École de Chimie, Polymères et Matériaux de Strasbourg

Premier semestre

Travaux dirigés de mécanique quantique
- Solutions -

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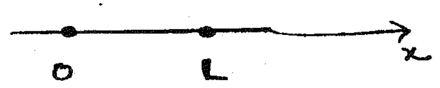
Particle confined along a segment of straight line



1_ The energy is only kinetic

2_ General case : $-\frac{\hbar^2}{2m}\nabla^2\psi + \underset{\text{potential energy}}{V}.\psi = E.\psi$

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

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

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

Let us prove that $E \geq 0$:

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

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

Thus $\boxed{E \geq 0}$

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

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

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

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

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

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

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

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

energies are quantized

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

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

$$\psi_{-n}(x) = -\frac{B_{-n}}{B_n}\psi_n(x) \Rightarrow$$ 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 $\int_{-\infty}^{+\infty}|\psi_n(x)|^2 dx = 1 \longleftarrow$ for a physical Solution.

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

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

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

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

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

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

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 mean 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

<u>Comment on the wave functions $\psi_n(x)$:</u>

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

This ensures the orthogonality of the solutions

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

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

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

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

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

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

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

<u>Comment on the probability densities:</u>

As n increases, the number of maxima of the probability density increases.
Let x_p^n denote one of the maxima: according to (7)

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

$$\Rightarrow \boxed{\begin{array}{l} x_p^n = \dfrac{(2p+1)}{2n} L \\ p = 0, 1, \ldots, n-1 \end{array}}$$

Therefore $x_{p+1}^n - x_p^n = \frac{L}{n} \xrightarrow[n \to +\infty]{} 0$

which means that for large quantum numbers the density of probability becomes uniform
$\Rightarrow$ <u>classical limit</u>

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 $(L \to +\infty)$

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

which means that we get a <u>continuum</u> of values for k_n and thus for E_n (the energy is not quantized anymore).
In reality L is of course <u>finite</u> (very large but not infinite) which means that the energy levels are very very close to each other, looking like a continuum. Note that

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

$E_2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \xrightarrow[L \to +\infty]{} 0 \quad . \quad \psi_2(x) \xrightarrow[L \to +\infty]{} 0$

$\vdots$

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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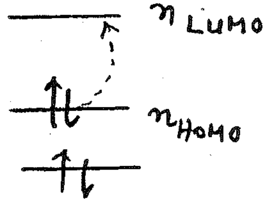


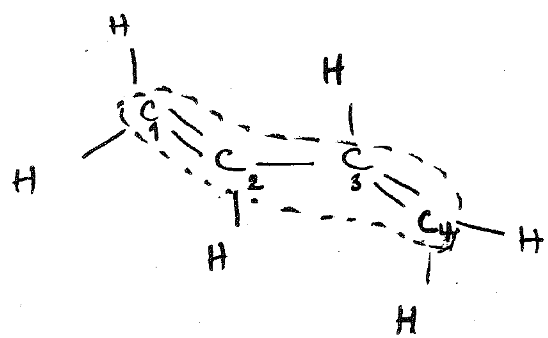
LUMO : Lowest Unoccupied Molecular Orbital
HOMO : Highest Occupied Molecular Orbital

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

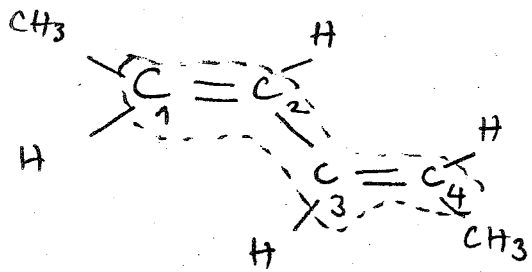
$$h\frac{c}{\lambda} = E_{n_{LUMO}} - E_{n_{HOMO}} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_{LUMO}^2 - n_{HOMO}^2\right)$$

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

Applications:



butadiene



hexa-2,4-diene

In both cases, there are 4 π electrons therefore

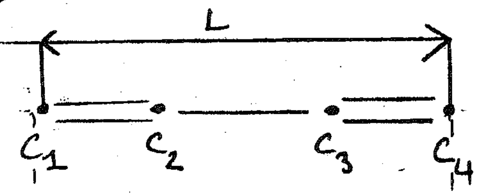
$n_{HOMO} = 2$

and

$n_{LUMO} = 3$.

Value of L ?

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



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

$L = 2 \times 135 + 154$

$L = 424\ pm$

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

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

<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

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

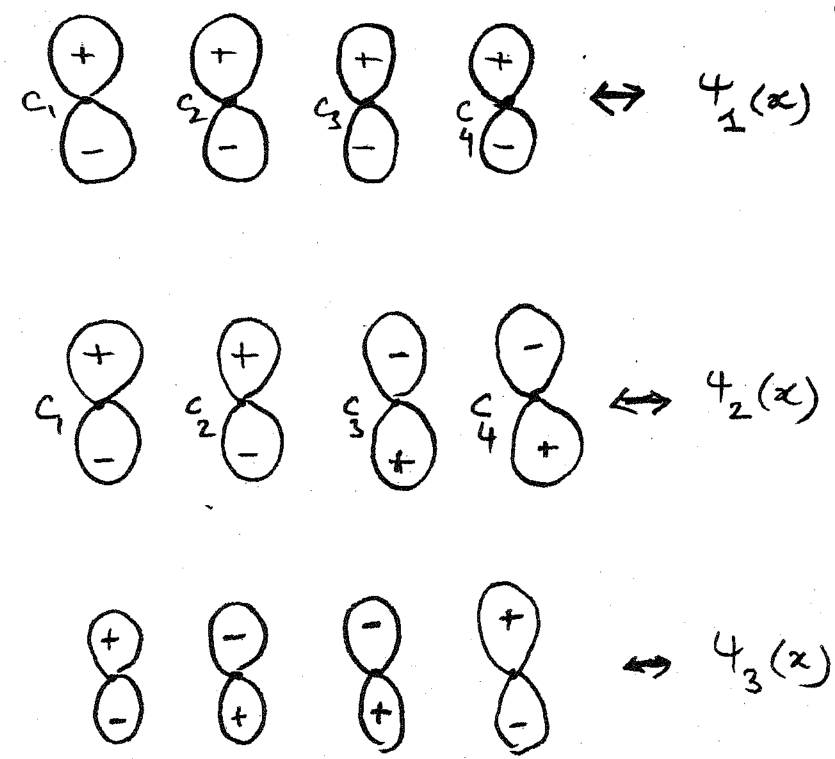
$\Rightarrow \underline{\lambda' = 220{,}4\ nm}$

which is rather close to the experimental values

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

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

Let us look at the π orbitals ...



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

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

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

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

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

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

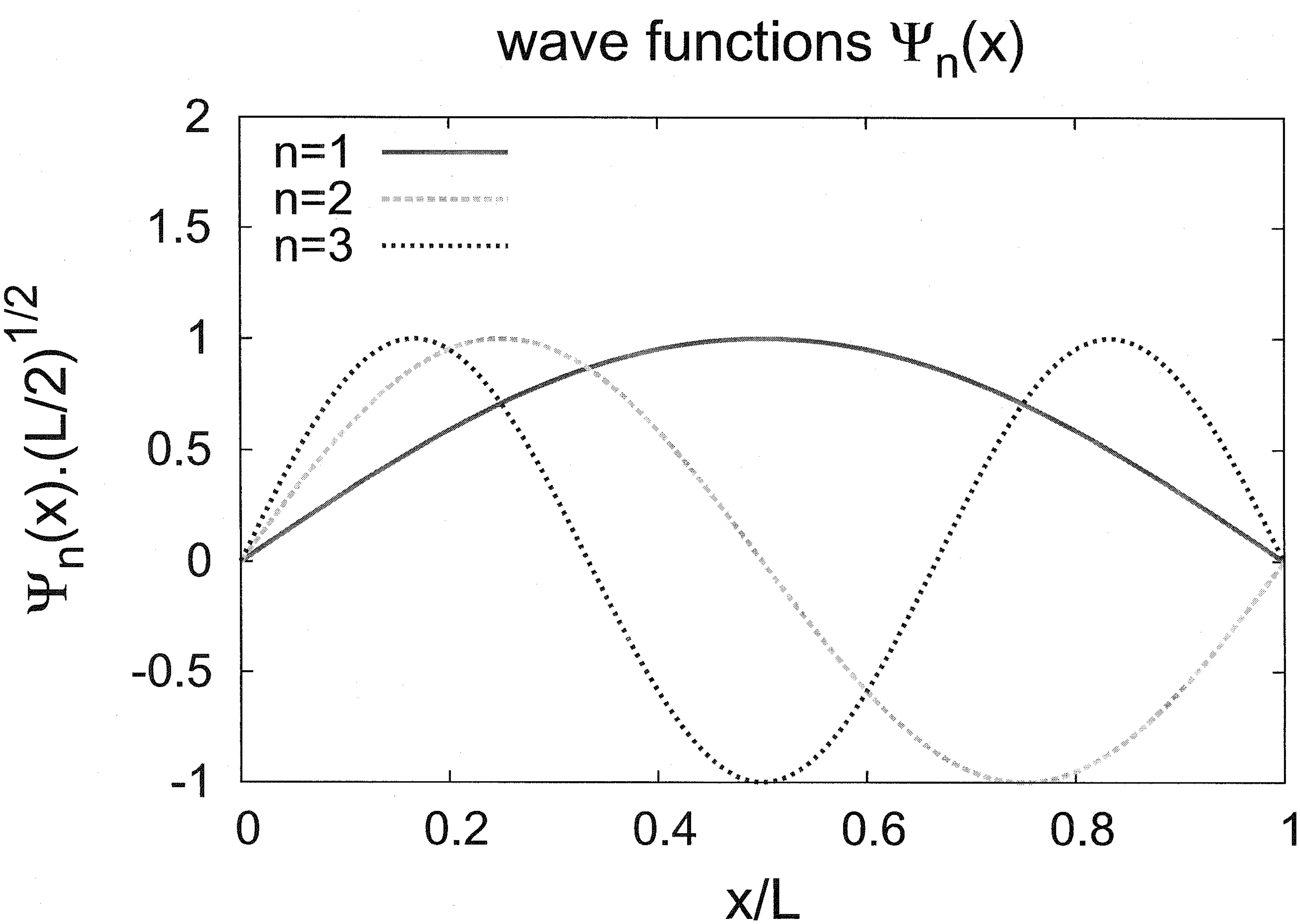
13- $$\langle p_x\rangle_n = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)$$

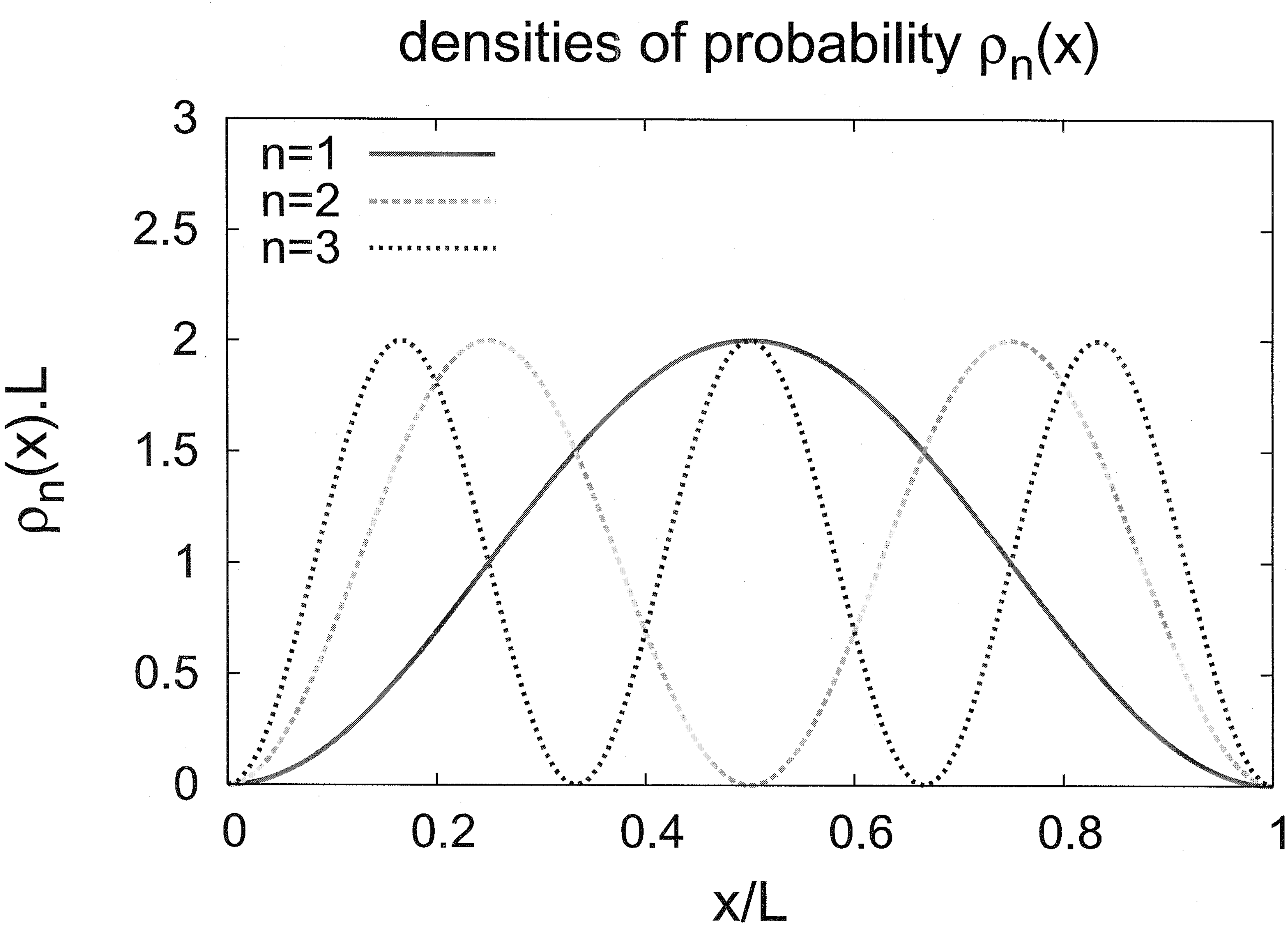
since $\forall x \quad \psi_n(x) \in \mathbb{R} \Rightarrow \psi_n^*(x) = \psi_n(x)$ and therefore $\langle p_x\rangle_n$ is imaginary ($\langle p_x\rangle_n = i\alpha$ where $\alpha \in \mathbb{R}$)

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

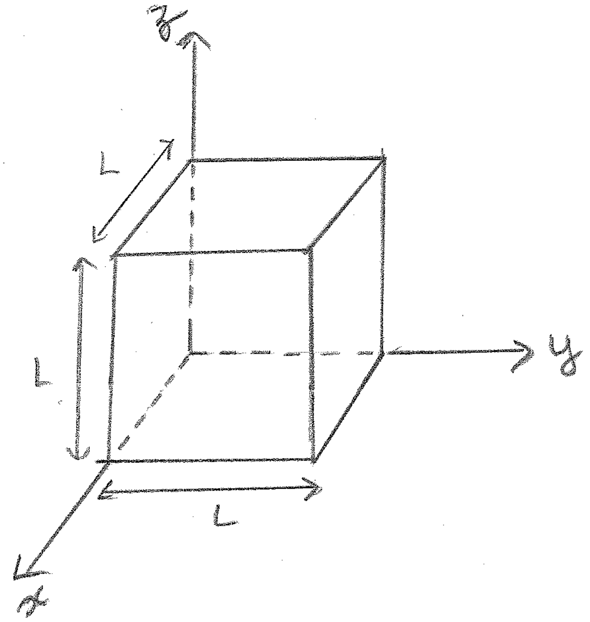
$$\langle p_x\rangle_n^* = \langle p_x\rangle_n = i\alpha = -i\alpha$$

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


wave functions Ψn(x)
Ψn(x).(L/2)1/2
x/L
n=1
n=2
n=3
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 : $\Psi(x,y,z) = \varphi_x(x).\varphi_y(y).\varphi_z(z)$

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

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

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 :

$$\begin{cases}\partial_x f(x) = 0\\ \partial_y g(y) = 0\\ \partial_z h(y) = 0\end{cases} \quad \text{donc on peut écrire} \quad \begin{cases} f(x) = -\dfrac{\hbar^2}{2m}\dfrac{1}{\varphi_x(x)}\dfrac{\partial^2\varphi_x(x)}{\partial x} = E_x\\ g(y) = -\dfrac{\hbar^2}{2m}\dfrac{1}{\varphi_y(y)}\dfrac{\partial^2\varphi_y(y)}{\partial y} = E_y\\ h(z) = -\dfrac{\hbar^2}{2m}\dfrac{1}{\varphi_z(z)}\dfrac{\partial^2\varphi_z(z)}{\partial z} = E_z\end{cases}$$

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)

$$\Psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right)$$

$$E = \frac{\pi^2\hbar^2}{2L^2 m}\left(n_x^2 + n_y^2 + n_z^2\right)$$

avec $n_x, n_y, n_z \in \mathbb{N}^*$

6)

E

$\vdots$

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

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

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

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

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)

Tutorial – Hydrogen atom

a) $$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\vec{r}) - \frac{e^2}{4\pi\varepsilon_0 r}\times\psi(\vec{r}) = E\,\psi(\vec{r})$$

energy   wave function

b) $$\psi_{1s}(\vec{r}) = \underbrace{\frac{1}{\sqrt{\pi}\,a_0^{3/2}}}_{\text{constant}}\ \underbrace{e^{-r/a_0}}_{\bar{\psi}_{1s}(\vec{r})}$$

$$\frac{\partial}{\partial x}e^{-r/a_0} = -\frac{1}{a_0}\frac{\partial r}{\partial x}e^{-r/a_0}$$

$$\frac{\partial^2}{\partial x^2}e^{-r/a_0} = -\frac{1}{a_0}\left[e^{-r/a_0}\frac{\partial^2 r}{\partial x^2} - \frac{1}{a_0}\left(\frac{\partial r}{\partial x}\right)^2 e^{-r/a_0}\right]$$

where $$\frac{\partial r}{\partial x} = \frac{1}{2}\,2x\left(x^2+y^2+z^2\right)^{-1/2} = \frac{x}{r}$$

and $$\frac{\partial^2 r}{\partial x^2} = \frac{1}{r} + x\times\frac{\partial}{\partial x}\left(\frac{1}{r}\right) = \frac{1}{r} - x\frac{\partial r}{\partial x}\frac{1}{r^2}$$

$$= \frac{1}{r} - \frac{x^2}{r^3}$$

Therefore $$\frac{\partial^2}{\partial x^2}e^{-r/a_0} = -\frac{1}{a_0}e^{-r/a_0}\left[\frac{1}{r} - \frac{x^2}{r^3} - \frac{1}{a_0}\frac{x^2}{r^2}\right]$$

Similarly we obtain $$\frac{\partial^2}{\partial y^2}e^{-r/a_0} = -\frac{1}{a_0}e^{-r/a_0}\left[\frac{1}{r} - \frac{y^2}{r^3} - \frac{1}{a_0}\frac{y^2}{r^2}\right]$$

and $$\frac{\partial^2 e^{-r/a_0}}{\partial z^2} = -\frac{1}{a_0}e^{-r/a_0}\left[\frac{1}{r} - \frac{z^2}{r^3} - \frac{z^2}{a_0 r^2}\right]$$

thus leading to

$$-\frac{\hbar^2}{2m_e}\nabla^2\bar{\psi}_{1s}(\vec{r}) = +\frac{\hbar^2}{2m_e a_0}e^{-r/a_0}\left[\frac{3}{r} - \frac{r^2}{r^3} - \frac{r^2}{a_0 r^2}\right]$$

$$= \frac{\hbar^2 e^{-r/a_0}}{2m_e a_0}\left(\frac{2}{r} - \frac{1}{a_0}\right)$$

Moreover $$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

$\Rightarrow$

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\bar{\psi}_{1s}(\vec{r}) = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r} - \frac{1}{a_0}\right)\bar{\psi}_{1s}(\vec{r}) - \frac{e^2}{4\pi\varepsilon_0 r}\bar{\psi}_{1s}(\vec{r})$$

$$= -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0}\bar{\psi}_{1s}(\vec{r})$$

Conclusion:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi_{1s}(\vec{r}) = -\underbrace{\frac{e^2}{2(4\pi\varepsilon_0)a_0}}\psi_{1s}(\vec{r})$$

$$-\frac{1}{2}\frac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2} = -E_I$$

c) $\psi_{1s}(\vec{r}=\vec{0}) = \dfrac{1}{\sqrt{\pi}\, a_0^{3/2}} \Rightarrow |\psi_{1s}(\vec{r}=\vec{0})|^2 = \dfrac{1}{\pi a_0^3} \neq 0$

We may be tempted to interpret this non-zero value as a non-zero probability of finding the electron at the nucleus, which is a bit strange. This point is discussed in the following.

d) • Normalization condition:

$$\int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi} \underbrace{|\psi(r',\theta,\varphi)|^2 r'^2 \sin\theta \, dr' d\theta \, d\varphi}_{d\mathcal{P}(r,\theta,\varphi)} = 1$$

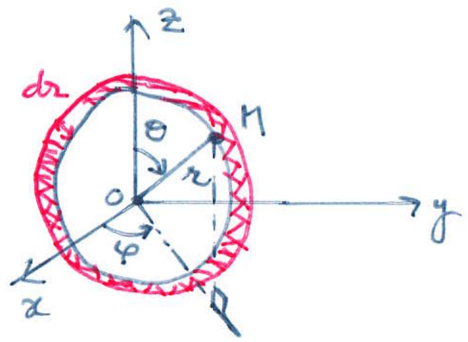
$d\mathcal{P}(r,\theta,\varphi) \leftarrow$ probability to find the electron "at position (r,θ,φ)"

• If we integrate partially in r', for example for $0 \leq r' \leq r$, but fully in θ and φ, then

$$\mathcal{P}(r) = \int_0^r dr' \int_0^{\pi}\int_0^{2\pi} |\psi(r',\theta,\varphi)|^2 r'^2 \sin\theta \, dr' d\theta \, d\varphi$$

Corresponds to the probability of finding the electron in the sphere centred at the origin of the frame O and with radius r.

• $d\mathcal{P}(r) = \underbrace{\mathcal{P}(r+dr) - \mathcal{P}(r)}_{\substack{\text{probability of finding the electron} \\ \text{at a distance between } r+dr \text{ and } r \text{ from} \\ \text{the nucleus. (red zone on the figure)}}} = \dfrac{d\mathcal{P}(r)}{dr}\, dr$



Note that $\displaystyle\int_0^{+\infty} d\mathcal{P}(r) = \int_0^{+\infty} \underbrace{\frac{d\mathcal{P}(r)}{dr}}_{\rho(r)} dr = \underbrace{\mathcal{P}(+\infty)}_{1} - \underbrace{\mathcal{P}(0)}_{0}$

it is a radial density of probability since, once multiplied by dr and integrated over all possible distances, it gives 1 (normalization condition).

e) $\displaystyle\mathcal{P}_{1s}(r) = \int_0^r dr' \int_0^{\pi}\int_0^{2\pi} \frac{e^{-2r'/a_0}}{\pi a_0^3} r'^2 \sin\theta \, dr' d\theta \, d\varphi$

$$= \frac{4}{a_0^3}\int_0^r dr' \, e^{-2r'/a_0} r'^2$$

$$\rightarrow \boxed{\rho_{1s}(r) = \frac{d\mathcal{P}_{1s}(r)}{dr} = \frac{4}{a_0^3} r^2 e^{-2r/a_0}}$$

$\rho_{1s}(0) = 0 \leftarrow$ the electron cannot be at the nucleus :-)

Maximum of $\rho_{1s}(r)$: $\frac{d\rho_{1s}}{dr} = 0 = e^{-2r/a_0}\left[2r - \frac{2}{a_0} r^2\right] = 2e^{-2r/a_0} r\left(1 - \frac{r}{a_0}\right)$

$\Rightarrow \boxed{r = a_0} \leftarrow$ like in Bohr's model

f) ψ_{1s} and ψ_{2s} do not vary with θ and φ. They only depend on $r \longrightarrow$ They have spherical symmetry.

$$\rho_{2s}(r) = \frac{dP_{2s}(r)}{dr} = \int_0^{\pi}\int_0^{2\pi} \frac{e^{-r/a_0}}{32\pi a_0^3}\left(2 - \frac{r}{a_0}\right)^2 r^2 \sin\theta \, d\theta \, d\varphi$$

$$\boxed{\rho_{2s}(r) = \frac{1}{8a_0} e^{-r/a_0}\left(2 - \frac{r}{a_0}\right)^2\left(\frac{r}{a_0}\right)^2}$$

The 1s orbital has no node.
The 2s orbital has one node (at $r = 2a_0$).
A node corresponds to a change of sign in the wavefunction
$\rightarrow$ it ensures that 1s and 2s orbitals are orthogonal.

g) $\psi_{2p_z}(\vec{r}) = \frac{e^{-r/2a_0}}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r\cos\theta}{a_0}$

$\Rightarrow |\psi_{2p_z}(r_0, \theta, \varphi)| \sim |\cos\theta|$

$\sim$ means it is proportional to ...
(the coefficient is a constant as it does not depend on θ and φ)

Conclusion: The $2p_z$ orbital will be represented by the following parametrized surface:

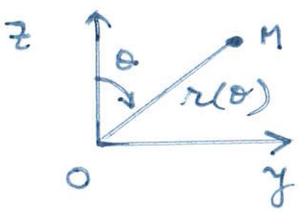
$$\theta, \varphi \longmapsto M(\underbrace{|\cos\theta|}_{r(\theta,\varphi)}, \theta, \varphi)$$

$r(\theta, \varphi) = r(\theta) \leftarrow$ invariance by rotation around the z axis

$r(\pi - \theta) = |\cos(\pi - \theta)| = |\cos\theta| = r(\theta)$

$\Rightarrow$ Symmetry with respect to the xOy plane.

h)

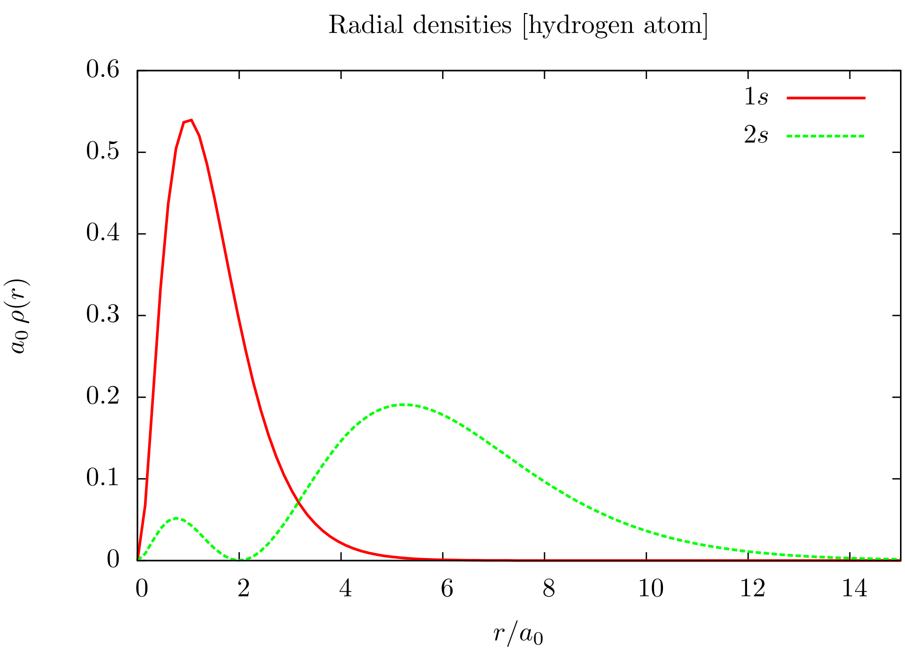


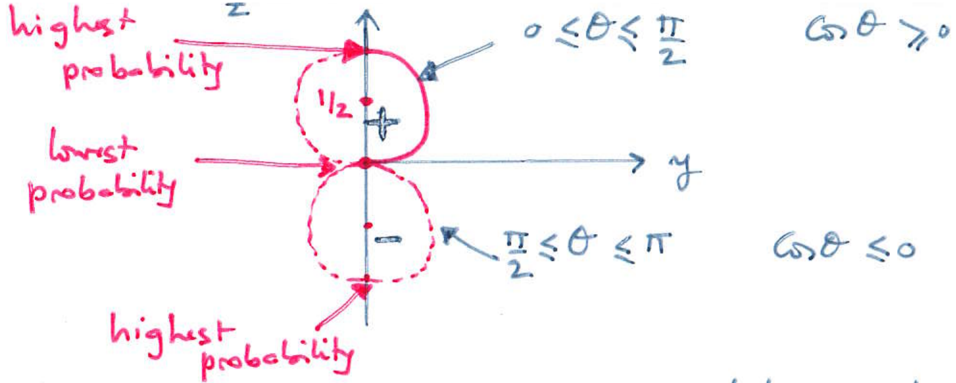
$0 \leq \theta \leq \frac{\pi}{2} \Rightarrow |\cos\theta| = \cos\theta = r(\theta)$

$OM = \frac{z}{\cos\theta} = \frac{z}{OM}$ if M belongs to the surface representing $2p_z$.

$\Rightarrow OM^2 = y^2 + z^2 = z \Rightarrow \boxed{y^2 + \left(z - \frac{1}{2}\right)^2 = \frac{1}{4}}$

This is the equation of a circle centered in $(y = 0, z = \frac{1}{2})$ with radius $\frac{1}{2}$.


Radial densities [hydrogen atom]
$a_0\,\rho(r)$
r/a_0
$1s$
$2s$
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
12
14



Lowest probability of finding the $2p_z$ electron: when $r(\theta) = 0 \Rightarrow$ in the xOy plane ($\Uparrow$ $\theta = \pi/2$)

Highest probability " : when $r(\theta) = 1 \Rightarrow$ along the z axis ($\Uparrow$ $\theta = 0$ or π)

<u>Complement:</u>

i) $\hat{H}(z)|\psi(z)\rangle = E(z)|\psi(z)\rangle \Rightarrow E(z)\underbrace{\langle\psi(z)|\psi(z)\rangle}_{1} = \langle\psi(z)|\hat{H}(z)|\psi(z)\rangle$

$$\Rightarrow \boxed{E(z) = \langle\psi(z)|\hat{H}(z)|\psi(z)\rangle}$$

$$\frac{dE(z)}{dz} = \langle\psi(z)|\frac{\partial\hat{H}(z)}{\partial z}|\psi(z)\rangle + \underbrace{\langle\frac{d\psi(z)}{dz}|\underbrace{\hat{H}(z)|\psi(z)\rangle}_{E(z)|\psi(z)\rangle}}_{E(z)\langle\frac{d\psi(z)}{dz}|\psi(z)\rangle} + \underbrace{\langle\psi(z)|\hat{H}(z)|\frac{d\psi(z)}{dz}\rangle}_{\langle\hat{H}(z)\psi(z)|\frac{d\psi(z)}{dz}\rangle = E^*(z)\langle\psi(z)|\frac{d\psi(z)}{dz}\rangle,\ E^*(z) = E(z)}$$

$$\Rightarrow \frac{dE(z)}{dz} = \langle\psi(z)|\frac{\partial\hat{H}(z)}{\partial z}|\psi(z)\rangle + E(z)\underbrace{\frac{d}{dz}\overbrace{\langle\psi(z)|\psi(z)\rangle}^{1}}_{0} \Rightarrow \boxed{\frac{dE(z)}{dz} = \langle\psi(z)|\frac{\partial\hat{H}(z)}{\partial z}|\psi(z)\rangle}$$

j) $$-\frac{\hbar^2}{2m_e}\nabla^2_{\vec{r}}\psi(Z,\vec{r}) - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi(Z,\vec{r}) = E(Z)\psi(Z,\vec{r}) \quad (1)$$

<u>Change of variables:</u> $\vec{\tilde{r}} = Z\vec{r} \Rightarrow \tilde{r} = Zr$

<u>Definition:</u> $\psi(Z,\vec{r}) = \psi\left(Z, \frac{\vec{\tilde{r}}}{Z}\right) = \tilde{\psi}(Z,\vec{\tilde{r}}) = \tilde{\psi}(Z, Z\vec{r})$

$$\Rightarrow \frac{\partial}{\partial x}\psi(Z,\vec{r}) = \frac{\partial}{\partial x}\left(\tilde{\psi}(Z,Z\vec{r})\right) = Z\,\frac{\partial}{\partial \tilde{x}}\left(\tilde{\psi}(Z,\vec{\tilde{r}})\right)\Big|_{\vec{\tilde{r}}=Z\vec{r}}$$

$$\Rightarrow \frac{\partial^2}{\partial x^2}\psi(Z,\vec{r}) = Z^2\,\frac{\partial^2}{\partial \tilde{x}^2}\left(\tilde{\psi}(Z,\vec{\tilde{r}})\right)\Big|_{\vec{\tilde{r}}=Z\vec{r}}$$

Similarly we obtain $\nabla^2_{\vec{r}}\psi(Z,\vec{r}) = Z^2\nabla^2_{\vec{\tilde{r}}}\tilde{\psi}(Z,\vec{\tilde{r}})\Big|_{\vec{\tilde{r}}=Z\vec{r}}$

$$(1) \Rightarrow -\frac{\hbar^2 Z^2}{2m_e}\nabla^2_{\vec{\tilde{r}}}\tilde{\psi}(Z,\vec{\tilde{r}}) - \frac{Z^2e^2}{4\pi\varepsilon_0\tilde{r}}\tilde{\psi}(Z,\vec{\tilde{r}}) = E(Z)\tilde{\psi}(Z,\vec{\tilde{r}})$$

$$\Rightarrow \boxed{-\frac{\hbar^2}{2m_e}\nabla^2_{\vec{\tilde{r}}}\tilde{\psi}(Z,\vec{\tilde{r}}) - \frac{e^2}{4\pi\varepsilon_0\tilde{r}}\tilde{\psi}(Z,\vec{\tilde{r}}) = \frac{E(Z)}{Z^2}\tilde{\psi}(Z,\vec{\tilde{r}})}$$

← Schrödinger equation for the hydrogen atom ($Z=1$)!

<u>Conclusions:</u> $\frac{E(Z)}{Z^2} = E(1)$ ← spectrum of the hydrogen atom.

$\tilde{\psi}(Z,\vec{\tilde{r}}) = \psi(1,\vec{\tilde{r}})$ ← corresponding eigenfunction (*)

(*) In fact
$$\tilde{\psi}(Z,\vec{\tilde{r}}) = C\,\psi(1,\vec{\tilde{r}}) \qquad \text{Eq. (2)}$$
C ← normalization factor.

$\forall Z$

$$\langle\psi(Z)|\psi(Z)\rangle = 1 = \int d\vec{r}\,|\psi(Z,\vec{r})|^2$$
$$= \int d\vec{\tilde{r}}\,|\psi(1,\vec{\tilde{r}})|^2$$
$$= \int d\vec{r}\,|\tilde{\psi}(Z,Z\vec{r})|^2$$
$$= \int d\vec{\tilde{r}}\,\frac{|\tilde{\psi}(Z,\vec{\tilde{r}})|^2}{Z^3}$$

change of variables
$\vec{r} \rightarrow \vec{\tilde{r}} = Z\vec{r}$

Thus leading to (according to Eq. (2))

$$\int d\vec{\tilde{r}}\,|\psi(1,\vec{\tilde{r}})|^2 = \frac{C^2}{Z^3}\int d\vec{\tilde{r}}\,|\psi(1,\vec{\tilde{r}})|^2$$

$$\Rightarrow \boxed{C = Z^{3/2}}$$

Conclusion: $\tilde{\psi}(Z,\vec{\tilde{r}}) = Z^{3/2}\,\psi(1,\vec{\tilde{r}})$

for $\vec{\tilde{r}} = Z\vec{r}$ we finally obtain

$$\tilde{\psi}(Z, Z\vec{r}) = \boxed{\psi(Z,\vec{r}) = Z^{3/2}\,\psi(1, Z\vec{r})}$$

The 1s orbital in the hydrogen-like atom can therefore be expressed as

$$\psi_{1s}(Z,\vec{r}) = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{\pi}}\, e^{-Zr/a_0}$$

- The energy is quantized as $E_n = -\frac{E_I}{n^2} \leftarrow E(1)$ in the hydrogen atom. It is therefore quantized as follows in the hydrogen-like atom

$$\boxed{E_n(Z) = -\frac{Z^2 E_I}{n^2}} \qquad \text{Eq. (3)}$$

k) $H(Z)\,|\psi_n(Z)\rangle = E_n(Z)\,|\psi_n(Z)\rangle$

According to the Hellmann-Feynman theorem

$$\frac{dE_n(Z)}{dZ} = \langle \psi_n(Z)|\,\underbrace{\frac{\partial \hat{H}(Z)}{\partial Z}}_{-\frac{e^2}{4\pi\varepsilon_0 r}\times}\,|\psi_n(Z)\rangle \underset{\substack{\uparrow \\ \text{according to} \\ \text{Eq. (3)}}}{=} -\frac{2Z E_I}{n^2}$$

Therefore $\left\langle \frac{1}{r}\right\rangle_{\psi_n(Z)} = \langle \psi_n(Z)|\,\frac{1}{r}\times|\psi_n(Z)\rangle = \frac{4\pi\varepsilon_0}{e^2} \times \frac{2Z E_I}{n^2}$

Since $E_I = \frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2} = \frac{e^2}{2(4\pi\varepsilon_0)}\frac{1}{a_0}$

it comes $\boxed{\left\langle \frac{1}{r}\right\rangle_{\psi_n(Z)} = \frac{Z}{n^2 a_0}}$

If the electron occupies the orbital $\psi_n(Z)$, its distance from the nucleus "is" about $n^2 \frac{a_0}{Z}$.

- According to Eq. (4)

$$\langle \psi_n(Z)|\,\frac{-Ze^2}{4\pi\varepsilon_0 r}\times|\psi_n(Z)\rangle$$

$$= +2E_n(Z) \quad \leftarrow \text{Virial theorem!}$$

Thus leading to

$$\left\langle \frac{p^2}{2m_e}\right\rangle_{\psi_n(Z)} = \langle \psi_n(Z)|\,-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m_e}\,|\psi_n(Z)\rangle$$

$$= E_n(Z) - \langle \psi_n(Z)|\,-\frac{Ze^2}{4\pi\varepsilon_0 r}\times|\psi_n(Z)\rangle \quad \leftarrow \text{Eq. (4)}$$

$$= -E_n(Z) = +\frac{Z^2 E_I}{n^2}$$

Since $E_I = \frac{1}{2} m_e c^2 \underbrace{\left[\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right]^2}_{\alpha^2}$

it comes
$$\frac{\langle p^2/2m_e\rangle_{\psi_n(Z)}}{m_e^2 c^2/2m_e} = \frac{2Z^2 E_I}{n^2 m_e c^2}$$

$$\Rightarrow \boxed{\frac{\langle p^2/2m_e\rangle_{\psi_n(Z)}}{m_e^2 c^2/2m_e} = \frac{(Z\alpha)^2}{n^2}}$$

can be interpreted as $\left(\frac{v_n}{c}\right)^2$ velocity from a classical point of view.

$$\Rightarrow \boxed{\frac{v_n}{c} = \frac{Z\alpha}{n}}$$

When $Z \sim 100$ relativistic effects become huge.
The Schrödinger equation is not valid anymore.
The (relativistic) Dirac equation should be used instead.

Problème : états de spin de l'électron en présence d'un champ magnétique

a) $\hat{H}|+\rangle = \frac{\hbar\omega_0}{2}|+\rangle \Rightarrow |+\rangle$ est un état propre de l'hamiltonien.

$\boxed{\text{C'est donc un état stationnaire}}$ $\Rightarrow$ si $|\psi(0)\rangle = |+\rangle$ alors $|\psi(t)\rangle$ reste colinéaire à $|+\rangle$ (puisque l'hamiltonien ne dépend pas du temps) et donc orthogonal à $|-\rangle$. La probabilité d'être dans l'état $|-\rangle$, qui vaut $|\langle -|\psi(t)\rangle|^2$, est donc nulle.

b) • Pour $\vec{B} = B_0\vec{e}_x$, $\hat{H}|+\rangle = \frac{\hbar\omega_0}{2}|-\rangle$ et $\hat{H}|-\rangle = \frac{\hbar\omega_0}{2}|+\rangle$

donc $\hat{H}|1\rangle = \frac{1}{\sqrt{2}}(\hat{H}|+\rangle - \hat{H}|-\rangle) = \frac{1}{\sqrt{2}}\left(\frac{\hbar\omega_0}{2}|-\rangle - \frac{\hbar\omega_0}{2}|+\rangle\right)$

soit $\hat{H}|1\rangle = -\frac{\hbar\omega_0}{2}\underbrace{(|+\rangle - |-\rangle)\frac{1}{\sqrt{2}}}_{|1\rangle}$

$\rightarrow$ $\boxed{\hat{H}|1\rangle = -\frac{\hbar\omega_0}{2}|1\rangle}$

De même $\hat{H}|2\rangle = \frac{1}{\sqrt{2}}(\hat{H}|+\rangle + \hat{H}|-\rangle) = \frac{1}{\sqrt{2}}\left(\frac{\hbar\omega_0}{2}|-\rangle + \frac{\hbar\omega_0}{2}|+\rangle\right)$

soit $\boxed{\hat{H}|2\rangle = \frac{\hbar\omega_0}{2}|2\rangle}$

• Comme $\langle +|+\rangle = \langle -|-\rangle = 1$ et $\langle +|-\rangle = 0$

il vient $\langle 1|2\rangle = \frac{1}{2}\left(\langle +|+\rangle + \cancel{\langle +|-\rangle} - \cancel{\langle -|+\rangle} - \langle -|-\rangle\right)$

$\boxed{\langle 1|2\rangle = 0}$

$\boxed{\begin{array}{l}\langle 1|1\rangle = \frac{1}{2}(1+1) = 1\\ \langle 2|2\rangle = \frac{1}{2}(1+1) = 1\end{array}}$

c) $|\psi(t)\rangle = c_1(t)|1\rangle + c_2(t)|2\rangle$

$\downarrow$

vérifie l'équation de Schrödinger dépendante du temps $\hat{H}|\psi(t)\rangle = i\hbar\frac{d}{dt}|\psi(t)\rangle$

soit $c_1(t)\underbrace{\hat{H}|1\rangle}_{-\frac{\hbar\omega_0}{2}|1\rangle} + c_2(t)\underbrace{\hat{H}|2\rangle}_{+\frac{\hbar\omega_0}{2}|2\rangle} = i\hbar\dot{c}_1|1\rangle + i\hbar\dot{c}_2|2\rangle$

d'où $\begin{cases} i\hbar\dot{c}_1 = -\frac{\hbar\omega_0}{2}c_1 \\ i\hbar\dot{c}_2 = \frac{\hbar\omega_0}{2}c_2 \end{cases}$

soit $\dot{c}_1 = \frac{i\omega_0}{2}c_1$ et $\dot{c}_2 = -\frac{i\omega_0}{2}c_2$

$\boxed{c_1(t) = c_1(0)e^{\frac{i\omega_0 t}{2}}}$ $\boxed{c_2(t) = c_2(0)e^{-\frac{i\omega_0 t}{2}}}$

d) $|\psi(0)\rangle = |+\rangle$ or $|1\rangle = \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle)$

et $|2\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$

donc $|1\rangle + |2\rangle = \frac{2}{\sqrt{2}}|+\rangle$ soit

$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \Rightarrow \boxed{c_1(0) = c_2(0) = \frac{1}{\sqrt{2}}}$

e) $\mathcal{P}_+(t) = |\langle + | \psi(t)\rangle|^2$

avec $|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{i\frac{\omega_0 t}{2}} |1\rangle + \frac{1}{\sqrt{2}} e^{-i\frac{\omega_0 t}{2}} |2\rangle$

Comme $\langle + | 1\rangle = \frac{1}{\sqrt{2}} = \langle + | 2\rangle$

il vient $\langle + | \psi(t)\rangle = \frac{1}{2} e^{i\omega_0 t/2} + \frac{1}{2} e^{-i\omega_0 t/2}$

soit $\langle + | \psi(t)\rangle = \cos(\omega_0 t/2)$

$\rightarrow \mathcal{P}_+(t) = \cos^2(\omega_0 t/2) = \frac{1}{4}\left(e^{i\omega_0 t/2} + e^{-i\omega_0 t/2}\right)\left(e^{-i\omega_0 t/2} + e^{+i\omega_0 t/2}\right)$

$= \frac{1}{4}\left[2 + \underbrace{e^{i\omega_0 t} + e^{-i\omega_0 t}}_{2\cos\omega_0 t}\right]$

$$\boxed{\mathcal{P}_+(t) = \frac{1}{2}(1 + \cos\omega_0 t)}$$

L'électron oscille entre les états $|+\rangle$ et $|-\rangle$ avec une pulsation égale à celle de Larmor.

f) D'après le théorème d'Ehrenfest

$$\frac{d}{dt}\langle \psi(t)|\hat{H}|\psi(t)\rangle = \frac{1}{i\hbar}\langle \psi(t)|\underbrace{[\hat{H},\hat{H}]}_{0}|\psi(t)\rangle$$

donc $\boxed{\langle \psi(t)|\hat{H}|\psi(t)\rangle = \langle \psi(0)|\hat{H}|\psi(0)\rangle} = \langle + |\hat{H}| + \rangle$

$= \frac{\hbar\omega_0}{2}\langle + | - \rangle$

soit $\boxed{\langle \psi(t)|\hat{H}|\psi(t)\rangle = 0}$

Commentaire : on peut le vérifier facilement ici.

$$\hat{H}|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{i\omega_0 t/2} \underbrace{(\hat{H}|1\rangle)}_{-\frac{\hbar\omega_0}{2}|1\rangle} + \frac{1}{\sqrt{2}} e^{-i\omega_0 t/2} \underbrace{(\hat{H}|2\rangle)}_{\frac{\hbar\omega_0}{2}|2\rangle}$$

d'où

$$\langle \psi(t)|\hat{H}|\psi(t)\rangle = -\frac{\hbar\omega_0}{2\sqrt{2}} e^{i\omega_0 t/2}\langle \psi(t)|1\rangle + \frac{\hbar\omega_0}{2\sqrt{2}} e^{-i\omega_0 t/2}\langle \psi(t)|2\rangle$$

avec $\langle 1|\psi(t)\rangle = \frac{e^{i\omega_0 t/2}}{\sqrt{2}}$

et $\langle 2|\psi(t)\rangle = \frac{e^{-i\omega_0 t/2}}{\sqrt{2}}$

Ainsi

$$\langle \psi(t)|\hat{H}|\psi(t)\rangle = -\frac{\hbar\omega_0}{4} + \frac{\hbar\omega_0}{4} = 0$$

Complement – spin states of the electron

- Ehrenfest theorem: $\langle A\rangle(t) = \langle\psi(t)|\hat{A}|\psi(t)\rangle$

$$\frac{d\langle A\rangle(t)}{dt} = \left\langle \frac{\hat{H}}{i\hbar}\psi(t)\middle|\hat{A}\middle|\psi(t)\right\rangle + \left\langle\psi(t)\middle|\hat{A}\frac{\hat{H}}{i\hbar}\middle|\psi(t)\right\rangle$$

$$= \frac{1}{i\hbar}\langle\psi(t)|[\hat{A},\hat{H}]|\psi(t)\rangle$$

$$\frac{d^2\langle A\rangle(t)}{dt^2} = \frac{1}{i\hbar}\left\langle\frac{d\psi(t)}{dt}\middle|[\hat{A},\hat{H}]\middle|\psi(t)\right\rangle + \frac{1}{i\hbar}\left\langle\psi(t)\middle|[\hat{A},\hat{H}]\middle|\frac{d\psi(t)}{dt}\right\rangle$$

$$= \frac{1}{i\hbar}\left\langle\frac{\hat{H}\psi(t)}{i\hbar}\middle|[\hat{A},\hat{H}]\middle|\psi(t)\right\rangle + \frac{1}{i\hbar}\left\langle\psi(t)\middle|[\hat{A},\hat{H}]\frac{\hat{H}}{i\hbar}\middle|\psi(t)\right\rangle$$

$$= \left(\frac{1}{i\hbar}\right)^2\langle\psi(t)|[\hat{A},\hat{H}]\hat{H} - \hat{H}[\hat{A},\hat{H}]|\psi(t)\rangle$$

because $\hat{H}^+ = \hat{H}$

Thus leading to

$$\boxed{\frac{d^2\langle A\rangle(t)}{dt^2} = \frac{1}{\hbar^2}\langle\psi(t)|[\hat{H},[\hat{A},\hat{H}]]|\psi(t)\rangle} \quad (1)$$

- In the particular case $\hat{A} = |+\rangle\langle+|$ we have

$$[\hat{A},\hat{H}] = |+\rangle\underbrace{\langle+|\hat{H}}_{\langle\hat{H}+|} - \underbrace{\hat{H}|+\rangle}_{\frac{\hbar\omega_0}{2}|-\rangle}\langle+| = \frac{\hbar\omega_0}{2}\left(|+\rangle\langle-| - |-\rangle\langle+|\right)$$

$$[\hat{H},[\hat{A},\hat{H}]] = \frac{\hbar\omega_0}{2}\hat{H}\left(|+\rangle\langle-| - |-\rangle\langle+|\right) - \frac{\hbar\omega_0}{2}\left(|+\rangle\langle-| - |-\rangle\langle+|\right)\hat{H}$$

$$= \frac{\hbar\omega_0}{2}\left(\frac{\hbar\omega_0}{2}|-\rangle\langle-| - \frac{\hbar\omega_0}{2}|+\rangle\langle+|\right)$$

$$- \frac{\hbar\omega_0}{2}\left(|+\rangle\frac{\hbar\omega_0}{2}\langle+| - |-\rangle\frac{\hbar\omega_0}{2}\langle-|\right)$$

$$[\hat{H},[\hat{A},\hat{H}]] = \left(\frac{\hbar\omega_0}{2}\right)^2(2)\left(|-\rangle\langle-| - |+\rangle\langle+|\right)$$

Using the resolution of the identity $|+\rangle\langle+| + |-\rangle\langle-| = \hat{1\!\!1}$

leads to $\boxed{[\hat{H},[\hat{A},\hat{H}]] = \left(\frac{\hbar\omega_0}{2}\right)^2(\hat{1\!\!1} - 2|+\rangle\langle+|).}$ (2)

- $\langle A\rangle(t) = \langle\psi(t)|+\rangle\langle+|\psi(t)\rangle = |\langle+|\psi(t)\rangle|^2$
$= P_+(t).$

Therefore, from (1) and (2), it comes

$$\frac{d^2P_+(t)}{dt^2} = \frac{1}{2}\omega_0^2\Big(\underbrace{\langle\psi(t)|\psi(t)\rangle}_{1} - 2\underbrace{\langle\psi(t)|+\rangle\langle+|\psi(t)\rangle}_{P_+(t)}\Big)$$

thus leading to

$$\boxed{\frac{d^2P_+(t)}{dt^2} = \omega_0^2\left(\frac{1}{2} - P_+(t)\right)} \quad (3)$$

- The solution obtained previously $P_+(t) = \frac{1}{2}(1+\cos\omega_0 t)$ does fulfill the equation (3). Indeed,

$$\frac{dP_+(t)}{dt} = -\frac{1}{2}\omega_0\sin\omega_0 t \quad \text{and} \quad \frac{d^2P_+(t)}{dt^2} = -\frac{\omega_0^2}{2}\underbrace{\cos\omega_0 t}_{(2P_+(t)-1)}.$$