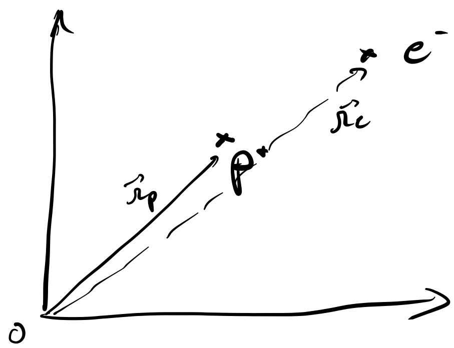
I Description et modélisation du système



m_p proton
m_e électron

$m_p \gg m_e$
proton fixe et électron en mouvement.

$$\hat{H} = \frac{\hat{\vec{p}}_p^{\,2}}{2m_p} + \frac{\hat{\vec{p}}_e^{\,2}}{2m_e} + V(\vec{r})$$

Référentiel du centre de masse

$$\begin{cases} \vec{R} = \dfrac{m_p \vec{r}_p + m_e \vec{r}_e}{m_p + m_e} \simeq \vec{r}_p \\ \vec{P} = \vec{p}_p + \vec{p}_e \end{cases}$$

Mouvement relatif
$$\begin{cases} \vec{r} = \vec{r}_e - \vec{r}_p \\ \vec{p} = \dfrac{m_e \vec{p}_e - m_p \vec{p}_p}{m_e + m_p} \end{cases}$$

$$\hat{H} = \underbrace{\frac{\vec{P}^2}{2M}}_{\hat{H}_{cm}} + \underbrace{\left[\frac{\hat{\vec{p}}^{\,2}}{2\mu} + V(\vec{r})\right]}_{\hat{H}_{rel}}$$

avec $m_p + m_e = M$
et $\mu = \dfrac{m_e m_p}{m_e + m_p} \simeq m_e$.

* Comment se restreindre à $\hat{H}_{rel}$
→ Argument conservat° de la quantité de mouvement
$\vec{p}_1 + \vec{p}_2 = \vec{P} = cte$.

Argument mathématique.

$[H, \mathcal{P}]$ commute $\longrightarrow$ vecteur propre de $\mathcal{P}$

onde plane $e^{i\vec{K}.\vec{R}}$

solution du type $e^{i\vec{K}.\vec{R}} \Psi(r)$.

$$\hat{H} e^{iKR} \Psi(r) = \frac{K^2}{2M} \Psi(r) e^{iKR} + H_{rel} \Psi(r) e^{i\vec{K}.\vec{R}}$$

$$E_{propre} = \frac{K^2}{2M} + E_{rel} \quad / \quad H_{rel} \Psi(r) = E_{rel} \Psi(r)$$

But Etat stationnaire de $\hat{H}_{rel} + V(r)$

$$\left[-\frac{\hbar^2}{2m} \Delta + V(r) \right] \Psi(r) = E \Psi(r)$$

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

$$= \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right)$$

en coord sph

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2m_e r^2} \underbrace{\left[-\hbar^2 \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]}_{\vec{L}^2} + V(r) \right] \Psi(r) = E \Psi(r)$$

$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}}$ Moment cinétique orbital

$$= -i\hbar \begin{pmatrix} y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \\ z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \\ \cdots \end{pmatrix} = \begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ L_z \end{pmatrix}$$

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Interêt de cette decomposition

$$\hat{H} = \hat{A}(r) + \frac{1}{2m_e r^2}\hat{L}^2$$

ne depend que de θ et φ.

$\hat{H}$ et $\hat{L}^2$ commutent

$\hookrightarrow$ $\exists$ base propre commune à $\hat{H}$ et $\hat{L}^2$

$\hat{L}^2(\theta, \varphi, \cancel{r}) \to \phi_{l,m}(\theta, \varphi)$ vp de $\hat{L}^2$.

Dans chaque espace propre $\{l, m\}$ de $\hat{L}^2$ on cherche

Les vp de $\hat{H}$ $\longrightarrow$ partie liée à r

Resoudre.

$$\left[\hat{A}(r) - \frac{1}{2m_e \hat{r}^2}\cdot\hat{L}^2\right] R_{l,m}^n(r)\,\phi_{lm}(\theta,\varphi) = E_{lm}^n R_{l,m}^n\,\phi_{l,m}(\theta,\varphi)$$

avec $\hat{L}^2\,\phi_{lm}(\theta,\varphi) = L_{l,m}\,\phi_{l,m}(\theta,\varphi)$

II Moment cinétique

A) Orbital

$$\vec{L} = \hat{\vec{r}} \times \hat{\vec{p}} \to (\hat{L}_x, \hat{L}_y, \hat{L}_z)$$

$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ $\qquad$ $\hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}}$

$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$ $\qquad$ Moment cinétique $\hat{\vec{J}} \times \hat{\vec{J}} = i\hbar\hat{\vec{J}}$

$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$

B) Moment cinétique

1) Base propre

3 dof couplés par les relations de commutations

↳ à priori au mieux 2 dof

↳ 2 observable qui commutent

$$\left\{ \hat{\vec{J}}^2 , \hat{J}_z \right\} \qquad J^2 = J_x^2 + J_y^2 + J_z^2$$

$$[J^2, J_z] \overset{\text{exo}}{=} 0$$

$\Rightarrow$ On cherche une base commune à $\hat{J}^2$ et $\hat{J}_z$

$$\begin{cases} J^2 |j,m\rangle = j(j+1)\hbar^2 |j,m\rangle \\ J_z |j,m\rangle = m\hbar |j,m\rangle \end{cases}$$

2) Quantificat° du moment cinétique

$$\hat{J}^+ = \hat{J}_x + i\hat{J}_y$$
$$J^- = J_x - iJ_y$$

Action de J^+

* $J^2 \left(J^+ |j,m\rangle \right) = J^+ \left(J^2 |j,m\rangle \right) = j(j+1)\hbar^2 J^+ |j,m\rangle$
* $J_z J_+ |j,m\rangle = \left(J_z J_x + i J_z J_y \right) |j,m\rangle$ exo
$= \hbar (m+1) J^+ |j,m\rangle$

$J_+ |j,m\rangle \propto |j,m+1\rangle = c\,|j,m+1\rangle$ operateur montant

$J_- |j,m\rangle \propto |j,m-1\rangle = c\,|j,m-1\rangle$ —— descendant.

$$\| J_+ |j,m\rangle \|^2 = \langle j,m| \underbrace{J_+^*}_{\substack{(J_x+iJ_y)^* \\ = \\ J_-}} J_+ |j,m\rangle$$

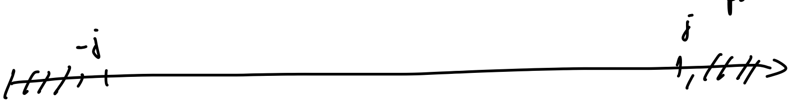
$$J_- J_+ \overset{\text{cNO}}{=} J^2 - J_z^2 - \hbar J_z$$

$$\| J_+ |j,m\rangle \|^2 = j(j+1)\hbar^2 - m^2\hbar^2 - m\hbar^2$$

$$= \hbar^2 \left(j(j+1) - m(m+1) \right) \geq 0$$

$$\Rightarrow m \leq j$$

$$\| J_- |j,m\rangle \|^2 \longrightarrow m \geq -j$$



$\exists\, m_{max}$ $|j, m_{max}\rangle$ etat propre

et $J^+|j, m_{max}\rangle$ n'est pas un etat propre.

$$\| J_+ |j, m_{max}\rangle \|^2 = 0 \Rightarrow m_{max} = j \Rightarrow m + \underset{\in \mathbb{N}}{N} = j$$

$$m_{min} = -j \Rightarrow m - \underset{\in \mathbb{N}}{N'} = -j$$

$$\frac{N + N'}{2} = j$$

<u>Conc</u>

$$\begin{cases} J^2 |j,m\rangle = j(j+1)\hbar \ |j,m\rangle \\ J_z |j,m\rangle = \hbar\, m \ |j,m\rangle \\ j \text{ est entier ou demi-entier} \\ m \in [-j, j] \text{ et entier ou demi entier} \end{cases}$$

3) Moment cinétique orbital : Application

$$\left. \begin{aligned} \hat{L}_z &= \frac{\hbar}{i} \frac{\partial}{\partial \varphi} \\ \hat{L}_z\, \Psi_{j,m}(\vec{r}) &= m\hbar\, \Psi_{j,m}(\vec{r}) \end{aligned} \right\} \text{ et } \Psi_{j,m}(\vec{r}) = \Phi_m(r,\theta)\, e^{im\varphi}$$

φ 2π period $\quad e^{im\varphi} = e^{im(\varphi + 2\pi)}$

$$e^{im2\pi} = 1 \rightarrow \left| \begin{array}{l} m \text{ entier.} \\ \ell \text{ entier} \end{array} \right.$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin\theta} \frac{\partial^2}{\partial\varphi^2} \right)$$

solution harmonique sphérique

$$Y_{\ell,m}(\theta,\varphi) = F_{\ell,m}(\theta)\, e^{im\varphi}$$

III Retour sur l'atome d'hydrogène

On cherche $\Psi(r,\theta,\varphi) = R_{\ell,m}(r)\, Y_{\ell,m}(\theta,\varphi)$

$$\frac{\partial^2}{\partial r^2}\left(r . R_{\ell,m}(r)\right)$$

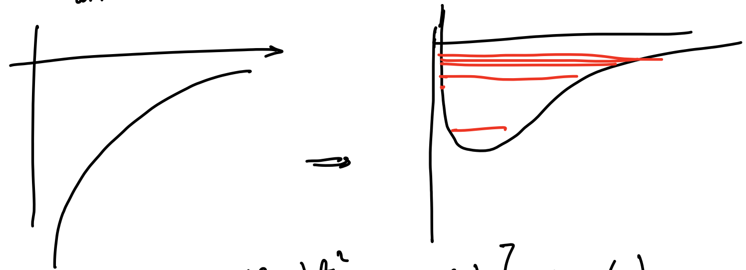
$$H\Psi = E\Psi$$

$$\Updownarrow$$

$$\left[-\frac{\hbar^2}{2m r}\frac{\partial^2}{\partial r^2} r + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2m_e r^2} + V(r)}_{V_{eff}}\right] R_{\ell,m}(r) = E\, R_{\ell,m}(r)$$

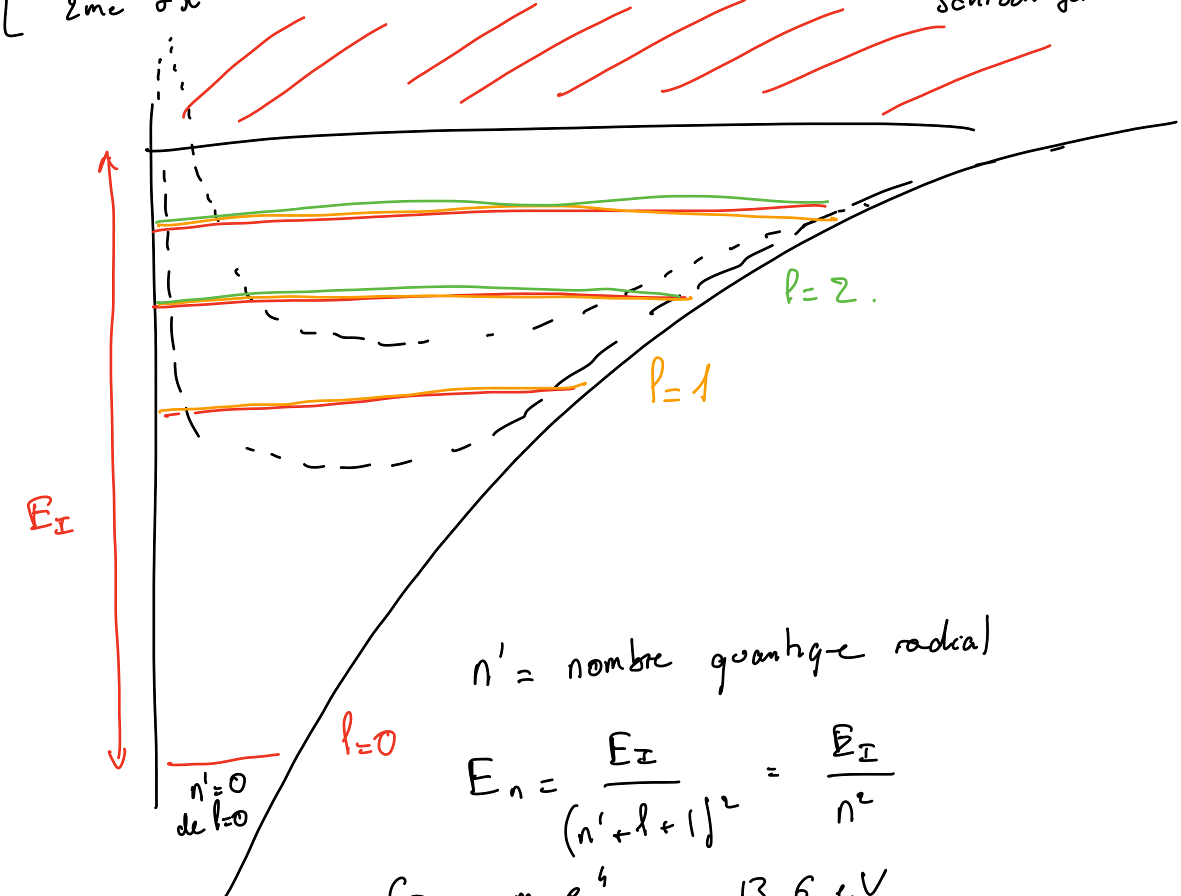
$$U_{\ell,m}(r) = r\, R_{\ell,m}(r)$$

attract° coulombienne + force centrifuge



$$\left[-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} + V(r)\right] U_{\ell,m}(r) = E_{\ell,m}\, U_{\ell,m}(r).$$

Schrodinger 1D.



n' = nombre quantique radial

$$E_n = \frac{E_I}{(n'+\ell+1)^2} = \frac{E_I}{n^2}$$

avec $\begin{cases} E_I = \dfrac{m_e e^4}{2\hbar^2} \sim 13,6 \text{ eV} \\ n \text{ nombre quantique principale} \end{cases}$

$$\psi_{n,l,m}(\vec{r}) = Y_{l,m}(\theta,\varphi)\, e^{-\frac{r}{n a_1}} \left(\frac{r}{a_1}\right)^{l} \left[C_0 + C_1 \frac{r}{a_1} + C_2 \frac{r^2}{a_1^2} + \dots + C_{n-l-1} \left(\frac{r}{a_1}\right)^{n-l-1}\right]$$

C_i coeff des poly de Laguerre

$a_1 = a_b = \frac{\hbar^2}{m_e e^2} \simeq 0.5\ \text{Å}$ rayon de Bohr.