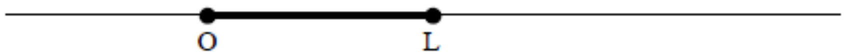
Particle confined on a segment



A particle of mass m is confined on a segment of length L: this model is used to describe free electrons in metals or electrons in conjugated polyenes.

1. The particle is assumed to be free on the segment. What does that mean for its energy?

2. Write the Schrödinger equation for the particle.

3. Solve the differential equation and write down the solutions in terms of cosine and sine functions.

4. Using the boundary condition at x=0, simplify the expression of the solutions Ψ.

5. Using the second boundary condition, the one on Ψ(x) at x=L, show that the energy is quantized, i.e. that it depends on a quantum number n.

6. Show that the quantum number n can be taken positive. Is n= 0 a physical solution?

7. Derive the normalization factor of the wave function associated to the quantum number n.

8. What represents Ψ*(x) Ψ(x) dx? Then, what represents Ψ*(x) Ψ(x)?

9. Draw the wave functions and the densities of probability associated to the energy levels n=1, 2, 3. Comment.

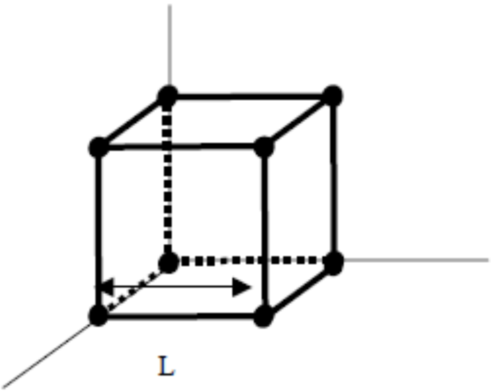
10. Show that in the case of a macroscopic system (L goes to infinity), the energy is not quantized anymore. Show that for large quantum numbers, the density of probability is uniform along the segment [OL]. Explain why this is referred to as classical limit.

11. Derive the expectation value of the position of the particle for a given n value. Comment.

12. Derive the expectation value of the momentum for a given n value. Comment.

13. We use the model of the confined particle along the segment [OL] to interpret the behavior of π electrons of double bonds in conjugated polyenes. The π electrons are considered to be free to move along the axis of the molecule, which is assumed to be a straight line. An electronic transition (absorption spectrum) happens between the highest occupied energy level (Pauli principle) and the first unoccupied one. The frequency of this transition obeys the Bohr equation: ΔE = hν.
We shall take two examples: hexa-2,4-diene (6C) and butadiene (4C). For each case, derive the relation between λ, the wavelength associated to this transition, and D, the length of the molecule. Compute λ in each case ($m=9{,}11.10^{-31}$ kg; $c=3.10^{8}$ $m.s^{-1}$; $h=6{,}63\ 10^{-34}$ J.s, C-C = 154 pm, C=C = 135 pm). The experimental values are λ_{exp6} =227 nm and λ_{exp4} =217 nm. Comment.

Particle confined in a cubic box



We consider a “free” particle of mass m trapped into a cubic box of volume L x L x L.

Purpose of the exercise: we want to know what are the possible energies of the trapped particle. Note that such a question arises in statistical physics when considering the ideal gas model.

1. Write the Schrödinger equation for the particle and give the six boundary conditions.

2. Let us write the solution as $\Psi(x,y,z)= \varphi_x(x)\varphi_y(y)\varphi_z(z)$. Insert this expression into the Schrödinger equation and divide then by $\Psi(x,y,z)$.

3. Show that the Schrödinger equation obtained in question 2 leads to three independent equations, which can be formally considered as Schrödinger equations for a particle confined on a segment along the x, y or z axis. The corresponding energies are denoted E_x, E_y and E_z in the following. Express the total energy E of the particle in the box with respect to E_x, E_y and E_z.

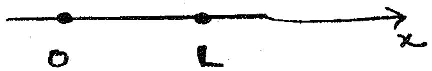
4. According to the tutorial "Particle confined on a segment”, and using boundary conditions, what are the possible values for E_x, E_y and E_z?

5. What are then the possible energies E for the particle in the box?

6. Give the expression of the corresponding wave function $\Psi(x,y,z)$.

7. What happens to the energy levels when the volume of the box becomes infinite?

Particle confined along a segment of straight line



1 - the energy is only kinetic

2 - General case : $-\dfrac{\hbar^2}{2m}\nabla^2\psi + V.\psi = E.\psi$ ← "potential energy"

$$\begin{cases} \text{one-dimension problem} & \psi(x,y,z) = \psi(x) \quad (2) \\ \text{for } 0 \leq x \leq L & V(x,y,z) = V(x) = 0 \quad (1) \\ \text{for } x \geq L \text{ and } x \leq 0 & \psi(x) = 0 \end{cases}$$

(1) and (2) $\Rightarrow$ $\boxed{-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} = E\psi}$ (3)

3 - (3) $\Leftrightarrow$ $\dfrac{d^2\psi}{dx^2} = -\dfrac{2mE}{\hbar^2}\psi$ (4)

Let us prove that $E \geq 0$:

(4) $\Rightarrow$ $\underbrace{\displaystyle\int_{-\infty}^{+\infty}\psi^*\frac{d^2\psi}{dx^2}}_{I} = -\dfrac{2m}{\hbar^2}\,E\,\underbrace{\displaystyle\int_{-\infty}^{+\infty}\psi^*\psi\,dx}_{\geq 0}$

$I = \underbrace{\left[\psi^*\dfrac{d\psi}{dx}\right]_{-\infty}^{+\infty}}_{0} - \displaystyle\int_{-\infty}^{+\infty}\underbrace{\frac{d\psi}{dx}\cdot\frac{d\psi^*}{dx}}_{\left|\frac{d\psi}{dx}\right|^2}dx \leq 0$

Thus $\boxed{E \geq 0}$

Let $k^2 = \dfrac{2mE}{\hbar^2}$

(4) $\Leftrightarrow$ $\dfrac{d^2\psi}{dx^2} + k^2\psi = 0$

$\Leftrightarrow$ $\boxed{\psi(x) = A\cos kx + B\sin kx}$ (5)

4 - Boundary conditions $\psi(x=0) = 0$

(5) $\Rightarrow$ $A = 0$ $\rightarrow$ $\psi(x) = B\sin kx$

5. Second boundary condition $\psi(x=L)=0$

$\Rightarrow \quad \sin kL = 0 \Leftrightarrow \boxed{kL = n\pi \quad n \in \mathbb{Z}}$

$\Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2 = E_n$

energies are quantized

6. $\psi_n(x) = B_n \sin\left(\frac{n\pi}{L} x\right)$ (6)

$\psi_{-n}(x) = B_{-n} \sin\left(-\frac{n\pi}{L} x\right) = - B_{-n} \sin\left(\frac{n\pi x}{L}\right)$

$\psi_{-n}(x) = - \frac{B_{-n}}{B_n} \psi_n(x) \Rightarrow$ ψ_{-n} and ψ_n are "collinear"

If we choose $B_n \in \mathbb{R}^{+*} \; \forall n \in \mathbb{Z}$

the normalisation of ψ_n and ψ_{-n} imposes

$B_n^2 = B_{-n}^2 \Rightarrow B_n = B_{-n}$

Thus $\boxed{\psi_{-n}(x) = -\psi_n(x)}$

They both contain the same "physics"
meaning that ψ_{-n} is NOT a new solution.

Therefore $n \in \mathbb{N}$.

if $n=0 \quad \psi_n(x) = \psi_0(x) = 0$

This wave function cannot describe the particle
since the normalization condition must be fulfilled,
that is $\int_{-\infty}^{+\infty} |\psi_n(x)|^2 dx = 1$ ← for a physical solution.

Thus $\boxed{n \in \mathbb{N}^*}$

7. Normalization $\int_{-\infty}^{+\infty} |\psi_n(x)|^2 dx = 1$

(6) $\Rightarrow \quad B_n^2 \int_0^L \underbrace{\sin^2\left(\frac{n\pi}{L} x\right)}_{\frac{1}{2}\left(1 - \cos\left(\frac{2n\pi}{L} x\right)\right)} dx = 1$

$\Rightarrow \quad \frac{B_n^2}{2} \left[L - \underbrace{\int_0^L \cos\left(\frac{2n\pi x}{L}\right) dx}_{\left[\frac{\sin(2n\pi x/L)}{(2n\pi/L)}\right]_0^L = 0} \right] = 1$

$\Rightarrow \quad B_n = \frac{\sqrt{2}}{\sqrt{L}}$

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

8- $\psi^*(x)\psi(x)\,dx = d\mathcal{P}(x)$: probability that the particle is at position x,

$\rho(x) = \psi^*(x)\psi(x)$ is the density of probability,

The normalization means that the particle must be somewhere on the line

$$\underbrace{\int_{-\infty}^{+\infty} d\mathcal{P}(x)}_{\text{sum of all probabilities}} = 1 = \int_{-\infty}^{+\infty} \rho(x)\,dx = \int_{-\infty}^{+\infty} \psi^*(x)\psi(x)\,dx$$

9- $\rho_n(x) = |\psi_n(x)|^2 = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)$

$$\rho_n(x) = \frac{2}{L}\left(\frac{1 - \cos(2n\pi x/L)}{2}\right)$$

$$\boxed{\rho_n(x) = \frac{1 - \cos(2n\pi x/L)}{L}} \quad (7)$$ see enclosed figures

Comment on the wave functions $\psi_n(x)$:

The number of nodes (where $\psi_n(x)$ changes sign) increases with n and thus with the energy

$n=1$	no nodes
$n=2$	1 node
$n=3$	2 nodes
$\vdots$	

This ensures the orthogonality of the solutions

$$\langle\psi_n|\psi_m\rangle = \int_0^L dx\, \psi_n^*(x)\psi_m(x)$$

$$= \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx$$

$$= \frac{\cancel{2}}{L}\int_0^L \frac{1}{\cancel{2}}\left(\cos\left((n-m)\frac{\pi x}{L}\right) - \cos\left((n+m)\frac{\pi x}{L}\right)\right)dx$$

$$= \frac{1}{L}\int_0^L \cos\left((n-m)\frac{\pi x}{L}\right)dx$$

$$\underbrace{-\frac{1}{L}\left[\frac{\sin\left((n+m)\frac{\pi x}{L}\right)}{(n+m)\frac{\pi}{L}}\right]_0^L}_{0}$$

if $n \neq m \Rightarrow \langle \psi_n | \psi_m \rangle = \frac{1}{L}\left[\frac{\sin\left((n-m)\pi \frac{x}{L}\right)}{(n-m)\frac{\pi}{L}} \right]_0^L = 0$

Therefore $\boxed{\langle \psi_n | \psi_m \rangle = \delta_{nm}}$

Comment on the probability densities:

As n increases, the number of maxima of the probability density increases.

Let x_p^n denote one of the maxima: according to (7)

$$\frac{2n\pi x_p^n}{L} = (2p+1)\pi$$

$$\Rightarrow \boxed{x_p^n = \frac{(2p+1)}{2n} L \qquad p = 0, 1, \dots, n-1}$$

Therefore $x_{p+1}^n - x_p^n = \frac{L}{n} \underset{n \to +\infty}{\longrightarrow} 0$

which means that for large quantum numbers the density of probability becomes uniform

$\Rightarrow$ classical limit

10 - We have shown in question 5 that the confinement of the particle induces a quantization of its energy $\longrightarrow E_n = \frac{\hbar^2 k_n^2}{2m}$

where $k_n = \frac{n\pi}{L}$. In the classical limit ($L \to +\infty$)

$$k_{n+1} - k_n = \frac{\pi}{L} \longrightarrow 0$$

which means that we get a continuum of values for k_n and thus for E_n (the energy is not quantized anymore).

In reality L is of course finite (very large but not infinite) which means that the energy levels are very very close to each other, looking like a continuum. Note that

$$E_1 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \underset{L \to +\infty}{\longrightarrow} 0 \qquad \psi_1(x) \underset{L \to +\infty}{\longrightarrow} 0$$

$$E_2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \underset{L \to +\infty}{\longrightarrow} 0 \qquad \psi_2(x) \underset{L \to +\infty}{\longrightarrow} 0$$

$\vdots$

but for sufficiently large n values, E_n won't be small (since L is finite).

In this respect, investigating the classical limit requires the investigation of large quantum numbers.

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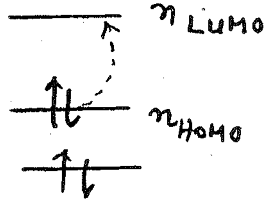


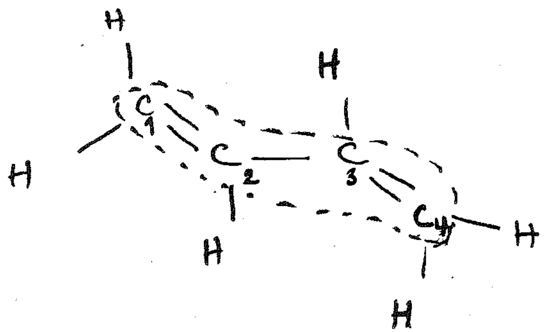
LUMO : Lowest Unoccupied Molecular Orbital
HOMO : Highest Occupied Molecular Orbital

We consider the electronic transition from the HOMO to the LUMO.
The corresponding wave length λ fulfills

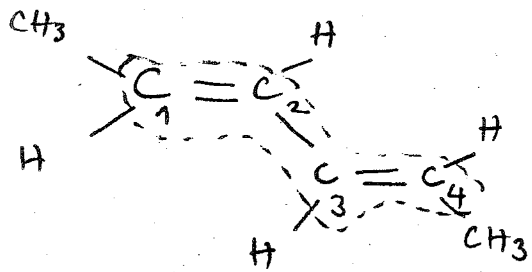
$$h\frac{c}{\lambda} = E_{n_{LUMO}} - E_{n_{HOMO}} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_{LUMO}^2 - n_{HOMO}^2\right)$$

$$\Rightarrow \boxed{\lambda = \frac{8mL^2c}{h\left(n_{LUMO}^2 - n_{HOMO}^2\right)}}$$

Applications:



butadiene



hexa-2,4-diene

In both cases, there are 4 π electrons therefore

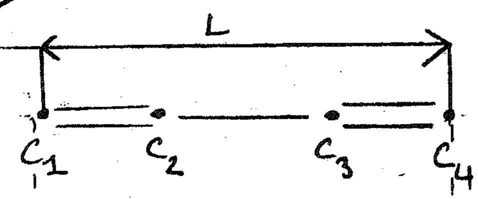
$n_{HOMO} = 2$

and

$n_{LUMO} = 3$.

Value of L ?

In our model we assume that the π electrons are on a straight line



$L = 2d_{C=C} + d_{C-C}$

$L = 2 \times 135 + 154$

$L = 424$ pm

$$\lambda = \frac{8\times 9{,}11\cdot 10^{-31}\,(424)^2\,10^{-24}\cdot 3\,10^{8}}{6{,}63\;10^{-34}\;(5)}$$

$$\lambda = 1{,}186\cdot 10^{-7}\,\mathrm{m} = \underline{118{,}6\ \mathrm{nm} = \lambda}$$

<u>Improvement of the model:</u>

Add on both sides half of the radius of a carbon atom ($d_{C-C}/2$). Thus we get

$$L' = L + d_{C-C} = 578\ \mathrm{pm}$$

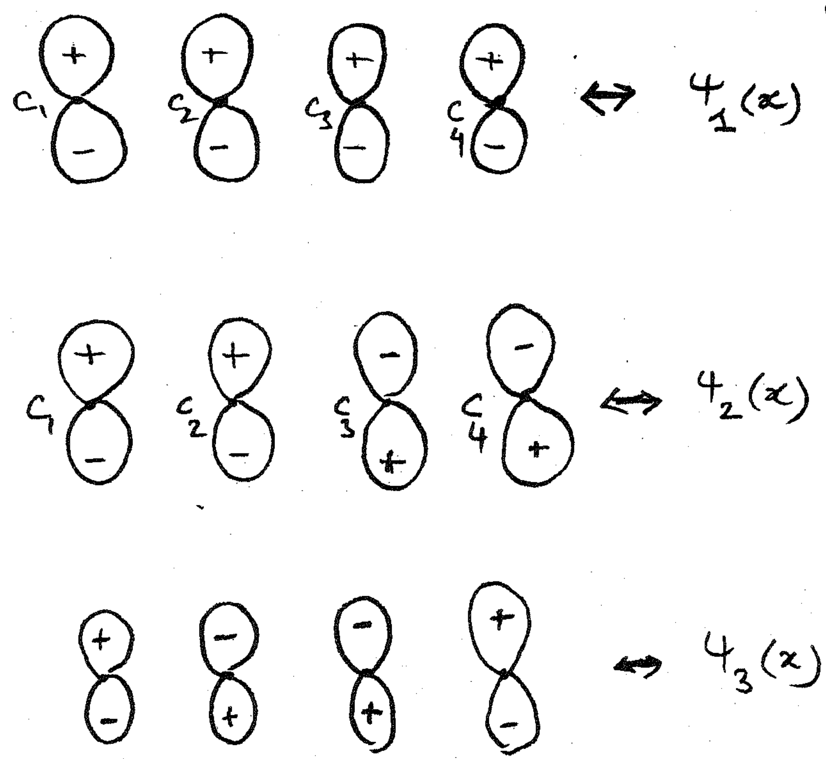
$$\Rightarrow \underline{\lambda' = 220{,}4\,\mathrm{nm}}$$

which is rather close to the experimental values

$$\lambda_{exp6} = 227\ \mathrm{nm} \quad \text{and} \quad \lambda_{exp4} = 217\ \mathrm{nm}$$

<u>Why this crude model makes sense?</u>

Let us look at the π orbitals ...



12- $\langle x\rangle_n = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\, x\, \psi_n(x) = \int_0^L \frac{2}{L}\, x \sin^2\left(\frac{n\pi x}{L}\right) dx$

$= \frac{2}{L}\int_0^L \frac{x}{2}\left(1-\cos(2n\pi x/L)\right) dx$

$= \frac{1}{L}\underbrace{\int_0^L x\,dx}_{\frac{L^2}{2}} - \frac{1}{L}\underbrace{\int_0^L x\cos(2n\pi x/L)\,dx}_{\underbrace{\left[\frac{x\sin(2n\pi x/L)}{(2n\pi/L)}\right]_0^L}_{=0} - \underbrace{\int_0^L \frac{\sin(2n\pi x/L)}{(2n\pi/L)}dx}_{\frac{1}{(2n\pi/L)}\underbrace{\left[\frac{-\cos(2n\pi x/L)}{(2n\pi/L)}\right]_0^L}_{=0}}}$

$\Rightarrow \boxed{\langle x\rangle_n = \frac{L}{2} \quad \forall n \in \mathbb{N}^*}$

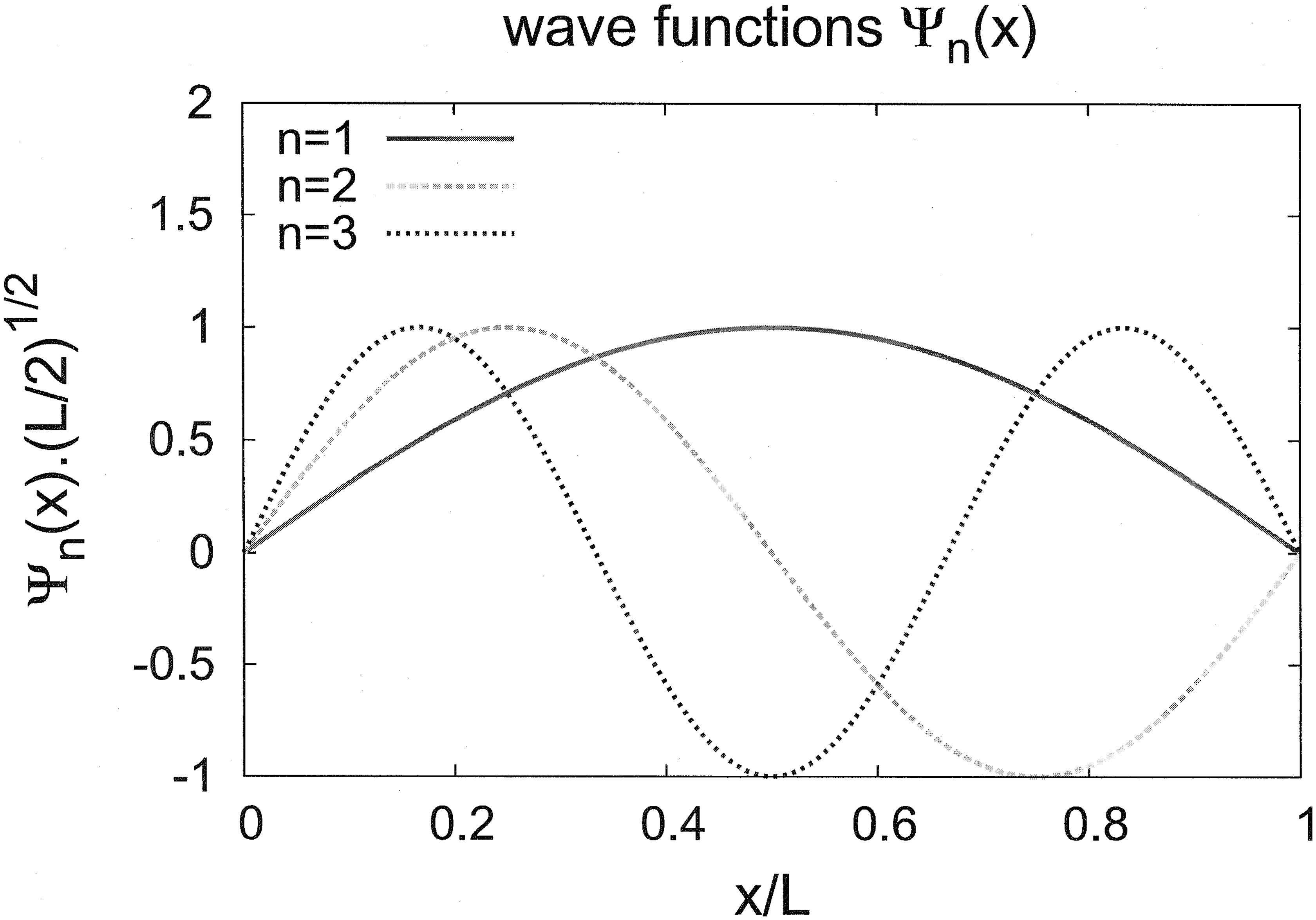
13- $\langle p_x\rangle_n = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)$

since $\forall x \quad \psi_n(x) \in \mathbb{R} \Rightarrow \psi_n^*(x) = \psi_n(x)$ and therefore $\langle p_x\rangle_n$ is imaginary ($\langle p_x\rangle_n = i\alpha$ where $\alpha \in \mathbb{R}$)

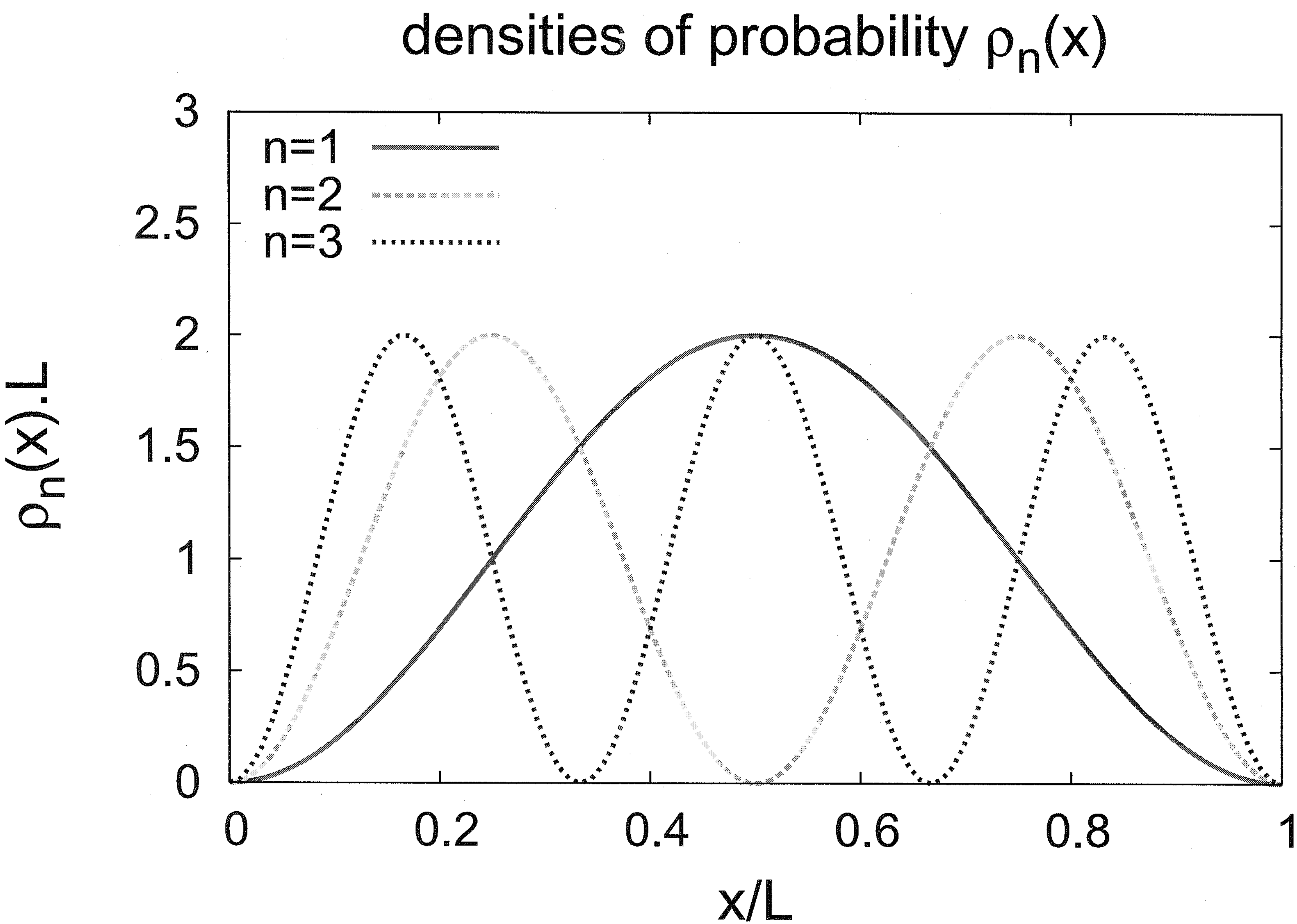
Moreover: $\langle p_x\rangle_n^* = \int_{-\infty}^{+\infty} dx\, \psi_n(x)\left(+i\hbar\frac{d}{dx}\right)\psi_n^*(x) = \underbrace{\left[\psi_n(x)(i\hbar)\psi_n^*(x)\right]_{-\infty}^{+\infty}}_{0} - \int_{-\infty}^{+\infty}\left(\frac{d\psi_n}{dx}\right) i\hbar\, \psi_n^*\, dx$

$\langle p_x\rangle_n^* = \langle p_x\rangle_n = i\alpha = -i\alpha$

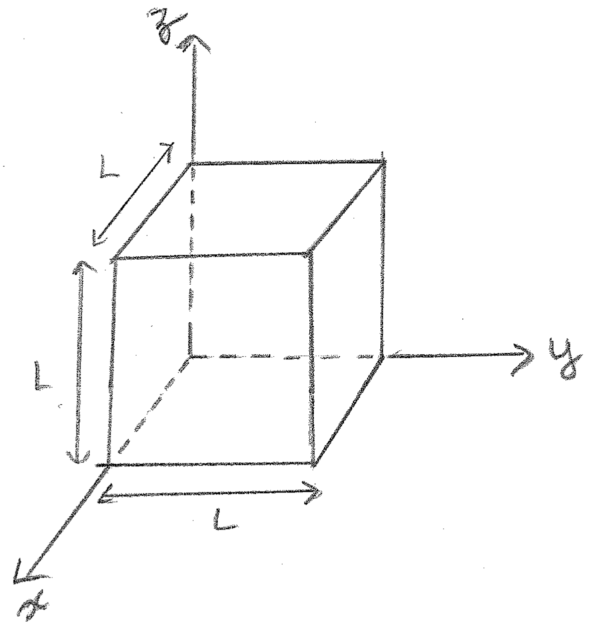
$\Rightarrow \quad \alpha = 0 \quad \Rightarrow \quad \boxed{\langle p_x\rangle_n = 0}$



wave functions Ψn(x)
n=1
n=2
n=3
Ψn(x).(L/2)1/2
x/L
2
1.5
1
0.5
0
-0.5
-1
0
0.2
0.4
0.6
0.8
1


densities of probability ρn(x)
n=1
n=2
n=3
ρn(x).L
x/L
0
0.5
1
1.5
2
2.5
3
0
0.2
0.4
0.6
0.8
1

Particule dans une boîte cubique



1) Equation de Schrödinger : $\hat{H}\,\Psi(x,y,z) = E\,\Psi(x,y,z)$

$0 \leq x \leq L$
$0 \leq y \leq L$
$0 \leq z \leq L$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z) = E\,\Psi(x,y,z)$$

conditions aux limites : $\Psi(0,y,z) = \Psi(L,y,z) = 0 \quad \forall y,z$

$\Psi(x,0,z) = \Psi(x,L,z) = 0 \quad \forall x,z$

$\Psi(x,y,0) = \Psi(x,y,L) = 0 \quad \forall x,y$

2) Séparation des variables : $\Psi(x,y,z) = \varphi_x(x)\cdot\varphi_y(y)\cdot\varphi_z(z)$

équation de Schrödinger divisée par $\varphi_x(x)\,\varphi_y(y)\,\varphi_z(z)$

$\forall x,y,z \quad (1) \quad \Rightarrow -\dfrac{\hbar^2}{2m}\left(\dfrac{1}{\varphi_x(x)}\dfrac{\partial^2\varphi_x(x)}{\partial x^2}+\dfrac{1}{\varphi_y(y)}\dfrac{\partial^2\varphi_y(y)}{\partial y^2}+\dfrac{1}{\varphi_z(z)}\dfrac{\partial^2\varphi_z(z)}{\partial z^2}\right) = E$

3) l'équation (1) est de la forme $f(x)+g(y)+h(z) = E \quad \forall x,y,z$

si on la dérive par rapport à x, à y, ou à z, on obtient :

$$\begin{cases}\partial_x f(x) = 0\\ \partial_y g(y) = 0\\ \partial_z h(y) = 0\end{cases}$$

donc on peut écrire

$$\begin{cases} f(x) = -\dfrac{\hbar^2}{2m}\dfrac{1}{\varphi_x(x)}\dfrac{\partial^2\varphi_x(x)}{\partial x} = E_x\\ g(y) = -\dfrac{\hbar^2}{2m}\dfrac{1}{\varphi_y(y)}\dfrac{\partial^2\varphi_y(y)}{\partial y} = E_y\\ h(z) = -\dfrac{\hbar^2}{2m}\dfrac{1}{\varphi_z(z)}\dfrac{\partial^2\varphi_z(z)}{\partial z} = E_z\end{cases}$$

avec E_x, E_y et E_z des constantes

Les trois équations ainsi obtenues sont indépendante les unes des autres si on remplace $f(x)$, $g(y)$ et $h(z)$ dans l'équation (1), on trouve

$$\boxed{E_x + E_y + E_z = E}$$

4) conditions aux limites $\Rightarrow$ même solutions que pour particule sur une ligne

ex : $\Psi(0,y,y) = \varphi_x(0)\,\cancel{\varphi_y(y)}\,\cancel{\varphi_z(z)} = \varphi_x(L)\,\cancel{\varphi_y(y)}\,\cancel{\varphi_y(z)} = \Psi(L,x,y)$
$= 0$

$$\Rightarrow \quad \varphi_x(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n_x \pi x}{L}\right) \qquad E_x = \frac{n_x^2 \pi^2 \hbar^2}{2L^2 m}$$

$$\varphi_y(y) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n_y \pi x}{L}\right) \qquad E_y = \frac{n_y^2 \pi^2 \hbar^2}{2L^2 m}$$

$$\varphi_z(z) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n_z \pi x}{L}\right) \qquad E_z = \frac{n_z^2 \pi^2 \hbar^2}{2L^2 m}$$

5)

$$\boxed{\begin{gathered}\Psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \\ E = \frac{\pi^2 \hbar^2}{2L^2 m}\left(n_x^2 + n_y^2 + n_z^2\right) \\ \text{avec } n_x, n_y, n_z \in \mathbb{N}^*\end{gathered}}$$

6)

E

$\frac{11\pi^2\hbar^2}{2L^2m}$: $(1,1,3)$ ou $(1,3,1)$ ou $(3,1,1)$

$\frac{9\pi^2\hbar^2}{2L^2m}$: $(n_x,n_y,n_z)=(1,2,2)$ ou $(2,1,2)$ ou $(2,2,1)$

$\frac{6\pi^2\hbar^2}{2L^2m}$: $n_x=n_y=1, n_z=2$ ou $n_x=n_z=1, n_y=2$ ou $n_y=n_z=1$, $n_x=2$

$\frac{3\pi^2\hbar^2}{2L^2m}$: $n_x=n_y=n_z=1$

Rq : certains niveaux sont dégénérés.

7. Lorsque le volume de la boîte devient infini, l'énergie n'est plus quantifiée. ($\Delta E \xrightarrow[L\to+\infty]{} 0$ entre 2 niveaux)