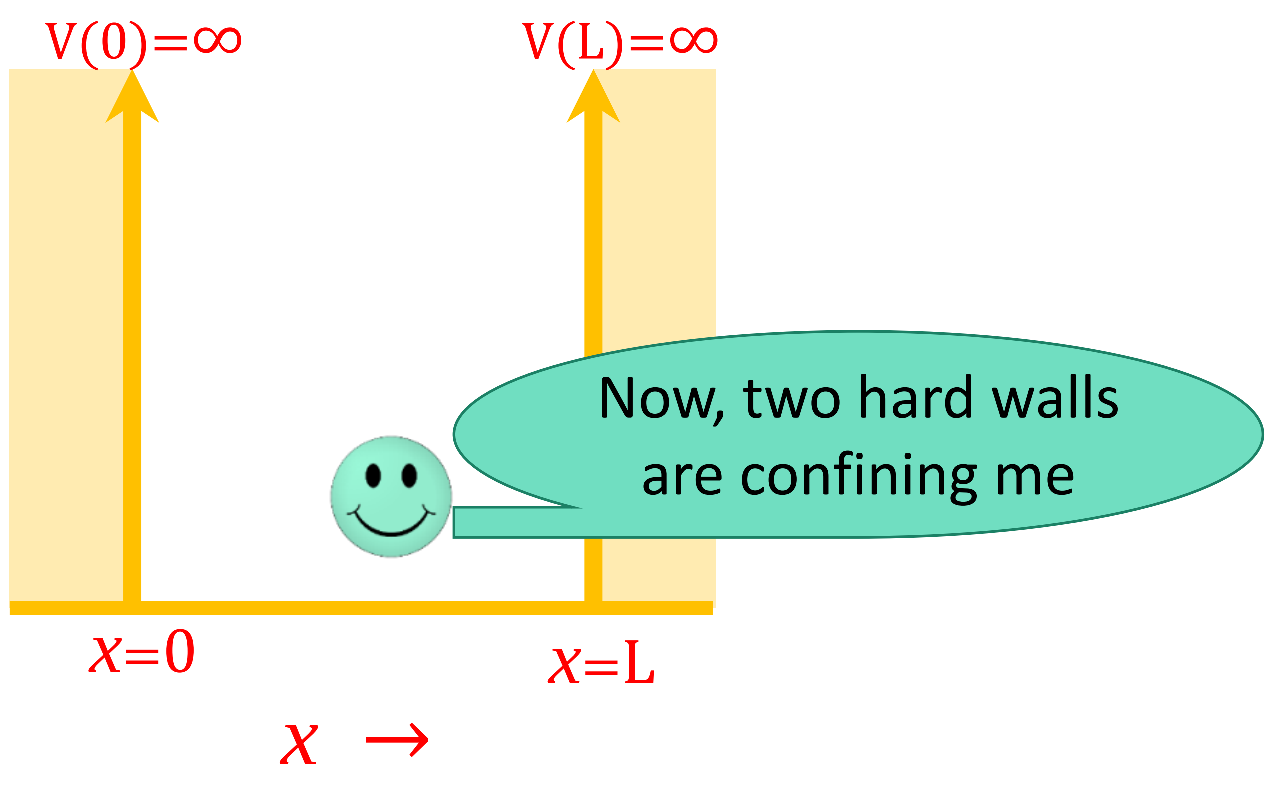
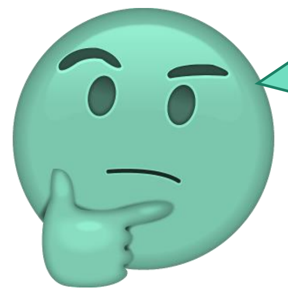


$$\hat{V}(x) = 0 \quad when \quad 0 \leq x \leq L$$
$$= \infty \; otherwise$$

$$\psi(x) = 0 \quad for \quad x \leq 0 \; and \; x \geq L$$

Am I still allowed to have any value of energy?



Let's see what Schrödinger Equation is suggesting

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

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x); \qquad 0 \leq x \leq L$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) = -k^2\psi(x)$$

where $k = \frac{\sqrt{2mE}}{\hbar}$

Possible solution

$$\psi(x) = ASin(kx) + BCos(kx)$$

- A, B, and k are constants which are to be determined using two boundary conditions and one normalization condition on the wavefunction

- **First boundary condition:** $\psi(x = 0) = 0$

$Sin(x = 0) = 0$ and $Cos(x = 0) = 1 \Rightarrow B = 0$

$$\Rightarrow \psi(x) = ASin(kx)$$

$$\Rightarrow \psi(x) = ASin(kx) = ASin\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$

- **Second boundary condition that** $\psi(x = \mathrm{L}) = 0$

$$\Rightarrow \psi(x = L) = ASin\left(\frac{\sqrt{2mE}}{\hbar}L\right) = 0$$

- If we take **A = 0**, then ***ψ*(*x*)=0** for all *x*. This will conflict with the Born interpretation that the particle must be somewhere within the box

$$\Rightarrow ASin\left(\frac{\sqrt{2mE}}{\hbar}L\right) = 0$$

$$\Rightarrow \frac{\sqrt{2mE}}{\hbar}L = kL = n\pi; \quad \text{where} \quad n = 1{,}2{,}\ldots$$

$$\Rightarrow E \,\&\, k \quad \text{are quantized}$$

- $n = 0$ is ruled out because $\psi(x)=0$ for all x

$$E \equiv E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad ; \quad n = 1, 2, \ldots$$

Energy of the particle is quantized, and the quantization arises from the boundary conditions that ψ must satisfy.

$$k \equiv k_n = \frac{n\pi}{L} \; ; \qquad n = 1, 2, \ldots$$

Zero-point energy: Because n cannot be 0 (zero), the *lowest energy that the particle may possess is not zero* (as would be allowed by classical mechanics, corresponding to a stationary particle). The lowest possible energy is: $E_1 = \frac{h^2}{8mL^2}$

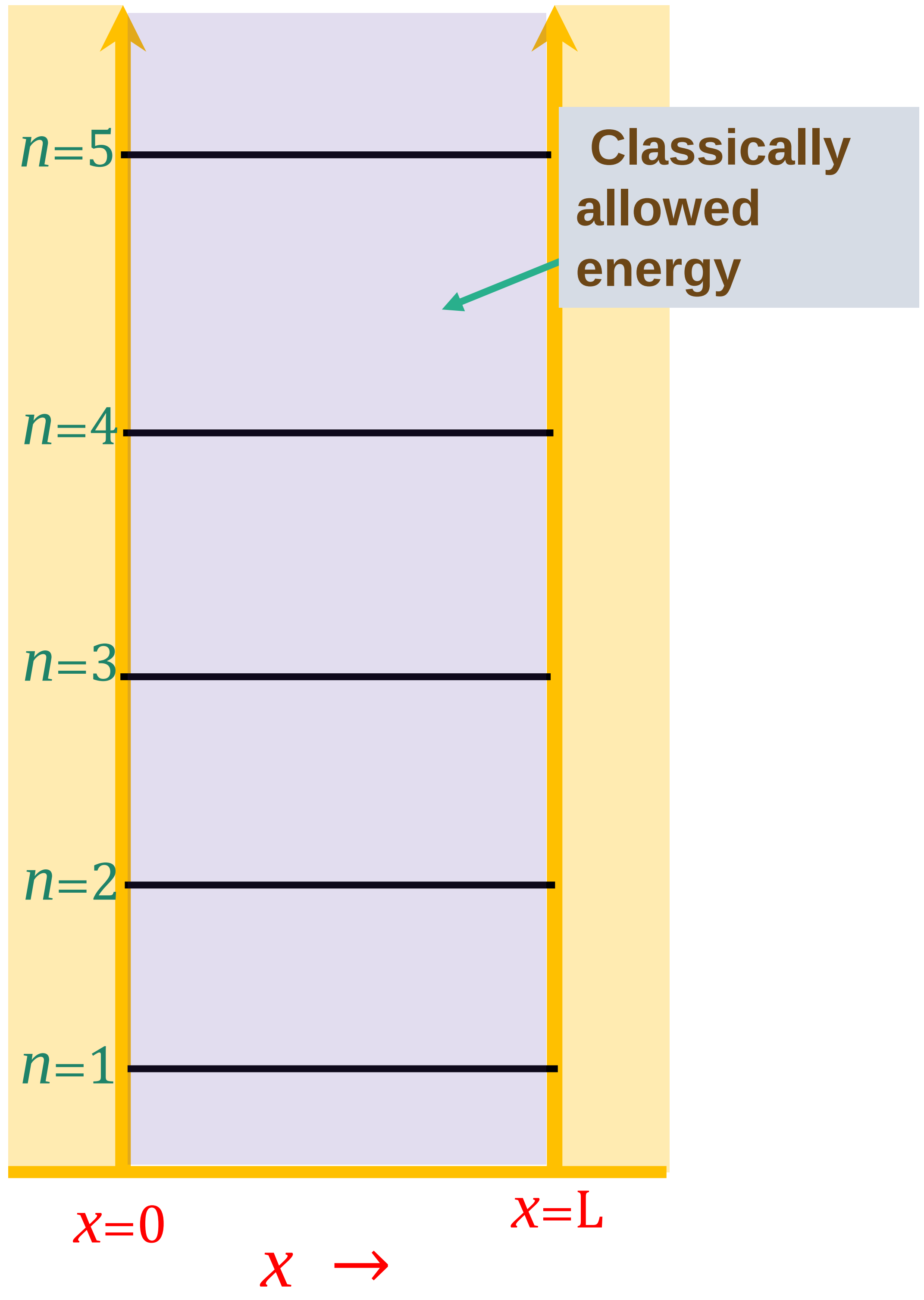
⇒ Zero-point energy is not zero!

The separation between adjacent energy levels with quantum numbers n and $(n+1)$ is

$$\Delta E_n = E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2}$$

$$\Delta E_n = (2n+1)\frac{h^2}{8mL^2}$$

- Note that the energy of the levels increase as n^2, and that their separation increases linearly with n.
- The separation of adjacent levels becomes zero when the walls are infinitely far apart



The wavefunction and probability density

$$\Rightarrow \psi_n(x) = ASin(k_n x) = ASin\left(\frac{\sqrt{2mE_n}}{\hbar}x\right)$$

- **Normalization of the wavefunction**

$$\int_0^L \psi_n^* \psi_n dx = 1 \Rightarrow A^2 \overbrace{\int_0^L Sin^2\left(\frac{n\pi x}{L}\right)}^{\frac{L}{2}} = A^2 \frac{L}{2} = 1$$

$$\Rightarrow A = \sqrt{\left(\frac{2}{L}\right)}$$

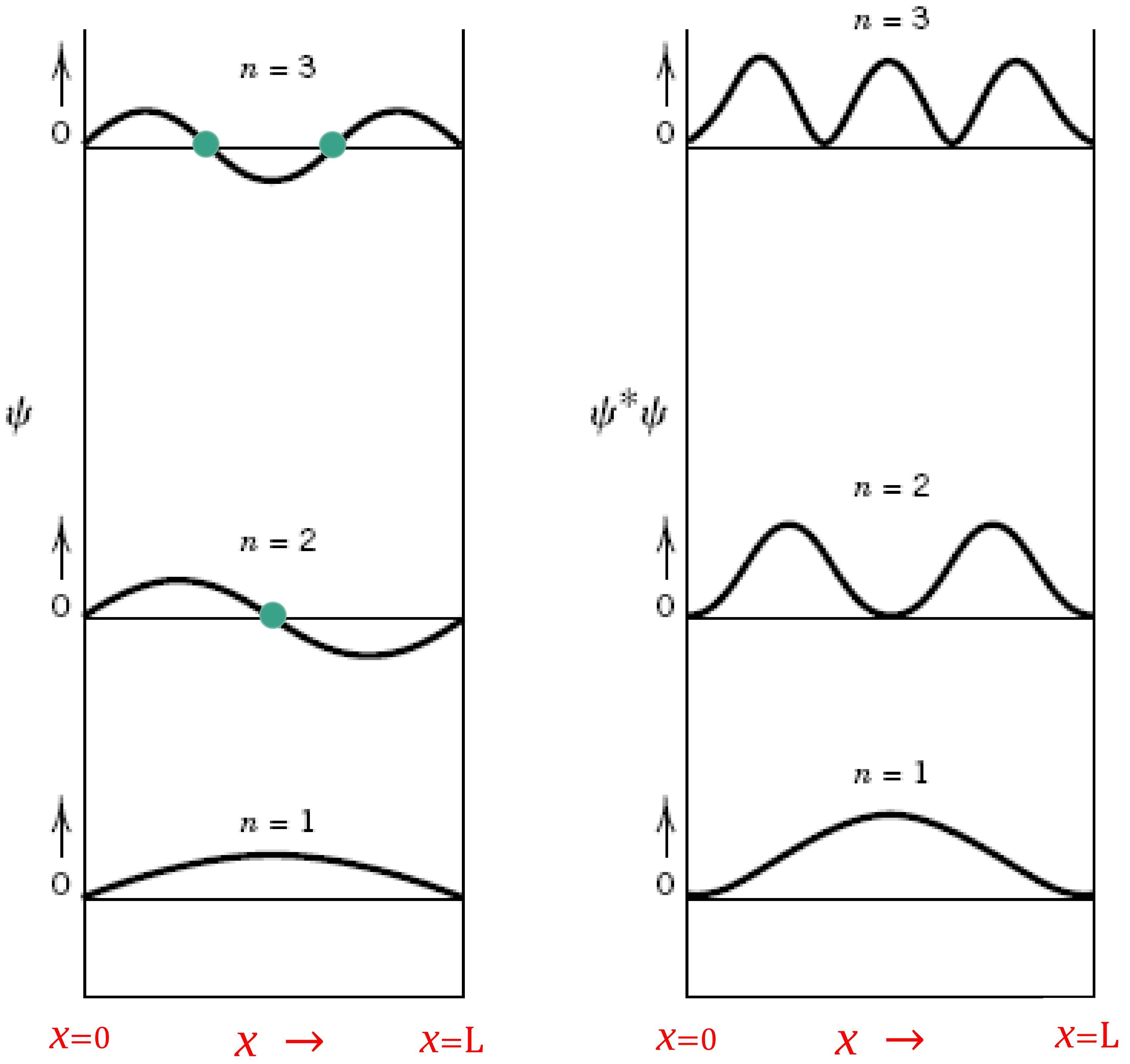
$$\Rightarrow \begin{array}{l} \psi_n(x) = \sqrt{\left(\frac{2}{L}\right)} Sin\left(\frac{n\pi x}{L}\right) \quad for\ 0 \le x \le L \\ \psi_n(x) = 0 \ \ otherwise \end{array}$$

The probability density for a particle in a 1D box is

$$\psi_n^2(x) = \frac{2}{L} Sin^2\left(\frac{n\pi x}{L}\right)$$

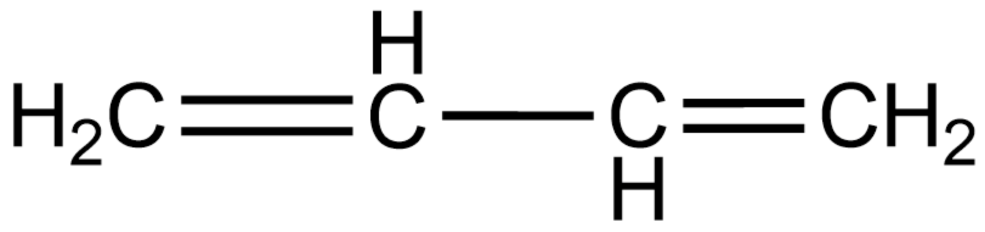
- $\psi_n^2(x)$ is not uniform and changes with position.
- The nonuniformity is pronounced when n is small.
- $\psi_n^2(x)$ tend to be uniform when n increases.

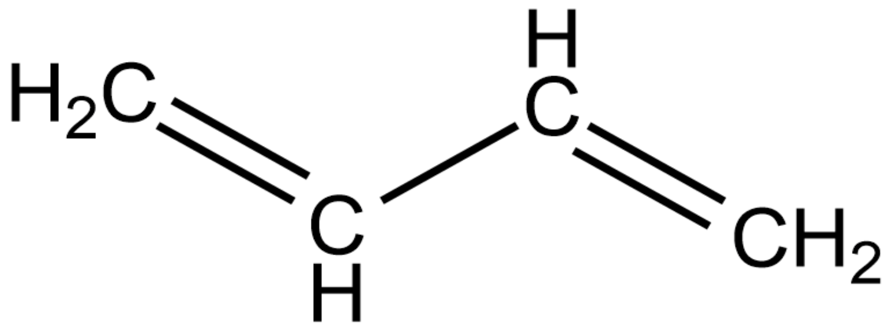
● node **The number of nodes: $(n-1)$**



π electrons in linear carbon hydrocarbons (Ex. 1,3-Butadien)

- **No. of π electrons = 4**

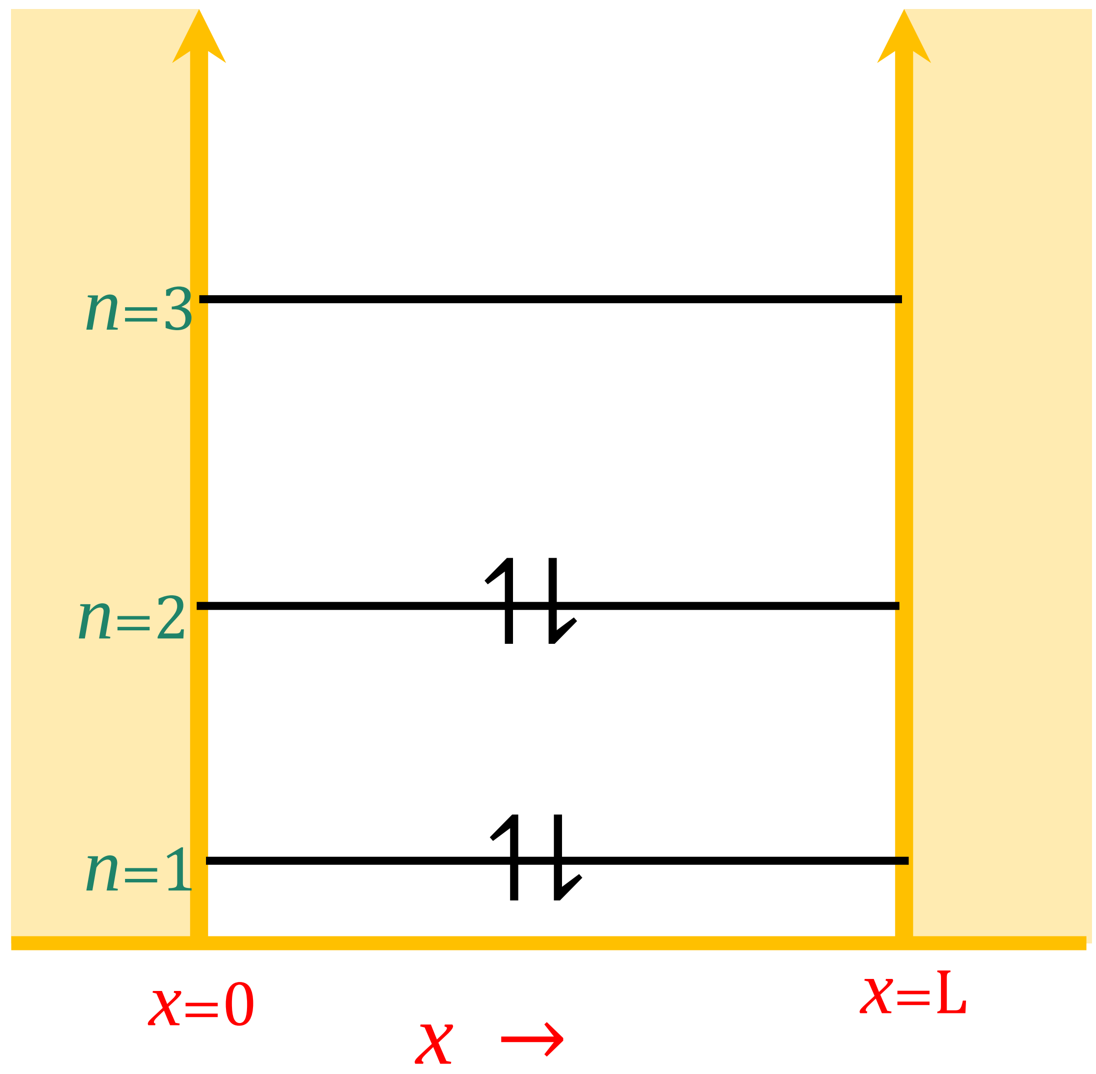




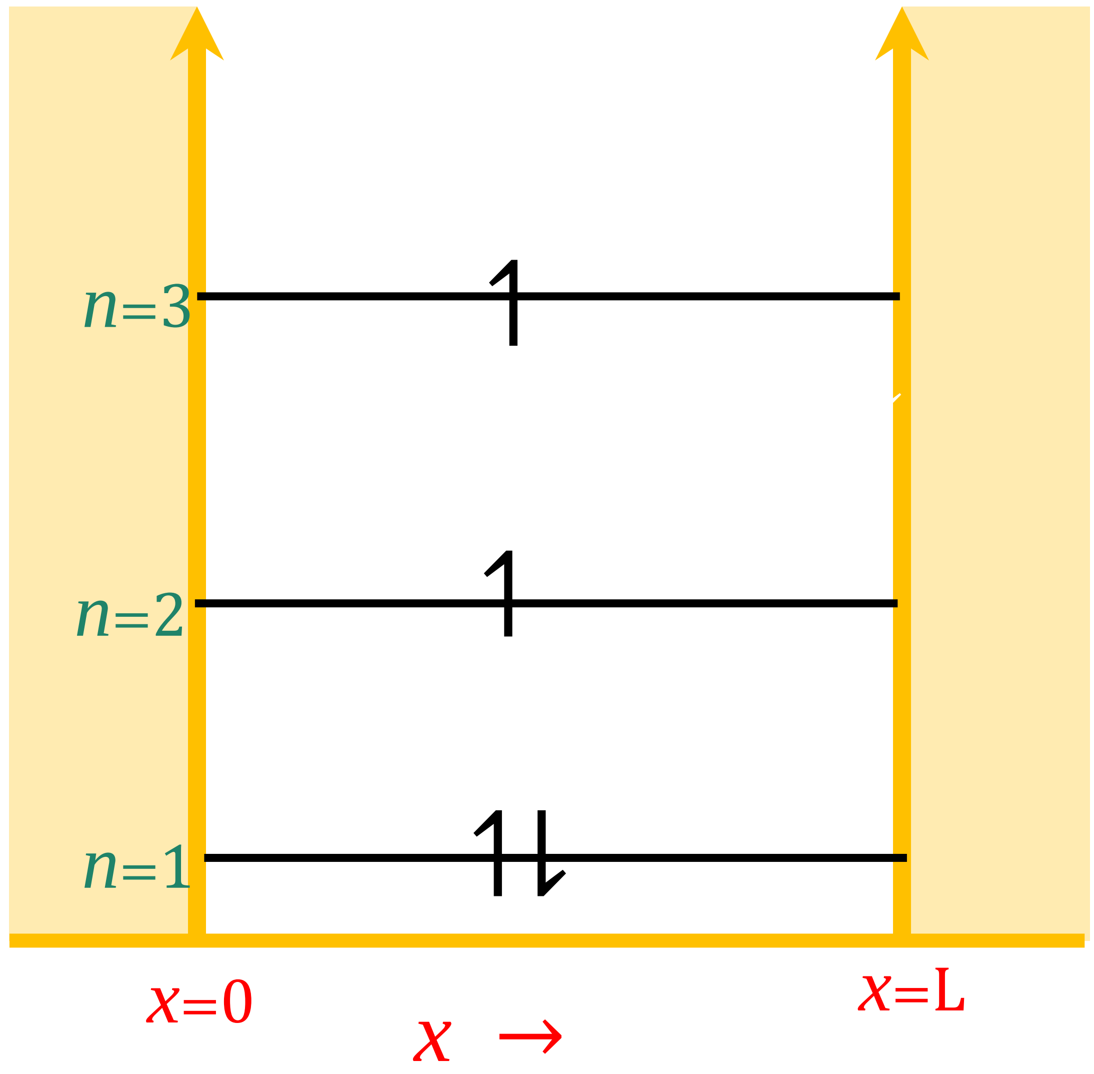
$$L = 2\ell_{C=C} + \ell_{C-C} + b = 2 \times 1.35\ \text{Å} + 1.54\ \text{Å} + b = 5.78\ \text{Å}$$

$$E_{gs} = \frac{h^2}{8mL^2}\left(2\times 1^2 + 2\times 2^2\right) = \frac{10h^2}{8mL^2}$$

$$E_{first,es} = \frac{h^2}{8mL^2}\left(2\times 1^2 + 1\times 2^2 + 1\times 3^2\right) = \frac{15h^2}{8mL^2}$$



Ground state configuration



Excited state configuration

$$\Delta E = E_{first,es} - E_{gs} = \frac{5h^2}{8mL^2}$$

$$\Delta E = \frac{hc}{\lambda_{em}} = \frac{5h^2}{8mL^2}$$

$$\lambda_{em} = \frac{5h}{8mcL^2}$$