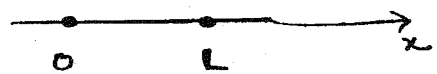
Université de Strasbourg

L3 – 1$^{\text{er}}$ semestre

Travaux dirigés de mécanique quantique pour la chimie – solutions

Emmanuel Fromager

Particle confined along a segment of straight line



1 – The energy is only kinetic

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

one-dimension problem $\psi(x,y,z) = \psi(x)$ (2)

for $0 \leq x \leq L$ $\quad V(x,y,z) = V(x) = 0$ (1)

for $x \geqslant L$ and $x \leqslant 0$ $\quad \psi(x) = 0$

(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 $E \geqslant 0$:

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

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

Thus $\boxed{E \geqslant 0}$

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 $\psi(x=L)=0$

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

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

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 $\int_{-\infty}^{+\infty} |\psi_n(x)|^2 dx = 1 \longleftarrow$ for a physical solution.

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

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

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

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

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

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

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

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

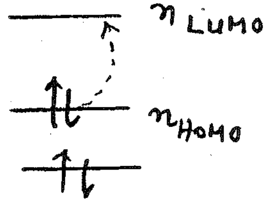
$$E_2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \underset{L \to +\infty}{\longrightarrow} 0 \qquad \psi_2(x) \underset{L \to +\infty}{\longrightarrow} 0$$

$\vdots$

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.

11 -



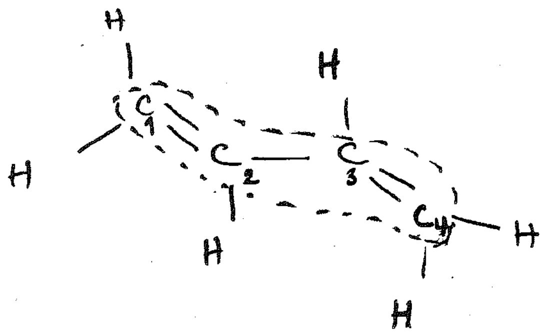
LUMO : Lowest Unoccupied Molecular Orbital
HOMO : Highest Occupied Molecular Orbital

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

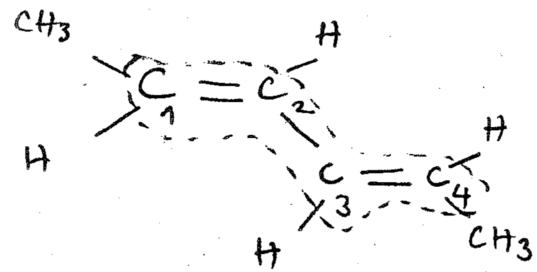
$$h\frac{c}{\lambda} = E_{n_{LUMO}} - E_{n_{HOMO}} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_{LUMO}^2 - n_{HOMO}^2\right)$$

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

Applications:



butadiene



hexa - 2,4 - diene

In both cases, there are 4 π electrons therefore

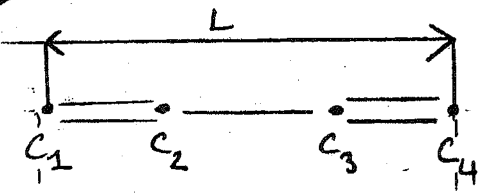
$n_{HOMO} = 2$

and

$n_{LUMO} = 3$.

Value of L?

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



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

$L = 2 \times 135 + 154$

$L = 424\ pm$

$$\lambda = \frac{8 \times 9{,}11.10^{-31} (424)^2 \, 10^{-24} . 3\,10^8}{6{,}63\ 10^{-34}\ (5)}$$

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

<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

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

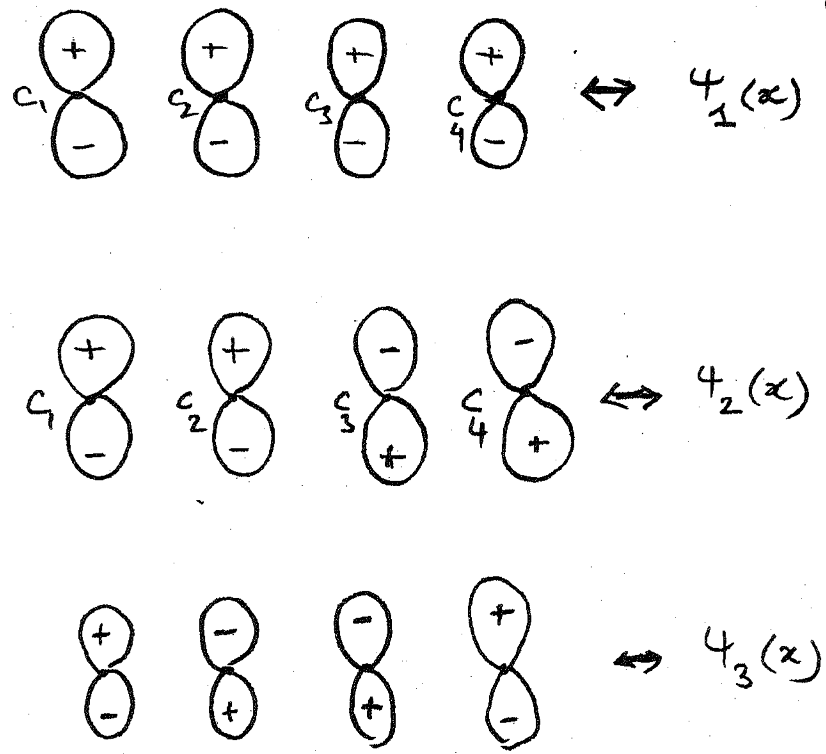
$$\Rightarrow \underline{\lambda' = 220{,}4\,nm}$$

which is rather close to the experimental values

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

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

Let us look at the π orbitals ...



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

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

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

$\left[\frac{x \sin(2n\pi x/L)}{(2n\pi/L)}\right]_0^L = 0$

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

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

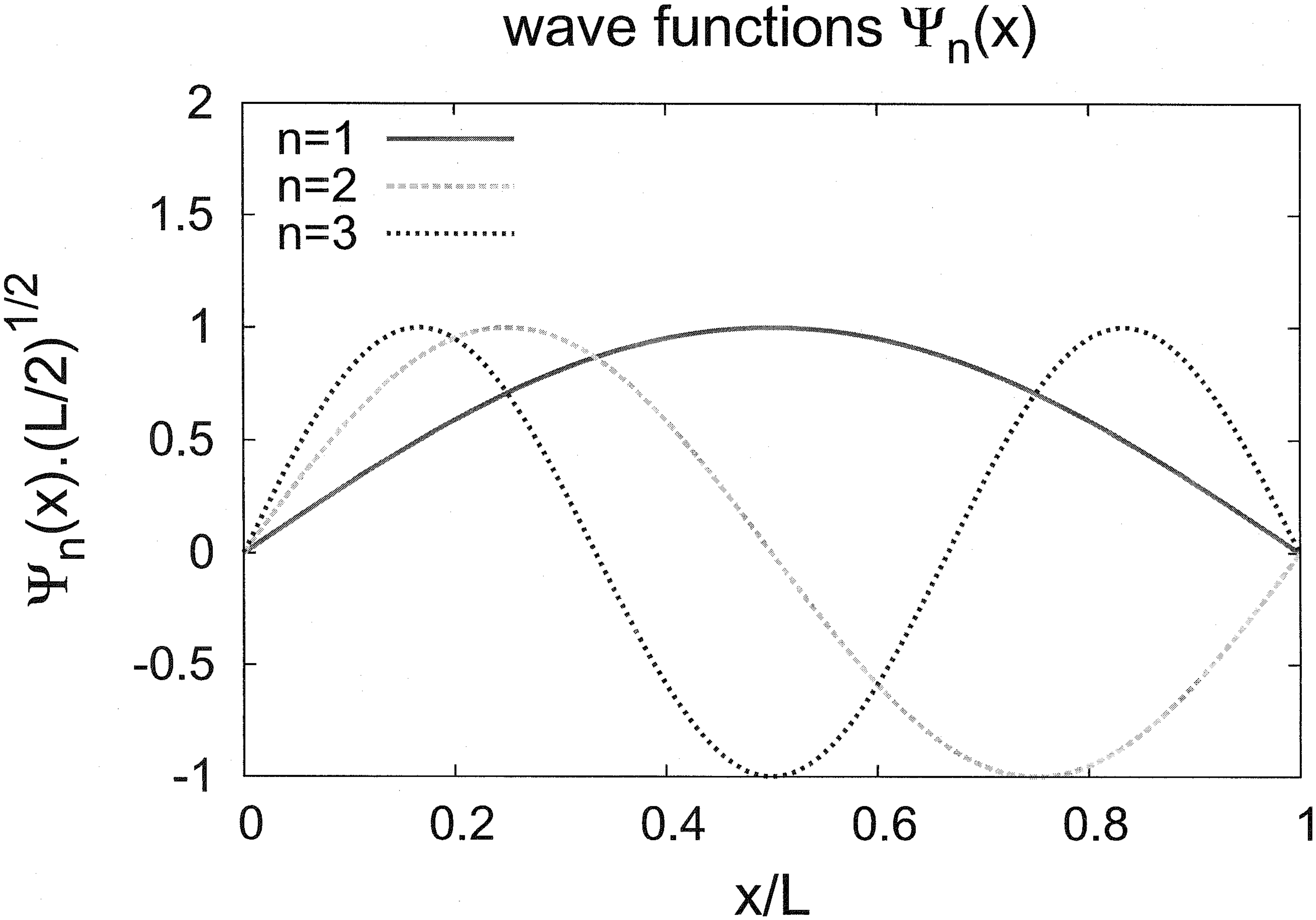
13- $\langle p_x\rangle_n = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi_n(x)$

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 $\alpha \in \mathbb{R}$)

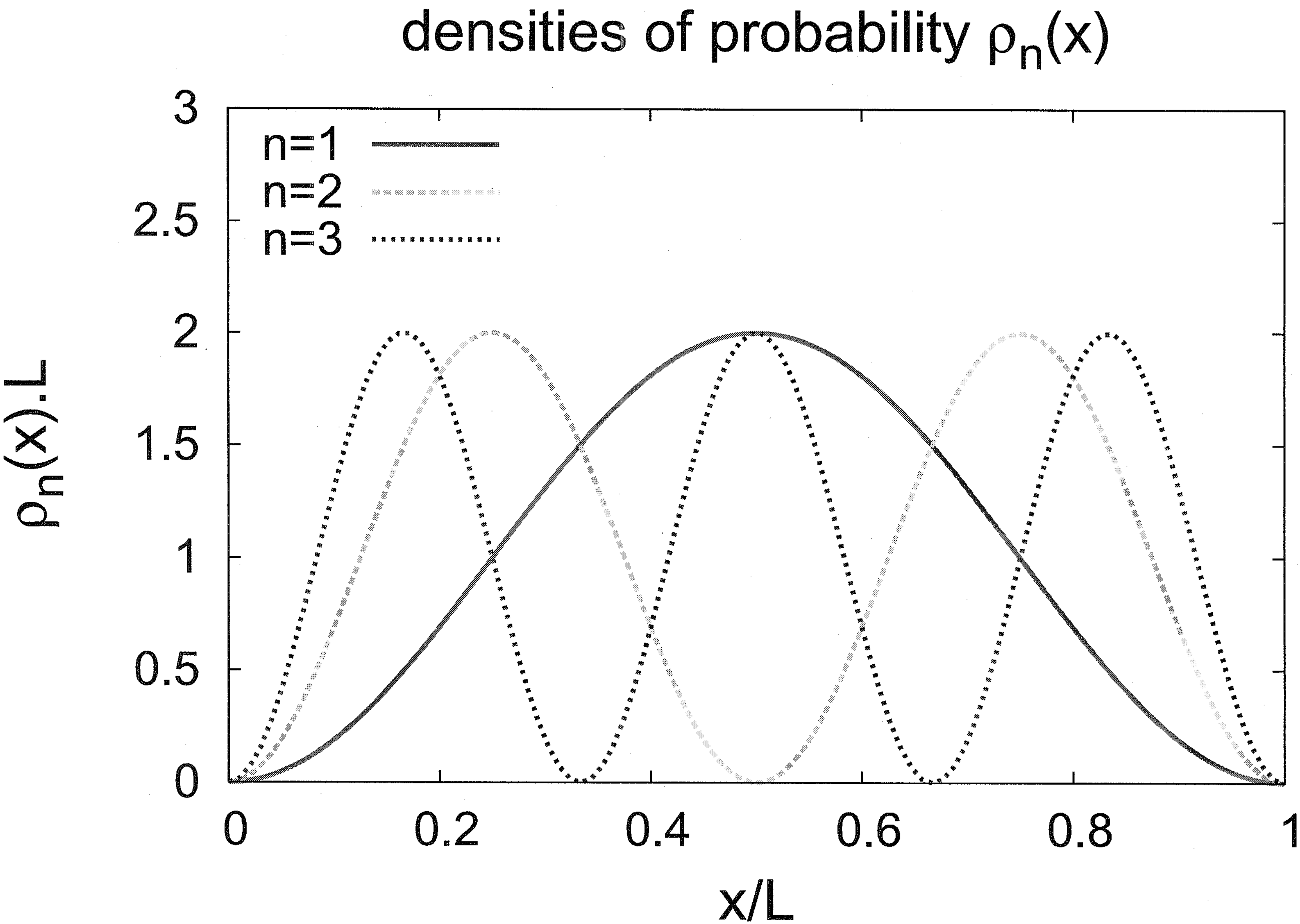
Moreover: $\langle p_x\rangle_n^* = \int_{-\infty}^{+\infty} dx\, \psi_n(x) \left(+i\hbar \frac{d}{dx}\right) \psi_n^*(x) = \underbrace{\left[\psi_n(x)\,(i\hbar)\,\psi_n^*(x)\right]_{-\infty}^{+\infty}}_{0} - \int_{-\infty}^{+\infty} \left(\frac{d\psi_n}{dx}\right) i\hbar\, \psi_n^*\, dx$

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

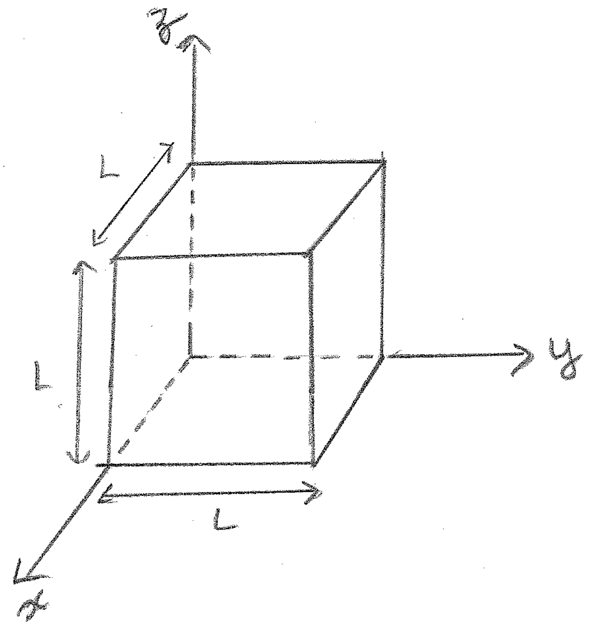
$\Rightarrow \quad \alpha = 0 \quad \Rightarrow \quad \boxed{\langle p_x\rangle_n = 0}$



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


densities of probability $\rho_n(x)$
n=1
n=2
n=3
$\rho_n(x).L$
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 :

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

donc on peut écrire

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

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

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

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

6)

E

$\vdots$

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

TD Postulats et formalisme de Dirac (1/Ex1)

1 - Opérateurs, fonctions propres et valeurs propres

1 -
$$\hat{x}\,\Psi(x,y,z) = x \times \Psi(x,y,z)$$
$$\hat{y}\,\Psi(x,y,z) = y \times \Psi(x,y,z)$$
$$\hat{z}\,\Psi(x,y,z) = z \times \Psi(x,y,z)$$
$$\hat{p}_x\Psi(x,y,z) = -i\hbar \frac{\partial \Psi(x,y,z)}{\partial x}$$
$$\hat{p}_y\Psi(x,y,z) = -i\hbar \frac{\partial \Psi(x,y,z)}{\partial y}$$
$$\hat{p}_z\Psi(x,y,z) = -i\hbar \frac{\partial \Psi(x,y,z)}{\partial z}$$

2 -
$$H_{libre} = \frac{1}{2} m v^2 = \frac{p_x^2+p_y^2+p_z^2}{2m}$$
$$\hat{H}_{libre} = \frac{\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$
$$\hat{H}_{libre}\Psi(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z)$$

3 -
$$[\hat{x},\hat{p}_x]\Psi = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\Psi = -x\, i\hbar\frac{\partial\Psi}{\partial x} + i\hbar\frac{\partial}{\partial x}(x.\Psi)$$
$$= \cancel{-x\, i\hbar\frac{\partial\Psi}{\partial x}} + i\hbar\Psi + \cancel{i\hbar\, x\frac{\partial\Psi}{\partial x}}$$
$$[\hat{x},\hat{p}_x] = i\hbar \quad \Leftarrow \quad = +i\hbar\Psi$$

on ne peut pas mesurer simult^t la position et la qté de mvt.

$$[\hat{p}_x,\hat{H}_{libre}]\Psi = \hat{p}_x\hat{H}_{libre}\Psi - \hat{H}_{libre}\hat{p}_x\Psi = -i\hbar\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi\right)$$
$$+\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) i\hbar\frac{\partial}{\partial x}\Psi$$

(*)
$$= +\frac{i\hbar^3}{2m}\left(\frac{\partial^3}{\partial x^3}\Psi + \frac{\partial}{\partial x}\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial}{\partial x}\frac{\partial^2\Psi}{\partial z^2}\right) - \frac{i\hbar^3}{2m}\left(\frac{\partial^3}{\partial x^3}\Psi + \frac{\partial^2}{\partial y^2}\frac{\partial\Psi}{\partial x}+\frac{\partial^2}{\partial z^2}\frac{\partial\Psi}{\partial x}\right)$$
$$= 0$$

de même $[\hat{p}_y,\hat{H}_{libre}]\Psi = [\hat{p}_z,\hat{H}_{libre}]\Psi = 0$

Il est possible de mesurer simultanément la quantité de mouvement et l'énergie.

(2/Ex2)

4 - •
$$\hat{H}_{libre}\cdot x^{k_x} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 x^{k_x}}{\partial x^2} + \cancel{\frac{\partial^2 x^{k_x}}{\partial y^2}}^{\,0} + \cancel{\frac{\partial^2 x^{k_x}}{\partial z^2}}^{\,0}\right)$$
$$= -\frac{\hbar^2}{2m}k_x\frac{\partial x^{k_x-1}}{\partial x} = -\frac{\hbar^2}{2m}k_x(k_x-1).x^{k_x-2} \neq Cste.\,x^{k_x}$$

la fonction x^{k_x} n'est pas fonction propre de $\hat{H}_{libre}$

•
$$\hat{H}_{libre}\, e^{ik_x x} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 e^{ik_x x}}{\partial x^2} + \cancel{\frac{\partial^2 e^{ik_x x}}{\partial y^2}}^{\,0} + \cancel{\frac{\partial^2 e^{ik_x x}}{\partial z^2}}^{\,0}\right)$$
$$= -\frac{\hbar^2}{2m}\cdot ik_x\frac{\partial e^{ik_x x}}{\partial x} = +\frac{\hbar^2}{2m}\cdot k_x^2 . e^{ik_x x}$$

La fonction $e^{ik_x x}$ est fonction propre de $\hat{H}_{libre}$, de valeur propre $+\frac{\hbar^2}{2m}k_x^2$

•
$$\hat{H}_{libre}\sin(k_x x) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \sin k_x x}{\partial x^2} + \cancel{\frac{\partial^2 \sin k_x x}{\partial y^2}}^{\,0} + \cancel{\frac{\partial^2 \sin k_x x}{\partial z^2}}^{\,0}\right)$$
$$= -\frac{\hbar^2}{2m}k_x\frac{\partial \cos k_x x}{\partial x} = +\frac{\hbar^2}{2m}k_x^2 . \sin k_x x$$

la fonction $\sin k_x . x$ est fonction propre de $\hat{H}_{libre}$, de valeur propre $\frac{\hbar^2}{2m}k_x^2$

Rq :
$$\hat{H}_{libre}(\sin k_x x) = \hat{H}_{libre}\left(\frac{e^{ik_x x} - e^{-ik_x x}}{2i}\right)$$
$$= \frac{1}{2i}\cdot\left(+\frac{\hbar^2}{2m}k_x^2 e^{ik_x x} - \frac{\hbar^2}{2m}k_x^2 e^{-ik_x x}\right) = +\frac{\hbar^2}{2m}k_x^2(\sin k_x x)$$

$\Rightarrow \sin(k_x x)$ est une combinaison linéaire de 2 fonctions propres de même valeur propre $\Rightarrow \sin(k_x x)$ est fonction propre de $\hat{H}_{libre}$.

(*) Rq :
$$[\hat{p}_x,\hat{H}_{libre}] = \left[\hat{p}_x, \frac{\hat{p}_x^2}{2m}+\frac{\hat{p}_y^2}{2m}+\frac{\hat{p}_z^2}{2m}\right]$$
$$= \underbrace{\frac{[\hat{p}_x,\hat{p}_x^2]}{2m}}_{0} + \underbrace{\frac{[\hat{p}_x,\hat{p}_y^2]}{2m}}_{0} + \underbrace{\frac{[\hat{p}_x,\hat{p}_z^2]}{2m}}_{0} = 0$$

car $[\hat{p}_x,\hat{p}_y]=0$ car $[\hat{p}_x,\hat{p}_z]=0$

Exercise 3 : $\hat{L}_z$ operator

1. $\forall \psi, \chi$ $\quad \langle \psi | \hat{L}_z | \chi \rangle = \int_0^{2\pi} d\varphi \; \psi^*(\varphi) \, (\hat{L}_z \chi)(\varphi) = \int_0^{2\pi} d\varphi \; \psi^*(\varphi) \left(-i\hbar \frac{\partial \chi}{\partial \varphi} \right)$

$$= -i\hbar \int_0^{2\pi} d\varphi \; \psi^* \frac{\partial \chi}{\partial \varphi} = -i\hbar \left(\left[\psi^* \chi \right]_0^{2\pi} - \int_0^{2\pi} d\varphi \; \chi \frac{\partial \psi^*}{\partial \varphi} \right)$$

$\varphi = 0$ and $\varphi = 2\pi$ correspond to the same position in space

$\Rightarrow \quad \psi^*(0)\chi(0) = \psi^*(2\pi)\chi(2\pi)$

$\Rightarrow \quad \langle \psi | \hat{L}_z | \chi \rangle = i\hbar \int_0^{2\pi} d\varphi \; \chi \frac{\partial \psi^*}{\partial \varphi} = \int_0^{2\pi} d\varphi \, (\hat{L}_z \psi)^* \chi = \langle \chi | \hat{L}_z | \psi \rangle^*$

Since $\hat{L}_z \psi = -i\hbar \frac{\partial \psi}{\partial \varphi}$

$\Rightarrow$ $\underline{\hat{L}_z \text{ is hermitian.}}$

2. Let Φ be eigenfunction of $\hat{L}_z$ associated to l_z

$\hat{L}_z \Phi = l_z \Phi \quad (2)$

Since $\hat{L}_z$ is hermitian, $\underline{l_z \in \mathbb{R}}$

Proof :

$\langle \Phi | \hat{L}_z | \Phi \rangle = \langle \Phi | \hat{L}_z | \Phi \rangle^*$ according to question 1

thus $\quad l_z \underbrace{\langle \Phi | \Phi \rangle}_{\neq 0} = l_z^* \langle \Phi | \Phi \rangle$.

$\Rightarrow \quad l_z = l_z^* \Rightarrow \quad l_z \in \mathbb{R}$.

$(2) \Leftrightarrow \quad -i\hbar \frac{\partial \Phi}{\partial \varphi} = l_z \Phi$

$\Leftrightarrow \quad \Phi(\varphi) = c \, e^{-l_z / i\hbar \, \varphi}$

$$\Phi(\varphi=0) = \Phi(\varphi=2\pi) \Rightarrow c\, e^{+\frac{i l_z}{\hbar} 2\pi} = c$$

$$\Rightarrow e^{\frac{2i\pi l_z}{\hbar}} = 1 \Rightarrow \frac{2\pi l_z}{\hbar} = 2\pi m \quad m \in \mathbb{Z}$$

$$\Rightarrow \boxed{l_z = m\hbar \quad m \in \mathbb{Z}}$$

Corresponding eigenfunction $\Phi_m = C_m e^{im\varphi}$ (we choose $C_m \in \mathbb{R}$)

Normalization : $\langle \Phi_m | \Phi_m \rangle = 1 = \int_0^{2\pi} C_m^* e^{-im\varphi} . C_m e^{im\varphi} d\varphi = C_m^2 . 2\pi$

$$\Rightarrow \boxed{C_m = \frac{1}{\sqrt{2\pi}}} \Rightarrow \Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

3- $\psi_0(\varphi) = A\cos^2(\varphi) = \frac{A}{4}\underbrace{(e^{i\varphi}+e^{-i\varphi})^2}_{(e^{2i\varphi}+2+e^{-2i\varphi})}$

$$\psi_0(\varphi) = \frac{A}{4}\left(2\times\sqrt{2\pi}\,\Phi_0 + \sqrt{2\pi}\,\Phi_2 + \sqrt{2\pi}\,\Phi_{-2}\right)$$

$$\boxed{\psi_0(\varphi) = \frac{A\sqrt{2\pi}}{4}\left(2\Phi_0 + \Phi_2 + \Phi_{-2}\right)}$$

Dirac notations :

$$|\psi_0\rangle = \frac{A\sqrt{2\pi}}{4}\left(2|\Phi_0\rangle + |\Phi_2\rangle + |\Phi_{-2}\rangle\right)$$

$$\boxed{\text{if } m \neq l \text{ then } \langle \Phi_m | \Phi_l \rangle = 0}$$

Proof: According to question 1-

$$\langle \Phi_m | \hat{L}_z | \Phi_l \rangle = \langle \Phi_l | \hat{L}_z | \Phi_m \rangle^*$$

$$l\hbar \langle \Phi_m | \Phi_l \rangle = \left(m\hbar \langle \Phi_l | \Phi_m \rangle\right)^*$$

$$= m\hbar \langle \Phi_m | \Phi_l \rangle$$

$$\Rightarrow (l-m)\langle \Phi_m | \Phi_l \rangle = 0$$

$$\Rightarrow \langle \Phi_m | \Phi_l \rangle = 0.$$

Therefore $\langle \psi_0 | \psi_0 \rangle = 1 = \frac{A\sqrt{2\pi}}{4}\left(2\underbrace{\langle \psi_0 | \Phi_0 \rangle}_{A\sqrt{2\pi}.\frac{2}{4}} + \underbrace{\langle \psi_0 | \Phi_2 \rangle}_{\frac{A\sqrt{2\pi}}{4}} + \underbrace{\langle \psi_0 | \Phi_{-2} \rangle}_{\frac{A\sqrt{2\pi}}{4}}\right)$

$$\langle \psi_0 | \psi_0 \rangle = \frac{A^2(2\pi)}{16}(4+1+1) = \frac{\pi A^2}{8}.6 = \frac{3\pi A^2}{4} = 1$$

$$\Rightarrow A^2 = \frac{4}{3\pi} \Rightarrow \boxed{A = \frac{2}{\sqrt{3\pi}}} \Rightarrow \frac{A\sqrt{2\pi}}{4} = \frac{\sqrt{2\pi}}{4}.\frac{2}{\sqrt{3\pi}} = \frac{1}{\sqrt{6}}$$

Thus $|\psi_0\rangle = \frac{1}{\sqrt{6}} \left(2|\Phi_0\rangle + |\Phi_2\rangle + |\Phi_{-2}\rangle\right)$

4 -

0 can be measured with probability $|\langle\Phi_0|\psi_0\rangle|^2 = \frac{4}{6} = \frac{2}{3}$

$+2\hbar$ ———— $|\langle\Phi_2|\psi_0\rangle|^2 = \frac{1}{6}$

$-2\hbar$ ———— $|\langle\Phi_{-2}|\psi_0\rangle|^2 = \frac{1}{6}$

5 - $\langle \hat{L}_z\rangle_{\psi_0} = \langle\psi_0|\hat{L}_z|\psi_0\rangle$ where $\langle\psi_0|\psi_0\rangle = 1$

$$= \langle\psi_0|\left(\frac{2}{\sqrt{6}}\underbrace{\hat{L}_z|\Phi_0\rangle}_{0} + \frac{1}{\sqrt{6}}\underbrace{\hat{L}_z|\Phi_2\rangle}_{2\hbar|\Phi_2\rangle} + \frac{1}{\sqrt{6}}\underbrace{\hat{L}_z|\Phi_{-2}\rangle}_{-2\hbar|\Phi_{-2}\rangle}\right)$$

$$\langle\hat{L}_z\rangle_{\psi_0} = \frac{2\hbar}{\sqrt{6}}\underbrace{\langle\psi_0|\Phi_2\rangle}_{\frac{1}{\sqrt{6}}} - \frac{2\hbar}{\sqrt{6}}\underbrace{\langle\psi_0|\Phi_{-2}\rangle}_{\frac{1}{\sqrt{6}}}$$

$$\boxed{\langle\hat{L}_z\rangle_{\psi_0} = 0}$$

Comment: Let A be an observable and $\hat{A}$ its corresponding hermitian operator. We denote $\{|u_i\rangle\}_i$ an orthonormal basis of eigenvectors of $\hat{A}$.

At time t_0 the quantum state $|\psi_0\rangle$ can be written in the basis $\{|u_i\rangle\}_i$ as follows

$|\psi_0\rangle = \sum_i c_i |u_i\rangle$ where $\hat{A}|u_i\rangle = a_i|u_i\rangle$ and

$\langle\psi_0|\psi_0\rangle = 1$. The expectation value of $\hat{A}$ for the state $|\psi_0\rangle$ can be written as

$$\langle\hat{A}\rangle_{\psi_0} = \langle\psi_0|\hat{A}|\psi_0\rangle = \sum_i c_i \langle\psi_0|\hat{A}|u_i\rangle$$

$$= \sum_i c_i a_i \langle\psi_0|u_i\rangle$$

Since $\langle u_j|\psi_0\rangle = \sum_i c_i \underbrace{\langle u_j|u_i\rangle}_{\delta_{ij}} = c_j \quad \forall j$

$\langle\psi_0|u_i\rangle = \langle u_i|\psi_0\rangle^* = c_i^*$

Therefore $\langle\hat{A}\rangle_{\psi_0} = \sum_i |c_i|^2 a_i = \boxed{\sum_i \mathcal{P}_i a_i = \langle\hat{A}\rangle_{\psi_0}}$

where $\mathcal{P}_i = |c_i|^2 = |\langle u_i|\psi_0\rangle|^2$ is the probability of being in state $|u_i\rangle$ at time t_0.

We can apply directly this formula for $\hat{L}_z$

$\Rightarrow \langle\hat{L}_z\rangle_{\psi_0} = 0\times\frac{2}{3} + 2\hbar\times\frac{1}{6} - 2\hbar\times\frac{1}{6} = 0$

$$\hat{L}_z^2 |\psi_0\rangle = \frac{1}{\sqrt{6}} \Big(\underbrace{2\hat{L}_z^2 |\Phi_0\rangle}_{= 0} + \underbrace{\hat{L}_z^2 |\Phi_2\rangle}_{(2\hbar)^2 |\Phi_2\rangle} + \underbrace{\hat{L}_z^2 |\Phi_{-2}\rangle}_{(-2\hbar)^2 |\Phi_{-2}\rangle} \Big)$$

$$= \frac{4\hbar^2}{\sqrt{6}} \left(|\Phi_2\rangle + |\Phi_{-2}\rangle \right)$$

$$\langle \hat{L}_z^2 \rangle_{\psi_0} = \langle \psi_0 | \hat{L}_z^2 | \psi_0 \rangle = \frac{4\hbar^2}{\sqrt{6}} \Big(\underbrace{\langle \psi_0 | \Phi_2 \rangle}_{\frac{1}{\sqrt{6}}} + \underbrace{\langle \psi_0 | \Phi_{-2} \rangle}_{\frac{1}{\sqrt{6}}} \Big)$$

$$= \frac{4\hbar^2}{\sqrt{6}} \cdot \frac{2}{\sqrt{6}} = \frac{8\hbar^2}{6} = \frac{4\hbar^2}{3}$$

Comment: We can therefore calculate the standard deviation for the angular momentum projection L_z at time t_0

$$(\Delta L_z)^2_{\psi_0} = \frac{4}{3}\hbar^2 \Rightarrow (\Delta L_z)_{\psi_0} = \frac{2\hbar}{\sqrt{3}} .$$

$$= \langle \hat{L}_z^2 \rangle_{\psi_0} - \langle \hat{L}_z \rangle^2_{\psi_0}$$

Ecart type et interprétation

1. $\langle\psi|(\hat{A}-\langle A\rangle_\psi)^2|\psi\rangle = \langle(\hat{A}-\langle A\rangle_\psi)^\dagger\psi|\hat{A}-\langle A\rangle_\psi|\psi\rangle$

Définition de l'opérateur adjoint

Formules utiles :

① $\forall |\psi\rangle, |\varphi\rangle \quad \langle\psi|\hat{A}|\varphi\rangle = \langle\hat{A}^\dagger\psi|\varphi\rangle = \langle\varphi|\hat{A}^\dagger|\psi\rangle^*$

② $\forall |\psi\rangle, |\varphi\rangle \quad \langle\psi|\hat{A}+\hat{B}|\varphi\rangle = \langle\psi|\hat{A}|\varphi\rangle + \langle\psi|\hat{B}|\varphi\rangle$

$$= \langle\hat{A}^\dagger\psi|\varphi\rangle + \langle\hat{B}^\dagger\psi|\varphi\rangle$$

$$= \langle\underbrace{(\hat{A}^\dagger+\hat{B}^\dagger)}_{(\hat{A}+\hat{B})^\dagger}\psi|\varphi\rangle$$

soit $\boxed{(\hat{A}+\hat{B})^\dagger = \hat{A}^\dagger+\hat{B}^\dagger}$

③ $\forall \alpha \in \mathbb{C}, \forall |\psi\rangle, |\varphi\rangle$

$$\langle\psi|\alpha\hat{A}|\varphi\rangle = \alpha\langle\psi|\hat{A}|\varphi\rangle = \alpha\langle\hat{A}^\dagger\psi|\varphi\rangle$$

$$= \langle\alpha^*\hat{A}^\dagger\psi|\varphi\rangle$$

soit $\boxed{(\alpha\hat{A})^\dagger = \alpha^*\hat{A}^\dagger}$

$\hat{A}-\langle A\rangle_\psi$ est une notation simple pour

$\hat{A}-\langle A\rangle_\psi \hat{\mathbb{1}} \to$ opérateur identité ($\hat{\mathbb{1}}|\psi\rangle = |\psi\rangle$)

D'après la formule ②

$$(\hat{A}-\langle A\rangle_\psi\hat{\mathbb{1}})^\dagger = \hat{A}^\dagger + (-\langle A\rangle_\psi\hat{\mathbb{1}})^\dagger$$

$$= \hat{A}^\dagger - \langle A\rangle_\psi^* \underbrace{\hat{\mathbb{1}}^\dagger}_{\hat{\mathbb{1}}} \leftarrow \text{formule ③}$$

Comme $\hat{A}$ est hermitique $\hat{A}^\dagger = \hat{A}$ et

$$\langle A\rangle_\psi^* = \langle\psi|\hat{A}|\psi\rangle^* = \langle\hat{A}\psi|\psi\rangle$$

$$= \langle\hat{A}^\dagger\psi|\psi\rangle$$

$$= \langle\psi|\hat{A}|\psi\rangle$$

$$= \langle A\rangle_\psi$$

donc $(\hat{A}-\langle A\rangle_\psi)^\dagger = \hat{A}-\langle A\rangle_\psi$

et $\langle\psi|(\hat{A}-\langle A\rangle_\psi)^2|\psi\rangle = \langle(\hat{A}-\langle A\rangle_\psi)\psi|(\hat{A}-\langle A\rangle_\psi)|\psi\rangle$

$$= \|(\hat{A}-\langle A\rangle_\psi)|\psi\rangle\|^2 \geqslant 0$$

- Comme $(\hat{A}-\langle A\rangle_\psi)^2 = \hat{A}^2 - 2\langle A\rangle_\psi\hat{A} + \langle A\rangle_\psi^2$

il vient

$$\langle\psi|(\hat{A}-\langle A\rangle_\psi)^2|\psi\rangle = \langle\psi|\hat{A}^2|\psi\rangle - 2\langle A\rangle_\psi \underbrace{\langle\psi|\hat{A}|\psi\rangle}_{\langle A\rangle_\psi} + \langle A\rangle_\psi^2 \underbrace{\langle\psi|\psi\rangle}_{1}$$

$$= \langle A^2\rangle_\psi - 2\langle A\rangle_\psi^2 + \langle A\rangle_\psi^2$$

donc $\langle A^2\rangle_\psi - \langle A\rangle_\psi^2 = \langle\psi|(\hat{A}-\langle A\rangle_\psi)^2|\psi\rangle \geqslant 0$

L'écart type est donc bien défini.

2. • $\hat{A}|\psi_a\rangle = a|\psi_a\rangle \Rightarrow \langle\psi_a|\hat{A}|\psi_a\rangle = \langle A\rangle_{\psi_a} = a\langle\psi_a|\psi_a\rangle = a$

car $|\psi_a\rangle$ est normé

• $\hat{A}^2|\psi_a\rangle = \hat{A}(\hat{A}|\psi_a\rangle) = a\hat{A}|\psi_a\rangle = a^2|\psi_a\rangle$

$\Rightarrow \langle\psi_a|\hat{A}^2|\psi_a\rangle = a^2\langle\psi_a|\psi_a\rangle = a^2 = \langle A^2\rangle_{\psi_a} = \langle A\rangle_{\psi_a}^2$

soit $(\Delta A)_{\psi_a} = 0$

3. $|\psi\rangle = \frac{1}{\sqrt{1+\delta^2}}(|\psi_a\rangle + \delta|\psi_b\rangle)$

$$\langle\psi|\psi\rangle = \frac{1}{(1+\delta^2)}\langle\psi_a+\delta\psi_b|\psi_a+\delta\psi_b\rangle$$

$$= \frac{1}{(1+\delta^2)}\left[\underbrace{\langle\psi_a|\psi_a\rangle}_{1} + \delta\underbrace{\langle\psi_a|\psi_b\rangle}_{0} + \underset{\delta}{\delta^*}\underbrace{\langle\psi_b|\psi_a\rangle}_{0} + \delta^2\underbrace{\langle\psi_b|\psi_b\rangle}_{1}\right]$$

soit $\langle\psi|\psi\rangle = 1$.

• $\hat{A}|\psi\rangle = \frac{1}{\sqrt{1+\delta^2}}(\hat{A}|\psi_a\rangle + \delta\hat{A}|\psi_b\rangle)$

$$= \frac{1}{\sqrt{1+\delta^2}}(a|\psi_a\rangle + \delta b|\psi_b\rangle)$$

$$\langle A\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle = \frac{1}{1+\delta^2}\langle\psi_a+\delta\psi_b|a\psi_a+\delta b\psi_b\rangle$$

$$= \frac{1}{1+\delta^2}\left[a\langle\psi_a|\psi_a\rangle + \delta b\langle\psi_a|\psi_b\rangle + \delta^* a\langle\psi_b|\psi_a\rangle + \underbrace{|\delta|^2}_{\delta^2} b\langle\psi_b|\psi_b\rangle\right]$$

car δ est réel

donc $\boxed{\langle A\rangle_\psi = \frac{a+b\delta^2}{1+\delta^2}}$

$$\langle A\rangle_\psi^2 = \frac{a^2+2ab\delta^2+b^2\delta^4}{(1+\delta^2)^2}$$

• $\hat{A}^2|\psi\rangle = \hat{A}(\hat{A}|\psi\rangle)$

$$= \frac{1}{\sqrt{1+\delta^2}}(a\hat{A}|\psi_a\rangle + \delta b\hat{A}|\psi_b\rangle)$$

Soit $\hat{A}^2|\psi\rangle = \frac{1}{\sqrt{1+\delta^2}}(a^2|\psi_a\rangle + \delta b^2|\psi_b\rangle)$

$$\langle \psi | \hat{A}^2 | \psi \rangle = \frac{1}{(1+\delta^2)} \langle \psi_a + \delta \psi_b | a^2 \psi_a + \delta b^2 \psi_b \rangle$$

$$\langle A^2 \rangle_\psi = \frac{1}{(1+\delta^2)} \left[a^2 + b^2 \delta^2 \right]$$

D'où $(\Delta A)^2_\psi = \frac{1}{(1+\delta^2)^2} \Big[\underbrace{(a^2+b^2\delta^2)(1+\delta^2)}_{\cancel{a^2} + \delta^2 a^2 + b^2\delta^2 + \cancel{b^2\delta^4}} - \cancel{a^2} - 2ab\delta^2 - \cancel{b^2\delta^4} \Big]$

Ainsi

$$(\Delta A)^2_\psi = \frac{1}{(1+\delta^2)^2} \left[\delta^2 \right] \left(a^2 + b^2 - 2ab \right) = \frac{\delta^2 (a-b)^2}{(1+\delta^2)^2}$$

$$\Rightarrow \boxed{(\Delta A)_\psi = \frac{\delta |a-b|}{(1+\delta^2)}}$$

$|\psi\rangle$ n'est état propre de $\hat{A}$ que lorsque $\delta = 0$ ou $\delta \to +\infty$ puisque $a \neq b$. Dans ces deux situations, le résultat de la mesure de A est connu. Ce sera a $(\delta = 0)$ ou b $(\delta \to +\infty)$. Pour $0 < \delta < +\infty$, la probabilité de mesurer a est $|\langle \psi_a | \psi \rangle|^2 = \frac{1}{1+\delta^2}$

et celle de mesurer b est $|\langle \psi_b | \psi \rangle|^2 = \frac{\delta^2}{1+\delta^2}$, et

$(\Delta A)_\psi \neq 0$ Il rend compte de l'incertitude avant la mesure.

Relations d'incertitude d'Heisenberg

1. Mesurer simultanément x et p_x revient à dire que, juste après la mesure, x et p_x sont connus et donc qu'il n'y a aucune incertitude sur leurs valeurs. Ainsi le système (ici la particule) serait dans un état quantique $|\psi\rangle$ tel que $(\Delta x)_\psi = 0$ ET $(\Delta p_x)_\psi = 0$

Soit $(\Delta x)_\psi (\Delta p_x)_\psi = 0 \longleftarrow$ impossible d'après la relation d'incertitude d'Heisenberg.

2. $N(\alpha) = \langle \psi(\alpha) | \psi(\alpha) \rangle = \langle \hat{\Delta}(\alpha) \psi | \hat{\Delta}(\alpha) \psi \rangle$

où $\hat{\Delta}(\alpha) = \hat{p}_x - \langle p_x \rangle_\psi + i\alpha(\hat{x} - \langle x \rangle_\psi)$

Formule utile: $\hat{A}$ opérateur quelconque.

$\forall |\psi\rangle, |\varphi\rangle \quad \langle \hat{A}\psi | \varphi \rangle = \langle \varphi | \hat{A} | \psi \rangle^*$

$= (\langle A^\dagger \varphi | \psi \rangle)^*$

$= \langle \psi | A^\dagger | \varphi \rangle$

donc $\boxed{(\hat{A}^\dagger)^\dagger = \hat{A}}$

Ainsi $N(\alpha) = \langle \psi | \hat{\Delta}^\dagger(\alpha) \hat{\Delta}(\alpha) | \psi \rangle$

où $\hat{\Delta}^\dagger(\alpha) = \underset{\hat{p}_x}{\hat{p}_x^\dagger} - \underbrace{\langle p_x \rangle_\psi^*}_{\langle p_x \rangle_\psi} - i\underset{\alpha \text{ puisque } \alpha \text{ est réel}}{\alpha^*}(\overset{\hat{x}}{\hat{x}^\dagger} - \overbrace{\langle x \rangle_\psi^*}^{\langle x \rangle_\psi})$

⚠

soit $\hat{\Delta}^\dagger(\alpha) = \hat{p}_x - \langle p_x \rangle_\psi - i\alpha(\hat{x} - \langle x \rangle_\psi)$

et $\hat{\Delta}^\dagger(\alpha)\hat{\Delta}(\alpha) = \left(\hat{p}_x - \langle p_x \rangle_\psi - i\alpha(\hat{x} - \langle x \rangle_\psi)\right)$

$\cdot \left(\hat{p}_x - \langle p_x \rangle_\psi + i\alpha(\hat{x} - \langle x \rangle_\psi)\right)$

$= \hat{p}_x^2 - \langle p_x \rangle_\psi \hat{p}_x + i\alpha\left(\hat{p}_x \hat{x} - \langle x \rangle_\psi \hat{p}_x\right)$

$- \langle p_x \rangle_\psi \hat{p}_x + \langle p_x \rangle_\psi^2 - i\alpha\left(\langle p_x \rangle_\psi \hat{x} - \langle p_x \rangle_\psi \langle x \rangle_\psi\right)$

$+ \alpha^2\left(\hat{x}^2 - 2\langle x \rangle_\psi \hat{x} + \langle x \rangle_\psi^2\right)$

$- i\alpha(\hat{x} - \langle x \rangle_\psi)(\hat{p}_x - \langle p_x \rangle_\psi)$

donc

$N(\alpha) = \underbrace{\langle p_x^2 \rangle_\psi} - \underbrace{\langle p_x \rangle_\psi^2} + i\alpha \langle \psi | \underbrace{\hat{p}_x \hat{x}} | \psi \rangle$

$- i\alpha \langle x \rangle_\psi \cancel{\langle p_x \rangle_\psi} - \cancel{\langle p_x \rangle_\psi^2} + \cancel{\langle p_x \rangle_\psi^2}$

$- i\alpha \cancel{\langle p_x \rangle_\psi} \langle x \rangle_\psi + i\alpha \cancel{\langle p_x \rangle_\psi} \langle x \rangle_\psi$

$+ \alpha^2 \underbrace{\langle x^2 \rangle_\psi} - 2\alpha^2 \underbrace{\langle x \rangle_\psi^2} + \alpha^2 \underbrace{\langle x \rangle_\psi^2}$

$- i\alpha \langle \psi | \underbrace{\hat{x} \hat{p}_x} | \psi \rangle + i\alpha \cancel{\langle p_x \rangle_\psi} \cancel{\langle x \rangle_\psi}$

$+ i\alpha \langle x \rangle_\psi \cancel{\langle p_x \rangle_\psi} - i\alpha \cancel{\langle x \rangle_\psi} \langle p_x \rangle_\psi$

$N(\alpha) = (\Delta p_x)_\psi^2 + \alpha^2 (\Delta x)_\psi^2 + i\alpha \langle \psi | \hat{p}_x \hat{x} - \hat{x} \hat{p}_x | \psi \rangle$

$$\boxed{N(\alpha) = (\Delta x)_\psi^2\ \alpha^2 - i\alpha \langle \psi | [\hat{x}, \hat{p_x}] | \psi \rangle + (\Delta p_x)_\psi^2}$$

3. Comme $[\hat{x}, \hat{p_x}] = i\hbar$

$$N(\alpha) = (\Delta x)_\psi^2 \alpha^2 + \alpha\hbar + (\Delta p_x)_\psi^2$$

$$= (\Delta x)_\psi^2 \left[\alpha^2 + \frac{\hbar\alpha}{(\Delta x)_\psi^2} + \frac{(\Delta p_x)_\psi^2}{(\Delta x)_\psi^2} \right]$$

$$= (\Delta x)_\psi^2 \left[\left(\alpha + \frac{\hbar}{2(\Delta x)_\psi^2}\right)^2 + \frac{(\Delta p_x)_\psi^2}{(\Delta x)_\psi^2} - \frac{\hbar^2}{4(\Delta x)_\psi^4} \right]$$

donc

$$N(\alpha) = (\Delta x)_\psi^2 \left[\left(\alpha + \frac{\hbar}{2(\Delta x)_\psi^2}\right)^2 + \frac{1}{(\Delta x)_\psi^2} \left[(\Delta p_x)_\psi^2 - \frac{\hbar^2}{4(\Delta x)_\psi^2} \right] \right]$$

$$N\left(-\frac{\hbar}{2(\Delta x)_\psi^2}\right) = (\Delta p_x)_\psi^2 - \frac{\hbar^2}{4(\Delta x)_\psi^2} \geqslant 0$$

puisque $N(\alpha) = \langle \psi(\alpha) | \psi(\alpha) \rangle$

norme au carré !

d'où $\quad (\Delta p_x)_\psi^2 \geqslant \dfrac{\hbar^2}{4(\Delta x)_\psi^2} \Rightarrow (\Delta p_x)_\psi^2 (\Delta x)_\psi^2 \geqslant \dfrac{\hbar^2}{4}$

soit $\quad \boxed{(\Delta x)_\psi (\Delta p_x)_\psi \geqslant \frac{\hbar}{2}}$

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:

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

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

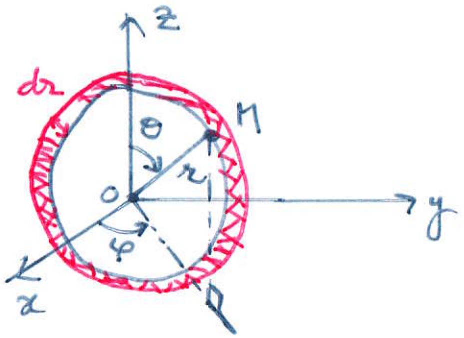
• If we integrate partially in r', for example for $0 \leq r' \leq r$, but fully in θ and φ, then

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

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

• $$d\mathcal{P}(r) = \underbrace{\mathcal{P}(r+dr) - \mathcal{P}(r)}_{} = \frac{d\mathcal{P}(r)}{dr}\, dr$$

probability of finding the electron at a distance between $r+dr$ and r from the nucleus. (red zone on the figure)



Note that $$\int_0^{+\infty} d\mathcal{P}(r) = \int_0^{+\infty} \overset{\rho(r)}{\overset{\parallel}{\frac{d\mathcal{P}(r)}{dr}}}\, dr$$

$$= \underbrace{\mathcal{P}(+\infty)}_{1} - \underbrace{\mathcal{P}(0)}_{0}$$

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

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

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

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

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

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

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

f) ψ_{1s} and ψ_{2s} do not vary with θ and φ. They only depend on r ⟶ 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
→ it ensures that 1s and 2s orbitals are orthogonal.

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

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

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:

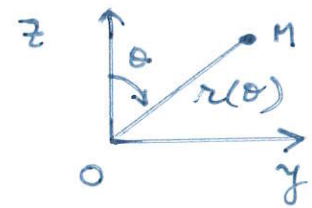
$$\theta,\varphi \longmapsto M(\underbrace{|\cos\theta|}_{r(\theta,\varphi)},\theta,\varphi)$$

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

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

⇒ Symmetry with respect to the xOy plane.

h)



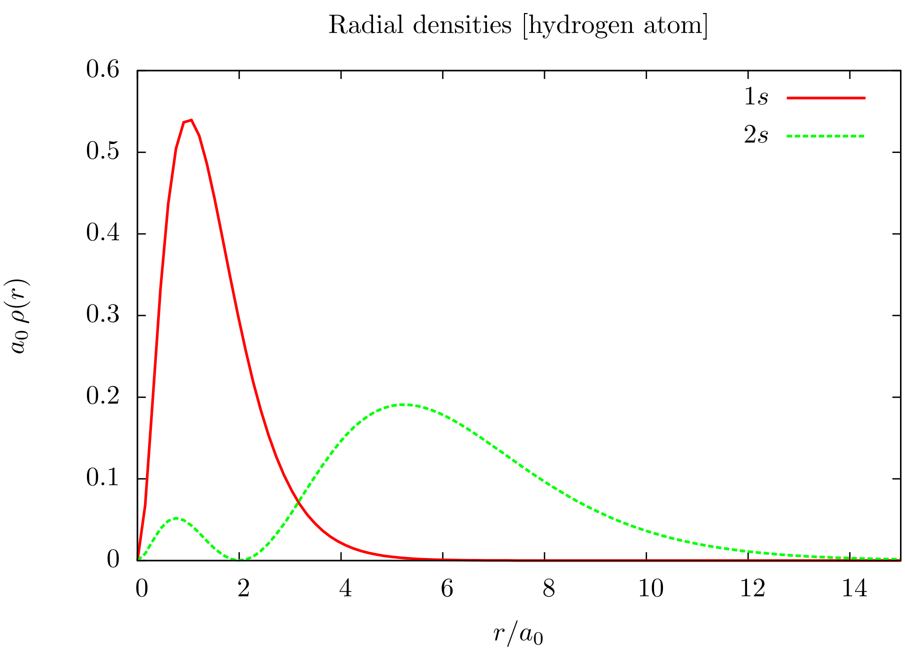
$0 \le \theta \le \frac{\pi}{2} \Rightarrow |\cos\theta| = \cos\theta = r(\theta)$

$OM = \frac{z}{\cos\theta} = \frac{z}{OM}$

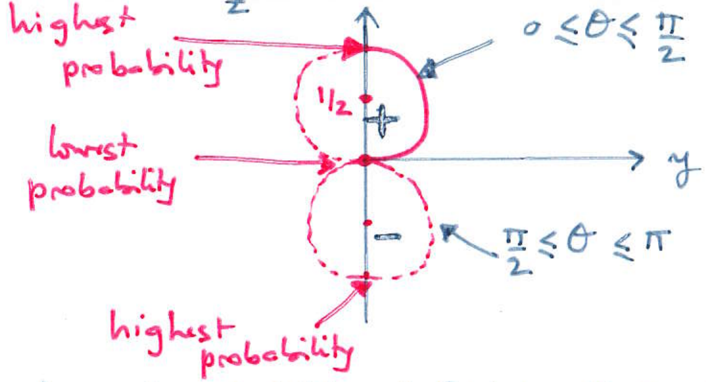
if M belongs to the surface representing $2p_z$.

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

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



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



$0 \leq \theta \leq \frac{\pi}{2}$ $\cos\theta \geq 0$

$\frac{\pi}{2} \leq \theta \leq \pi$ $\cos\theta \leq 0$

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

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

Complement:

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

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

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

$$\langle\hat{H}(z)\psi(z)|\frac{d\psi(z)}{dz}\rangle = E^*(z)\langle\psi(z)|\frac{d\psi(z)}{dz}\rangle, \quad E^*(z) = E(z)$$

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

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

$$\tilde{\psi}(Z,\vec{\tilde{r}}) = \underbrace{C}_{\text{normalization factor.}}\psi(1,\vec{\tilde{r}}) \quad \text{Eq. (2)}$$

$\forall Z$

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

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 $E_n = -\frac{E_I}{n^2}$ ← $E(1)$ 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

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

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

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

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

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

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

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

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

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.

L'oscillateur harmonique (1)

1- a) $E_{tot} = \frac{1}{2m} p_x^2 + \frac{1}{2} k x^2$ $\quad \hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} k \hat{x}^2 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}\omega^2 m \hat{x}^2$

b) $\hat{X} = \sqrt{\frac{m\omega}{\hbar}}\, \hat{x}$; $\hat{P}_x = \frac{1}{\sqrt{m\hbar\omega}} \hat{p}_x$; $\hat{H} = \hbar\omega\left(\frac{1}{2}\hat{P}_x^2 + \frac{1}{2}\hat{X}^2\right)$

$$[\hat{x}, \hat{P}_x]\Psi = \sqrt{\frac{m\omega}{\hbar}}\, x \frac{1}{\sqrt{m\hbar\omega}} \frac{\hbar}{i}\frac{\partial \Psi(x)}{\partial x} - \sqrt{\frac{m\omega}{\hbar}} \frac{1}{\sqrt{m\hbar\omega}} \frac{\hbar}{i}\frac{\partial}{\partial x}\left(x\Psi(x)\right)$$

$$= -\frac{1}{i}\Psi(x) = i\Psi(x) \Rightarrow [\hat{X}, \hat{P}_x] = i$$

c) Rappel : $(\hat{A}+\hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$; $(\hat{A}+i\hat{B})^\dagger = \hat{A}^\dagger - i\hat{B}^\dagger$; $(AB)^\dagger = B^\dagger A^\dagger$

$\hat{X}$ et $\hat{P}_x$ hermitiques donc $\hat{X}^\dagger = \hat{X}$ et $\hat{P}_x^\dagger = \hat{P}_x$

$(\hat{a})^\dagger = \frac{1}{\sqrt{2}}(\hat{X}^\dagger - i\hat{P}_x^\dagger) = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P}_x) = \hat{a}^\dagger$ $\quad$ $\hat{a}$ et $\hat{a}^\dagger$ sont adjoints

$$[\hat{a}, \hat{a}^\dagger]\Psi(x) = \left[\frac{1}{\sqrt{2}}(\hat{X}+i\hat{P}_x)\frac{1}{\sqrt{2}}(\hat{X}-i\hat{P}_x) - \frac{1}{2}(\hat{X}-i\hat{P}_x)(\hat{X}+i\hat{P}_x)\right]\Psi(x)$$

$$= \frac{1}{2}\left(\hat{X}^2\cancel{\Psi(x)} + i\hat{P}_x\hat{X}\Psi(x) - i\hat{X}\hat{P}_x\Psi(x) + \hat{P}_x^2\cancel{\Psi(x)}\right)$$

$$- \frac{1}{2}\left(\hat{X}^2\cancel{\Psi(x)} - i\hat{P}_x\hat{X}\Psi(x) + i\hat{X}\hat{P}_x\Psi(x) + \hat{P}_x^2\cancel{\Psi(x)}\right)$$

$$= i[\hat{P}_x, \hat{X}]\Psi(x) = i(-i)\Psi(x) = \Psi(x) \Rightarrow [\hat{a}, \hat{a}^\dagger] = 1$$

$\hat{a}$ et $\hat{a}^\dagger$ ne sont pas hermitiques $\Rightarrow$ pas associés à des observables

d) $\hat{N} = \hat{a}^\dagger\hat{a}$, $\hat{N}^\dagger = (\hat{a}^\dagger\hat{a})^\dagger = a^\dagger(\hat{a}^\dagger)^\dagger = \hat{a}^\dagger\hat{a} = \hat{N}$

$\Rightarrow \hat{N}$ est hermitique

$$\hat{N} = \frac{1}{2}(\hat{X} - i\hat{P}_x)(\hat{X} + i\hat{P}_x) = \frac{1}{2}\left(\hat{X}^2 + i\underbrace{[\hat{X}, \hat{P}_x]}_{i} + \hat{P}_x^2\right) = \frac{1}{2}\left(\hat{X}^2 + \hat{P}_x^2 - 1\right)$$

$$\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)$$

$|\Psi\rangle$ vecteur propre de $\hat{N}$ $\Rightarrow$ $\hat{N}|\Psi\rangle = \lambda|\Psi\rangle \Leftrightarrow \hbar\omega\hat{N}|\Psi\rangle = \hbar\omega\lambda|\Psi\rangle$

$\Leftrightarrow \hbar\omega(\hat{N} + \frac{1}{2})|\Psi\rangle = \underbrace{\hbar\omega(\lambda + \frac{1}{2})}_{E}|\Psi\rangle \Leftrightarrow \hat{H}|\Psi\rangle = E|\Psi\rangle$

$|\Psi\rangle$ est vecteur propre de $\hat{N}$, de valeur propre λ et vecteur propre de $\hat{H}$, de valeur propre $E = \hbar\omega(\lambda + \frac{1}{2})$

$\Rightarrow$ si l'on calcule λ, on pourra calculer l'énergie du système.

(2)

2) a) $[\hat{N}, \hat{a}]\Psi = \hat{N}\hat{a}\Psi - \hat{a}\hat{N}\Psi = (\hat{a}^\dagger\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger\hat{a})\Psi$

$= (\underbrace{[\hat{a}^\dagger, \hat{a}]}_{-1}\hat{a})\Psi = -\hat{a}\Psi$, $[\hat{N}, \hat{a}] = -\hat{a}$

$[\hat{N}, \hat{a}^\dagger]\Psi = (\hat{N}\hat{a}^\dagger - \hat{a}^\dagger\hat{N})\Psi = (a^\dagger\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a})\Psi = \hat{a}^\dagger\underbrace{[\hat{a}, \hat{a}^\dagger]}_{1}\Psi = \hat{a}^\dagger\Psi$

$\Leftrightarrow [\hat{N}, \hat{a}^\dagger] = +\hat{a}^\dagger$

b) $\hat{N}$ est hermitique $\Leftrightarrow \lambda \in \mathbb{R}$

$\hat{N}|\Psi_\lambda\rangle = \lambda|\Psi_\lambda\rangle = \hat{a}^\dagger\hat{a}|\Psi_\lambda\rangle$ $\quad \times \langle\Psi_\lambda|$

$\Leftrightarrow \quad \lambda\langle\Psi_\lambda|\Psi_\lambda\rangle = \langle\Psi_\lambda|\hat{a}^\dagger\hat{a}|\Psi_\lambda\rangle$

$\Leftrightarrow \quad \lambda\underbrace{\langle\Psi_\lambda|\Psi_\lambda\rangle}_{>0} = \underbrace{\|\hat{a}|\Psi_\lambda\rangle\|^2}_{\geq 0} \quad \Leftrightarrow \lambda \geq 0$

Rq : si $\lambda = 0$; $\|\hat{a}|\Psi_\lambda\rangle\|^2 = 0 \Leftrightarrow a|\Psi_\lambda\rangle = 0$

c) de même si $\lambda \neq 0$, $\hat{a}|\Psi_\lambda\rangle \neq 0$ $\quad ([\hat{N}, \hat{a}] = -\hat{a})$

$\hat{a}|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$: $\hat{N}\hat{a}|\Psi_\lambda\rangle = -\hat{a}|\Psi_\lambda\rangle + \hat{a}\hat{N}|\Psi_\lambda\rangle$

$= -\hat{a}|\Psi_\lambda\rangle + \hat{a}\lambda|\Psi_\lambda\rangle$

$\hat{N}\hat{a}|\Psi_\lambda\rangle = (\lambda - 1)\hat{a}|\Psi_\lambda\rangle$

$\Rightarrow$ valeur propre associée à $|\Psi_\lambda\rangle$: $(\lambda - 1)$

si $\lambda \neq 0$ $\hat{a}^+|\Psi_\lambda\rangle \neq 0$

et $\hat{N}\hat{a}^+|\Psi_\lambda\rangle = \hat{a}^+|\Psi_\lambda\rangle + \hat{a}^+\hat{N}|\Psi_\lambda\rangle = (\lambda + 1)\hat{a}^+|\Psi_\lambda\rangle$

$\hat{a}^+$ opérateur création, si on l'applique à $|\Psi_\lambda\rangle$, on passe du niveau λ à $\lambda + 1$

$\hat{a}$ opérateur annihilation, ——— $|\Psi_\lambda\rangle$, ——— λ à $\lambda - 1$

d) Supposons λ non entier $\Leftrightarrow \lambda = m + q$ avec $m \in \mathbb{N}$ et $0 < q < 1$

$\hat{a}|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$, de valeur propre $\lambda - 1$

$\hat{a}^2|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$, de valeur propre $\lambda - 2$

...

$\hat{a}^{m+1}|\Psi_\lambda\rangle$ ——— $\hat{N}$, ——— $\lambda - m - 1$

or $\lambda = m + q$ avec $0 < q < 1$ donc $\lambda - m - 1 < 0$, ce qui n'est pas possible puisque les valeurs propres $\in \mathbb{R}^+$.

Donc λ ne peut pas ~~ne~~ pas être entier $\Rightarrow \lambda \in \mathbb{N}$

2) d) Que se passe-t-il si $\lambda = m \in \mathbb{N}$?

$\hat{a}^m|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$, de valeur propre $\lambda - m = 0$

d'après 2) b) on sait que $\hat{a}^{m+1}|\Psi_\lambda\rangle = 0$

$\Rightarrow$ dans ce cas on n'obtient pas de $|\Psi\rangle$ non nul vecteur propre de $\hat{N}$ de valeur propre <0 $\Rightarrow$ c'est possible $\Rightarrow m \in \mathbb{N}$.

e) $\hat{a}^m|\Psi_\lambda\rangle$ est le vecteur propre $|\Psi_0\rangle$ de valeur propre $\lambda = 0$

si j'applique $\hat{a}^+$ à $|\Psi_0\rangle$ j'ai $\hat{a}^+|\Psi_0\rangle$ ——— $\lambda = 1$

$\hat{a}^{+2}|\Psi_0\rangle$ ——— $\lambda = 2$

⋮

et $\forall k \in \mathbb{N}$, $\hat{a}^{+k}|\Psi_0\rangle$ ——— $\lambda = k$

donc tous les vecteurs propres $|\Psi_m\rangle$ peuvent être obtenus en appliquant $\hat{a}^+$, à partir de $|\Psi_0\rangle$

f) Pour $\lambda = 0$, $\hat{a}|\Psi_0\rangle = 0 \Leftrightarrow \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}_x)|\Psi_0\rangle = 0$

$$\Leftrightarrow \sqrt{\frac{m\omega}{\hbar}}\, x\,\Psi_0(x) + \frac{i}{\sqrt{m\hbar\omega}}\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_0(x) = 0$$

$$\Leftrightarrow \frac{m\omega}{\hbar}x\,dx = -\frac{d\Psi_0(x)}{\Psi_0(x)}$$

$$\Leftrightarrow \Psi_0(x) = K\, e^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2}$$

$\Rightarrow$ la solution est unique car toutes les fonctions solutions de l'équation sont proportionnelles entre elles.

$\Rightarrow$ normalisation $\displaystyle\int_{-\infty}^{+\infty}\Psi_0^*\Psi_0\,dx = \int_{-\infty}^{+\infty}K^2 e^{-\frac{m\omega}{\hbar}x^2} = K^2\sqrt{\frac{\pi\hbar}{m\omega}} = 1$

$$\Leftrightarrow K = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

$$\Rightarrow \boxed{\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}}$$

g) Les valeurs propres de $\hat{H}$ sont $\hbar\omega(m+\frac{1}{2})$ avec $m \in \mathbb{N}$ (cf question 1.d)

$\Rightarrow$ pour $m=0$: $E_0 = \frac{\hbar\omega}{2}$ et $\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$

2) g) (suite) On construit les autres fonctions d'onde à partir de Ψ_0, en utilisant $\hat{a}^+$

$$|\Psi_1\rangle = \frac{\hat{a}^+|\Psi_0\rangle}{\underbrace{\sqrt{\langle\hat{a}^+\Psi_0|\hat{a}^+\Psi_0\rangle}}_{\text{normalisation}}} = \frac{\hat{a}^+|\Psi_0\rangle}{\sqrt{\langle\Psi_0|\hat{a}\hat{a}^+|\Psi_0\rangle}}$$

or $\hat{a}\hat{a}^+ = 1 + \hat{a}^+\hat{a} = 1 + \hat{N} \Leftrightarrow \langle\Psi_0|1+\hat{N}|\Psi_0\rangle = (1+0)\underbrace{\langle\Psi_0|\Psi_0\rangle}_{1}$

$\Leftrightarrow |\Psi_1\rangle = \frac{\hat{a}^+|\Psi_0\rangle}{\sqrt{1}}$ avec $E_1 = \hbar\omega(1+\frac{1}{2}) = \frac{3}{2}\hbar\omega$

de même $|\Psi_2\rangle = \frac{\hat{a}^+|\Psi_1\rangle}{\sqrt{\langle a^+\Psi_1|a^+\Psi_1\rangle}} = \frac{\hat{a}^{+2}|\Psi_0\rangle}{\sqrt{1\times 2}}$ avec $E_2 = \hbar\omega(2+\frac{1}{2}) = \frac{5}{2}\hbar\omega$

⋮

$|\Psi_m\rangle = \frac{(\hat{a}^+)^m|\Psi_0\rangle}{\sqrt{m!}}$ avec $E_m = \hbar\omega(m+\frac{1}{2})$

↳ ce sont les polynômes d'Hermite.

Dégénérescence ? Supposons $|\Psi_m\rangle$ vecteur propre de $\hat{N}$ de valeur propre m et non dégénéré

$\hat{N}|\Psi_m\rangle = m|\Psi_m\rangle$

est-ce que $|\Psi_{m+1}\rangle$ est également non dégénéré ?

on sait que $\hat{a}|\Psi_{m+1}\rangle$ est vecteur propre de $\hat{N}$, de valeur propre m

or, on suppose $|\Psi_m\rangle$ non dégénéré donc $|\Psi_m\rangle$ et $\hat{a}|\Psi_{m+1}\rangle$ sont proportionnels

$\hat{a}|\Psi_{m+1}\rangle = C\,|\Psi_m\rangle$

$\Leftrightarrow \hat{a}^+\hat{a}|\Psi_{m+1}\rangle = C\,\hat{a}^+|\Psi_m\rangle$

$\Leftrightarrow \hat{N}|\Psi_{m+1}\rangle = C\,\hat{a}^+|\Psi_m\rangle$

$\Leftrightarrow (m+1)|\Psi_{m+1}\rangle = C\,\hat{a}^+|\Psi_m\rangle$

$\Leftrightarrow |\Psi_{m+1}\rangle = \frac{C}{m+1}\hat{a}^+|\Psi_m\rangle$

$\Leftrightarrow \hat{a}^+|\Psi_m\rangle$ et $|\Psi_{m+1}\rangle$ sont proportionnels et associés à la même valeur propre

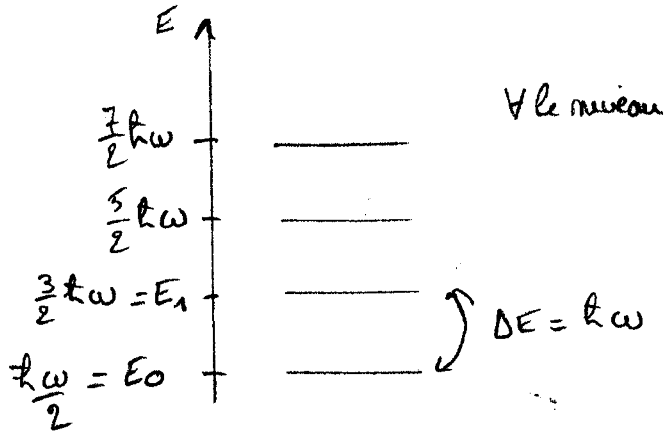
$\Rightarrow |\Psi_{m+1}\rangle$ non dégénéré.

or $|\Psi_0\rangle$ est non dégénéré $\Rightarrow |\Psi_1\rangle$ est non dégénéré

$\Rightarrow |\Psi_2\rangle$ ———

$\Rightarrow |\Psi_m\rangle$ est non dégénéré

Energie entre deux niveaux successifs : $\Delta E = E_{m+1} - E_m = \hbar\omega$ ne dépend pas de m



(seule transition permise)

∀ le niveau, pour passer au niveau supérieur, on absorbe toujours la même énergie $\hbar\omega$, donc le spectre d'absorption de vibration ne contient qu'une bande d'absorption correspondant à cette énergie.

2) b) L'énergie de l'état fondamental (appelé aussi l'énergie du vide), n'est pas nulle !

3) Molécule H-I, $k = 313{,}8\ N.m^{-1} = \omega^2 m \Rightarrow \omega = \sqrt{\frac{k}{m}}$

fréquence de l'oscillateur : $\nu_0 = \frac{\omega}{2\pi} = 6{,}89.10^{13}\ Hz$ et $\Delta E = \hbar\omega = \nu_0 h = 4{,}56.10^{-20} J$

$E = \frac{hc}{\lambda} \Rightarrow \lambda = 4{,}35.10^{-6}\ m \ \hat{=}\ \frac{1}{\lambda} = \frac{\nu_0}{c} = 2299\ cm^{-1}$

on observe une bande d'absorption caractéristique de la vibration de la liaison H-I dans l'infra-rouge.

4 - Model of the point charge elastically bound, in an electric field

- $\hat{H}(\mathcal{E}) = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - q\mathcal{E}\hat{x}$

- Schrödinger equation $\hat{H}(\mathcal{E})\chi = E(\mathcal{E})\chi$

energy in the presence of the electric field

wave function in the presence of the electric field

$$\Updownarrow$$

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + \frac{1}{2}m\omega^2x^2\chi - q\mathcal{E}x\chi = E(\mathcal{E})\chi$$

Since $\frac{1}{2}m\omega^2x^2 - q\mathcal{E}x = \frac{1}{2}m\omega^2\left(x^2 - \frac{2q\mathcal{E}}{m\omega^2}x\right)$

$$= \frac{1}{2}m\omega^2\left[\left(x - \frac{q\mathcal{E}}{m\omega^2}\right)^2 - \frac{q^2\mathcal{E}^2}{m^2\omega^4}\right]$$

$$(1) \Leftrightarrow \boxed{-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + \frac{1}{2}m\omega^2(x-x_0)^2\chi = \left(E(\mathcal{E}) + \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2}\right)\chi}$$

Let $x_0 = \frac{q\mathcal{E}}{m\omega^2}$, $E' = E(\mathcal{E}) + \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2}$ (2)

Change of variable $u = x - x_0$

$$\chi(x) = \chi(u + x_0) = \Phi(u)$$

$$\left.\frac{d\Phi}{du}\right|_u = \left.\frac{d\chi}{dx}\right|_{u+x_0} \quad \text{and} \quad \left.\frac{d^2\Phi}{du^2}\right|_u = \left.\frac{d^2\chi}{dx^2}\right|_{u+x_0}$$

Therefore (1) can be rewritten as

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\Phi}{du^2} + \frac{1}{2}m\omega^2u^2\Phi = E'\Phi} \quad (3)$$

(3) is formally identical to the Schrödinger equation of a 1D harmonic oscillator of energy E' and corresponding eigenfunction Φ.

- We know from section 2 that E' is quantized and can be written as $E'_n = (n + \frac{1}{2})\hbar\omega \quad n \in \mathbb{N}$

According to (2), the energy of a 1D harmonic oscillator in the presence of a static electric field is quantized and equals

$$E_n(\mathcal{E}) = E'_n - \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2}$$

$$\boxed{E_n(\mathcal{E}) = (n + \tfrac{1}{2})\hbar\omega - \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2} \quad , n \in \mathbb{N}}$$

- From section 2 we know that the eigenfunction Φ_n associated to E_n' is equal to ψ_n (← we explained previously how it can be obtained from the creation operator $\hat{a}^+$ and the vacuum wave function ψ_0)

$$\Phi_n(u) = \psi_n(u) = \chi_n(u + x_0)$$

Therefore the eigenfunction χ_n of the bound system in the presence of the electric field, associated to $E_n(\mathcal{E})$, is equal to

$$\boxed{\chi_n(x) = \psi_n(x - x_0)} \quad (4)$$

In the following we denote $\psi_n(\mathcal{E}) = \chi_n$ ← depends on $\mathcal{E}$ since $x_0 = \dfrac{q\mathcal{E}}{m\omega^2}$

We thus rewrite the Schrödinger equation as

$$\hat{H}(\mathcal{E})\psi_n(\mathcal{E}) = E_n(\mathcal{E})\psi_n(\mathcal{E}) \qquad \forall \mathcal{E}.$$

$$\Rightarrow \quad E_n(\mathcal{E})\langle \psi_n(\mathcal{E})|\psi_n(\mathcal{E})\rangle = \langle \psi_n(\mathcal{E})|\hat{H}(\mathcal{E})|\psi_n(\mathcal{E})\rangle$$

$$\Rightarrow \quad \frac{dE_n(\mathcal{E})}{d\mathcal{E}} = \frac{d}{d\mathcal{E}}\langle \psi_n(\mathcal{E})|\hat{H}(\mathcal{E})|\psi_n(\mathcal{E})\rangle$$

$$= \left\langle \frac{d\psi_n(\mathcal{E})}{d\mathcal{E}}\right|\hat{H}(\mathcal{E})|\psi_n(\mathcal{E})\rangle + \langle \psi_n(\mathcal{E})|\frac{\partial \hat{H}(\mathcal{E})}{\partial \mathcal{E}}|\psi_n(\mathcal{E})\rangle + \langle \psi_n(\mathcal{E})|\hat{H}(\mathcal{E})\left|\frac{d\psi_n(\mathcal{E})}{d\mathcal{E}}\right\rangle$$

$$= E_n(\mathcal{E})\left\langle\frac{d\psi_n(\mathcal{E})}{d\mathcal{E}}\middle|\psi_n(\mathcal{E})\right\rangle + \underbrace{\left\langle \hat{H}(\mathcal{E})\psi_n(\mathcal{E})\middle|\frac{d\psi_n(\mathcal{E})}{d\mathcal{E}}\right\rangle}_{E_n^*(\mathcal{E})\langle \psi_n(\mathcal{E})|\frac{d\psi_n(\mathcal{E})}{d\mathcal{E}}\rangle} + \langle \psi_n(\mathcal{E})|\frac{\partial \hat{H}(\mathcal{E})}{\partial \mathcal{E}}|\psi_n(\mathcal{E})\rangle$$

$$E_n^*(\mathcal{E}) = E_n(\mathcal{E})$$

<u>Comment:</u> Note that χ_n is normalized since, according to Eq.(4)

$$\langle \chi_n|\chi_n\rangle = \langle \psi_n(\mathcal{E})|\psi_n(\mathcal{E})\rangle = \int_{-\infty}^{+\infty} dx\, |\chi_n(x)|^2 = \int_{-\infty}^{+\infty} dx\, |\psi_n(x - x_0)|^2$$

$$= \int_{-\infty}^{+\infty} du\, |\psi_n(u)|^2 = 1$$

← the solution ψ_n of the 1D harmonic oscillator is normalized.

$$\frac{dE_n(\xi)}{d\xi} = E_n(\xi)\underbrace{\frac{d\langle\psi_n(\xi)|\psi_n(\xi)\rangle}{d\xi}}_{0} + \langle\psi_n(\xi)|\frac{\partial\hat{H}(\xi)}{\partial\xi}|\psi_n(\xi)\rangle$$

since $\langle\psi_n(\xi)|\psi_n(\xi)\rangle = 1 \;\; \forall \xi$

we thus obtain the Hellmann–Feynman theorem:

$$\boxed{\frac{dE_n(\xi)}{d\xi} = \langle\psi_n(\xi)|\frac{\partial\hat{H}(\xi)}{\partial\xi}|\psi_n(\xi)\rangle}$$

$$\frac{\partial\hat{H}(\xi)}{\partial\xi} = -q\hat{x} = -\hat{D}$$

$$\Rightarrow \boxed{\frac{dE_n(\xi)}{d\xi} = -\langle\hat{D}\rangle_{\psi_n(\xi)}}$$

$$E_n(\xi) = (n+\tfrac{1}{2})\hbar\omega - \frac{1}{2}\frac{q^2\xi^2}{m\omega^2} \rightarrow \frac{dE_n(\xi)}{d\xi} = -\frac{q^2\xi}{m\omega^2}$$

$$\Rightarrow \boxed{\langle\hat{D}\rangle_{\psi_n(\xi)} = \frac{q^2\xi}{m\omega^2}}$$

Static polarizability $\alpha(0) = \left.\frac{d\langle\hat{D}\rangle_{\psi_n(\xi)}}{d\xi}\right|_0 = \frac{q^2}{m\omega^2}$

↓

note that the static polarizability is a property of the system (nucleus + particle). It does not depend on the electric field!

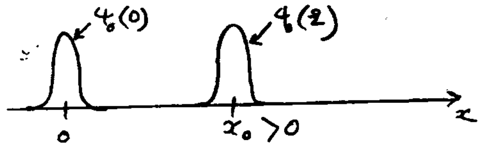
$$\langle\hat{D}\rangle_{\psi_n(\xi)} = \frac{q^2\xi}{m\omega^2} = q\underbrace{\langle\psi_n(\xi)|\hat{x}|\psi_n(\xi)\rangle}_{\langle\hat{x}\rangle_{\psi_n(\xi)}}$$

$$\Rightarrow \boxed{\langle\hat{x}\rangle_{\psi_n(\xi)} = \frac{q\xi}{m\omega^2} = x_0}$$

Comment: In the ground state ($n=0$) the wave function equals

$$\psi_0(\xi)_{(x)} = \chi_0(x) = \psi_0(x-x_0) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}(x-x_0)^2}$$

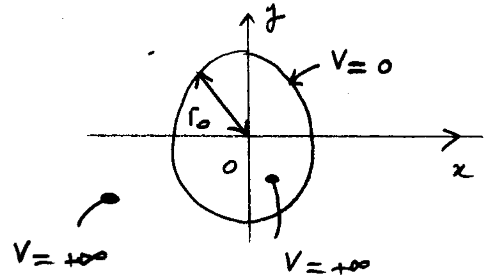
if $q>0$ and $\xi>0$: $x_0>0$ which is consistent with classical mechanics



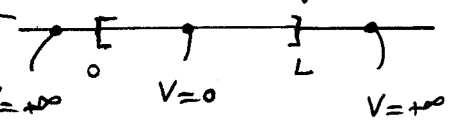
Tutorial: rotational energy of a diatomic molecule

1. Planar rotator

1-1.

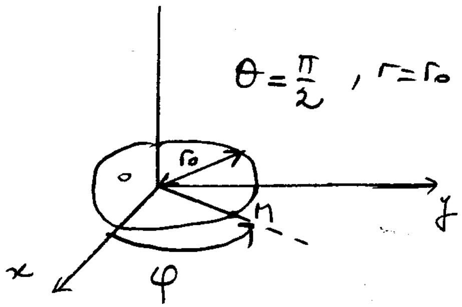


The potential energy is infinite inside and outside the circle. It equals zero on the circle. Thus the particle is "free" to move on the circle.
For the particle on a straight line we had the potential energy infinite outside the segment and $V=0$ on the segment



1-2.

$\theta = \frac{\pi}{2}$, $r = r_0$



Schrödinger equation $\hat{H}\psi = E\psi$ on the circle

where $\psi(r,\theta,\varphi) = \psi(\varphi)$

and $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2$

Thus $\hat{H}\psi = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\mathrm{tg}\,\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\right]\psi$

$\frac{\partial^2}{\partial r^2} r\psi = \frac{\partial}{\partial r}\left(\psi + r\underbrace{\frac{\partial\psi}{\partial r}}_{0}\right) = 0$

$\frac{\partial\psi}{\partial\theta} = 0$

$\Rightarrow \hat{H}\psi = -\frac{\hbar^2}{2\mu r_0^2}\frac{\partial^2}{\partial\varphi^2}\psi$

The Hamiltonian of a planar rotator can therefore be written as

$$\boxed{\hat{H}_{PR} = -\frac{\hbar^2}{2\mu r_0^2}\frac{\partial^2}{\partial\varphi^2}}$$

1-3. $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi} \Rightarrow \hat{L}_z^2 = -\hbar^2\frac{\partial^2}{\partial\varphi^2}$

$$\boxed{\hat{H}_{PR} = \frac{\hat{L}_z^2}{2I}}$$

1-4- $[\hat{H}_{PR}, \hat{L}_z] = \frac{1}{2I}[\hat{L}_z^2, \hat{L}_z] = 0$

$\hat{H}_{PR}$ and $\hat{L}_z$ are two commuting hermitian operators. We can therefore find a common orthonormal basis of eigenfunctions

1-5- According to Exercise 3 in the tutorial "postulats of quantum mechanics and Dirac formalism" the normalized eigenfunctions of $\hat{L}_z$ are $\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$ $(m \in \mathbb{Z})$ with the associated eigenvalue $m\hbar$.

1-6- Let us check that Φ_m is also an eigenfunction of $\hat{H}_{PR}$:

$$\hat{H}_{PR}\Phi_m = \frac{1}{2I}\hat{L}_z(\hat{L}_z\Phi_m) = \frac{1}{2I}\hat{L}_z(m\hbar\Phi_m) = \frac{m\hbar}{2I}\underbrace{\hat{L}_z\Phi_m}_{m\hbar\Phi_m}$$

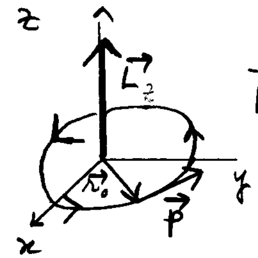
$$\boxed{\hat{H}_{PR}\Phi_m = E_m\Phi_m \quad \text{with} \quad \underbrace{\underset{m\in\mathbb{Z}}{E_m = \frac{(m\hbar)^2}{2I}}}_{\text{quantized energy}}}$$

For $m \neq 0$ the degeneracy is 2 since Φ_m and Φ_{-m} are associated to the same energy. (*)

With $B = \frac{h^2}{8\pi^2 I} = \frac{\hbar^2}{2I}$

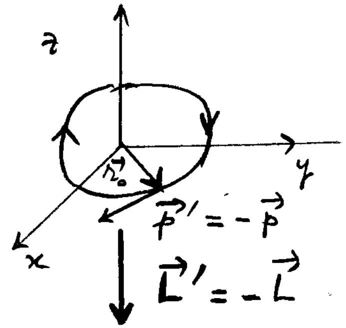
$$\boxed{E_m = m^2 B}$$

(*) Comment: $m > 0$ means, from a classical mechanics point of view, that the particle rotates this way



$\vec{L} = \vec{r}_0 \wedge \vec{p} = \underbrace{L_z}_{>0}\vec{e}_z$

And $m < 0$ means that the particle rotates the other way around



$\vec{L}' = \vec{r}_0 \wedge \vec{p}' = \underbrace{L'_z}_{<0}\vec{e}_z$, $\quad L'_z = -L_z$

In both cases the kinetic energy should be the same since $p' = p$ ⇒ We get the same result in quantum mechanics.

if $m = 0$ $\quad E_0 = 0$ and $\Phi_0(\varphi) = \frac{1}{\sqrt{2\pi}} \neq 0$

$m = 0$ is a physical solution

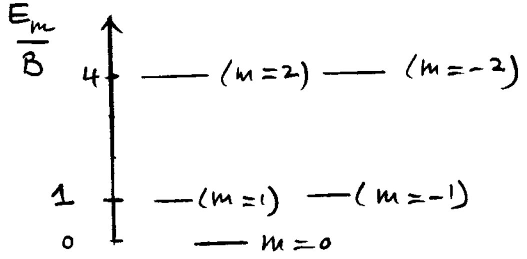
1-7- $E_{m+1} - E_m = (m+1)^2 B - m^2 B = \boxed{B(2m+1) = \Delta E_m}$

ΔE_m is not constant like for the harmonic oscillator.

$E_0 = 0$

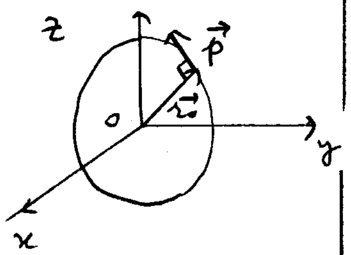
$E_1 = B$

$E_2 = 4B$



2- Rigid rotator

2-1- In classical mechanics



$\vec L = \vec r_0 \wedge \vec p$ and $\vec r_0 \perp \vec p$

since the particle moves on a sphere

Therefore $\|\vec L\| = r_0 \cdot p$

$L^2 = r_0^2 p^2$

The energy is only kinetic

$$\boxed{E = \frac{p^2}{2\mu} = \frac{L^2}{2\mu r_0^2}}$$

In quantum mechanics; the Hamiltonian of the rigid rotator equals then

$$\boxed{\hat H_{RR} = \frac{\hat L^2}{2I}}$$

2.2 $[\hat H_{RR}, \hat L^2] = \frac{1}{2I}[\hat L^2, \hat L^2] = 0 \rightarrow$ common orthonormal basis of eigenfunctions

The eigenfunctions of $\hat L^2$ are the spherical harmonics

$\hat L^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2 Y_l^m(\theta,\varphi) \quad l \in \mathbb{N}$

$\hat L_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi) \quad m \in \mathbb{Z}$, $-l \leq m \leq +l$

$$\hat H_{RR} Y_l^m = \frac{1}{2I} \hat L^2 Y_l^m = \frac{l(l+1)\hbar^2 Y_l^m}{2I}$$

$$\boxed{\hat H_{RR} Y_l^m = E_l Y_l^m \quad \text{with } E_l = l(l+1)B, \ l \in \mathbb{N}}$$

The energy is quantized and the degeneracy equals to $2l+1$ since $m = -l, -l+1, \dots, 0, 1, \dots, l$ give the same energy E_l

2-3- $\Delta E_\ell = E_{\ell+1} - E_\ell = (\ell+2)(\ell+1)B - \ell(\ell+1)B$

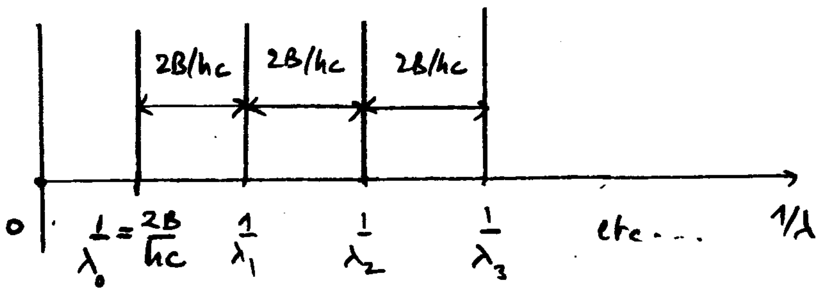
$\boxed{\Delta E_\ell = 2(\ell+1)B} \neq$ constant.

The frequency ν_ℓ corresponding to the transition $\ell \to \ell+1$ fulfills $h\nu_\ell = \Delta E_\ell = 2(\ell+1)B$

$$\lambda_\ell = \frac{c}{\nu_\ell} \Rightarrow \frac{1}{\lambda_\ell} = \frac{\nu_\ell}{c} = \boxed{\frac{2(\ell+1)B}{hc} = \frac{1}{\lambda_\ell}}$$

$$\boxed{\frac{1}{\lambda_{\ell+1}} - \frac{1}{\lambda_\ell} = \frac{2B}{hc} = cst}$$

If transitions occur only between adjacent levels the adsorption spectrum should look like:



3- Applications

3-1-1- The experimental spectrum in figure 1 matches the theoretical one with $\frac{2B}{hc} = 20{,}7\ cm^{-1}$.

Note that the transition $1 \to 2$ should occur, according to question 2-3, for the wave number

$$\frac{1}{\lambda_1} = 2 \times \frac{2B}{hc} = 41{,}4\ cm^{-1}$$

according to experiment

and that is what can be seen on the experimental spectrum.

Everything is consistent!

The selection rule is therefore $\Delta\ell = \pm 1$ for purely rotational transitions ($\Delta\ell = +1$ for absorption and $\Delta\ell = -1$ for emission)

3-1-2-

* $\frac{1}{\lambda_{\ell+1}} - \frac{1}{\lambda_\ell} = 2\bar{B} = \frac{2B}{hc} \Rightarrow \bar{B} = \frac{B}{hc}$

* $\bar{B} = \frac{1}{hc} \cdot \frac{h^2}{8\pi^2 \mu r_0^2}$ where $\mu = \frac{35\, m_p^2}{36\, m_p}$

$\mu = \frac{35}{36} m_p$

$$\boxed{r_0^2 = \frac{h}{c} \cdot \frac{1}{8\pi^2 \bar{B}} \frac{36}{35\, m_p}}$$

$r_0 \simeq 1{,}3$ Å

3-2-1- transition of lowest energy $0 \rightarrow 1$ $(\Delta E_1 = 2B)$

3-2-2- $\frac{1}{\lambda_0} = 3.84235\ cm^{-1} \Rightarrow \lambda_0 \simeq \underbrace{2{,}6\ 10^{-3}\ m}_{\text{microwave}}$

Vibrational transitions occur in the infrared domain (with $\Delta n = \pm 1$), that is for smaller wave lengths. $(\lambda_{microwave} > \lambda_{infrared})$
We can thus conclude that adjacent rotational energy levels are much closer to each other energetically than adjacent vibrational levels.

3-2-3- $\frac{1}{\lambda_0} = \frac{2B}{hc} \Rightarrow B = \frac{hc}{2\lambda_0} \simeq 3{,}816\ 10^{-23}\ J$

3-2-4- $B = \frac{h^2}{8\pi^2 I} \Rightarrow I = \frac{h^2}{8\pi^2 B} \simeq 1{,}457\ 10^{-46}\ m^2 kg$

$r_0^2 = \frac{I}{\mu} \Rightarrow r_0 = \left(\frac{I}{\mu}\right)^{1/2} \simeq \boxed{1{,}13\ \mathring{A} \simeq r_0}$