Ex. 1

1. $H = -\frac{1}{2}\vec{\nabla}_1^2 - \frac{1}{2}\vec{\nabla}_2^2 - \frac{1}{2}\vec{\nabla}_3^2 - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}}$

où $\vec{\nabla}_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ (laplacien)

$r_i = |\vec{r}_i| =$ distance de l'électron i du noyau

$r_{ij} = |\vec{r}_i - \vec{r}_j| =$ distance entre les électrons i et j

2. (a) $1s^2$: 2 électrons dans l'état $1s$ $(n=1, l=0)$

$4d^1$: 1 électron dans l'état $4d$ $(n=4, l=2)$

(b) La configuration $1s^2$ n'est pas dégénérée (couche remplie)

la configuration $4d^1$ est 10-fois dégénérée $\left(m_l = \pm 2, \pm 1, 0 \quad m_s = \pm \frac{1}{2}\right)$

$\hookrightarrow (1s^2)(4d^1)$ est 10-fois dégénérée

(c) $L = 0+2 = 2$ et $S = \frac{1}{2}$ $\Rightarrow J = \frac{3}{2}$ ou $\frac{5}{2}$

$J = \frac{3}{2}$: 4-fois dégénérée $\left(m_J = \pm\frac{3}{2}, \pm\frac{1}{2}\right)$

$J = \frac{5}{2}$: 6-fois dég. $\left(m_J = \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}\right)$

3. $Z = 3 \hookrightarrow 3$ électrons. Nb. quantiques : $(1, 0, 0, \frac{1}{2})$

$(1, 0, 0, -\frac{1}{2})$

$(2, 0, 0, \frac{1}{2})$

$$|\Psi\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{100}(\vec{x}_1)\,|+\rangle_1 & \psi_{100}(\vec{x}_1)\,|-\rangle_1 & \psi_{200}(\vec{x}_1)\,|+\rangle_1 \\ \psi_{100}(\vec{x}_2)\,|+\rangle_2 & \psi_{100}(\vec{x}_2)\,|-\rangle_2 & \psi_{200}(\vec{x}_2)\,|+\rangle_2 \\ \psi_{100}(\vec{x}_3)\,|+\rangle_3 & \psi_{100}(\vec{x}_3)\,|-\rangle_3 & \psi_{200}(\vec{x}_3)\,|+\rangle_3 \end{vmatrix}$$

4. Système hydrogenoïde avec $Z_{eff} = 1$, $n = 2$

$\hookrightarrow V_{ion} = \frac{13.6\text{ eV}}{2^2} = 3.4\text{ eV}$

5. (a)

$$\text{H-F}: \left(-\frac{1}{2}\vec{\nabla}^2 - \frac{3}{|\vec{x}|} + \sum_{\substack{\lambda=(100+),\\(100-),\\(200+)}} V_{d,\lambda}(\vec{x})\right)\psi_{100-}(\vec{x}) - \sum_{\substack{\lambda=(100+),\\(100-),\\(200+)}} \int V^\ell_{ex,(100-)\lambda}(\vec{x},\vec{y})\,\psi_{100-}(\vec{y})\,d^3y$$

$$= \epsilon_{100-}\,\psi_{100-}(\vec{x})$$

Or $V^\ell_{ex,\kappa\lambda} \propto \delta_{m_s^{(\kappa)} m_s^{(\lambda)}} \Rightarrow V^\ell_{ex,(100+)(100-)} = 0,\ V^\ell_{ex,(200+)(100-)} = 0$

et $\displaystyle\int V^\ell_{ex,(100-)(100-)}(\vec{x},\vec{y})\,\psi_{100-}(\vec{y})\,d^3y = \int d^3y\,\frac{|\psi_{100-}(\vec{y})|^2}{|\vec{x}-\vec{y}|}\,\psi_{100-}(\vec{x})$

$$= V_{d,(100-)}(\vec{x})\,\psi_{100-}(\vec{x})$$

H-F devient $\displaystyle\left(-\frac{1}{2}\vec{\nabla}^2 - \frac{3}{|\vec{x}|} + \sum_{\lambda\neq(100-)} V_{d,\lambda}(\vec{x})\right)\psi_{100-}(\vec{x}) = \epsilon_{100-}\,\psi_{100-}(\vec{x})$

ce qui est l'éq. de Hartree.

(b) Grands r: $V_{eff}(r) \sim -\frac{1}{r}\left(1 + \text{exponentiellement supprimé}\right)$

$\sim -\frac{1}{r}$ potentiel écrantée avec charge effective $Z_{eff} = Z-2 = 1$

Petits r: $V_{eff}(r) \sim -\frac{1}{r}\left(1+1+1+\mathcal{O}(r)\right)$

$\sim -\frac{3}{r} + \text{const.} + \mathcal{O}(r)$

l'électron voit la charge nucléaire "nue", les effets des autres électrons se compensent en moyenne

Ex. 2

A) (a) état fondamental 1s $\Rightarrow$ premier terme $\vec{L}\cdot\vec{\mu}_I$ s'annule car $L=0$

deuxième terme : $Y_1^0 = Y_1^{0*} = \text{const.}$

$$\Rightarrow \langle 1,0,0,m_s',m_I' | \sum_q g(R) C_q Y_2^q(\theta,\phi) \mu_q | 1,0,0,m_s,m_I \rangle$$

$$\propto \sum_q \underbrace{\int d\phi \int d\cos\theta \, Y_2^q(\theta,\phi)}_{=0} = 0$$

troisième terme : $\langle 1,0,0,m_s',m_I' | \frac{8\pi}{3} \vec{\mu}_S\cdot\vec{\mu}_I \, \delta(\vec{R}) | 1,0,0,m_s,m_I \rangle$

$$= \frac{8\pi}{3} \frac{g_P \mu_n}{\hbar} \frac{g_e \mu_e}{\hbar} \int d^3R \, \psi_{100}^*(\vec{R}) \, \delta(\vec{R}) \, \psi_{100}(\vec{R}) \, \langle m_s', m_I' | \vec{S}\cdot\vec{I} | m_s, m_I \rangle$$

(avec $\psi_{100}(\vec{R}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-R/a_0}$, $g_e = 2$, $\mu_n = \frac{e\hbar}{2M_p c}$, $\mu_e = \frac{e\hbar}{2m_e c}$)

$$= \underbrace{\frac{4}{3} \frac{g_p e^2}{M_p m_e c^2 a_0^3}}_{\equiv A} \langle m_s', m_I' | \vec{I}\cdot\vec{S} | m_s, m_I \rangle$$

(b) i. Vu que $[\vec{F}^2, \vec{I}\cdot\vec{S}] = 0$ et $[F_z, \vec{I}\cdot\vec{S}] = 0$, la perturbation est diagonale dans la base $\{|F, m_F\rangle\}$

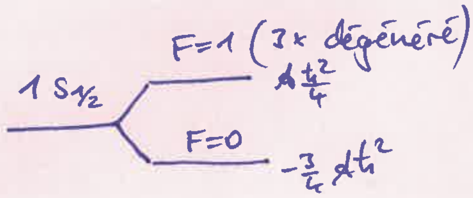
ii. $\vec{F}^2 = (\vec{L}+\vec{S}+\vec{I})^2 = \vec{L}^2 + \vec{S}^2 + \vec{I}^2 + 2\vec{L}\cdot\vec{I} + 2\vec{L}\cdot\vec{S} + 2\vec{I}\cdot\vec{S}$

$\Leftrightarrow \vec{I}\cdot\vec{S} = \frac{1}{2}(\vec{F}^2 - \vec{L}^2 - \vec{S}^2 - \vec{I}^2 - 2\vec{L}\cdot\vec{I} - 2\vec{L}\cdot\vec{S})$

avec $L=0$, $s=\frac{1}{2}$, $I=\frac{1}{2}$: valeurs propres de $A\,\vec{I}\cdot\vec{S}$

$$= A\frac{\hbar^2}{2}\left(F(F+1) - \frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right) = A\frac{\hbar^2}{2}\left(F(F+1) - \frac{3}{2}\right)$$

iii. $F = \frac{1}{2} - \frac{1}{2} = 0$ ou $F = \frac{1}{2} + \frac{1}{2} = 1$



iv. $\Delta L = 0 \Rightarrow$ pas dipolaire électrique

$$\Delta E = A\hbar^2 = \frac{4}{3} g_p \frac{m_e^2 c^2}{m_p} = \frac{\hbar c}{\lambda} \Rightarrow \lambda = 21\text{ cm}$$

B)

(a) $l = 0 \Rightarrow$ le terme $-\vec{B}_0 \cdot \vec{\mu}_L$ ne contribue pas

$M_p >> m_e \Rightarrow \vec{B}_0 \cdot \vec{\mu}_I$ négligeable devant $\vec{B}_0 \cdot \vec{\mu}_S$

$$H_{pert} \approx A\, \vec{I} \cdot \vec{S} - \vec{B}_0 \cdot \vec{\mu}_S = A\, \vec{I} \cdot \vec{S} + \frac{e B_0}{m_e c} S_z$$

(b)

$$|F=0, m_F=0\rangle = \frac{1}{\sqrt{2}}\left(|m_S = \tfrac{1}{2}, m_I = -\tfrac{1}{2}\rangle - |m_S = -\tfrac{1}{2}, m_I = \tfrac{1}{2}\rangle\right)$$

$$\equiv \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right)$$

$$|F=1, m_F=1\rangle = |++\rangle$$

$$|F=1, m_F=0\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right)$$

$$|F=1, m_F=-1\rangle = |--\rangle$$

$$S_z|1,1\rangle = S_z|++\rangle = \frac{\hbar}{2}|++\rangle = \frac{\hbar}{2}|1,1\rangle$$

$$S_z|1,-1\rangle = S_z|--\rangle = -\frac{\hbar}{2}|--\rangle = -\frac{\hbar}{2}|1,-1\rangle$$

$$S_z|1\,0\rangle = \frac{1}{\sqrt{2}}\left(S_z|+-\rangle + S_z|-+\rangle\right) = \frac{1}{\sqrt{2}}\left(+\frac{\hbar}{2}|+-\rangle - \frac{\hbar}{2}|-+\rangle\right)$$

$$= \frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right) = \frac{\hbar}{2}|0,0\rangle$$

$$S_z|0\,0\rangle = \frac{1}{\sqrt{2}}\left(S_z|+-\rangle - S_z|-+\rangle\right) = \frac{1}{\sqrt{2}}\left(+\frac{\hbar}{2}|+-\rangle + \frac{\hbar}{2}|-+\rangle\right)$$

$$= \frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right) = \frac{\hbar}{2}|1,0\rangle$$

$$\hookrightarrow \mathcal{M} = \frac{\hbar}{2}\begin{pmatrix} 1 & & & \\ & -1 & & \\ & & 0 & 1 \\ & & 1 & 0 \end{pmatrix}$$

$$H_{pert} = \begin{pmatrix} \frac{A\hbar^2}{4} + \hbar\omega_0 & & & \\ & \frac{A\hbar^2}{4} - \hbar\omega_0 & & \\ & & \frac{A\hbar^2}{4} & \hbar\omega_0 \\ & & \hbar\omega_0 & -\frac{3}{4}A\hbar^2 \end{pmatrix}$$

$$\omega_0 = \frac{\hbar e B_0}{2 m_e c}$$

(c) valeurs propres: $\frac{A\hbar^2}{4} \pm \hbar\omega_0$

et les valeurs propres de $\begin{pmatrix} \frac{A\hbar^2}{4} & \hbar\omega_0 \\ \hbar\omega_0 & -\frac{3}{4}A\hbar^2 \end{pmatrix}$

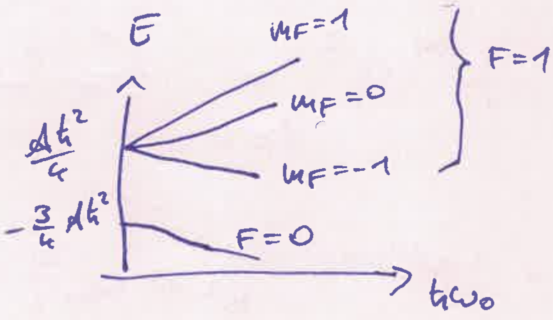
Ex. 2 B) (c)

$$\begin{vmatrix} \frac{A\hbar^2}{4} - \lambda & \hbar\omega_0 \\ \hbar\omega_0 & -\frac{3}{4}A\hbar^2 - \lambda \end{vmatrix} = 0$$

$$\Leftrightarrow -\left(\frac{A\hbar^2}{4} - \lambda\right)\left(\frac{3}{4}A\hbar^2 + \lambda\right) - \hbar^2\omega_0^2 = 0$$

$$\Leftrightarrow \lambda^2 + \frac{A\hbar^2}{2}\lambda - \frac{3A^2\hbar^4}{16} - \hbar^2\omega_0^2 = 0$$

$$\Leftrightarrow \lambda_{1,2} = -\frac{A\hbar^2}{4} \pm \sqrt{\frac{A^2\hbar^4}{4} + \hbar^2\omega_0^2}$$



Ex. 3

1. $E_{12} = E_2 - E_1 = \left(\frac{1}{4} - 1\right) E_1 = -\frac{3}{4} \times (-13.6\,eV) = 10.2\,eV$

2. $\vec{E} = \theta(t)\vec{E}_0 e^{-t/\tau}$ en direction $\vec{e}_z \Rightarrow \Phi = e\theta(t) e^{-t/\tau} E_0 z$

$$\langle 210 | \Phi | 100 \rangle = \int_0^\infty r^2 dr \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi \, \frac{1}{4\pi\sqrt{2}a_0^4} r^2 \cos^2\theta \, e^{-\frac{3}{2}\frac{r}{a_0}} eE_0\theta(t)e^{-t/\tau}$$

$$= \frac{eE_0}{4\pi\sqrt{2}a_0^4}\theta(t)e^{-t/\tau} 2\pi \underbrace{\int_0^\infty r^4 e^{-\frac{3}{2}\frac{r}{a_0}} dr}_{= \left(\frac{2a_0}{3}\right)^5 \underbrace{\int_0^\infty x^4 e^{-x} dx}_{=24}} \underbrace{\int_{-1}^{1} \cos^2\theta \, d\cos\theta}_{=\frac{2}{3}}$$

$$\left(\begin{array}{l} x = \frac{3r}{2a_0} \\ dr = \frac{2a_0}{3} dx \\ r^4 = \frac{16}{81} a_0^4 x^4 \end{array} \right)$$

$$= eE_0 a_0 \times \frac{2^{15/2}}{3^5} \theta(t) e^{-t/\tau}$$

$$c^{(1)}(t) = \frac{1}{i\hbar}\int_0^t dt' \, e^{-t'/\tau} e^{\frac{i}{\hbar}E_{21}t'} \langle 210 | \Phi | 100 \rangle$$

$$c^{(1)}(t) = -\frac{ieE_0 a_0}{\hbar} \frac{2^{15/2}}{3^5} \frac{1 - e^{\left(\frac{i}{\hbar}E_{21} - \frac{1}{\tau}\right)t}}{\frac{i}{\hbar}E_{21} - \frac{1}{\tau}}$$

$$|c^{(1)}(t)|^2 \underset{t \gg \tau}{=} \frac{2^{15}}{3^{10}} \frac{e^2 E_0^2 a_0^2}{\hbar^2} \frac{1}{\omega_{21}^2 + \frac{1}{\tau^2}} \qquad \omega_{21} = \frac{E_{21}}{\hbar}$$

3. indép. si $\frac{1}{\tau^2} \gg \omega_{21}^2 \iff \tau \ll \frac{\hbar}{E_{21}}$