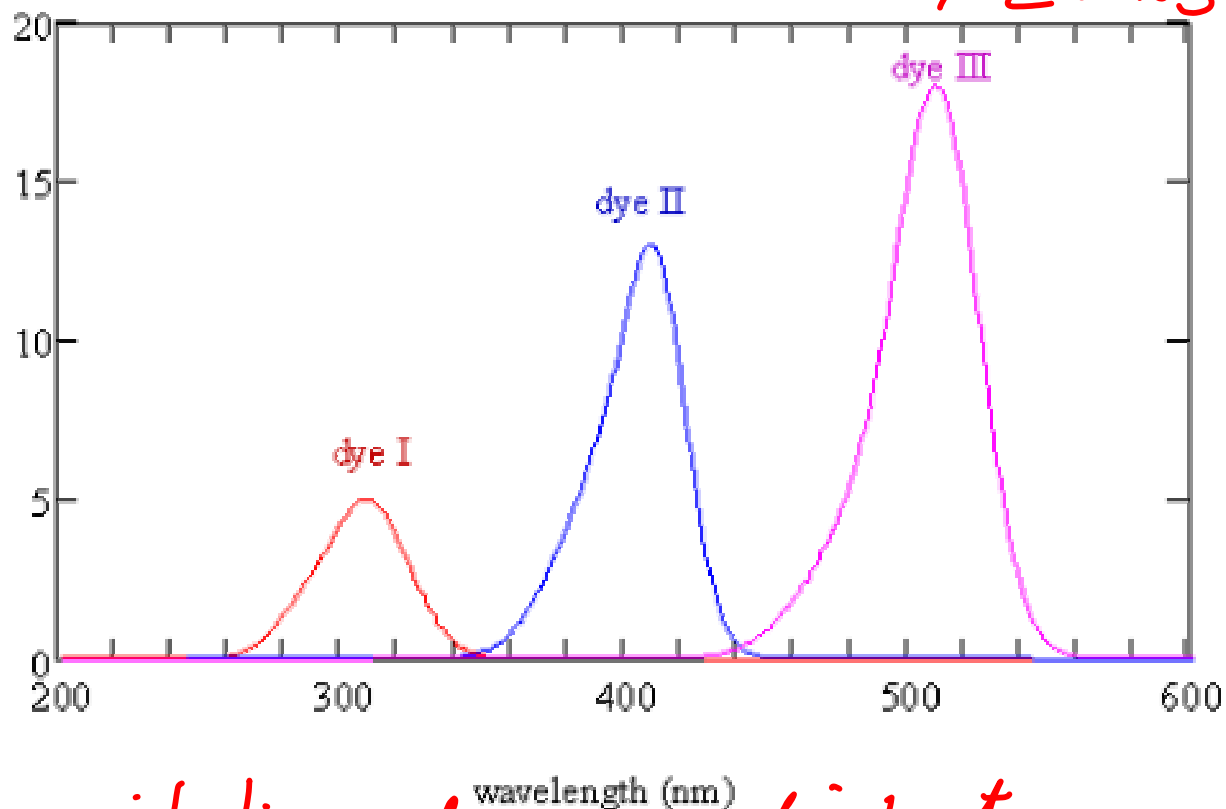


Focus attention on the π -electrons (6 of them)



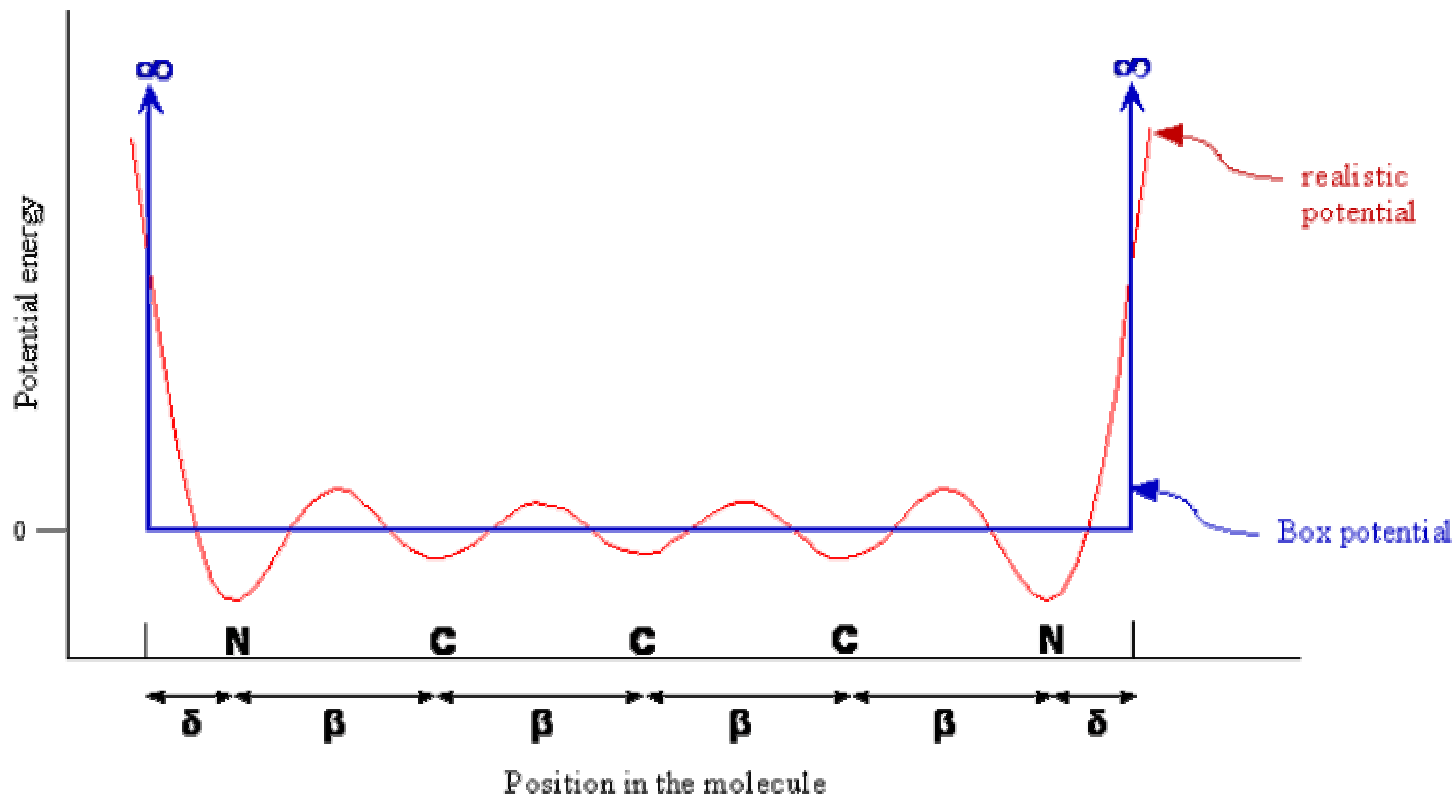


dye I : $n = 1$, dye II : $n = 2$,
dye III : $n = 3$



Electronic excitation from the highest occupied level to the lowest unoccupied level

- 1) π -electrons are independent (one electron does not feel the other)
- 2) Real potential is the red line (approximated by $\hat{P}\hat{I}\hat{B}$)
- 3) Pauli exclusion principle.



Dye I has 6 π -electrons. E_4

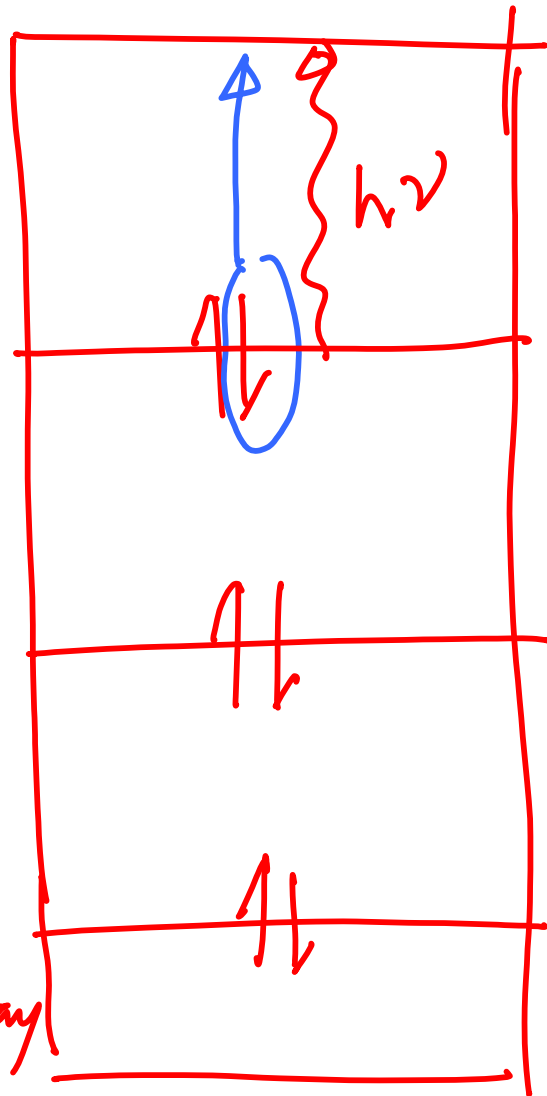
The three lowest energy states

of a PIB each take E_3
two electrons

When light of frequency $\nu = \frac{E_4 - E_3}{h}$ shines on

the dye, it is absorbed. E_4

Color observed is complementary
of color absorbed



Dye II -

- 1) 8 π electrons
- 2) length of the box is longer than dye I
- 3) Transition freq is $E_5 - E_4$ which is lower than dye I
(Try to explain this yourself)

Dye III - 10 π electrons
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