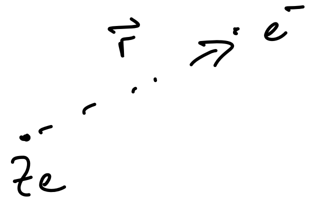
Structure principale de l'atome de H

(Théorie non-relativiste de Schrödinger)

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\vec r} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



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

$$\mathcal{H}|n l m\rangle = E_n |n l m\rangle$$

$$E_n = -\frac{R_y(Z)}{n^2} \qquad l = 0, 1, \dots, n-1$$

$$n = 1, 2, \dots, \infty$$

$$|nlm\rangle \to \psi_{nlm}(r,\theta,\phi) = N_{nl}\, Y_{lm}(\theta,\phi)\, \underbrace{R_{nl}(r)}_{P_{n-1}\left(\frac{Zr}{na_0}\right) e^{-\frac{rZ}{na_0}}}$$

$$\underbrace{P_{n-1}\left(\frac{Zr}{na_0}\right)}_{\left(\frac{Zr}{a_0}\right)^l L^{2l+1}_{n+l}\left(\frac{2rZ}{na_0}\right)}$$

$$1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, r^2 |Y_{lm}|^2 |R_{nl}|^2$$

$P(r)$

Effets relativistes

$\vec{S}$

e^-, m

$\hat{\vec{S}} = (\hat{S}^x, \hat{S}^y, \hat{S}^z)$

$[\hat{S}^\alpha, \hat{S}^\beta] = i\hbar \sum_\gamma \epsilon_{\alpha\beta\gamma} \hat{S}^\gamma$

$\alpha, \beta = x, y, z$ $\quad |\hat{\vec{S}}^2| \to \hbar^2 S(S+1)$

$S = \frac{1}{2}$

moment magnétique :

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

$\mu_B = \frac{e\hbar}{2m}$ magnéton de Bohr

$g \simeq -2$ facteur gyromagnétique de l'électron

$\underbrace{\hat{\vec{L}}, \hat{\vec{S}}}$ deux moments cinétiques de l'électron

$[\hat{L}^\alpha, \hat{S}^\beta] = 0$

Deux espaces de Hilbert : $\mathcal{H}_1, \mathcal{H}_2 \to \underbrace{\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2}$

$|\psi_1\rangle$ $\quad |\psi_2\rangle$ $\quad |\psi_1\rangle \otimes |\psi_2\rangle$

$\hat{\vec{L}} \to \underset{\mathcal{H}_1}{\hat{\vec{L}}} \otimes \underset{\mathcal{H}_2}{\hat{\mathbb{1}}}$ $\qquad \vec{S} \to \underset{\mathcal{H}_1}{\hat{\mathbb{1}}} \otimes \underset{\mathcal{H}_2}{\hat{\vec{S}}}$

Composition (somme) de moments cinétique en MQ

$\hat{\vec{L}}_1 \, , \, \hat{\vec{L}}_2 \longrightarrow H_1 \otimes H_2$

$\hat{L}_1^2 \to \hbar^2 \ell_1(\ell_1+1)$

$\hat{L}_1^z \to \hbar m_1$

$\hat{L}_2^2 \to \hbar^2 \ell_2(\ell_2+1)$

$\hat{L}_2^z \to \hbar m_2$

ℓ_1, ℓ_2 entiers ou demi-entiers

Base pour $H_1 \otimes H_2$: $|\ell_1 m_1\rangle \otimes |\ell_2 m_2\rangle$

$|\ell_1 m_1\rangle$: $\hat{\vec{L}}_1^2$, $\hat{L}_1^z$

$|\ell_2 m_2\rangle$: $\hat{\vec{L}}_2^2$, $\hat{L}_2^z$

$[\hat{L}_1^\alpha, \hat{L}_2^\beta] = 0$

ECOC
ensemble complet d'observables compatibles

ECOC alternatif : $\hat{L}_1^2, \hat{L}_2^2, \hat{L}^2, \hat{L}^z$

$\hat{\vec{L}} = \hat{\vec{L}}_1 + \hat{\vec{L}}_2 \to H_1 \otimes H_2$

$\left(= \hat{L}_1 \otimes \hat{\mathbb{1}}_2 + \hat{\mathbb{1}}_1 \otimes \hat{L}_2 \right)$

$[\hat{L}^\alpha, \hat{L}^\beta] = [\hat{L}_1^\alpha + \hat{L}_2^\alpha, \hat{L}_1^\beta + \hat{L}_2^\beta]$

$= [\hat{L}_1^\alpha, \hat{L}_1^\beta] + [\hat{L}_2^\alpha, \hat{L}_2^\beta]$

$$= i\hbar \sum_\gamma \epsilon_{\alpha\beta\gamma} (\hat{L}_1^\gamma + \hat{L}_2^\gamma)$$

$$\hat{L}^\gamma$$

$\hat{\vec{L}}^2$, $\hat{L}^z$ compatible

$\hbar^2 L(L+1)$ $\qquad \hbar M$

$$\hat{\vec{L}}^2 = \hat{\vec{L}}_1^2 + \hat{\vec{L}}_2^2 + \underbrace{\hat{\vec{L}}_1 \cdot \hat{\vec{L}}_2 + \hat{\vec{L}}_2 \cdot \hat{\vec{L}}_1}_{2 \vec{L}_1 \cdot \vec{L}_2}$$

$\vec{L}_1^2$ (2)

$$\hat{L}^z = \hat{L}_1^z + \hat{L}_2^z$$

$\hat{\vec{L}}_1^2$ (2)

$\hat{L}_1^z$, $\hat{L}_2^z$

$\vec{L}_1^2$, $\vec{L}_2^2$, $\vec{L}^2$, L^z : ECOC pour $H_1 \otimes H_2$

$|\ell_1 \ell_2 ; LM\rangle$ base pour $H_1 \otimes H_2$

Changement de base vers $|\ell_1 m_1\rangle \otimes |\ell_2 m_2\rangle$

$$|\ell_1 \ell_2 ; LM\rangle \neq |\psi_1\rangle \otimes |\psi_2\rangle$$

$\underbrace{\quad}_{H_1 \otimes H_2}$

$H_1 \otimes H_2$ intriqué ?

fixe ℓ_1, ℓ_2 quelles valeurs pour L et M ?

$$|\ell_1 m_1\rangle \otimes |\ell_2 m_2\rangle = \sum_{L,M} \left[\langle \ell_1 \ell_2 ; LM | \left(|\ell_1 m_1\rangle \otimes |\ell_2 m_2\rangle \right) \right] |\ell_1 \ell_2 ; LM\rangle$$

$$\left(\underline{\mathbb{1}}_{\ell_1 \ell_2} = \sum_{LM} |\ell_1 \ell_2 ; LM\rangle \langle \ell_1 \ell_2 ; LM| \right)$$

$$\left(\langle \ell_1 \ell_2 ; LM| \right) \left(|\ell_1 m_1\rangle \otimes |\ell_2 m_2\rangle \right) = C^{\ell_1 \ell_2}_{m_1 m_2 ; LM}$$

coefficients de Clebsch - Gordan

Somme de deux spins $s = 1/2$

$$\vec{L}_1 \to \vec{S}_1 \qquad |\vec{S}_1|^2 = \hbar^2 s(s+1) \qquad s = 1/2$$

$$\vec{L}_2 \to \vec{S}_2 \qquad (2)$$

$H_1 \otimes H_2$ $\qquad \dim(H_1 \otimes H_2) = \dim(H_1)\,\dim(H_2)$

$\pm 1/2$

$$|\ell_1 m_1\rangle \otimes |\ell_2 m_2\rangle \to |s = \tfrac{1}{2}, m_1\rangle \otimes |s = \tfrac{1}{2}, m_2\rangle$$

$\pm 1/2$

$$|s=\tfrac{1}{2}, m=\tfrac{1}{2}\rangle \Longrightarrow |\uparrow\rangle$$

$$|s=\tfrac{1}{2}, m=-\tfrac{1}{2}\rangle \rightarrow |\downarrow\rangle$$

$$|s=\tfrac{1}{2}, m_1\rangle \otimes |s=\tfrac{1}{2}, m_2\rangle = \left\{\begin{array}{l} |\uparrow\uparrow\rangle = |\uparrow_1\rangle\otimes|\uparrow_2\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{array}\right.$$

$$\left\{\begin{array}{l}
\underset{(2)}{S_1^x} = \frac{\hbar}{2}\underset{(2)}{\sigma_1^x} = \frac{\hbar}{2}\begin{array}{c c} & \begin{array}{cc}|\uparrow\rangle & |\downarrow\rangle\end{array} \\ \begin{array}{c}\langle\uparrow| \\ \langle\downarrow|\end{array} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\end{array} \rightarrow \underset{(2)}{\mathcal{H}_1} \\
\qquad\qquad\qquad\qquad \langle\uparrow|\sigma^x|\uparrow\rangle \\
\underset{(2)}{S_1^y} = \frac{\hbar}{2}\sigma_1^y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \rightarrow \underset{(2)}{\mathcal{H}_1} \\
\underset{(2)}{S_1^z} = \frac{\hbar}{2}\sigma_1^z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \rightarrow \underset{(2)}{\mathcal{H}_1}
\end{array}\right.$$

$$S^x = S_1^x + S_2^x \longrightarrow \mathcal{H}_1 \otimes \mathcal{H}_2$$

$$= \underset{\uparrow}{\frac{\hbar}{2}}\ \begin{array}{c c} & \begin{array}{cccc}|\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle\end{array} \\ \begin{array}{c}\langle\uparrow\uparrow| \\ \langle\uparrow\downarrow| \\ \langle\downarrow\uparrow| \\ \langle\downarrow\downarrow|\end{array} & \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}\end{array}$$

$$S^y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i & -i & 0 \\ i & 0 & 0 & -i \\ i & 0 & 0 & -i \\ 0 & i & i & 0 \end{pmatrix}$$

$$S^z = \frac{\hbar}{2}\begin{pmatrix} 2 & & & 0 \\ & 0 & & \\ & & 0 & \\ 0 & & & -2 \end{pmatrix}$$

$$\langle\uparrow\uparrow| S_1^z + S_2^z |\uparrow\uparrow\rangle = \frac{\hbar}{2} + \frac{\hbar}{2} = \hbar$$

$$|\vec{S}|^2 = \hbar^2 \begin{array}{c c} & \begin{array}{cccc} |\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \end{array} \\ \begin{array}{c} \langle\uparrow\uparrow| \\ \langle\uparrow\downarrow| \\ \langle\downarrow\uparrow| \\ \langle\downarrow\downarrow| \end{array} & \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \end{array}$$

$$\underbrace{\hbar^2 s(s+1)}_{\hbar L(L+1)}$$

$$\hbar^2 s(s+1) = 2\hbar^2$$

$$s = 1$$

$$\begin{vmatrix} 1-\lambda & 1 \\ 1 & 1-\lambda \end{vmatrix} = (1-\lambda)^2 - 1 = \lambda(\lambda-2) = 0$$

$$\underline{\lambda} = 0, 2$$

$$S(S+1)$$

$$\underline{S} = 0, 1$$

<u>3 fois dégénéré</u>

états propres de $\hat{\vec{S}}_1^2$, $\hat{\vec{S}}_2^2$, $\hat{\vec{S}}^2$, $\hat{S}^z$

$$|s_1, s_2 ; SM\rangle = |SM\rangle$$

$$|SM\rangle = \begin{cases} |1,1\rangle = |\uparrow\uparrow\rangle \\ |1,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\ |1,-1\rangle = |\downarrow\downarrow\rangle \\ \\ |0,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \end{cases}$$

triplets

singulet

Règles générales de composition de deux moments cinétiques

$$\underbrace{|l_1 m_1\rangle \otimes |l_2 m_2\rangle} \to |l_1 l_2 ; LM\rangle$$

$$C^{l_1 l_2}_{m_1 m_2 ; LM} \neq 0 \quad ?$$

$$L^z = L_1^z + L_2^z$$

$$\left(\qquad \right)$$

$$L^z \left(|l_1 m_1\rangle \otimes |l_2 m_2\rangle \right) \leftarrow$$

$$= (L_1^z + L_2^z) |l_1 m_1\rangle \otimes |l_2 m_2\rangle$$

$$= \hbar \underbrace{(m_1 + m_2)}_{L \quad M} |l_1 m_1\rangle \otimes |l_2 m_2\rangle$$

$$C^{l_1 l_2}_{m_1 m_2 ; LM} \sim \delta_{m_1 + m_2, M}$$

$$|l_1, m_1 = l_1\rangle \otimes |l_2, m_2 = l_2\rangle \qquad |l_1 l_2 ; LM\rangle$$

$$M = l_1 + l_2$$

$$M = -L, \dots, L$$

$$\Rightarrow \quad L \geq l_1 + l_2$$

$$\hat{L}^+ = \hat{L}_1^+ + \hat{L}_2^+ \qquad L = l_1 + l_2$$

$$\hat{L}^+ |l_1 l_1\rangle \otimes |l_2 l_2\rangle = 0$$

$$L^+ |l_1 l_2 ; L, l_1 + l_2\rangle = 0$$

$$l_1 + l_2$$

$$|l_1 l_1\rangle \otimes |l_2 l_2\rangle = |l_1 l_2 ; (l_1+l_2)\, (l_1+l_2)\rangle$$

$$L^- |l_1 l_1\rangle \otimes |l_2 l_2\rangle : \qquad L^- = L_1^- + L_2^-$$

$$L^- |l_1 l_2 ; (l_1+l_2)\, (l_1+l_2)\rangle$$

$$\sim |l_1 l_2 ; (l_1+l_2), (l_1+l_2)-1\rangle$$

$$= \frac{1}{\sqrt{2}} \underbrace{|l_1, l_1 - 1\rangle |l_2, l_2\rangle + |l_1, l_1\rangle |l_2, l_2 - 1\rangle}$$

$$|l_1, l_2 ; (l_1+l_2)-1, (l_1+l_2)-1\rangle$$

$$= \frac{1}{\sqrt{2}} |l_1, l_1 - 1\rangle |l_2\, l_2\rangle - |l_1, l_2\rangle |l_2, l_2 - 1\rangle$$

$\dots$

$$C^{l_1 l_2}_{m_1, m_2, LM} \neq 0 \qquad m_1 + m_2 = M$$

$$L = l_1 + l_2,\ l_1 + l_2 - 1,\ \dots,\ |l_1 - l_2|$$

$$\boxed{L = |l_1 - l_2|,\ |l_1 - l_2| + 1,\ \dots,\ l_1 + l_2}$$

$$(M = -L, \dots, L)$$

Ex. $\quad s_1 = \frac{1}{2} \qquad s_2 = \frac{1}{2}$

$$S = 0, 1$$

$$\dim(H_1 \otimes H_2) = \dim(H_1)\,\dim(H_2)$$

$$\dim(H_1) = 2l_1 + 1 \qquad m_1 = -l_1, \dots, l_1$$

$(1) \qquad (2)$

fixe l_1, l_2

$$\dim (\mathcal{H}_1 \otimes \mathcal{H}_2) = (2l_1+1)(2l_2+1)$$

$$|l_1 l_2 ; LM\rangle$$

$$\sum_{L=|l_1-l_2|}^{l_1+l_2} (2L+1)$$