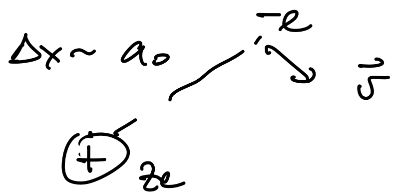
Effets relativistes dans la physique de l'atome de H

→ structure fine du spectre



$$p \sim \Delta p \gtrsim \frac{\hbar}{\Delta x}$$

$$v = \frac{p}{m} \gtrsim \frac{\hbar}{m a_0}$$

$$\frac{v}{c} = \frac{\hbar}{m a_0 c} = \alpha \simeq \frac{1}{137} \sim 10^{-2}$$

→ constante de structure fine

$$a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m e^2}$$

$$E = \underset{-\frac{R_y}{n^2}}{E_n} + o\left(\frac{v}{c}\right)^2$$

$$o\left(\frac{v}{c}\right)^4$$

$$\hat{H} = \underbrace{\frac{\vec{p}^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r}}_{\hat{H}_0} + \hat{H}_{so} + \hat{H}_{rel} + \hat{H}_D + \dots$$

- $\hat{H}_{so}$: couplage spin-orbite
- $\hat{H}_{rel}$: correction relativiste à l'énergie cinétique
- $\hat{H}_D$: terme de Darwin

$$\llcorner \; o\left(\frac{v}{c}\right)^2$$

Théorie semi-classique

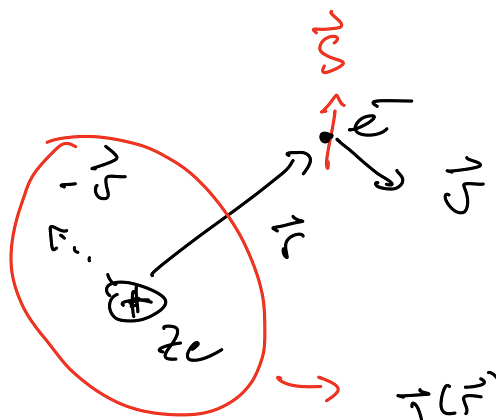
Théorie quantique + relativiste de l'atome de H

= équation de Dirac

e^- $\vec S$ $\qquad \vec m = \frac{g\mu_B}{\hbar}\vec S \qquad g \simeq -2$

$\uparrow \qquad\qquad \mu_B = \frac{e\hbar}{2m}$

Couplage spin-orbite



$\vec m$ moment magnétique

champ magnétique $\vec B$

$$E = -\vec m \cdot \vec B$$

$$\vec j(\vec r) = \rho(\vec r)\,\vec v(\vec r) = Ze\,\delta(\vec r)\,(-\vec v)$$

$$\vec B(\vec r) = \frac{\mu_0}{4\pi}\int d^3r'\,\frac{\vec j(\vec r')\times(\vec r-\vec r')}{|\vec r-\vec r'|^3}$$

dans le référentiel de e^-

Loi de Biot-Savart

$$= \frac{\mu_0}{4\pi m}(-Ze)\,\frac{\overbrace{m\vec v\times\vec r}^{-\vec L}}{r^3}$$

$$\vec L = \vec r\times\vec p = m\,\vec r\times\vec v$$

$$= -\frac{\mu_0\epsilon_0}{me}\left(-\frac{Ze^2}{4\pi\epsilon_0 r^3}\right)\vec L$$

$\mu_0\epsilon_0 = \frac{1}{c^2}$

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$-\frac{1}{r^3} = +\frac{1}{r}\left(\frac{\partial}{\partial r}\frac{1}{r}\right)$$

$$-\frac{Ze^2}{4\pi\epsilon_0 r^3} = \frac{1}{r}\frac{\partial}{\partial r}\underbrace{\left(\frac{Ze^2}{4\pi\epsilon_0 r}\right)}_{-V(r)}$$

$$= -\frac{1}{r}\frac{d}{dr}V(r)$$

$$= \frac{1}{mc^2 e}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec L$$

"orbite"

$$E_{so} = - \frac{g\mu_B}{\hbar} \hat{\vec{S}} \cdot \frac{1}{mc^2 e} \left(\frac{1}{r} \frac{dV}{dr} \right) \hat{\vec{L}}$$

spin-orbite

$$= + \frac{\cancel{g}}{\cancel{\hbar}} \frac{\cancel{e\hbar}}{\cancel{2}m} \frac{1}{mc^2 \cancel{e}} \left(\frac{1}{r} \frac{dV}{dr} \right) \hat{\vec{L}} \cdot \hat{\vec{S}}$$

$$= \frac{1}{2m^2c^2} \frac{1}{r} \left(\frac{dV}{dr} \right) \hat{\vec{L}} \cdot \hat{\vec{S}} = \hat{\mathcal{H}}_{so}$$

précession de Thomas

$\hat{\mathcal{H}}_{so}$ en perturbation par rapport à $\hat{\mathcal{H}}_0$

$$\hat{\mathcal{H}}_0 |nlm\rangle \otimes |sm_s\rangle = E_n |nlm\rangle \otimes |sm_s\rangle \quad \Big| \quad E_n = -\frac{R_y}{n^2}$$

$\hat{\mathcal{H}}_0 \quad \vec{L}^2 \quad L_z$

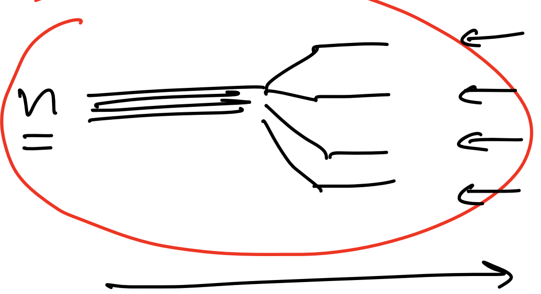
$D_n = 2n^2$ dégénérescence de E_n

$\rightarrow |nlm\rangle \otimes |sm_s\rangle$

$m_s = \pm \frac{1}{2} \qquad s = \frac{1}{2}$

théorie des perturbations dans le cas dégénéré

à l'ordre 1



perturbation

$(\mathcal{H}_{so})$

$$\Rightarrow \langle n\, l\, m | \otimes \langle s\, m_s |\ \hat{\mathcal{H}}_{so}\ | n\, l'\, m' \rangle \otimes | s\, m_s' \rangle$$

$$\hat{\mathcal{H}}_{so} = \frac{1}{2m^2c^2} \underbrace{\left(\frac{1}{r} \frac{d\hat{V}}{dr} \right)}_{\text{radiale}} \underbrace{\hat{\vec{L}} \cdot \hat{\vec{S}}}_{\text{angulaire / spin}}$$

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

moment cinétique total de l'électron

$$\hat{\vec{J}}^2 = \hat{\vec{L}}^2 + \hat{\vec{S}}^2 + 2\, \hat{\vec{L}} \cdot \hat{\vec{S}}$$

$$\Rightarrow \hat{\vec{L}} \cdot \hat{\vec{S}} = \frac{1}{2} \left(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2 \right)$$

$$| l\, m \rangle \otimes | s\, m_s \rangle \rightarrow | l, s; j\, m_j \rangle$$

$\vec{L}^2$ $\quad \vec{S}^2$ $\quad \vec{J}^2$ $\quad J_z$

valeurs propres de la matrice des perturbations

$$\Delta E^{(SO)}_{nls_j} = \langle n\, l s; j m_j | \left(\frac{1}{2m^2c^2} \left(\frac{1}{r}\frac{dV}{dr} \right) \vec{L}\cdot\vec{S} \right) | n l s; j m_j \rangle$$

$R_{nl}(r)$ $\qquad$ $R_{nl}(r)$

$$= \frac{1}{2m^2c^2} \left(\frac{1}{r}\frac{dV}{dr} \right)_{nl} \frac{\hbar^2}{2} \left(j(j+1) - l(l+1) - s(s+1) \right)$$

$$\int dr\, r^2 R_{nl}^2(r) \frac{1}{r}\frac{dV}{dr}$$

$$\Downarrow$$

$$\frac{Z^3}{l(l+\frac{1}{2})(l+1)(na_0)^3}$$

$$= \dots = \frac{1}{2} |E_n| \frac{Z^4 \alpha^2}{n l (l+\frac{1}{2})(l+1)} \left[j(j+1) - l(l+1) - s(s+1) \right]$$

Correction relativiste à l'énergie cinétique

$$E_{kin} = \sqrt{m^2c^4 + c^2p^2}$$

$$= mc^2 \sqrt{1 + \frac{p^2}{m^2c^2}} \simeq$$

$p \ll mc$

$v \ll c$

$$= mc^2\left(1+\frac{p^2}{2m^2c^2}-\underbrace{\frac{1}{8}\left(\frac{p^2}{m^2c^2}\right)^2}+O\left(\left(\frac{p^2}{m^2c^2}\right)^3\right)\right)$$

$$= mc^2+\frac{p^2}{2m}\underbrace{-\frac{1}{2}\left(\frac{p^2}{2m}\right)^2\frac{1}{mc^2}}_{E_{rel}}+\ --$$

$$\hat{H}_{rel} = -\frac{1}{2mc^2}\left(\frac{\hat{p}^2}{2m}\right)^2 \qquad \hat{H}_0 = \frac{p^2}{2m}-\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\left(\hat{H}_0+\frac{Ze^2}{4\pi\epsilon_0 r}\right)^2$$

$$= -\frac{1}{2mc^2}\left(\hat{H}_0^2+\hat{H}_0\frac{Ze^2}{4\pi\epsilon_0}\hat{\frac{1}{r}}+\underbrace{\frac{Ze^2}{4\pi\epsilon_0}\hat{\frac{1}{r}}\hat{H}_0}+\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\left(\hat{\frac{1}{r}}\right)^2\right)$$

$$|nlm\rangle\otimes|sm_s\rangle$$

$$\langle nlm|\ \hat{H}_{rel}\ |nlm\rangle = \Delta E_{nl}^{(rel)}$$

$$= -\frac{1}{2mc^2}\left[E_n^2+2E_n\frac{Ze^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle_{nl}+\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle_{nl}\right]$$

$$\frac{Z}{n^2a_0} \qquad \frac{Z^2}{n^3a_0^2(l+\frac{1}{2})}$$

$$= \cdots = -E_n\frac{Z^2\alpha^2}{n^2}\left[\frac{3}{4}-\frac{n}{l+1/2}\right]$$

Terme de Darwin

$$\Delta p \, \Delta x \geq \frac{\hbar}{2}$$

$$\underset{\substack{= \\ m \Delta v}}{\Delta p} \geq \frac{\hbar}{2 \Delta x}$$

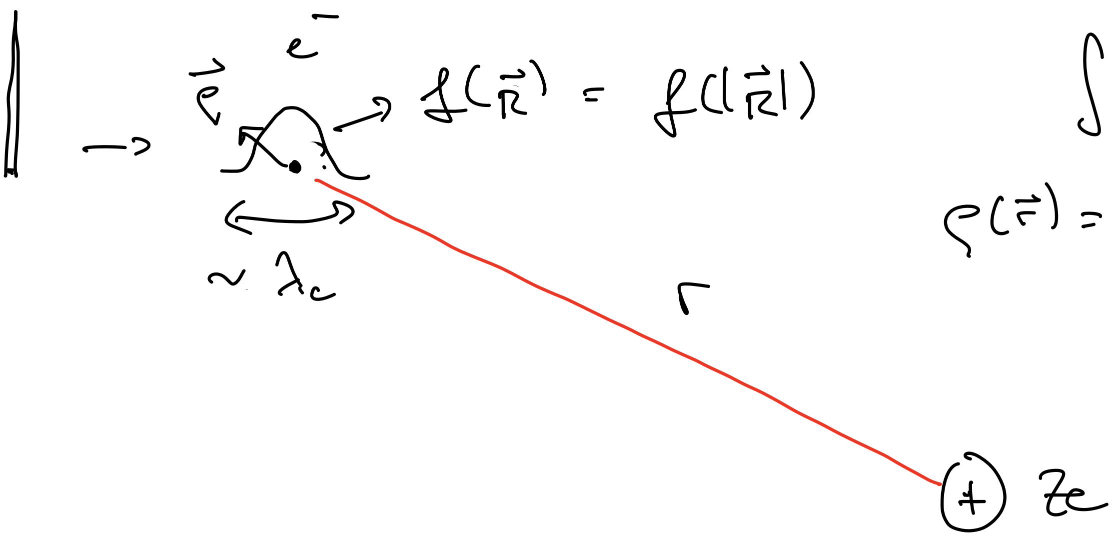
$$c > \Delta v \gtrsim \frac{\hbar}{m \Delta x}$$

$$\Delta x \gtrsim \frac{\hbar}{mc} = \lambda_c$$

= longueur de Compton de l'électron

$\simeq 4 \times 10^{-13}$ m

$a_0 \simeq 5 \times 10^{-11}$ m



$$f(\vec{R}) = f(|\vec{R}|)$$

$$\int f(|\vec{R}|) \, d^3R = 1$$

$$\rho(\vec{r}) = -e \, f(\underbrace{\vec{r} - \vec{r}_e}_{\vec{R}})$$

avant $\delta(\vec{r} - \vec{r}_e)$

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \longrightarrow -\int d^3R\, \frac{Ze^2}{4\pi\epsilon_0} f(\vec{R}) \frac{1}{|\vec{r}+\vec{R}|}$$

$$V(\vec{r}+\vec{R})$$

$$\downarrow$$

DL de $V(\vec{r}+\vec{R})$

autour de $\vec{R}=0$

$f(|\vec{R}|)$

$$= -\frac{Ze^2}{4\pi\epsilon_0} \int d^3R\, f(\vec{R}) \left(\frac{1}{r} + \left(\vec{\nabla}\frac{1}{r}\right)\cdot\vec{R} + \frac{1}{2}\sum_{ij}\left(\frac{\partial}{\partial x_i \partial x_j}\frac{1}{r}\right) R_i R_j + \dots \right)$$

0

δ_{ij}

$$\int d^3R\, f(\vec{R})\, R_i R_j = \delta_{ij} \int d^3R\, f(\vec{R})\, R_i^2$$

$$i=j \qquad = \frac{1}{3}\delta_{ij} \underbrace{\int d^3R\, f(\vec{R})\, R^2}_{\sim \lambda_c^2}$$

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \underbrace{\frac{1}{6}\frac{Ze^2}{4\pi\epsilon_0}\left(\nabla^2\frac{1}{r}\right)\lambda_c^2}_{\nabla^2\frac{1}{r} \to -4\pi\delta(\vec{r})} + \dots$$

$$= -\frac{Ze^2}{4\pi\epsilon_0 r} + \hat{H}_D$$

$$\mathcal{H}_D = - \frac{1}{6} \frac{Ze^2}{\epsilon_0} \, \lambda_c^{\,2} \, \delta(\vec{r})$$

$$\frac{1}{8}$$

notation

$E_n \rightarrow (n \ell m)$

$s \Rightarrow \ell = 0$

$p \Rightarrow \ell = 1$

$d \Rightarrow \ell = 2$ . .

$1s$, $2s$, $2p$, $3s$, $3p$, $3d$

$\ell = 0, 1, 2$

$S, P, D \ldots (\ell)$

notation spectroscopique pour les états de structure fine

$n L_j$