

Masa finita del Núcleo: conexión a la fórmula de Bohr

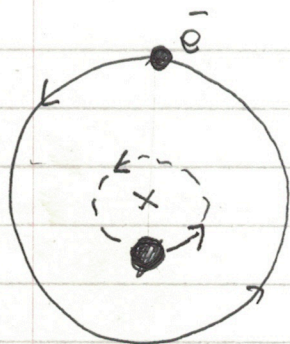
Escogiendo C. de coords. en el centro de masa

$$\mathbf{R} = \frac{m_e \vec{r}_e + M \vec{r}_N}{m + M} = 0 \Rightarrow m_e \vec{r}_e = M \vec{r}_N$$

$$\Rightarrow r_N = (m_e/M) r_e \quad (1)$$

hipótesis de De Broglie $\Leftrightarrow$ cuantización de $L = n\hbar$

$$m_e \omega_e r_e^2 + M \omega_N r_N^2 = n\hbar \quad (2)$$



$$\text{Coulomb} \Rightarrow \frac{ze^2}{(r_e + r_N)^2} = m_e \omega_e^2 r_e$$

$$\frac{ze^2}{r_e^2 (1 + \frac{m_e}{M})^2} = m_e \omega_e^2 r_e \quad (3)$$

$$(2) \rightarrow m_e \omega_e r_e^2 + m_e \omega_N^2 \left(\frac{m_e}{M}\right)^2 r_e^2 = n\hbar$$

$$m_e \omega_e^2 r_e \left(1 + \left(\frac{m_e}{M}\right)\right) = n\hbar \quad (2')$$

$$\frac{(2')^2}{(3)} \cdot \frac{m_e^2 \omega_e^2 r_e^4 \left(1 + \left(\frac{m_e}{M}\right)\right)^2}{m_e \omega_e^2 r_e^3} = \frac{n^2 \hbar^2}{ze^2} \left(1 + \frac{m_e}{M}\right)^2$$

$$\Rightarrow \frac{m_e^{-1} r_e^{-1}}{\left(1 + \frac{m_e}{M}\right)^2} = \frac{ze^2}{\left(1 + \frac{m_e}{M}\right)^2 n^2 \hbar^2} \Rightarrow \boxed{r_e = \frac{n^2 \hbar^2}{m_e z e^2} = \frac{a_0 n^2}{z}} \quad (4)$$

indep. de M (!)

$\Rightarrow$ radios son los mismos para todos los isótopos del Hidrógeno

Energía: $E = \frac{1}{2} m \omega^2 r^2 + \frac{1}{2} M \omega^2 r_N^2 - \frac{ze^2}{(r_N + r_e)}$

$$= \frac{1}{2} m \omega^2 r^2 + \frac{1}{2} M \omega^2 \left(\frac{m}{M}\right)^2 r^2 - \frac{ze^2}{r(1 + \frac{m}{M})}$$

$$= \frac{1}{2} m \omega^2 r^2 \left(1 + \frac{m}{M}\right) - \frac{ze^2}{r(1 + \frac{m}{M})}$$

pero $m \omega^2 r^2 \stackrel{(a)}{=} \frac{ze^2}{r(1 + \frac{m}{M})^2}$

$$\Rightarrow E = - \frac{ze^2}{2r(1 + \frac{m}{M})} = - \frac{ze^2 m ze^2}{2n^2 \hbar^2 (1 + \frac{m}{M})}$$

$$E = - \frac{\mu z^2 e^4}{2n^2 \hbar^2}$$

(s) where

$$\mu = \frac{m}{1 + \frac{m}{M}}$$

masa reducida

cuando $M \rightarrow \infty$, $\mu \rightarrow m$.

$M = 1836 m$ para el H

$$\Rightarrow \mu = \frac{1836 m}{1837}$$

ATOMO DE HIDROGENO

La soluc. del problema del átomo de H fue uno de los peu y mayor triunfos de la E. de S.

→ imposible de resolver exacto para átomos con más de un electrón → desarrollo de técnicas numéricas y aprox. que permiten altos grados de precisión.

Átomo de H : 2 partículas → $\Psi(x_p, y_p, z_p, x_e, y_e, z_e, t)$

$$E. \text{ total} : \frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} + V(r) \quad (1)$$

$$\text{o sea, } -\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(r) \quad (2)$$

$$\text{donde } V(r) = -e^2/r$$

$$\left(-\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(r) \right) \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (3)$$

$$\begin{array}{l} \text{C. de M.: } X = \frac{m_e x_e + m_p x_p}{m_e + m_p}, \quad x = x_e - x_p \\ Y = \frac{m_e y_e + m_p y_p}{m_e + m_p}, \quad y = y_e - y_p \\ Z = \frac{m_e z_e + m_p z_p}{m_e + m_p}, \quad z = z_e - z_p \end{array} \quad (4)$$

$$(4) \Rightarrow \left. \begin{aligned} M\ddot{X} &= m_e \ddot{x}_e + m_p \ddot{x}_p \\ X &= x_e - x_p \end{aligned} \right\} \begin{array}{l} m_p \\ m_e \end{array}$$

$$\Rightarrow \left. \begin{aligned} M\ddot{X} &= m_e \ddot{x}_e + m_p \ddot{x}_p \\ m_p \ddot{x}_p &= m_p \ddot{x}_e - m_p \ddot{x}_p \end{aligned} \right\} \Rightarrow \begin{aligned} M\ddot{X} + m_p \ddot{x}_p &= (m_e + m_p) \ddot{x}_e \\ \Rightarrow \ddot{x}_e &= \ddot{X} + \frac{m_p}{M} \ddot{x}_p \end{aligned}$$

$$\text{wird, } \left[\ddot{y}_e = \ddot{Y} + \frac{m_p}{M} \ddot{y}_p \right], \left[\ddot{z}_e = \ddot{Z} + \frac{m_p}{M} \ddot{z}_p \right] \quad (5)$$

$$\text{funktion, } \left. \begin{aligned} M\ddot{X} &= m_e \ddot{x}_e + m_p \ddot{x}_p \\ m_e \ddot{x}_e &= m_e \ddot{x}_e - m_e \ddot{x}_p \end{aligned} \right\} M\ddot{X} - m_e \ddot{x}_e = m_p \ddot{x}_p$$

$$\Rightarrow \left[\ddot{x}_p = \ddot{X} - \frac{m_e}{M} \ddot{x}_e \right] \text{ und } \left[\ddot{y}_p = \ddot{Y} - \frac{m_e}{M} \ddot{y}_e \right] \text{ und } \left[\ddot{z}_p = \ddot{Z} - \frac{m_e}{M} \ddot{z}_e \right] \quad (6)$$

$$\begin{aligned} \Rightarrow & \frac{1}{2} m_e (\dot{x}_e^2 + \dot{y}_e^2 + \dot{z}_e^2) + \frac{1}{2} m_p (\dot{x}_p^2 + \dot{y}_p^2 + \dot{z}_p^2) = \\ & = \frac{1}{2} m_e \left\{ \dot{X}^2 + \left(\frac{m_p}{M}\right)^2 \dot{x}_e^2 + 2\frac{m_p}{M} \dot{x}_e \dot{X} + \dot{Y}^2 + \left(\frac{m_p}{M}\right)^2 \dot{y}_e^2 + 2\frac{m_p}{M} \dot{y}_e \dot{Y} + \dot{Z}^2 + \left(\frac{m_p}{M}\right)^2 \dot{z}_e^2 + 2\left(\frac{m_p}{M}\right) \dot{z}_e \dot{Z} \right\} \\ & + \frac{1}{2} m_p \left\{ \dot{X}^2 + \left(\frac{m_e}{M}\right)^2 \dot{x}_p^2 - 2\frac{m_e}{M} \dot{x}_p \dot{X} + \dot{Y}^2 + \left(\frac{m_e}{M}\right)^2 \dot{y}_p^2 - 2\left(\frac{m_e}{M}\right) \dot{y}_p \dot{Y} + \dot{Z}^2 + \left(\frac{m_e}{M}\right)^2 \dot{z}_p^2 - 2\left(\frac{m_e}{M}\right) \dot{z}_p \dot{Z} \right\} \\ & = \frac{1}{2} (m_e + m_p) [\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2] + \frac{1}{2} \frac{m_e m_p}{(m_e + m_p)} (\dot{x}_e^2 + \dot{y}_e^2 + \dot{z}_e^2) \\ & = \frac{1}{2} M [\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2] + \frac{1}{2} \mu (\dot{x}_e^2 + \dot{y}_e^2 + \dot{z}_e^2) \end{aligned}$$

$$P_x = M \dot{X} ; P_y = M \dot{Y} ; P_z = M \dot{Z}$$

$$E = \frac{P_x^2 + P_y^2 + P_z^2}{2M} + \frac{P_x^2 + P_y^2 + P_z^2}{2\mu} \quad (7)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2M} \nabla_{cm}^2 - \frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (8)$$

$$\Psi(X, Y, Z, x, y, z, t) = U(x, y, z) V(X, Y, Z) e^{-i(E+E')t/\hbar} \quad (9)$$

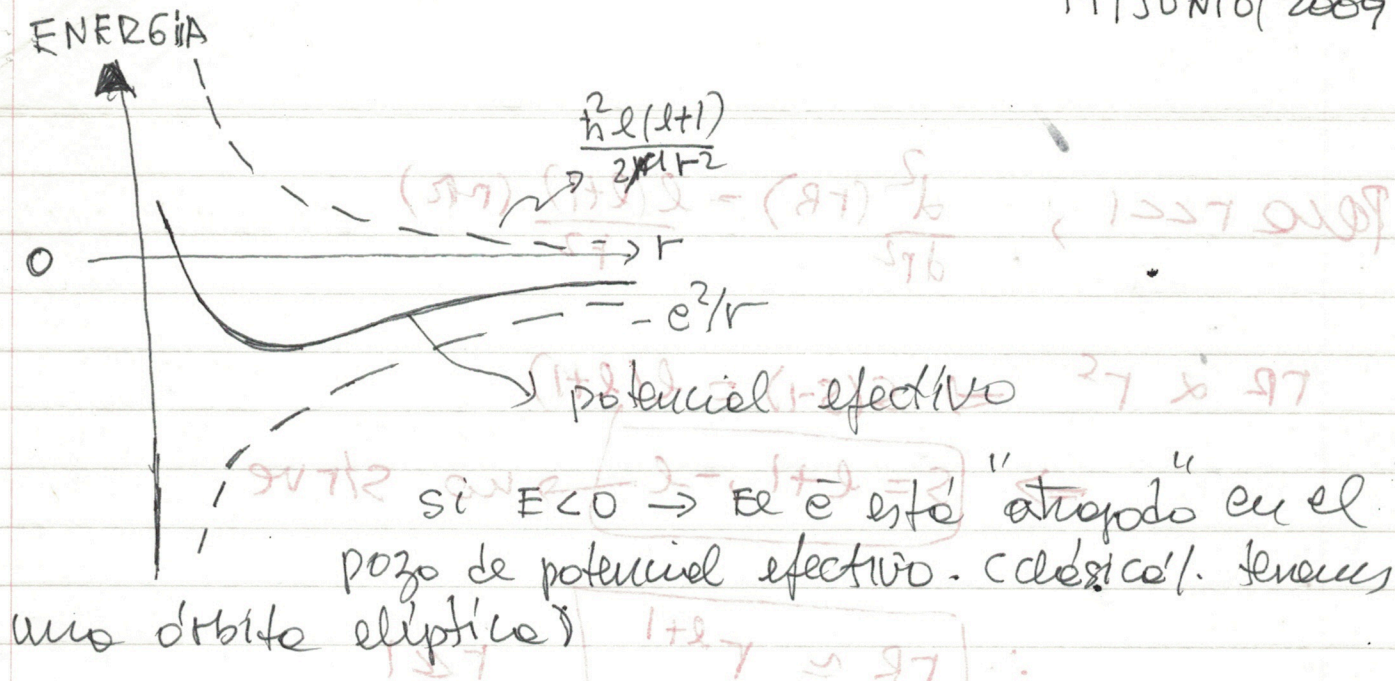
$$\Rightarrow -\frac{\hbar^2}{2M} \nabla_{cm}^2 U = E' U \quad (10)$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] U = E U \quad (11)$$

(11) Represento a 1 partícula efectiva bajo la influencia de un potencial con simetría esférica $\Rightarrow$ ya conocemos la dependencia angular, dada por $Y_{lm}(\theta, \phi)$

$$U(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi)$$

$$\frac{d^2}{dr^2} (rR) = -\frac{2M}{\hbar^2} \left[\underbrace{E - V(r)}_{\text{término Coulombiano}} - \underbrace{\frac{\hbar^2 l(l+1)}{2\mu r^2}}_{\text{potencial centrifugo}} \right] (rR) \quad (12)$$



Solución [Estimada]:

$$\frac{d^2}{dr^2} (rR) = -\frac{2\mu}{\hbar^2} \left[E_n + \frac{ze^2}{r} - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] (rR) \quad (1)$$

$$\text{Def: } \alpha_n = \sqrt{-2\mu E_n / \hbar^2} ; C = 2\mu ze^2 / \hbar^2 \quad (2)$$

$$\Rightarrow \frac{d^2}{dr^2} (rR) = \left[\alpha_n^2 - \frac{C}{r} + \frac{l(l+1)}{r^2} \right] (rR) \quad (3)$$

$$r \gg 1: \frac{d^2}{dr^2} (rR) = \alpha_n^2 (rR) \Rightarrow \boxed{rR = e^{-\alpha_n r}} \quad (4)$$

$\Rightarrow$ razonable suponer $rR(r) = g(r) e^{-\alpha_n r}$ $\xrightarrow{\text{serie en } r}$

$$\Rightarrow \frac{d^2 g}{dr^2} - 2\alpha_n \frac{dg}{dr} + \frac{Cg}{r} - \frac{l(l+1)}{r^2} g = 0 \quad (5)$$

For $r \ll 1$, $\frac{d^2}{dr^2}(rR) = \frac{l(l+1)}{r^2}(rR)$

$rR \propto r^s \Rightarrow s(s-1) = l(l+1)$

$\Rightarrow s = l+1, -l$ ~~no s/rve~~

$\therefore rR \approx r^{l+1}$ $r \ll 1$

(1) $\frac{d}{dr} \left[\frac{1}{r^2} \frac{d}{dr} (r^2 R) \right] + \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] R = 0$

(5) $\frac{d}{dr} \left[\frac{1}{r^2} \frac{d}{dr} (r^2 R) \right] + \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] R = 0$

(3) $\frac{d}{dr} \left[\frac{1}{r^2} \frac{d}{dr} (r^2 R) \right] + \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] R = 0$

(4) $\frac{d}{dr} \left[\frac{1}{r^2} \frac{d}{dr} (r^2 R) \right] + \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] R = 0$

$\Rightarrow$ asymptotic behavior $R(r) \sim e^{-\kappa r}$ as $r \rightarrow \infty$

(2) $0 = \frac{d}{dr} \left[\frac{1}{r^2} \frac{d}{dr} (r^2 R) \right] + \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] R$

se plantea una solución del tipo:

$$g(r) = r^s \sum_{q=0}^{\infty} b_q r^q \quad \text{y se sustituye en (5),}$$

imponiendo que $\lim_{r \rightarrow \infty} g(r) \rightarrow 0$

lo $\exists$ de condiciones de borde para un $R(r)$ aceptable físicamente $\Rightarrow$

$$E_n = -\frac{\mu \epsilon^4}{2\hbar^2 n^2} \quad (6) \quad \text{donde } n=1, 2, 3, \dots$$

$l=0, 1, 2, \dots, n-1$

$\rightarrow$ # cuántico radial.

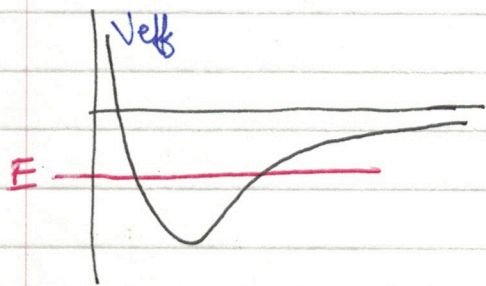
$$\text{y } R_{nl} \propto r^{l+1} e^{-\alpha n r} \text{ Pol}(r) \quad (7)$$

E_n NO depende de l : NO entero! - cierto

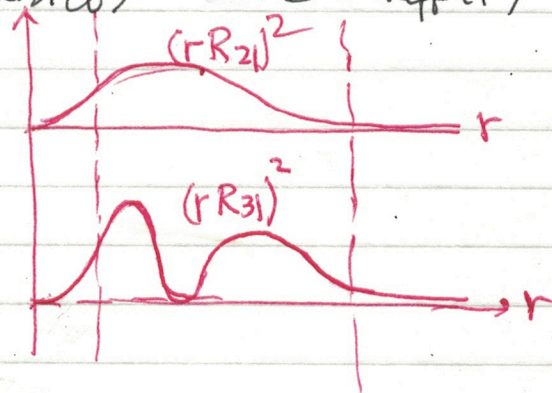
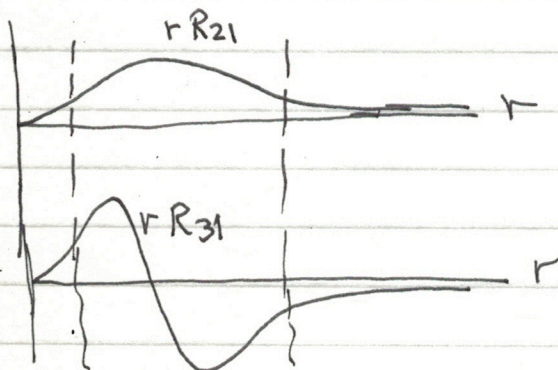
$$\Psi(r, \theta, \phi) = R_{ne}(r) Y_{em}(\theta, \phi) \quad (1)$$

donde $r R_{ne}(r)$ satisface una eq. tipo S 1-D.

$$\frac{d^2}{dr^2} (r R_{ne}) = -\frac{2\mu}{\hbar^2} [E - V_{eff}(r)] (r R_{ne}) \quad (2)$$



$E < V_{eff} \Rightarrow (r R_{ne})'' = -\alpha^2 (r R_{ne})$
 $\Rightarrow$ crec. o decaimiento exponencial
 $E > V_{eff} \Rightarrow (r R_{ne})'' = -\alpha^2 (r R_{ne})$
 $\Rightarrow$ oscilación entre los pto. de retorno clásico
 $E = V_{eff}(r)$



$$P(r) = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |R_{ne}(r) Y_{em}(\theta, \phi)|^2 r^2 \sin\theta d\theta d\phi = r^2 |R_{ne}(r)|^2 \quad (3)$$

Notar que $\lim_{r \rightarrow 0} [r R_{ne}(r)] = 0 \Rightarrow$ Es imposible $\frac{1}{r}$ entre el e^- con el protón.

Notación (espectroscópica)

letra: s p d f g h i ... (algebraico)
 l : 0 1 2 3 4 5 6

$$U_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} e^{-\rho}$$

$$\rho = \frac{Zr}{a_0'}, \quad a_0' = a_0 \left(\frac{m_e + m_p}{m_p} \right)$$

$\downarrow$ masa Nucleo

$Z = \text{carga núcleo}$

$$U_{200} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} (2-\rho) e^{-\rho/2}$$



$$U_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} \rho \cos\theta e^{-\rho/2}$$

$$U_{21,\pm 1} = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} \rho \sin\theta e^{-\rho/2 \pm i\phi}$$

$$U_{300} = \frac{1}{8\sqrt{3\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} (27-18\rho+2\rho^2) e^{-\rho/3}$$

$$U_{310} = \frac{\sqrt{2}}{8\sqrt{\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} (6-\rho) \rho \cos\theta e^{-\rho/3}$$

$$U_{31,\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} (6-\rho) \rho \sin\theta e^{-\rho/3 \pm i\phi}$$

$$U_{320} = \frac{1}{8\sqrt{6\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} \rho^2 (3\cos^2\theta - 1) e^{-\rho/3}$$

$$U_{32,\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} \rho^2 \sin\theta \cos\theta e^{-\rho/3 \pm i\phi}$$

$$U_{32,\pm 2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0'} \right)^{3/2} \rho^2 \sin^2\theta e^{-\rho/3 \pm 2i\phi}$$

Ejercicio

Demuestre que, para este estado, la probabilidad de medir $l=0$ y $l=1$ es idénticamente nula, mientras que la probabilidad de medir $l=2$ es 1.

$$\psi(x, y, z) = (xy + yz + zx) e^{-\alpha r^2}$$

$$x = r \sin \theta \cos \phi ; \quad y = r \sin \theta \sin \phi ; \quad z = r \cos \theta$$

$$xy = r^2 \sin^2 \theta \sin \phi \cos \phi \quad (1)$$

$$yz = r^2 \sin \theta \cos \theta \sin \phi \quad (2)$$

$$zx = r^2 \sin \theta \cos \theta \cos \phi \quad (3)$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}} ; \quad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta ; \quad Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

Text

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) ; \quad Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

$$(1) \Rightarrow \sin^2 \theta \sin \phi \cos \phi = \frac{1}{2} \sin^2 \theta \sin(2\phi)$$

$$Y_{2,2} - Y_{2,-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta (e^{2i\phi} - e^{-2i\phi}) = \sqrt{\frac{15}{32\pi}} 2i \sin^2 \theta \sin(2\phi)$$

$$\boxed{\frac{(Y_{2,2} - Y_{2,-2})}{4i} \sqrt{\frac{32\pi}{15}} = \frac{1}{2} \sin^2 \theta \sin(2\phi)} \quad (4)$$

$$Y_{2,1} - Y_{2,-1} = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta (e^{i\phi} - e^{-i\phi})$$

$$= -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta (e^{i\phi} - e^{-i\phi})$$

$$= -2\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \sin\phi$$

$$\Rightarrow \boxed{\sin\theta \cos\theta \sin\phi = -\frac{1}{2} \sqrt{\frac{8\pi}{15}} (Y_{2,1} - Y_{2,-1})} \quad (5)$$

$$Y_{2,1} + Y_{2,-1} = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \left(\frac{e^{i\phi} - e^{-i\phi}}{2i} \right) 2i$$

$$= -2i \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \sin\phi$$

$$\boxed{\sin\theta \cos\theta \sin\phi = -\frac{1}{2i} \sqrt{\frac{8\pi}{15}} (Y_{2,1} + Y_{2,-1})} \quad (6)$$

$$XY + YZ + ZX = \left(\frac{8\pi}{15} \right)^{1/2} \left\{ \frac{(Y_{2,2} - Y_{2,-2})}{2i} - \frac{(Y_{2,1} - Y_{2,-1})}{2} + \frac{(Y_{2,1} + Y_{2,-1})}{2i} \right\}$$

Y_{00} : absent

$Y_{10}, Y_{1,\pm 1}$: absent

seul $l=2$ état présente.

$\Rightarrow$ la prob. de trouver $l=2$ is 1.

$$L^2 = \hbar^2 l(l+1) = 6\hbar^2$$