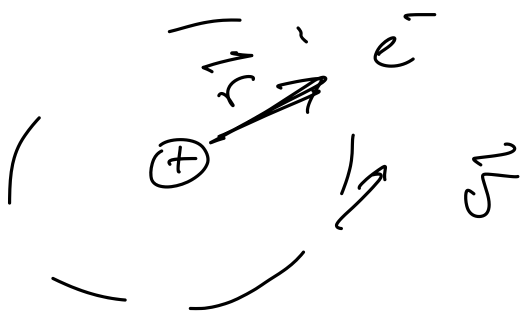
Corrections relativistes à l'atome de H
(structure fine)

v ?



$\Delta p \, \Delta x \gtrsim \hbar$

$a_0 \simeq 0.5 \times 10^{-10}$ m

$$v \simeq \frac{\Delta p}{m} \gtrsim \frac{\hbar}{m \Delta x}$$

$$\Delta x \simeq \frac{a_0}{(Z)}$$

$\dfrac{\hbar}{m a_0}$ devant c ?

$$\alpha = \frac{\hbar}{m a_0 c} \simeq \frac{1}{137}$$

constante de structure fine

(équation de Dirac)

$$H = \frac{\vec p^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r} + \underbrace{\Delta H}_{H_{so} + H_{rel} + H_D}$$

$\llcorner H_0 \longrightarrow$

$$E_n = -\frac{R_y}{n^2}$$

H_{so} : couplage spin-orbite

H_{rel} : correction relativiste à l'énergie cinétique

H_D : terme de Darwin

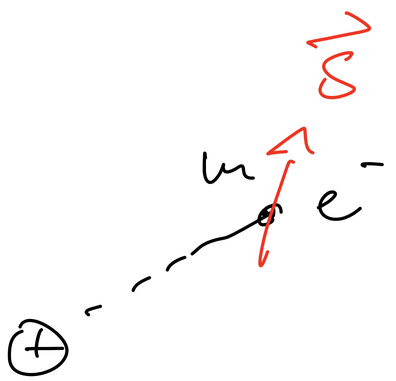
$Ry = 13.6\ eV$

$f = \frac{Ry}{h} \simeq 10^{15}\ Hz$

$\mathcal{O}(\alpha^2)\ Ry$

$f \simeq 10^{10}\ Hz$

Couplage spin-orbite



moment magnétique

$\vec{m} = g\mu_B \vec{S}/\hbar$

$g \simeq -2$

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

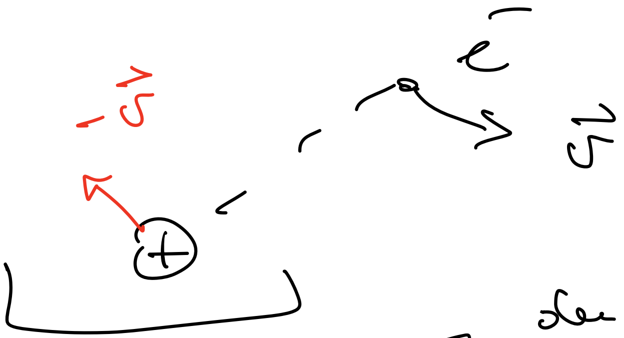
$\mathcal{H}$

$|n\ell m\rangle \otimes |s\ m_s\rangle$

$\vec{L}^2 \quad L^z \quad \vec{S}^2 \quad S^z$

$E_n = -\frac{Ry}{n^2}$

$D_n = 2n^2$



densité de charge

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

$$\rho = Ze\,\delta(\vec{r}) \qquad \epsilon_0\mu_0 = \frac{1}{c^2}$$

$4\pi \times 10^{-7}$ H/m

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

$$= -\frac{\mu_0\epsilon_0\,(Ze^2)}{m\,4\pi e\,\epsilon_0}\,\frac{(m\vec{v})\times\vec{r}}{r^3} \qquad m\vec{v} = \vec{p}$$

$$= \frac{1}{mc^2 e}\left(\frac{Ze^2}{4\pi\epsilon_0 r^3}\right)(\vec{r}\times\vec{p}) \rightarrow \vec{L}$$

$$\frac{1}{r}\frac{dV}{dr}$$

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

$$\vec{B}(\vec{r}) = \frac{1}{mec^2}\left(\frac{1}{r}\frac{dU}{dr}\right)\vec{L}$$

Spin-orbite

$$E_{SO} = -\vec{\mu}\cdot\vec{B}$$

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

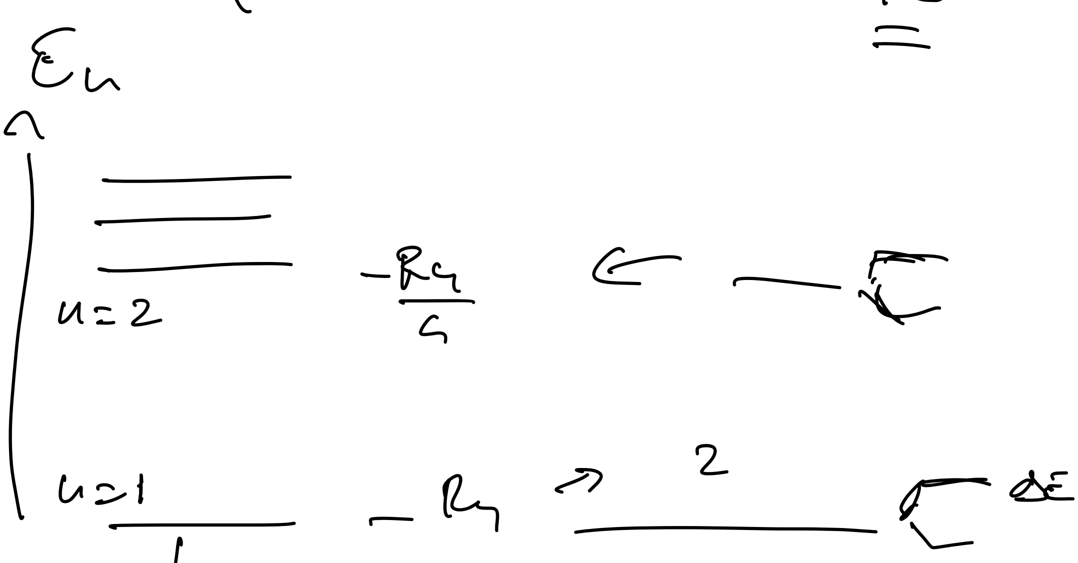
$$\mu_B = \frac{e\hbar}{2m}$$

$$= \frac{1}{2m^2c^2}\left(\frac{1}{r}\frac{dU}{dr}\right)\vec{L}\cdot\vec{S}$$

précession de Thomas

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

perturbation de $\underline{\underline{H_0}}$



$$D_n = 2n^2 \qquad |n\ell m\rangle \otimes |s\, m_s\rangle$$

théorie des perturbations dans le cas dégénéré

$$\langle n\ell m| \otimes \langle s m_s| \; H_{so} \; |n\ell' m'\rangle \otimes |s\, m_s'\rangle \sim \delta_{\ell\ell'}$$

$$H_0 \quad \vec{L}^2 \quad L^z \quad \vec{S}^2 \quad S^z$$

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

moment cinétique total de l'électron

$$|n\ell s;\, j\, m_j\rangle$$

$$H_0 \quad \vec{L}^2 \quad \vec{S}^2 \quad \vec{J}^2 \quad J^z$$

$$j = |\ell - s|, \ldots, \ell + s$$

$$j = \begin{cases} \ell - \frac{1}{2},\ \ell + \frac{1}{2} & \ell \neq 0 \\ \frac{1}{2} & \ell = 0 \end{cases}$$

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

$$\vec{L}\cdot\vec{S} = \underbrace{\frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]}$$

$$[\vec{L}\cdot\vec{S}, \vec{L}^2] = 0$$

$$[\quad , \vec{J}^2] = 0 \qquad [\vec{L}\cdot\vec{S}, \vec{S}^2] = 0$$

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

$$=$$

$$\Uparrow$$

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

$$\langle n l s; j m_j | \frac{1}{2m^2c^2} \underbrace{\left(\frac{1}{r}\frac{dV}{dr}\right)} \left(\vec{L}\cdot\vec{S}\right) | n l' s; j' m_j' \rangle$$

$$\frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]$$

$$= \delta_{l l'}\, \delta_{j j'}\, \delta_{m_j m_j'}$$

$$\frac{1}{2m^2c^2} \underbrace{\left\langle \frac{1}{r}\frac{dV}{dr} \right\rangle_{nl}} \qquad \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$$\Uparrow$$

$$\int_0^\infty dr\, r^2 R_{nl}^2 \frac{1}{r}\frac{dV}{dr}$$

$$[\vec{J}^2, J^z] = 0$$

$$[\vec{L}^2, J^z] = 0$$

$$[\vec{S}^2, J^z] = 0$$

$$\int_0^\infty dr \quad r^2 \quad \underline{\underline{R_{nl}}} \quad rP$$

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{Z^3}{l(l+1)(l+\frac{1}{2})(na_0)^3}$$

$$\Delta E_{nljs}^{(SO)} = \frac{1}{2m^2 c^2} \frac{Z^4 e^2}{4\pi\epsilon_0} \frac{1}{l(l+1)(l+\frac{1}{2})(na_0)^3}$$

$$\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$$\Rightarrow \quad \Delta E_{nljs}^{(SO)} = \frac{1}{2}|E_n| \frac{Z^4 \alpha^2}{n\, l(l+1)(l+\frac{1}{2})} \times$$

$$\left[j(j+1) - l(l+1) - s(s+1)\right]$$

Correction relativiste à l'énergie cinétique

$$E_{kin} = \frac{p^2}{2m} \to E_{kin,\,rel} = \sqrt{m^2c^4 + c^2p^2}$$

$$v = \frac{p}{m} \ll c$$

$$= mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} = mc^2\left[1 + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + o\left(\frac{p}{mc}\right)^6\right]$$

$$= mc^2 + \frac{1}{2}\frac{p^2}{m} \underbrace{- \frac{1}{8}\frac{p^4}{m^3c^2}}_{-\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2} + o\left(\frac{p}{mc}\right)^6 mc^2$$

$$\underbrace{\qquad\qquad}_{H_{rel}}$$

$$H_0 = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\frac{p^2}{2m} = H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\left[f(r), \vec{L}^2\right] = 0, \quad \vec{J}^2 = 0, \quad J^z = 0$$

$$\underline{\underline{H_{rel}}} = -\frac{1}{2mc^2}\left(H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2$$

$$|n\underline{l}s_i; jm_j\rangle$$

$$\langle nls_i; jm_j | H_{rel} | nl's_i; j'm_j'\rangle$$

$$= \left(\delta_{jj'}\,\delta_{m_j m_j'}\,\delta_{ll'}\right)\left(-\frac{1}{2mc^2}\right)\langle nls_i, jm_j|\Big[\underbrace{H_0^2}_{E_n^2}+\frac{Ze^2}{4\pi\epsilon_0 r}\underbrace{H_0}_{E_n}+\underbrace{H_0}_{E_n}\frac{Ze^2}{4\pi\epsilon_0 r}+\left(\frac{Ze^2}{4\pi\epsilon_0 r}\right)^2\Big]|nls_i, jm_j\rangle$$

$$H_0|nls_i, jm_j\rangle = E_n|nls_i, jm_j\rangle$$

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

$$\left\langle\frac{1}{r}\right\rangle_{nl} \to \frac{Z}{n^2 a_0} \qquad \left\langle\frac{1}{r^2}\right\rangle_{nl} \to \frac{Z^2}{n^3 a_0^2\left(l+\frac{1}{2}\right)}$$

$$\Delta E_{nl}^{(rel)} = \dots = -E_n\frac{Z^2\alpha^2}{n^2}\left[\frac{3}{4}-\frac{n}{l+1/2}\right]$$

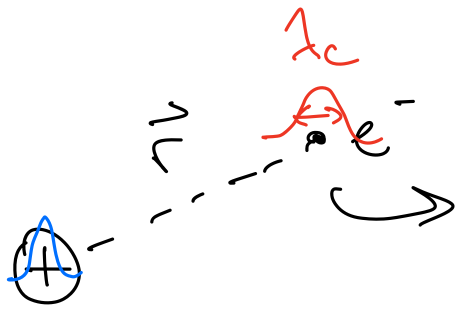
Terme de Darwin

$$c \geq v = \frac{\Delta p}{m} \geq \frac{\hbar}{m \Delta x}$$

$$\Delta x \geq \frac{\hbar}{mc} = \lambda_c$$ Longueur de Compton (réduite)

e^- : $\lambda_c = 3.87 \times 10^{-13}$ m

$$\alpha = \frac{\lambda_c}{a_0}$$



distribution de charge

$$\rho(\vec r) = -e f(\vec r)$$

$$\int d^3 r \, f(\vec r) = 1$$

$$V(\overset{\sim a_0}{\vec r}) = -\frac{Z e^2}{4\pi\epsilon_0 r} \longrightarrow \int d^3\vec R \, \underbrace{\frac{-Z e^2}{4\pi\epsilon_0 |\vec r + \vec R|}}_{V(\vec r + \vec R)} f(\overset{\sim \lambda_c}{\vec R})$$

$$|\vec r| \gg |\vec R|$$

$$= \int d^3R\, f(|\vec R|)\Big[\overset{1}{V(\vec r)} + \vec R \cdot \vec\nabla V(\vec r)$$

$$+ \frac{1}{2} \vec R^T H_V \vec R + o(R^3) \Big]$$

$$H_V = \left(\frac{\partial^2 V}{\partial r_i \partial r_j} \right)$$

$$= V(\vec r) + \vec\nabla V \cancelto{0}{\int d^3R\, \vec R\, f(|\vec R|)}$$

$$+ \frac{1}{2} \sum_{ij} \frac{\partial^2 V}{\partial r_i \partial r_j} \int d^3R\, R_i R_j\, f(|\vec R|) + \dots$$

$i = x, y, z$

$j =$

$$= \begin{cases} 0 & i \neq j \\ \underbrace{\int d^3R\, R_i^2 f(R)}_{\frac{1}{3} \int d^3R\, R^2 f(R)} & i = j \end{cases}$$

$$\int dR_x\, dR_y\, dR_z\, R_x R_y\, f(R) = 0$$

$$\lambda_c^2$$

$$V_{eff}(\vec{r}) = V(\vec{r}) + \frac{1}{6}\nabla^2 V \int d^3R\, R^2 f(R) + \dots$$

$$\nabla^2\left(-\frac{Ze^2}{4\pi\epsilon_0 r}\right) \qquad \nabla^2 \frac{1}{r} = -4\pi\delta(\vec{r})$$

$$V_{eff}(r) = V(r) + \underbrace{\frac{1}{6}\frac{Ze^2}{\epsilon_0}\lambda_c^2\,\delta(\vec{r})}_{\mathcal{H}_D}$$

$\frac{1}{8}$

$$\langle nls, jm_j | \mathcal{H}_D | nls, jm_j \rangle$$

$=$ $=$

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

seulement si $l=0$ $\Rightarrow$ $\neq 0$

$$\Delta E_{nl}^{(D)} = \delta_{l0} \frac{\pi \hbar^2 Z}{m^2 c^2} a_0 \, Ry \, \underbrace{\left| \psi_{n00}(0) \right|^2}_{\frac{Z^3}{\pi n^3 a_0^3}}$$

$$= \dots = -E_n \frac{Z^4 \alpha^2}{n} \delta_{l0}$$