Atomes & Molécules

Mécanique quantique

Physique atomique : → test le plus précis pour la mécanique quantique

→ contrôle sur l'état des atomes (et molécules)

→ métrologie quantique

→ simulation quantique

→ ordinateur quantique

Rappels de MQ

Etat d'un système $|\psi\rangle \in \mathcal{H}$ espace de Hilbert

Base de $\mathcal{H}$ $|\phi_n\rangle$ $n = 1, \dots, \dim(\mathcal{H})$

$$\sum_{n=1}^{\dim(\mathcal{H})} |\phi_n\rangle\langle\phi_n| = \mathbb{1}_{\mathcal{H}}$$

$$|\psi\rangle = \sum_{n=1}^{\dim(\mathcal{H})} \overbrace{\langle\phi_n|\psi\rangle}^{c_n} |\phi_n\rangle$$

$c_n \in \mathbb{C}$

$$|\psi\rangle \leftrightarrow (c_1, c_2, \dots, c_{\dim(\mathcal{H})}) \in \mathbb{C}^{\dim(\mathcal{H})}$$

Observables $\leftarrow$ $\hat{A}$ opérateurs (matrices)

hermitien : $\hat{A}^+ = \hat{A}$

$\langle \phi_n | \hat{A} | \phi_m \rangle = \langle \phi_m | \hat{A} | \phi_n \rangle^*$

nombre complexe

Base d'états propres de $\hat{A}$

$$\hat{A} | \psi_a \rangle = a | \psi_a \rangle$$

$a \in \mathbb{R}$ valeur propre

→ résultats possibles d'une mesure de $\hat{A}$

$\hat{A} = \hat{\mathcal{H}}$ Hamiltonien → énergie

$|\psi(0)\rangle$ au temps $t=0$

$$i\hbar \frac{d}{dt} |\psi\rangle = \hat{\mathcal{H}} |\psi\rangle$$

$\hat{\mathcal{H}}$ est indé pendant du temps

$\hbar = 1.054 \times 10^{-34}$ J-s

$$|\psi(t)\rangle = e^{-i/\hbar \hat{\mathcal{H}} t} |\psi(0)\rangle$$

États stationnaires → états propres de $\hat{\mathcal{H}}$

$$\hat{H}|\psi_E\rangle = E|\psi_E\rangle \qquad E \in \mathbb{R}$$

$$|\psi_E(t)\rangle = e^{-i/\hbar E t}|\psi_E\rangle$$

Évolution temporelle : existence de quantité conservée

$\exists \hat{A}_i$: $\langle\psi(t)|\hat{A}_i|\psi(t)\rangle$

$= \langle\psi(0)|\hat{A}_i|\psi(0)\rangle \quad \forall t$

$$\Updownarrow$$

$$[\hat{A}_i, \hat{H}] = \hat{A}_i\hat{H} - \hat{H}\hat{A}_i = 0$$

$\hat{A}_i$ et $\hat{H}$ commutent

$$e^{+i/\hbar \hat{H} t}\hat{A}_i e^{-i/\hbar \hat{H} t} = \hat{A}_i$$

$\hat{A}_i|\psi_{a_i}\rangle = a_i|\psi_{a_i}\rangle$

$i = 1, 2, \dots, M$

$\hat{H}|\psi_E\rangle = E|\psi_E\rangle$

admettent une base commune d'états propres

$\rightarrow |E, a_1, a_2, \dots a_M\rangle$

$\underbrace{E, a_1, a_2, \dots a_M}_{\text{nombres quantiques}}$

$$[\hat{A}_i, \hat{A}_j] = 0 \quad \forall i, j$$

si l'état est uniquement défini par $E, a_1, a_2 \ldots$ (pas de dégénérescence = je n'ai pas deux états différents avec les mêmes étiquettes)

$\Rightarrow$ ensemble <u>complet</u> d'observables qui commutent (ECOC)

Commutation $[\hat{H}, \hat{A}_i] = 0 \Rightarrow \hat{A}_i$ est conservé dans l'évolution temporelle

<u>symétrie</u> de $\hat{H}$

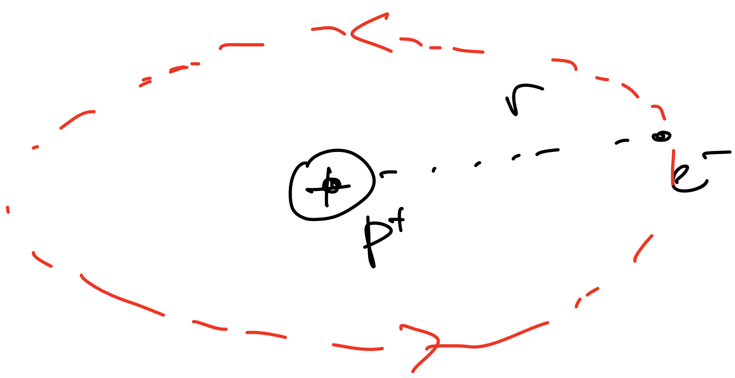
$$\downarrow$$

$$e^{i\varphi \hat{A}_i} \hat{H} e^{-i\varphi \hat{A}_i} = \hat{H}$$

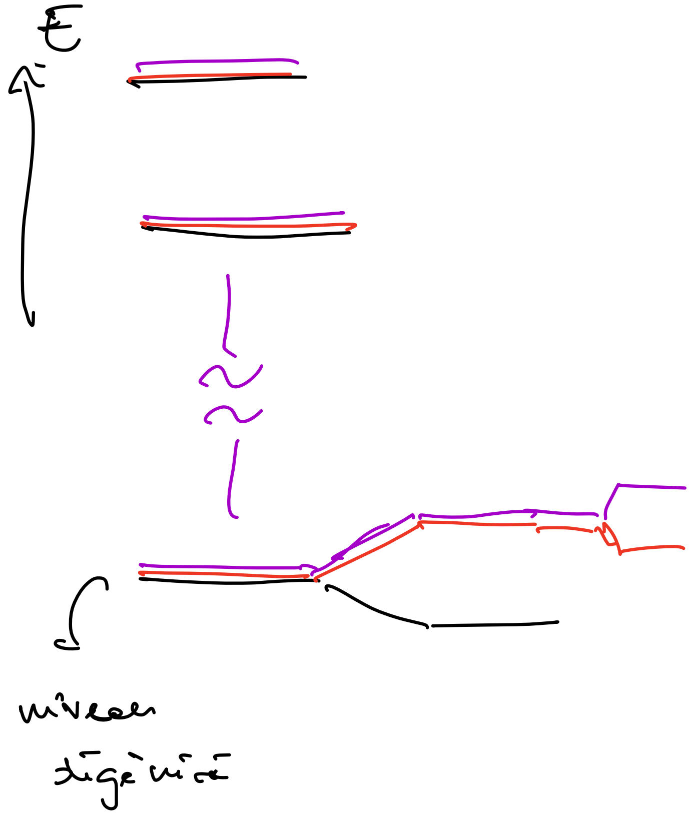
symétrie

$U^{-1} = U^{+}$

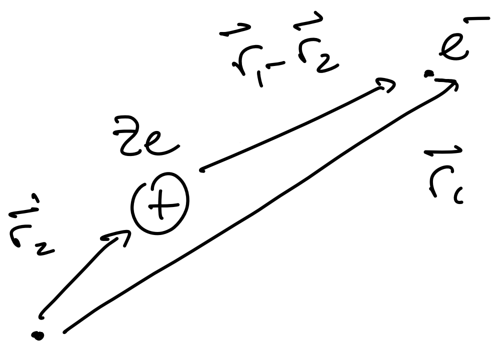
unitaire



symétrie $\Rightarrow |E, a_1, a_2, \ldots\rangle$



Atome d'hydrogène : Théorie non-relativiste / de Schrödinger



m : électron

M : noyau

$M \sim 10^3 \ m$

classique

$$E = \frac{1}{2} m \dot{\vec{r}}_1^{\,2} + \frac{1}{2} M \dot{\vec{r}}_2^{\,2} - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

Variable centre de masse

$$\vec{R} = \frac{m\vec{r}_1 + M\vec{r}_2}{m+M}$$

Variable relative $\qquad \vec{r} = \vec{r}_1 - \vec{r}_2$

$$E = \frac{1}{2}\mu \dot{\vec{r}}^{\,2} + \frac{1}{2}(m+M)\dot{\vec{R}}^{\,2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\mu = \frac{mM}{m+M} \simeq m$$

$$\vec{p} = \mu \dot{\vec{r}} \qquad \vec{P} = (m+M)\dot{\vec{R}}$$

$$E = \frac{\vec{P}^{\,2}}{2(m+M)} + \frac{\vec{p}^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

quantification de $\vec{p}, \vec{r}$

$$(p_x, p_y, p_z) \qquad (x, y, z)$$

$$(\hat{p}_x, \hat{p}_y, \hat{p}_z) \qquad (\hat{x}, \hat{y}, \hat{z})$$

$$[\hat{x}, \hat{p}_x] = i\hbar \qquad [\hat{x}, \hat{p}_y] = 0 \quad \text{(ex.)}$$

$$\hat{y} \quad \hat{p}_y \qquad [\hat{x}, \hat{y}] = 0$$

$$\hat{z} \quad \hat{p}_z$$

$$\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \hat{\frac{1}{r}} = \hat{f}(\hat{x}, \hat{y}, \hat{z}) = \frac{1}{\sqrt{\hat{x}^2 + \hat{y}^2 + \hat{z}^2}}$$

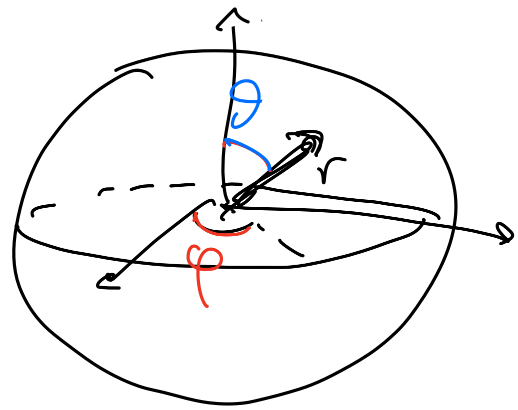
$$\hat{H}|\psi_E\rangle = E|\psi_E\rangle \quad \leftarrow$$

vecteurs propres de $\hat{x}, \hat{y}, \hat{z}$ $\quad |\vec{r}\rangle = |x, y, z\rangle$

$$\underbrace{\langle\vec{r}|\hat{H}|\psi_E\rangle}_{\uparrow} = E\underbrace{\langle\vec{r}|\psi_E\rangle}_{\psi(\vec{r})}$$

$$\left(-\frac{\hbar^2}{2\mu}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi(\vec{r}) = E\,\psi(\vec{r})$$

$$(x, y, z) \rightarrow (r, \vartheta, \varphi)$$



$$\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r(.)) + \frac{1}{r^2}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}(.)\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right]$$

Moment cinétique / angulaire

$$\vec{L} = \vec{r}\times\vec{p} \rightarrow \hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}}$$

$$= \left(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y,\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z,\ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \right)$$

$$\underline{\langle \vec{r} | \hat{p}_x | \psi \rangle} = \underline{-i\hbar \frac{\partial}{\partial x} \psi(\vec{r})}$$

representation
x

$$\vec{L} \rightarrow -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y},\ \cdots,\ \cdots \right)$$

$$\hat{L}^x \qquad \hat{L}^y \qquad L^z$$

$$\hat{L}^x \rightarrow i\hbar \left(\cos\phi \cot\vartheta \frac{\partial}{\partial \varphi} + \sin\varphi \frac{\partial}{\partial \vartheta} \right)$$

$$\hat{L}^y \rightarrow i\hbar \left(\sin\phi \cot\vartheta \frac{\partial}{\partial \varphi} - \cos\varphi \frac{\partial}{\partial \vartheta} \right)$$

$$\hat{L}^z \rightarrow -i\hbar \frac{\partial}{\partial \varphi}$$

$$\vec{L}^2 \rightarrow -\hbar^2 \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial \vartheta} \left(\sin\vartheta \frac{\partial}{\partial \vartheta} (\cdot) \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial \varphi^2} \right]$$

$$\hat{H} \rightarrow -\frac{\hbar^2}{2\mu} \underbrace{\frac{1}{r} \frac{\partial^2}{\partial r^2} (r(\cdot))} + \frac{\hat{\vec{L}}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$[\hat{H}, \hat{\vec{L}}^2] = 0 \qquad \leftarrow$$

Rappel du moment cinétique en MQ

$(\hat{L}^x, \hat{L}^y, \hat{L}^z)$ $\alpha = x, y, z$

β

γ

$$[\hat{L}^\alpha, \hat{L}^\beta] = i\hbar\, \epsilon_{\alpha\beta\gamma}\, \hat{L}^\gamma$$

$$\epsilon_{\alpha\beta\gamma} = \begin{cases} 1 & \alpha\beta\gamma \text{ est une permutation paire de } xyz \ (yzx,\ zxy) \\ -1 & \text{" " impaire "} \\ 0 & \text{autrement} \end{cases}$$

$$[\hat{L}^x, \hat{L}^y] = i\hbar \hat{L}^z$$

$$[\hat{L}^y, \hat{L}^z] = i\hbar \hat{L}^x$$

$$[\hat{\vec{L}}^2, \hat{L}^\alpha] = 0$$ $\underline{\underline{\alpha = z}}$

états simultanés de $\hat{\vec{L}}^2$ et $\hat{L}^z$

$|l, m\rangle$ l m

$$\begin{cases} \hat{\vec{L}}^2 \, |l, m\rangle = \hbar^2 l(l+1) \, |l, m\rangle \\ \hat{L}^z \, |l, m\rangle = \hbar m \, |l, m\rangle \end{cases}$$

$$l = 0, 1, 2, 3, \ldots \in \mathbb{N}$$

$$m = -l, -l+1, \ldots, l$$

$$\begin{cases} \langle r, \vartheta, \phi | \hat{L}^z | l m\rangle = \hbar m \langle r, \vartheta, \phi | l, m\rangle \\ \underbrace{\langle r, \vartheta, \phi | \hat{\vec{L}}^2 | l, m\rangle}_{} = \hbar^2 l(l+1) \langle r, \vartheta, \phi | l, m\rangle \end{cases}$$

$$(\varphi \leftrightarrow \phi)$$

$$\hat{\vec{L}}^2 \, \psi_{lm}(r, \vartheta, \phi) = \hbar^2 l(l+1) \, \psi_{lm}(r, \vartheta, \phi)$$

$$\psi_{lm}(r, \vartheta, \phi) = R_{lm}(r) \, \underbrace{Y_{lm}(\vartheta, \phi)}_{}$$

harmoniques sphériques

$$\underline{Y_{lm}(\vartheta, \phi)} = \Theta_{lm}(\vartheta) \, \frac{e^{im\phi}}{\sqrt{2\pi}} \in \mathbb{C}$$

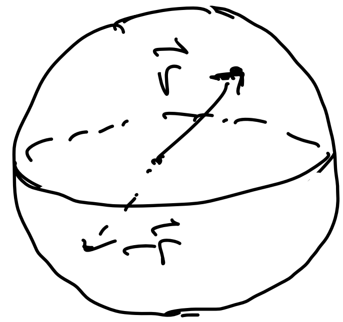
parité sous l'inversion de l'espace

$$Y_{lm}(\vartheta,\phi) \longrightarrow (-1)^{l}\, Y(\vartheta,\phi)$$

$\phi \to \phi + \pi$

$\vartheta \to \pi - \vartheta$

parité des harmoniques sphériques



Representation des $Y_{lm}(\vartheta\ \phi)$

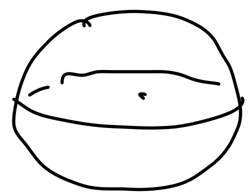
$Re[\,Y_{lm}(\vartheta,\phi)\,]$

surfaces telles que la distance de l'origine vaut $|Re[\,Y_{lm}(\vartheta\ \phi)\,]|$

normalisation $\displaystyle\int_0^{\pi} d\vartheta\ \sin\vartheta \int_0^{2\pi} d\phi\ |Y_{lm}|^2 = 1$

$l=0$

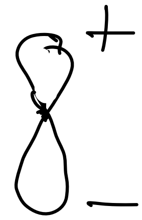
$$Y_{0,0}(\vartheta,\phi) = \frac{1}{\sqrt{4\pi}}$$



onde s

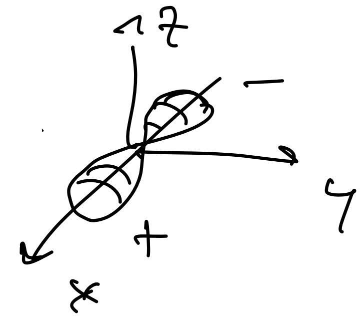
$l = 1 \qquad m = -1, 0, 1$

$$Y_{10}(\vartheta,\phi) = \sqrt{\frac{3}{4\pi}}\ \cos\vartheta$$



onde p

$$Y_{1,\pm 1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{\pm i\phi}$$



$l=2$ $(\ldots)$

Structure radiale des fonctions propres de l'atome d'hydrogène

$$\hat{H} \to -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial^2}{\partial r^2}(r(\cdot)) + \frac{\vec{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$[\hat{H}, \hat{L}^2] = 0$ $\quad [\hat{H}, \hat{L}_z] = 0$

$[\hat{L}^2, \hat{L}_z] = 0$ $\quad \hat{H}, \vec{L}^2, L_z = \text{ECOC}$

$$\Rightarrow \psi(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$$

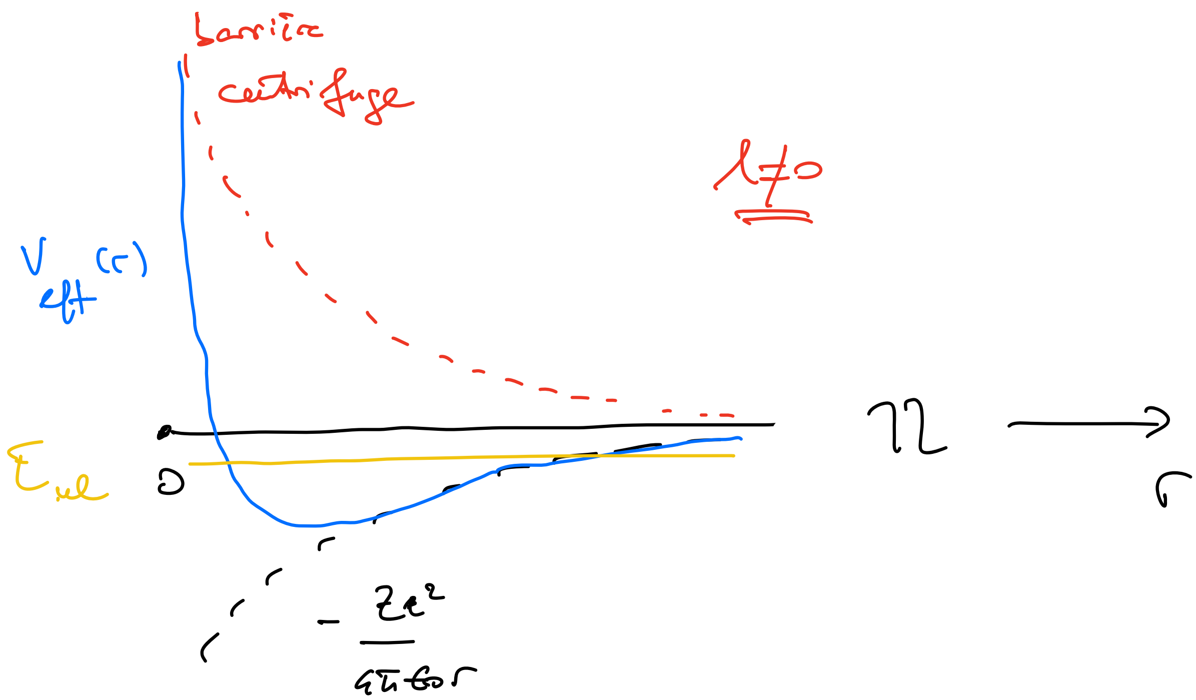
$$\Rightarrow H\psi = E\psi$$

$$H\psi = \left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}(r R_{nl}) + \frac{\hbar^2 l(l+1)}{2\mu r^2} R_{nl}\right.$$

$$-\frac{Ze^2}{4\pi\varepsilon_0 r} R_{nl} \Big] \cancel{Y_{lm}(\theta,\phi)} = E_{nl} R_{nl} \cancel{Y_{lm}}$$

$$R_{nl}(r) = \frac{u_{nl}(r)}{r}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} u_{nl}(r) + \underbrace{\left(\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)}_{V_{eff}(r)} u_{nl}(r) = E_{nl}\, u_{nl}$$



<u>états liés</u> $\underline{E_{nl} < 0}$

longueur adimensionnée $\rho = \frac{r}{a_0}$

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2 (Z)}$$

~~dans~~ la suite $Z = 1$

$\mu = m$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = \text{rayon de Bohr}$$

$$\simeq 0.5\ldots \text{Å}$$

$$= 5\ldots \times 10^{-11}\ m$$

$$\frac{\hbar^2}{2 m a_0^2} = Ry = \underline{13.6\ eV}$$

$$= 13.6 \times 1.6 \times 10^{-19}\ J$$

$$= \hbar \quad 2 \times 10^{16}\ Hz$$

$$\underbrace{-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} u_{nl}(r)} + \left(\overbrace{\frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2}} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) u_{nl}(r) = E_{nl}\, u_{nl}$$

$$v_{nl}(\rho) = u_{nl}(a_0 \rho) \qquad 2Ry$$

$$\left[-\frac{\hbar^2}{2\mu a_0^2} \frac{d^2}{d\rho^2} + \frac{\hbar^2}{2\mu a_0^2} \frac{l(l+1)}{\rho^2} - \frac{Ze^2}{4\pi\epsilon_0 a_0} \frac{1}{\rho} \right] v_{nl}$$

$$= E_{nl}\, v_{nl}$$

$$\left[-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{2}{\rho} \right] v_{nl} = \epsilon_{nl}\, v_{nl}$$

$$\epsilon_{nl} = \frac{E_{nl}}{Ry}$$

$\boxed{\rho \to \infty}$

$$\frac{d^2}{d\rho^2} v_{nl} \cong |\epsilon_{nl}| \, v_{nl}$$

$$v_{nl}(\rho) = e^{\pm \sqrt{|\epsilon_{nl}|} \, \rho}$$

$$\to e^{-\sqrt{|\epsilon_{nl}|} \, \rho} = e^{-\rho/\lambda_{nl}}$$

$$\lambda_{nl} = \frac{1}{\sqrt{|\epsilon_{nl}|}}$$

$\boxed{\rho \to 0}$ je postule que

$$v_{nl}(\rho) \sim \rho^{\beta}$$

$$-\beta(\beta-1)\, \rho^{\beta-2} + l(l+1)\, \rho^{\beta-2} \Rightarrow -2 \cancel{\rho^{\beta-1}} = \epsilon_{nl} \cancel{\rho^{\beta}}$$

$$\beta(\beta-1) = l(l+1) \quad \Rightarrow \quad \beta = l+1$$

$$\boxed{v_{nl}(\rho) \underset{\rho \to 0}{\sim} \rho^{l+1}}$$

Cherche une solution sous la forme

$$v_{nl}(\rho) = f_{nl}(\rho')\, e^{-\rho/\lambda_{nl}}$$

$$\rho' = \frac{2}{\lambda_{nl}}\rho$$

$$\downarrow$$

$$\left[\frac{d^2}{d(\rho')^2} - \frac{d}{d\rho'} - \frac{l(l+1)}{(\rho')^2} + \frac{\lambda_{nl}}{\rho'}\right] f_{nl}(\rho') = 0$$

$$f_{nl}(\rho' \to 0) \sim (\rho')^{l+1}$$

$$f_{nl}(\rho') = (\rho')^{l+1} \underbrace{\sum_{n=0}^{\infty} c_n (\rho')^n}_{=} = c_0(\rho')^{l+1} + \, + \dots (\rho')^{l+2}$$

$=$

$$c_0 \neq 0$$

$$c_{n+1} = \frac{n+l+1-\lambda_{nl}}{n(n+1) + (2l+2)(n+1)}\, c_n$$

$$\frac{c_{k+1}}{c_k} \underset{k\to\infty}{\simeq} \frac{k}{k(k+1)} = \frac{1}{k+1}$$

$$c_k \underset{k\to\infty}{\simeq} \alpha \frac{1}{k!} \qquad \frac{\cancel{\alpha}\, k!}{\cancel{\alpha}\,(k+1)!} = \frac{1}{k+1}$$

d

$$f_{nl}(\varsigma) \simeq (\rho')^{l+1} \sum_{k=0}^{\infty} \frac{\alpha}{k!} (\rho')^k$$

$$= (\rho')^{l+1} \alpha\, e^{\rho'}$$

$$e^{\frac{2\varsigma}{\lambda}}$$

$\exists\, k_0 :$ $\quad c_{k_0+1} = 0$

$$c_{k_0} \neq 0$$

d

$$c_{k+1} = \frac{k+l+1-\lambda_{nl}}{k(k+1)+(2l+2)(k+1)}\, c_k$$

$$k_0+l+1-\lambda_{nl} = 0$$

$$\lambda_{n\cancel{\ell}} = k_0 + \ell + 1 \in \mathbb{N}^*$$

$$= n$$

$$\lambda_{n\ell} = \frac{1}{\sqrt{|\epsilon_{n\ell}|}}$$

$$E_n = -|\epsilon_{n\ell}| \, Ry =$$

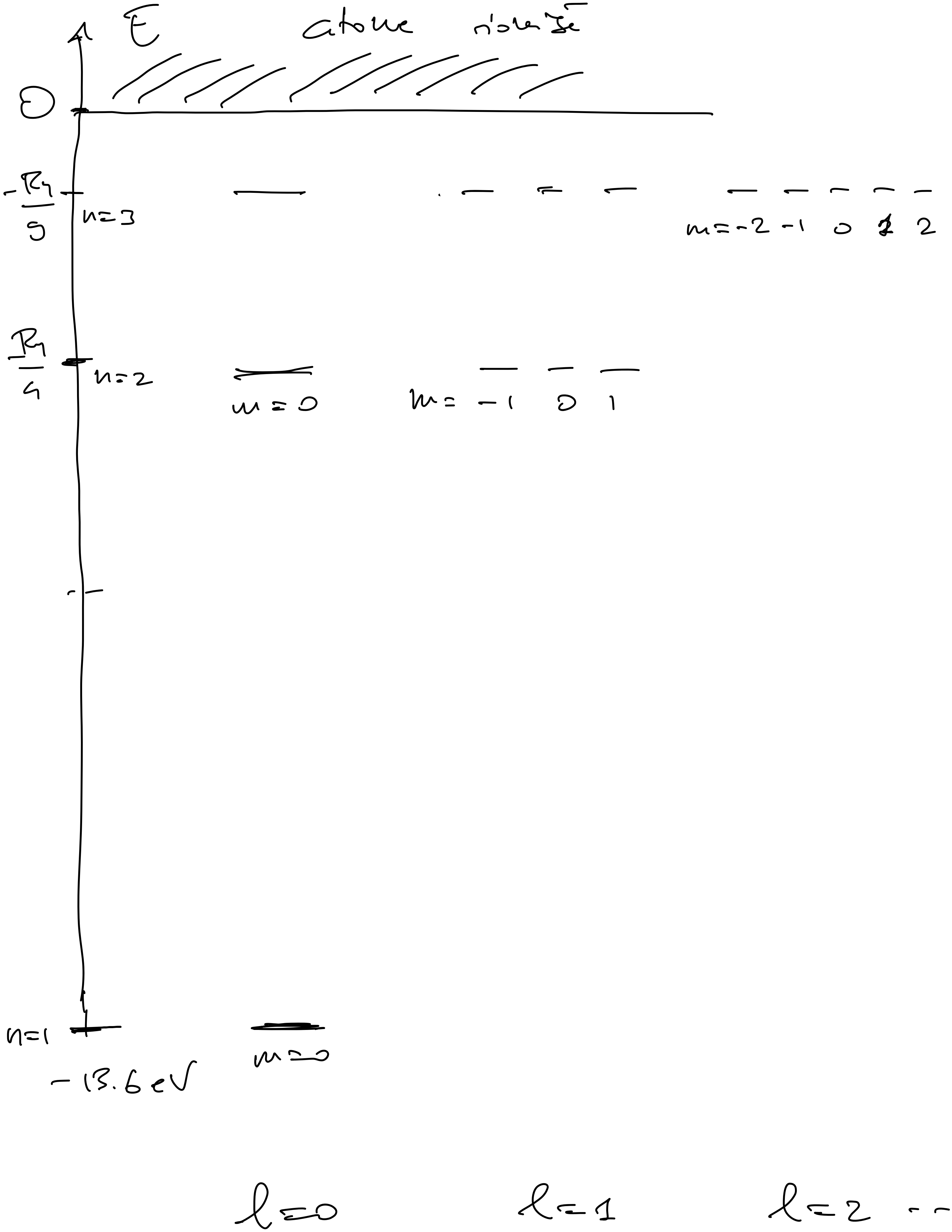
$$= -\frac{Ry}{\lambda_{n\ell}^2} \longrightarrow -\frac{Ry}{n^2}$$

$$\ell = n - 1 - k_0 \leq n - 1$$

$$k_0 = n - 1 - \ell$$

$$\ell = 0, 1, \ldots, n-1$$

$$E_n \longrightarrow \psi_{n\ell m}(r, \vartheta, \phi) = R_{n\ell}(r) \, Y_{\ell m}(\vartheta, \phi)$$



E
0
-Ry/9
n=3
m=-2 -1 0 1 2
Ry/4
n=2
m=0
m= -1 0 1
n=1
-13.6eV
m=0
l=0
l=1
l=2 --

dégénérescence

$$D_n \equiv \sum_{l=0}^{n-1} \underbrace{(2l+1)}_{=} \quad \text{valeurs possibles pour } m$$

$$= \cancel{2}\,\frac{n(n-\cancel{1})}{\cancel{2}} + \cancel{n} = n^2$$

$n =$ nombre quantique principale

Etats propres

$$\psi_{nlm}(r,\vartheta,\phi) = R_{nl}(r)\,Y_{lm}(\vartheta,\phi)$$

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} = \frac{v_{nl}(\rho)}{r}$$

$$= \frac{f_{nl}(\rho)\,e^{-\rho/\lambda_{nl}}}{r}$$

polynome d'ordre $n-1$

$$= N_{nl} \, (\rho)^{l+1} \sum_{k=0}^{k_0} c_k (\rho)^k \; e^{-\rho/\lambda_{nl}}$$

$\cancel{\rho}$

k_0

polynome d'ordre $\underline{n-l-1}$

$$L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$\frac{2\rho}{\lambda}$$

$$R_{nl}(r) = N_{nl} \, \mathrm{poly}_{n-1}^{(l)}(r) \; e^{-\frac{r}{na_0}}$$

$$\int_0^\infty dr \, \underbrace{r^2 |R_{nl}|^2}_{P_{nl}(r)} = 1$$

probabilité pour la variable radiale

$Z = 1 \longrightarrow Z > 1$

$a_0 \rightarrow \frac{a_0}{Z}$ $\qquad \frac{\hbar^2}{2\mu a_0^2} \rightarrow Z^2 \frac{\hbar^2}{2\mu a_0^2}$

$=$