Université Ibn Tofail
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Examen de Chimie Théorique, S5, SMC
Durée 1h, Pr. Rabaâ

I/ <u>**Question de Cours**</u>: (6 points)

1- Calculer le commutateur $[\hat{L}x, \hat{L}y]$ en coordonnées Cartésians?

2- Exprimer les opérateurs du moment cinétique orbitals, $\hat{L}z$ et $\hat{L}^2$ en coordonnées sphériques?

3- Calculer le commutateur $[\hat{L}z, \hat{L}^2]$? Commenter.

4- Quelle est la condition d'Hermiticité de ces opérateurs? Expliquer.

I/ L'<u>**Atome d'Hydrogène**</u> **(Z=1):** (14 points)

On considère l'atome d'hydrogène, composé d'un noyau de charge Z=1 et d'un électron de masse m_e. On suppose que le noyau est fixe:

1- Ecrire l'équation de Schrödinger générale de l'atome d'hydrogène en coordonnées sphériques)?

2- Sachant que l'état fondamental **1s** (n=1, l=0) de l'atome d'hydrogène de type **ϕ(1s) = C exp (-r/a_0)**, est solution de l'équation de Schrödinger. (C= Constante, r= Rayon, a_0 = Rayon de Bohr), que deviant l'équation de Schrödinger donnée en (1) ? Expliquer.

3- Calculer le facteur de normalisation, C?

4- Calculer la valeur moyenne de la distance noyau-électron. On donne:

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}$$

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I) Questions de cours

1) $\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$ et $\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ et $\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

* $[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \times -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - (-i\hbar)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)(-i\hbar)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

$$= -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) + \hbar^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$= -\hbar^2\left[y\frac{\partial}{\partial z}z\frac{\partial}{\partial x} - \cancel{y\frac{\partial}{\partial z}x\frac{\partial}{\partial z}} - \cancel{z\frac{\partial}{\partial y}z\frac{\partial}{\partial x}} + \cancel{z\frac{\partial}{\partial y}x\frac{\partial}{\partial z}}\right] + \hbar^2\left[\cancel{z\frac{\partial}{\partial x}y\frac{\partial}{\partial z}} - \cancel{z\frac{\partial}{\partial x}z\frac{\partial}{\partial y}} - \cancel{x\frac{\partial}{\partial z}y\frac{\partial}{\partial z}} + x\frac{\partial}{\partial z}z\frac{\partial}{\partial y}\right]$$

$$= -\hbar^2\left[y\frac{\partial z}{\partial z}\frac{\partial}{\partial x}\right] + \hbar^2\left[x\frac{\partial z}{\partial z}\frac{\partial}{\partial y}\right] = -\hbar^2\left(y\frac{\partial}{\partial x}\right) - \hbar^2\left(x\frac{\partial}{\partial y}\right).$$

$$= -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$$

$\left(\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \Rightarrow \left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) = \frac{\hat{L}_z}{i\hbar}\right.$

$\left.-\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) = -\hbar^2 \times \frac{\hat{L}_z}{i\hbar} = -\frac{\hbar}{i}\hat{L}_z = i\hbar\hat{L}_z\right)$

$\left(\frac{1}{i}\right) = -i$

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$

2) Les opérateurs de moment cinétique. $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$ $\hat{L}^2 = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$

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③ Commutateur $[\hat{L}_z, \hat{L}^2]$

$*[\hat{L}_z, \hat{L}^2] = \hat{L}_z\hat{L}^2 - \hat{L}^2\hat{L}_z$ $\quad * [\hat{L}_z, \hat{L}^2] = [\hat{L}_z, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] = [\hat{L}_z, \hat{L}_x^2] + [\hat{L}_z, \hat{L}_y^2] + [\hat{L}_z, \hat{L}_z^2]$

$[\hat{L}_z, \hat{L}^2] = [\hat{L}_z, \hat{L}_x^2] + [\hat{L}_z, \hat{L}_y^2] + [\hat{L}_z, \hat{L}_z^2] = [\hat{L}_z, \hat{L}_x\hat{L}_x] + [\hat{L}_z, \hat{L}_y\hat{L}_y] + [\hat{L}_z, \hat{L}_z\hat{L}_z]$

$[\hat{L}_z, \hat{L}^2] = [\hat{L}_z, \hat{L}_x]\hat{L}_x + \hat{L}_x[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_y]\hat{L}_y + \hat{L}_y[\hat{L}_z, \hat{L}_y] + [\hat{L}_z, \hat{L}_z]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_z]$

$= (\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z)\hat{L}_x + \hat{L}_x(\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z) + (\hat{L}_z\hat{L}_y - \hat{L}_y\hat{L}_z)\hat{L}_y + \hat{L}_y(\hat{L}_z\hat{L}_y - \hat{L}_y\hat{L}_z) +$

$(\hat{L}_z\hat{L}_z - \hat{L}_z\hat{L}_z)\hat{L}_z + \hat{L}_z(\hat{L}_z\hat{L}_z - \hat{L}_z\hat{L}_z)$

$= \hat{L}_z\cancel{\hat{L}_x}\hat{L}_x - \hat{L}_x\cancel{\hat{L}_z}\hat{L}_x + \hat{L}_x\cancel{\hat{L}_z}\hat{L}_x - \hat{L}_x\cancel{\hat{L}_x}\hat{L}_z + \hat{L}_z\hat{L}_y\hat{L}_y - \hat{L}_y\cancel{\hat{L}_z}\hat{L}_y + \hat{L}_y\cancel{\hat{L}_z}\hat{L}_y - \hat{L}_y\cancel{\hat{L}_y}\hat{L}_z +$
$\hat{L}_z\cancel{\hat{L}_z}\hat{L}_z - \hat{L}_z\cancel{\hat{L}_z}\hat{L}_z + \hat{L}_z\hat{L}_z\hat{L}_z - \hat{L}_z\cancel{\hat{L}_z}\hat{L}_z$

$[\hat{L}_z, \hat{L}^2] = 0$ $\quad \hat{L}_z$ et L^2 2 opérateurs commutent

④ Condition d'hermicité $\quad (\hat{L}_z) = (\hat{L}_z)^+$ et ② $\hat{L}^2 = (\hat{L}^2)^+$

$\begin{cases} (\hat{L}_z)^+ = \left(-i\hbar\frac{\partial}{\partial\varphi}\right)^+ = -(i)^+(\hbar)^+\left(\frac{\partial}{\partial\varphi}\right)^+ \\ (\hat{L}_z)^+ = -\hat{L}_z \end{cases}$ $= -x - i\hbar\frac{\partial}{\partial\varphi} = i\hbar\frac{\partial}{\partial\varphi}$

I) Atome d'hydrogène

① L'équation de Schrödinger de l'atome d'hydrogène en coordonnées sphérique

$$\left(\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\varphi}\right]-\frac{e^2}{4\pi\varepsilon_0 r}\right)\Psi(r,\theta,\varphi)=E\Psi(r,\theta,\varphi)$$

$$\left(\frac{-\hbar^2}{2m}\nabla^2+V\right)\Psi(r,\theta,\varphi)=E\Psi(r,\theta,\varphi)$$

②

$$\left[\frac{-\hbar^2}{2m}\nabla^2+V\right]\phi_{1s}(r,\theta,\varphi)=E\phi_{1s}(r,\theta,\varphi)$$

Avec $\begin{cases}\phi_{1s}=Ce^{-\frac{r}{a_0}}\\ \phi_{1s} \text{ dépend de } r\\ V=\frac{-e}{4\pi\varepsilon_0 r}\end{cases}$

$$\frac{-\hbar^2}{2m}\nabla^2\phi_{1s}-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\phi_{1s}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\phi_{1s}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\varphi}\phi_{1s}\right]-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Ce^{-r/a_0}}{\partial r}\right)\right]-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\times\frac{-C}{a_0}e^{-\frac{r}{a_0}}\right)\right]-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\times\frac{-C}{a_0}\frac{\partial}{\partial r}\left(r^2e^{-\frac{r}{a_0}}\right)\right]-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{-\hbar^2}{2m}\left[\frac{-C}{a_0r^2}\left(2re^{-\frac{r}{a_0}}-\frac{r^2}{a_0}e^{-\frac{r}{a_0}}\right)\right]-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{-\hbar^2}{2m}\left[\frac{-2}{ra_0}Ce^{-\frac{r}{a_0}}+\frac{C}{a_0^2}e^{-\frac{r}{a_0}}\right]-V\phi_{1s}-E\phi_{1s}=0$$

$$\frac{+\hbar^2}{ma_0}\left(\frac{Ce^{-\frac{r}{a_0}}}{r}\right)-\frac{\hbar^2}{2a_0^2m}\left(Ce^{-\frac{r}{a_0}}\right)-\frac{e^2}{4\pi\varepsilon_0}\frac{Ce^{-\frac{r}{a_0}}}{r}-ECe^{-\frac{r}{a_0}}=0$$

$$\frac{Ce^{-\frac{r}{a_0}}}{r}\left[\frac{+\hbar^2}{ma_0}-\frac{e^2}{4\pi\varepsilon_0}\right]+Ce^{-\frac{r}{a_0}}\left[\frac{-\hbar^2}{2a_0^2m}-E\right]=0$$

③

$$\frac{C e^{\frac{-r}{a_0}}}{r} \neq 0 \qquad \frac{+\hbar^2}{a_0 m} - \frac{e^2}{4\pi\varepsilon_0} = 0 \quad \text{et} \quad \frac{-\hbar^2}{2a_0^2 m} - E = 0$$

$$a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{e^2 m} \qquad E = \frac{-\hbar^2}{2a_0^2 m}$$

$$a_0 = 0{,}53 A^\circ \qquad E = -13{,}6\,eV$$

③ calculer la constante C $\quad \phi_{1s} = C e^{\frac{-r}{a_0}}$

$$\langle \phi_{1s} | \phi_{1s} \rangle = 1 \qquad \iiint |\psi|^2 dV = 1 \qquad dV = r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

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$$\iiint C^2 . e^{\frac{-2r}{a_0}} r^2 dr \sin\theta \, d\theta \, d\varphi = 1$$

$$C^2 \int_0^{+\infty} r^2 e^{\frac{-2r}{a_0}} dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\varphi = 1$$

$$C^2 \left[\left(\frac{2!}{\left(\frac{2}{a_0}\right)^3} \right) \times 2 \times 2\pi = 1 \Leftrightarrow 4\pi C^2 \times \frac{2a_0^3}{8} = 1 \Leftrightarrow C = \sqrt{\frac{1}{\pi a_0^3}}$$

④ Valeur moyenne distance noyau – électrons

$$\langle r \rangle = \frac{\langle \psi | r | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\iiint |\psi|^2 r \, dV}{\iiint |\psi|^2 dV = 1} = \iiint |\psi|^2 dV$$

$$\langle r \rangle = \iiint \frac{1}{\pi a_0^3} \times e^{\frac{-2r}{a_0}} \times r \, dV$$

$$= \frac{1}{\pi a_0^3} \int_0^{+\infty} r e^{\frac{-2r}{a_0}} dr = \frac{1}{\pi a_0^3} \times \left(\frac{1}{\left(\frac{2}{a_0}\right)^2} \right) = \frac{1}{\pi a_0^3} \times \frac{a_0^2}{4}$$

$$\langle r \rangle = \frac{1}{4\pi a_0}$$

④