ATOMES & MOLECULES

→ structure atomique, stabilité de la matière

→ test le plus sévère de la MQ

→ mesures les plus précises en physique ←

→ "règle" pour comprendre l'univers

→ technologies quantiques : → senseurs quantiques

→ simulateurs / ordinateurs quantiques

→ ...

Rappels de MQ

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

$$|\psi\rangle \to (c_1, c_2, c_3, \ldots)$$

$$\downarrow$$

$$\mathbb{C}$$

$D = \dim(\mathcal{H}) \to$ base $|\phi_n\rangle$ $n = 1, \ldots, D$

$$\underbrace{\mathbb{1}_{\mathcal{H}} = \sum_n |\phi_n\rangle\langle\phi_n|}$$

$$\langle\phi_n|\phi_m\rangle = \delta_{nm}$$

Observables physiques $\hat{A}$ opérateur hermitien

$$\hat{A}^\dagger = \hat{A}$$

$A_{nm} = \langle\phi_n|\hat{A}|\phi_m\rangle$

$$A^*_{nm} = A_{mn}$$

$$\hat{A}\,|\psi_a\rangle = \underline{\underline{a}}\,|\psi_a\rangle$$ résultats possibles d'une mesure

ex. $\hat{A}$ = Énergie = $\underline{\underline{\hat{H}}}$ Hamiltonien

Evolution d'un état

$$i\hbar \frac{d}{dt}|\psi\rangle = \underline{\underline{\hat{H}(t)}}\,|\psi\rangle$$ eq. de Schrödinger (dép. du temps)

$\hat{H}$ indep. du temps $\quad \underline{|\psi(t)\rangle} = \underbrace{e^{-i/\hbar\,\hat{H}t}}_{\hat{U}(t)}\,\underline{|\psi(0)\rangle}$

États stationnaires : états propres de $\hat{H}$

$$\hat{H}|\psi_E\rangle = E\,|\psi_E\rangle$$ éq. de Schrödinger <u>indép.</u> du temps

$$e^{-i/\hbar\,\hat{H}t}\,|\psi_E\rangle = e^{-i/\hbar\,Et}\,|\psi_E\rangle$$

Si $\hat{H}$ est indépendant de temps

→ Énergie se conserve

Autres quantités conservées $\hat{A}$

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

$\rightarrow$ $\hat{A}$, $\hat{\mathcal{H}}$ admettent une base commune de vecteurs propres

$|\psi\rangle = |E, a\rangle$

$$\begin{cases} \hat{\mathcal{H}}|E, a\rangle = E|E, a\rangle \\ \hat{A}|E, a\rangle = a|E, a\rangle \end{cases}$$

$\hat{A}_1, \hat{A}_2, \ldots \rightarrow [\hat{\mathcal{H}}, \hat{A}_i] = 0$

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

étiqueter les états $|E, a_1, a_2, \ldots\rangle$

quantités conservées $\Longleftrightarrow$ symétries

$[\hat{\mathcal{H}}, \hat{A}_j] = 0$

$\hat{U}_{A_j}(\phi) = e^{-i\phi\hat{A}_j}$

$\hat{U}^\dagger \hat{\mathcal{H}} \hat{U} = \hat{\mathcal{H}}$

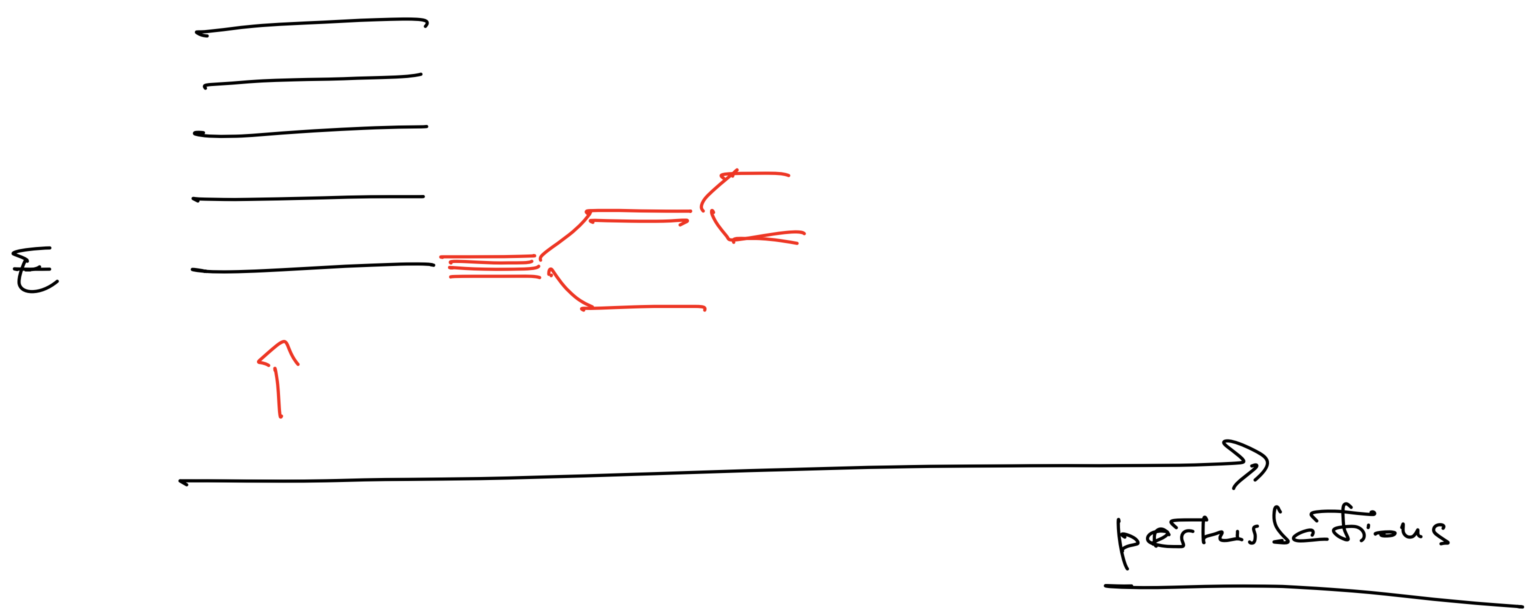
Pour résoudre eq. de Schrödinger indep. du temps

$\rightarrow$ identifier les symétries de $\hat{\mathcal{H}}$

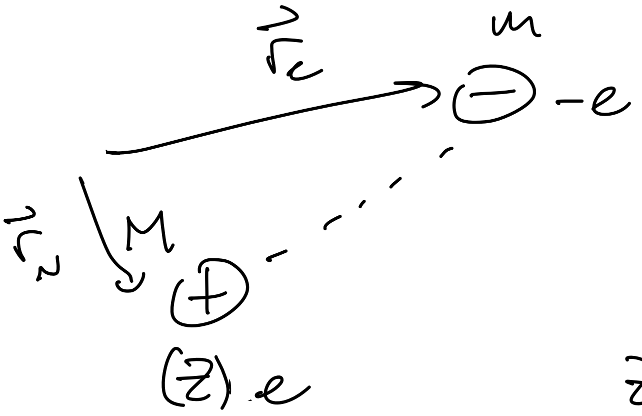
beaucoup de symétries

$$|\psi\rangle = |E, a_1, a_2, \ldots\rangle$$

(bons) nombres quantiques



Atome d'hydrogène : théorie non-relativiste
(théorie de Schrödinger)



$Z \geq 1$

Classique :

$$E = \frac{1}{2} m_e \dot{\vec{r}}_e^{\,2} + \frac{1}{2} m_N \dot{\vec{r}}_N^{\,2} - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_e - \vec{r}_N|}$$

$$\begin{cases} \vec{R} = \dfrac{m_e \vec{r}_e + m_N \vec{r}_N}{m_e + m_N} & \text{centre de masse} \\[2ex] \vec{r} = \vec{r}_e - \vec{r}_N & \text{variable relative} \end{cases}$$

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

$$\mu = \frac{m_e m_N}{m_e + m_N} \qquad \text{masse réduite}$$

$$M = m_e + m_N$$

$m_e \to m$

$$\frac{m_e}{m_N} \simeq 10^{-3} \qquad \mu \simeq m_e = m$$

$$E = \underbrace{\frac{\vec{p}^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}}_{\text{relative}} + \underbrace{\frac{\vec{P}^{\,2}}{2M}}_{\text{CdM}}$$

description en MQ

$$\vec{r},\ \vec{p} \longrightarrow \hat{\vec{r}},\ \hat{\vec{p}}$$

$$[\hat{r}_\alpha, \hat{p}_\beta] = i\hbar\,\delta_{\alpha\beta}$$

$\alpha = x, y, z$
$\beta = x, y, z$

$$\hat{H}_{rel}(\hat{\vec{r}}, \hat{\vec{p}}) = \frac{\hat{\vec{p}}^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 |\hat{\vec{r}}|}$$

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle \qquad \hat{r}_\alpha|\vec{r}\rangle = r_\alpha|\vec{r}\rangle$$

$$\langle\vec{r}|\hat{H}|\psi\rangle = E\,\underbrace{\langle\vec{r}|\psi\rangle} \rightarrow$$

fonction d'onde

$\psi(\vec{r})$ =

$$\underbrace{\left(-\frac{\hbar^2}{2\mu}\vec{\nabla}^2_{\vec{r}} - \frac{Ze^2}{4\pi\epsilon_0 r}\right)}_{\hat{\mathcal{H}}} \psi(\vec{r}) = E\,\psi(\vec{r})$$

$\vec{r} = (x, y, z)$

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

Moment cinétique angulaire en MQ

$\vec{L} = \vec{r} \times \vec{p}$ $\qquad \hat{\vec{p}} \to -i\hbar\vec{\nabla}$

$\downarrow$ MQ $\qquad \langle \vec{r} | \hat{\vec{p}} | \psi \rangle = -i\hbar\vec{\nabla}\psi(\vec{r})$

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

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

$\hat{p}_z \to -i\hbar\frac{\partial}{\partial z}$, $\quad \hat{p}_y \to -i\hbar\frac{\partial}{\partial y}$, $\quad \hat{p}_x \to -i\hbar\frac{\partial}{\partial x}$

Coordonnées polaires

$\vec{r} = r(\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)$

$r \geq 0$

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

$$= \frac{1}{r}\frac{\partial^2}{\partial r^2}\left(r(\cdot)\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(\cdot)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\begin{cases} \hat{L}_x \rightarrow i\hbar\left(\cos\phi\cot\theta\frac{\partial}{\partial\phi} + \sin\phi\frac{\partial}{\partial\theta}\right) \\ \hat{L}_y \rightarrow i\hbar\left(\sin\phi\cot\theta\frac{\partial}{\partial\phi} - \cos\phi\frac{\partial}{\partial\theta}\right) \\ \hat{L}_z \rightarrow -i\hbar\frac{\partial}{\partial\phi} \end{cases}$$

$$\hat{L}^2 \rightarrow -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(\cdot)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\vec{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}\left[r(\cdot)\right] - \frac{1}{\hbar^2 r^2}\underline{\underline{\hat{L}^2}}$$

II

$$\boxed{\hat{H} \to -\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2}\left[r(.)\right] + \frac{\vec{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}}$$

$$\left\{\begin{array}{l} [\hat{H}, \hat{\vec{L}}^2] = 0 \\ [\hat{H}, \hat{L}^\alpha] = 0 \qquad\qquad [\hat{\vec{L}}^2, \hat{L}^\alpha] = 0 \end{array}\right.$$

$\alpha = x, y, z$

<u>Rappel</u> : propriétés du MA en MQ

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

$$\epsilon_{\alpha\beta\gamma} = \begin{cases} 1 & \alpha\beta\gamma \text{ perm. paire de } (xyz) \\ -1 & \text{" " impaire} \\ 0 & \text{autrement} \end{cases}$$

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

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

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

$$\hat{\vec{L}}^2 = (\hat{L}^x)^2 + (\hat{L}^y)^2 + (\hat{L}^z)^2$$

$$[\hat{\vec{L}}^2, \hat{L}^x] = 0$$

états propres de moment angulaire

$|l\, m\rangle$ état propre de $\hat{\vec{L}}^2$ et $\hat{L}^z$

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

$l = 0, 1, 2, \ldots$?

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

$\underline{2l+1}$ valeurs possibles

$$\hat{L}^+ = \hat{L}^x + i \hat{L}^y \qquad \hat{L}^- = \hat{L}^x - i \hat{L}^y$$

$$\hat{L}^+ |l\, m\rangle = \hbar \sqrt{l(l+1) - m(m+1)}\, |l, m+1\rangle$$

$$\hat{L}^- |l m\rangle = \hbar\sqrt{l(l+1) - m(m-1)}\ |l, m-1\rangle$$

$\hat{\vec{L}}^2, \hat{L}^z$ Ensemble complet d'observables compatibles (ECOC)

$|l m\rangle$ n'impliquent que θ et ϕ

$$\langle \vec{r}| \hat{\vec{L}}^2 |\psi\rangle = \big(\qquad \big)\ \psi(\vec{r})$$

$$\langle \vec{r}| \hat{L}^z |\psi\rangle = \big(\qquad \big)\ \psi(\vec{r})$$

(r, θ, ϕ)

$$|l m\rangle \to |\vec{r}\rangle = |r, \theta, \phi\rangle$$

$$\langle r, \theta, \phi| \hat{L}^2 |l, m\rangle =$$

$$= \hbar^2 l(l+1) \underbrace{\langle r, \theta, \phi | l m\rangle}_{Y_{lm}(\theta, \phi)}$$

$$\langle r, \theta, \phi| \hat{L}^z |l m\rangle = \hbar m\, Y_{lm}(\theta, \phi)$$

$$\begin{cases} -\hbar^2 \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial}{\partial\vartheta} (\cdot) \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial\phi^2} \right] Y_{lm}(\vartheta,\phi) = -\hbar^2 l(l+1)\, Y_{lm}(\vartheta,\phi) \\ -i\hbar \frac{\partial}{\partial\phi} Y_{lm}(\vartheta,\phi) = \hbar m\, Y_{lm}(\vartheta,\phi) \end{cases}$$

$$Y_{lm}(\vartheta,\phi) = \underbrace{\Phi_m(\phi)}_{\frac{e^{im\phi}}{\sqrt{2\pi}}} \; \underbrace{\Theta_{lm}(\vartheta)}_{\text{polynôme de Legendre associé}}$$

$Y_{lm}(\vartheta,\phi)$ <u>harmoniques sphériques</u>

$l : 0, 1, \ldots, \infty \qquad m = -l, \ldots, l$

$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

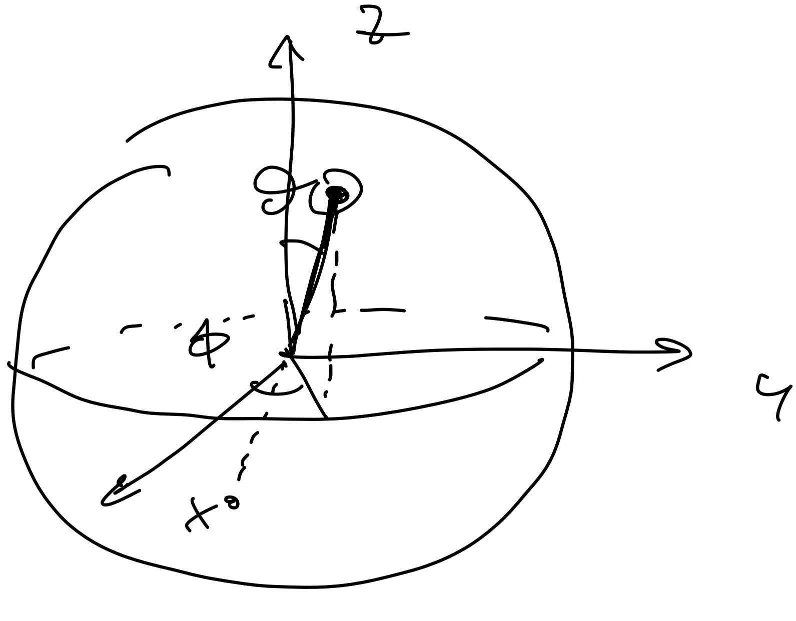
$$\int d\Omega\, |Y_{\ell m}|^2 = 1$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \,(\ldots)$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

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

$$Y_{20} = \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right)$$



$$|Y_{\ell m}|^2 \qquad \text{surface} \quad r(\theta,\phi) = |Y_{\ell m}|^2$$

parité des harmoniques sphériques

inversion de l'espace $\vec{r} \to -\vec{r}$

$\vartheta \to \pi - \vartheta$

$\phi \to \phi + \pi$

$$Y_{lm}(\vartheta, \phi) = (-1)^{l} Y_{lm}(\pi - \vartheta, \phi + \pi)$$

Equation de Schrödinger pour $\underline{\underline{H}}$

$$H_{rel} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r(\cdot)) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\varepsilon_0 = 8.85 \times 10^{-12} \frac{F}{m}$

$$+ \frac{\vec{L}^2}{2\mu r^2}$$

$$H_{rel}\,\psi(r,\vartheta,\phi) = E\,\psi(r,\vartheta,\phi)$$

$$\psi(r,\vartheta,\phi) = R_{nl}(r)\,\underline{\underline{Y_{lm}(\vartheta,\phi)}}$$

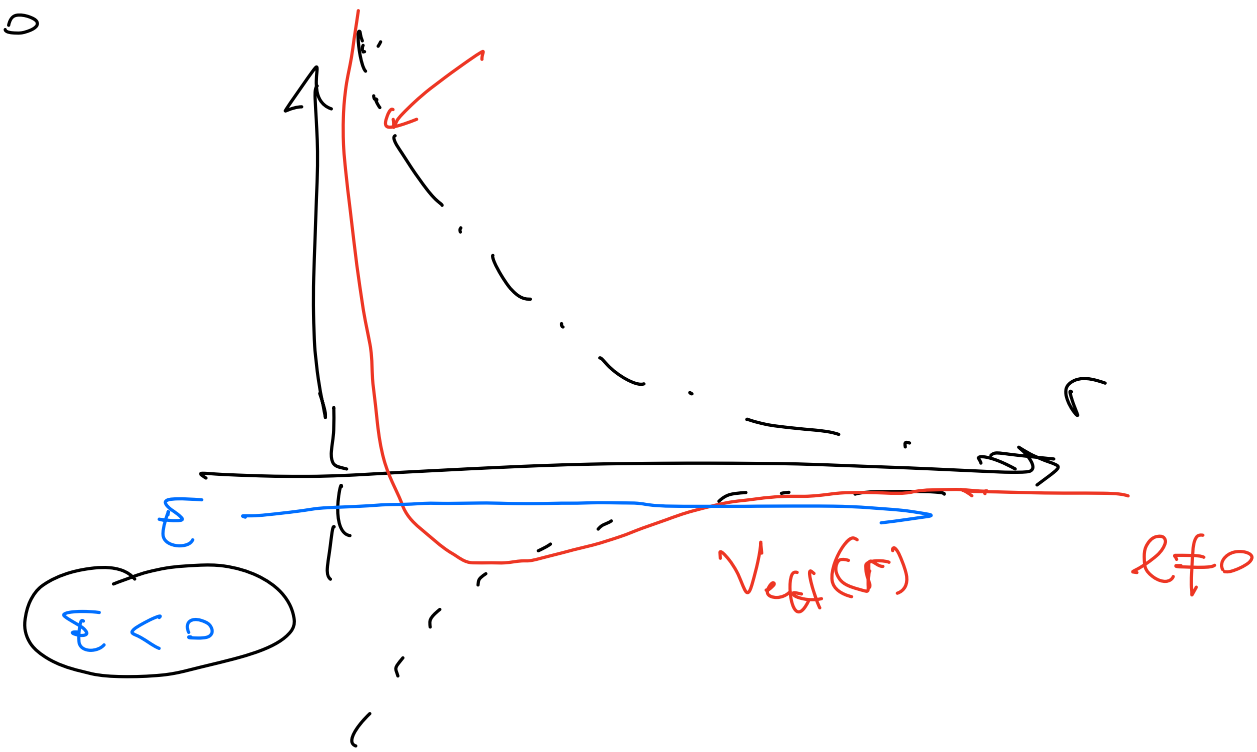
$$\left[-\frac{\hbar^2}{2\mu}\underbrace{\frac{1}{r}\frac{\partial^2}{\partial r^2}(r(\cdot))} - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right]\cancel{Y_{\ell m}} R_{n\ell}$$

$$= \varepsilon \cancel{Y_{\ell m}} R_{n\ell}$$

$$R_{n\ell}(r) = \frac{\overbrace{u_{n\ell}(r)}}{r}$$

$$\left[\underbrace{-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}} \underbrace{- \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}}_{V_{eff}(r)}\right] u_{n\ell}(r) = \underline{\varepsilon_{n\ell}}\, u_{n\ell}(r)$$

$r \geq 0$



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

$$v_{n\ell}(\rho) = u_{n\ell}(r) \quad r \to \rho a_0$$

$$\left[-\frac{\hbar^2}{2\mu a_0^2}\frac{d^2}{d\rho^2}-\frac{Ze^2}{4\pi\varepsilon_0 a_0}\frac{1}{\rho}+\frac{\hbar^2 \ell(\ell+1)}{2\mu a_0^2}\frac{1}{\rho^2}\right]v_{n\ell}$$

$$= E_{n\ell}\, v_{n\ell}$$

$$\frac{Ze^2}{4\pi\varepsilon_0 a_0} = \frac{\hbar^2}{\mu a_0^2}$$

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

$\mu \to m$

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \simeq 0.5\,\text{Å}$$

$$= 5\times10^{-11}\,m$$

rayon de Bohr

$$\frac{\hbar^2}{2ma_0^2} = Ry = 13.6\ eV$$

$$eV = 1.6\times10^{-19}\ J$$

$$\frac{Ry}{h} = 1.52\times10^{15}\ Hz$$

$$\left[-\frac{d^2}{d\rho^2}-\frac{2}{\rho}+\frac{\ell(\ell+1)}{\rho^2}\right]v_{n\ell}(\rho) = \frac{E_{n\ell}}{Ry}v_{n\ell}(\rho)$$

$$\epsilon_{n\ell}$$

$\varepsilon < 0$

$$\boxed{\frac{E_{nl}}{R_y} = \epsilon_{nl}}$$

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

$$\cancel{-}\frac{d^2}{d\rho^2} v_{nl}(\rho) \cong \cancel{-}|\epsilon_{nl}|\, v_{nl}(\rho)$$

$$\boxed{v_{nl}(\rho) \overset{\rho\to\infty}{\sim} e^{\cancel{\pm}\sqrt{|\epsilon_{nl}|}\,\rho} = e^{-\frac{\rho}{\lambda_{nl}}}}$$

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

$$\boxed{\rho \to 0}$$

churchu solution

$$v_{nl}(\rho) \underset{\rho\to 0}{\Rightarrow} \rho^{\beta}$$

$$v_{nl}(\rho) : \left[-\frac{d^2}{d\rho^2} - \cancel{\frac{2}{\rho}} + \frac{l(l+1)}{\rho^2}\right] v_{nl} \simeq 0$$

$$\underbrace{-\beta(\beta-1)}\,\rho^{\beta-2} - \cancel{2\rho^{\beta-1}} + \underbrace{l(l+1)}\,\rho^{\beta-2} \simeq 0$$

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

$$\boxed{\beta = l+1}$$

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

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

réinjecte dans l'équation.

$$\left[-\frac{d^2}{d\rho^2} + \frac{2}{\lambda}\frac{d}{d\rho} + \frac{l(l+1)}{\rho^2} - \frac{2}{\rho}\right] f = 0$$

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

d $\quad$ ρ

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

$$f\left(\frac{\lambda\rho'}{2}\right) = (\rho')^{l+1} \sum_{k=0}^{\infty} c_k (\rho')^{k}$$

$$c_0 \neq 0$$

condition de recurrence sur c_k

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

$k \to \infty$

$k_0 = 0 \Rightarrow c_0 \neq 0$

$l+1-n=0 \quad l=n-1$

$$\Rightarrow \frac{c_{k+1}}{c_k} \to \frac{k}{k(k+1)} = \frac{1}{k+1}$$

$$c_k \approx \frac{1}{k!}$$

$$\sum_{k=0}^{\infty} c_k (\rho')^k \to \sum_{k=0}^{\infty} \frac{(\rho')^k}{k!} = e^{\rho'}$$

$$= e^{2\rho/\lambda}$$

$$\rho \to \infty \qquad e^{-\rho/\lambda} f(\rho) \sim e^{-\rho/\lambda} e^{2\rho/\lambda}$$
$$\sim e^{\rho/\lambda}$$

troncature du <u>polynôme</u>

$$\underline{\exists k_0} : \quad c_{k_0+1} = \frac{k_0+l+1-\lambda}{k_0(k_0+1)+(2l+2)(k_0+1)} = 0$$

$k_0 \in \mathbb{N} \qquad k_0 = 0, 1, 2, \ldots$

$$\underset{=}{\lambda_{nl}} = k_0 + \underset{0,1,2\ldots}{l} + 1 = n \in \mathbb{N}^*$$

$n = 1, 2, 3, \ldots$

$$|\epsilon_{nl}| = \frac{1}{\lambda_{nl}^2} = \frac{1}{n^2}$$

$n = 1, 2, 3, \ldots$

$$\boxed{E_n = -Ry\,|\epsilon_{nl}| = -\frac{Ry}{n^2}}$$

structure principale du spectre

$$E_m - E_n = \underbrace{Ry\left(-\frac{1}{m^2}+\frac{1}{n^2}\right)}$$

$$= \hbar\,\omega_{mn}$$

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

$$E = E_{nlm} = E_n$$

$\underline{\underline{n}}$: quelles valeurs pour $\underline{l}$?

$$k_0 + l + 1 = n$$

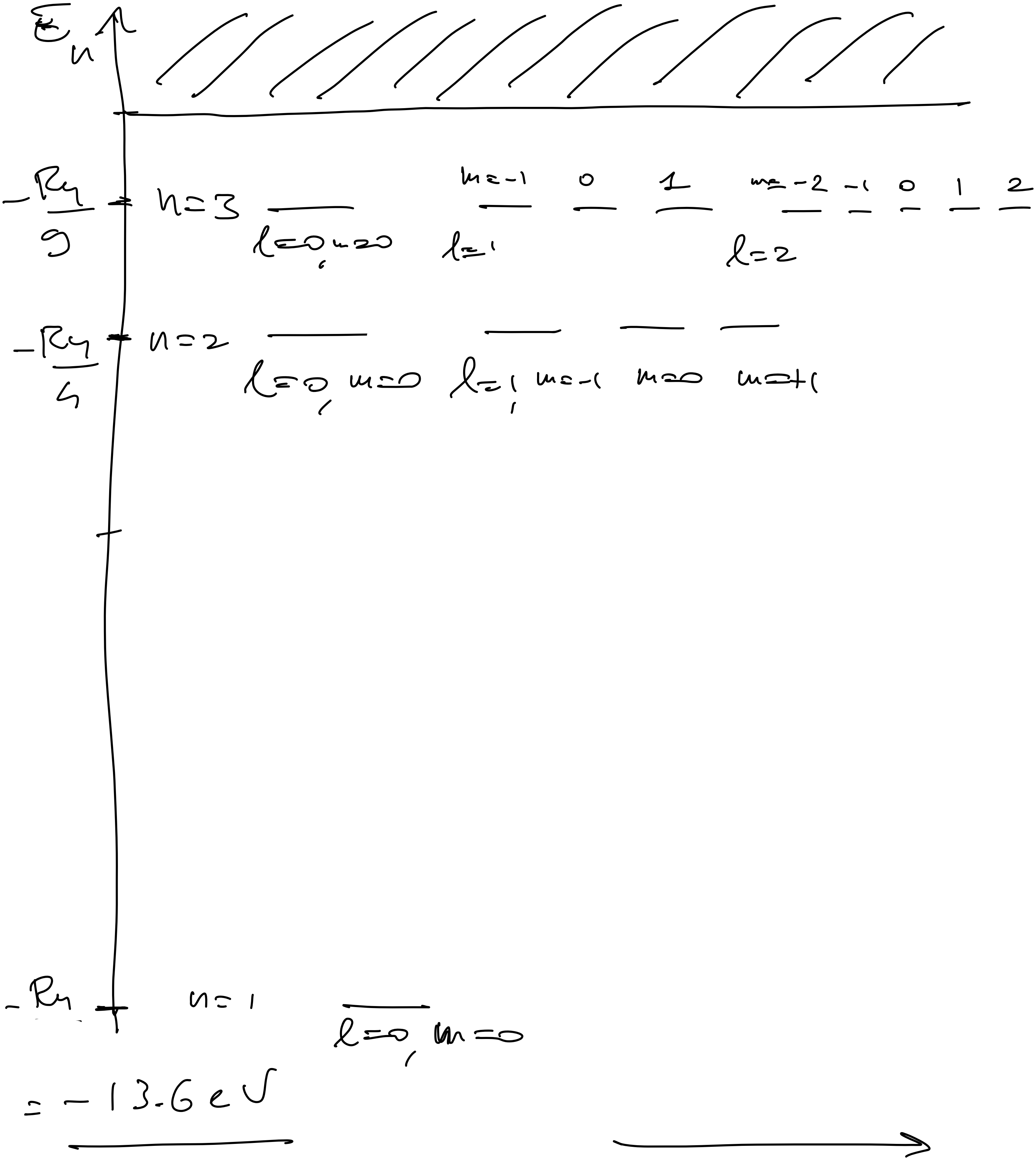
$$l = n - 1 - k_0 \qquad \underline{l \leq n-1}$$

$$n \to l = 0, 1, \dots, n-1 \to m = -l, \dots, l$$

dégénérescence de E_n

$$D_n = \sum_{l=0}^{n-1} (2l+1) = 2\,\frac{n(n-1)}{2} + n$$

$$= n^2$$



E_n
$-\frac{Ry}{9}$ $n=3$
$l=0, m=0$
$l=1$ $m=-1$ 0 1
$l=2$ $m=-2$ -1 0 1 2
$-\frac{Ry}{4}$ $n=2$
$l=0, m=0$
$l=1, m=-1$ $m=0$ $m=+1$
$-Ry$ $n=1$
$l=0, m=0$
$= -13.6\,eV$

$$\psi_{nlm}(r,\vartheta,\phi) = \langle \vec{r}, \vartheta, \phi \mid n\,l\,m \rangle$$

$$= Y_{lm}(\vartheta,\phi)\, N_{nl}\, e^{-\frac{r}{n a_0}}\, P_{n-1}\left(\frac{2r}{n a_0}\right)$$

polynome d'ordre n-1

$$R_{nl}(r) = \frac{u_{nl}}{r} = \frac{v_{nl}\left(\frac{r}{a_0}\right)}{r} \sim e^{-\frac{r}{a_0 n}}\, r \left(\frac{r}{a_0}\right)^{l+1} P_{n-l-1}(r)$$

$$k_0 + l + 1 - n = 0$$

$$k_0 = n - l - 1$$

$$L_{n+l}^{2l+1}\left(\frac{2r}{n a_0}\right)$$

$$\uparrow$$

$$e^{l}$$