

H_{sf} ?

$$H_{sf}\chi = E\chi$$

Atome H :

$$H_{sf} = \frac{p^2}{2m} + V - \underbrace{\frac{\mathbf{p}^4}{8m^3r^2}}_{W_{mv}} + \underbrace{\frac{\hbar^2 e^2 \pi}{2m^2 c^2} \delta(\mathbf{r})}_{W_D} + \underbrace{\frac{e^2}{2m^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S}}_{W_{so}}$$

Théorie des perturbations stationnaires

$$E_n^0 = -\frac{E_I}{n^2}; E_I = \frac{me^4}{2\hbar^2} = \frac{1}{2}mc^2\alpha^2$$

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

$$1S : E_{1s} = E_{1s}^0 + \langle 1S | W_{mv} + W_D | 1S \rangle = E_{1s}^0 - \frac{1}{8}mc^2\alpha^2$$

$$1S : E_{2s}^0 + \langle 2S | W_{mv} + W_D | 2S \rangle = -\frac{5}{128}mc^2\alpha^4$$

$$\dim \mathcal{E}_{n=2} = 8 \rightarrow (W_{sf})_{\mathcal{E}_{n=2}} \text{ à diagonaliser}$$

$$(W_{sf})_{\mathcal{E}_{n=2}} = \begin{pmatrix} 2 \times 2 & 0 \\ 0 & 6 \times 6 \end{pmatrix}$$

On a que

$$[\mathbf{L}, W_{mv}] = 0 \text{ car } [\mathbf{L}, \mathbf{P}^4] = 0$$

W_{mv} est donc un opérateur scalaire

$$\langle 2, 1, m | W_{mv} | 2, 1, m \rangle = \langle 2, 1, m | -\frac{1}{2} \frac{(H_0 - V)^2}{mc^2} | 2, 1, m \rangle$$

$$= -\frac{1}{2mc^2} \left(E_2^{(0)2} + 2e^2 E_2^0 \left\langle \frac{1}{R} \right\rangle_{2p} + e^2 \left\langle \frac{1}{R^2} \right\rangle_{2p} \right) = -\frac{7}{384}mc^2\alpha^4$$

$$\langle 2, 1, m | W_{so} | 2, 1, m \rangle = \langle 2, 1, m | \frac{e^2}{2m^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S} | 2, 1, m \rangle$$

Les éléments de la matrice ne seront pas tous diagonaux cette fois dans le sous-espace d'intérêt car $\mathbf{S} \cdot \mathbf{L}$ ne commute pas avec \mathbf{L}

$$\begin{aligned}
&= \frac{e^2}{2m^2c^2} \int \frac{r^2}{r^3} dr R_{21} R_{21} \langle 1, m | \mathbf{L} \cdot \mathbf{S} | 1, m \rangle \\
&= \frac{e^2}{2m^2c^2} \int \frac{dr}{r} \left(\frac{1}{24a_0^3} \right) \left(\frac{r}{a_0} \right)^2 e^{\frac{r}{a_0}} \langle \mathbf{L} \cdot \mathbf{S} \rangle \\
&= \xi_{2P} \langle \mathbf{L} \cdot \mathbf{S} \rangle
\end{aligned}$$

$$\langle L \cdot S \rangle = \langle \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2 \rangle = h^2 \left[\frac{1}{2} J(J+1) - \frac{11}{8} \right]$$