Ec. de Schrödinger en 3D

$$\check{T} + \check{V} = \check{H} \qquad (1)$$

$$\check{H} = \frac{\check{p}^2}{2m} + \check{V}, \qquad (2)$$

$$\check{p}^2 = \check{P}_x^2 + \check{P}_y^2 + P_z^2 = \left(-i\hbar\frac{\partial}{\partial x}\right)^2 + \left(-i\hbar\frac{\partial}{\partial y}\right)^2 + \left(-i\hbar\frac{\partial}{\partial z}\right)^2$$

$$= -\hbar^2\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] = -\hbar^2\nabla^2 \qquad (3)$$

$$\Rightarrow \check{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$$

$$-i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t) \qquad (4)$$

Estado estacionario: $\psi(\vec{r},t) = e^{-\frac{it}{\hbar}E}\psi(\vec{r})$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r}) \qquad (5)$$

autofunción — autoenergía ($\in \mathbb{R}$)

Caso sencillo: el oscilador harmónico en 3D

Partícula de masa m, moviéndose en 3D bajo el efecto del potencial:

$$V(\vec{r}) = \frac{1}{2} m\omega^2 r^2 \quad (1)$$
$$= \frac{1}{2} m\omega^2 (x^2+y^2+z^2) = V_x(x) + V_y(y) + V_z(z)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + V_x(x) + V_y(y) + V_z(z) \right] \psi(x,y,z) = E\, \psi(x,y,z)$$

separación de variables. $\psi(x,y,z) = X(x)\, Y(y)\, Z(z)$ (2)

$$\Rightarrow -X''YZ - XY''Z - XYZ'' + (V_xX)YZ + X(V_yY)Z + XY(V_zZ) = +K^2 XYZ \quad (3)$$

donde $K^2 \equiv 2mE/\hbar^2$ (4)

$$\Rightarrow -\frac{X''}{X} - \frac{Y''}{Y} - \frac{Z''}{Z} + V_x + V_y + V_z = +K^2$$

$$\underbrace{\left[-\frac{X''}{X} + V_x \right]}_{\text{sólo dep. de } x} + \underbrace{\left[-\frac{Y''}{Y} + V_y \right]}_{\text{sólo dep. de } y} + \underbrace{\left[-\frac{Z''}{Z} + V_z \right]}_{\text{sólo dep. de } z} = +K^2$$ ¡ojo!

i) $-\frac{X''}{X} + V_x(x) = k_x^2$

ii) $-\frac{Y''}{Y} + V_y(y) = k_y^2$

iii) $-\frac{Z''}{Z} + V_z(z) = k_z^2$

$$k_x^2 + k_y^2 + k_z^2 = K^2$$

$$\underbrace{\frac{\hbar^2 k_x^2}{2m}}_{E_x} + \underbrace{\frac{\hbar^2 k_y^2}{2m}}_{E_y} + \underbrace{\frac{\hbar^2 k_z^2}{2m}}_{E_z} = E$$

$$\begin{aligned} X(x)'' - (m\omega/\hbar)^2 x^2 X(x) &= -K_x^2 \\ Y(y)'' - (m\omega/\hbar)^2 y^2 Y(y) &= -K_y^2 \\ Z(z)'' - (m\omega/\hbar)^2 z^2 Z(z) &= -K_z^2 \end{aligned}$$

por los resultados de 1D sabemos que

$E_x = (n_x + \frac{1}{2})\hbar\omega \qquad n_x = 0, 1, 2, \ldots$

$E_y = (n_y + \frac{1}{2})\hbar\omega \qquad n_y = 0, 1, 2, \ldots$

$E_z = (n_z + \frac{1}{2})\hbar\omega \qquad n_z = 0, 1, 2, \ldots$

o sea $\quad E = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega$

$$\Psi_{n_x n_y n_z}(x,y,z,t) = e^{-\frac{i}{\hbar}Et}\left[\left(\frac{d}{dx} - ax\right)^{n_x} e^{-\frac{ax^2}{2}}\right]\left[\left(\frac{d}{dy} - ay\right)^{n_y} e^{-\frac{ay^2}{2}}\right]\left[\left(\frac{d}{dz} - az\right)^{n_z} e^{-\frac{az^2}{2}}\right]$$

sin normalizar

$(a \equiv m\omega^2/\hbar^2)$

$$1 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(x,y,z)|^2 \, dx\,dy\,dz = \int_{-\infty}^{\infty} |X_{n_x}(x)|^2 dx \int_{-\infty}^{\infty} |Y_{n_y}(y)|^2 dy \int_{-\infty}^{\infty} |Z_{n_z}(z)|^2 dz$$

Paridad: $(-1)^{n_x + n_y + n_z}$

n_x	n_y	n_z	N	E_N	Paridad	Deg
0	0	0	0	$\frac{3}{2}\hbar\omega$	+	1
1	0	0	1		−	
0	1	0	1	$\frac{5}{2}\hbar\omega$	−	3
0	0	1	1		−	
2	0	0	2		+	
0	2	0	2		+	
0	0	2	2	$\frac{7}{2}\hbar\omega$	+	6
1	1	0	2		+	
1	0	1	2		+	
0	1	1	2		+	
3	0	0	3		−	
0	3	0	3		−	
0	0	3	3		−	
2	1	0	3		−	
2	0	1	3	$\frac{9}{2}\hbar\omega$	−	10
0	2	1	3		−	
1	2	0	3		−	
1	0	2	3		−	
0	1	2	3		−	
1	1	1	3		−	

Formula general?

Degeneración

$$E_N = \hbar\omega\left(N + \frac{3}{2}\right) \qquad \text{donde } N = n_x + n_y + n_z$$

Sea $N = n_x + n_y + n_z$

para N fijo, $0 \le n_x \le N$

y para cada ~~nx~~ $0 \le n_x \le N$, tenemos

$$\underbrace{N - n_x}_{} = n_y + n_z$$

$$N' = n_y + n_z \quad \text{y} \quad 0 \le n_y \le N'$$

y para cada $0 \le n_y \le N'$, n_z está fijo

$$\# = \sum_{n_x=0}^{N} \sum_{n_y=0}^{N-n_x} 1 = \sum_{n_x=0}^{N} (N - n_x + 1) = \frac{(N+1)(N+2)}{2} \quad //$$

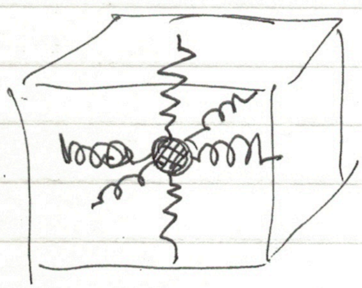
Otro caso fácil: El oscilador 3D anisotrópico

$$V(x,y,z) = \frac{1}{2}m\left(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right)$$

con $\omega_x^2 \neq \omega_y^2 \neq \omega_z^2$.

El potencial es aún separable $V = V_x(x) + V_y(y) + V_z(z)$

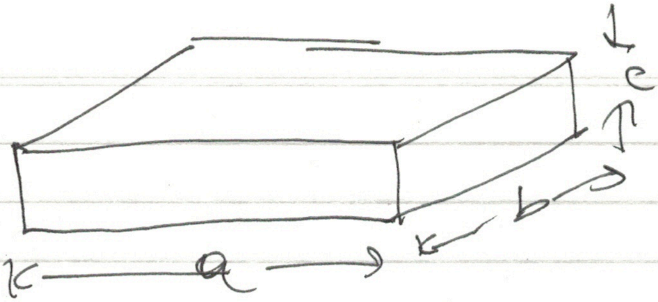
$$\Rightarrow E = E_x + E_y + E_z = (n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z$$



P. ejemplo si $\omega_y = 2\omega_x$ y $\omega_z = 3\omega_x$

$$\Rightarrow E = \hbar\omega_x\left[n_x + 2n_y + 3n_z + 6\right] \qquad n_x, n_y, n_z = 0, 1, 2, \ldots$$

Ej: Listar las primeras 10 energías con sus degeneraciones (if any).



$$E = \frac{\hbar^2}{2m}\left[\left(\frac{n_x\pi}{a}\right)^2 + \left(\frac{n_y\pi}{b}\right)^2 + \left(\frac{n_z\pi}{c}\right)^2\right]$$

$$\Psi(x,y,z) = \text{cte} \times \sin\left[\frac{n_x\pi}{a}x\right]\sin\left[\frac{n_y\pi}{b}y\right]\sin\left[\frac{n_z\pi}{c}z\right]$$

Potenciales con simetría esférica: $V(\vec{r}) = V(|\vec{r}|)$

fuerzas centrales: $\vec{F} = -\vec{\nabla}V(|\vec{r}|)$

p. ej. potencial Coulombiano, gravitacional.

→ conviene re-expresar todo en coords. esféricas

(∗) $r^2 = x^2 + y^2 + z^2$

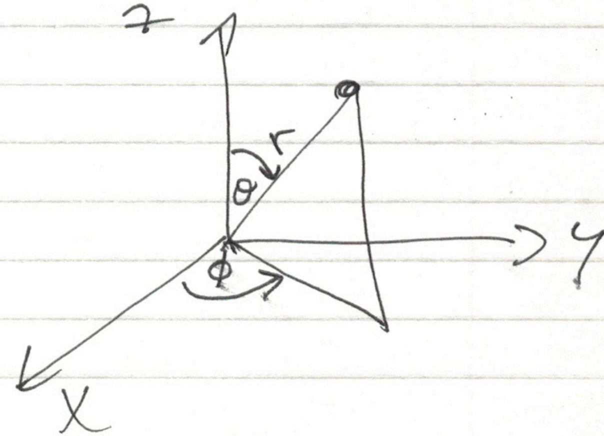
(∗) $\cos\theta = \frac{z}{r} = \frac{z}{\sqrt{x^2+y^2+z^2}}$

(∗) $\tan\phi = \frac{y}{x}$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$



objetivo: re-expresar la E. de S. en coords. esféric

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \phi}\frac{\partial \phi}{\partial x}$$

$$(0) \Rightarrow 2r\frac{\partial r}{\partial x} = 2x \Rightarrow \frac{\partial r}{\partial x} = \frac{x}{r} = \boxed{\sin\theta\cos\phi} \qquad (1)$$

$$(*) \Rightarrow -\sin\theta\frac{\partial \theta}{\partial x} = -\frac{1}{2}z(x^2+y^2+z^2)^{-3/2}\cdot 2x = -\frac{z}{r}\cdot\frac{x}{r^2} = -\frac{\cos\theta}{r}\sin\theta\cos\phi$$

$$\Rightarrow \boxed{\frac{\partial \theta}{\partial x} = \frac{1}{r}\cos\theta\cos\phi} \qquad (2)$$

$$(*) \Rightarrow (1+\tan^2\phi)\frac{\partial \phi}{\partial x} = \frac{-y}{x^2} = \frac{-y}{x}\cdot\frac{1}{x} = -\tan\phi\cdot\frac{1}{r\sin\theta\cos\phi}$$

$$\frac{1}{\cos^2\phi}\cdot\frac{\partial \phi}{\partial x} = -\frac{\tan\phi}{r\sin\theta\cos\phi} \rightarrow \frac{\partial \phi}{\partial x} = -\frac{\cos^2\phi\tan\phi}{r\sin\theta\cos\phi} = -\frac{\sin\phi}{r\sin\theta}$$

$$\therefore \boxed{\frac{\partial \phi}{\partial x} = -\frac{1}{r}\frac{\sin\phi}{\sin\theta}}$$

$$\therefore \frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial \theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial \phi} \qquad (3)$$

After "some" algebra:

$$\Rightarrow \nabla^2\Psi = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\Psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} \qquad (4)$$

y la ec. de S. looks like:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V(r)\Psi = E\psi \qquad (5)$$

ó $$\nabla^2\Psi = \frac{2m}{\hbar^2}(V(r)-E)\Psi \qquad (6)$$

tomar $$\Psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi) \qquad (7)$$

$$\frac{Y}{r}\frac{\partial^2}{\partial r^2}(rR) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \frac{2m}{\hbar^2}(V(r)-E)RY$$

multip. por $r^2/(RY)$:

$$\underbrace{\frac{r}{R}\frac{\partial^2}{\partial r^2}(rR)}_{\text{sólo dep. de } r} + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = \underbrace{\frac{2mr^2}{\hbar^2}(V(r)-E)}_{\text{sólo dep. de } r}$$

$$\therefore\ \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -\alpha \qquad (8)$$

$$\frac{r}{R}\frac{\partial^2}{\partial r^2}(rR) - \frac{2mr^2}{\hbar^2}(V(r)-E) = +\alpha \qquad (9)$$

$Y(\theta,\phi)$ en (8) describe la dependencia angular.

(8) puede escribirse como $\check{\Omega}\, Y = +\alpha Y$ (8')

Significado físico de $\check{\Omega}$

$$\underset{\text{energía cinética}}{K} = \frac{P_r^2}{2m} + \frac{L^2}{2mr^2}$$, donde $P_r = m v_r = m\, dr/dt$

→ La ec. de S. debiera ser de la forma

$$\left[\frac{\check{P}_r^2}{2m} + \frac{\check{L}^2}{2mr^2}\right] u = (E - V) u$$

Comparando, vemos que $\check{P}_r^2 u = -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}(r u)$

y $\check{L}^2 u = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial u}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2}$

EJ: a partir de $L_x = yP_z - zP_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

$$L_y = zP_x - xP_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_z = xP_y - yP_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

dem. que se obtiene:

$$\check{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\check{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\check{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

De aquí se halla $L^2 = \check{L}_x^2 + \check{L}_y^2 + \check{L}_z^2 = \hbar^2\check{\Omega}$

Autovalores de $\check{\Omega}$: $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

$$\Rightarrow \frac{\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2} = -\alpha\,\Theta\,\Phi \qquad / \sin^2\theta/\Theta\Phi$$

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}_{-\alpha - cte.} + \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{cte.} = -\alpha\sin^2\theta$$

Imponiendo $\Phi(\phi+2\pi) = \Phi(\phi) \Rightarrow cte = -m^2$, $m \rightarrow$ entero

$$\Phi'' = -m^2\Phi \Longrightarrow \Phi = A e^{im\phi}$$

Notar que $\Phi(\phi)$ es autofunción de $\check{L}_z$:

$$L_z\Phi = -i\hbar\frac{\partial}{\partial\phi}(\Phi(\phi)) = -i\hbar\frac{\partial}{\partial\phi}(Ae^{im\phi}) = m\hbar\Phi$$

$\Rightarrow$ El resultado de medir L_z es siempre un multiplo <u>entero</u> de $\hbar$.

Por otro lado, $\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = +m^2 - \alpha\sin^2\theta$

$$\Rightarrow \sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + (\alpha\sin^2\theta - m^2)\,\Theta = 0$$

se ve complicada. Def: $x = \cos\theta$

$$\Rightarrow \frac{d}{dx}\left[(1-x^2)\frac{dy}{dx}\right] - \frac{m^2 y}{1-x^2} = -\alpha y$$

Resolviendo por medio de una serie en x, se halla que la solución es finita $\forall \theta$ $(-1 < x < 1)$ sólo cuando

$\alpha = l(l+1)$ donde l entero y $l \geq |m|$

$$\Rightarrow \boxed{\check{\Omega} Y = l(l+1) Y} \quad \text{y como } L^2 = \hbar^2 \Omega$$

$$\Rightarrow \boxed{\check{L}^2 Y(\theta,\phi) = \hbar^2 l(l+1) Y(\theta,\phi)} \quad l = 0, 1, 2, \ldots$$

Autofunciones de $\check{L}^2$: $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

$$\underbrace{Y_{lm}(\theta,\phi)}_{\text{Armónicos esféricos}} = \underbrace{P_l^{|m|}}_{\text{Pols. Asociados de Legendre}}(\cos\theta)\, e^{im\phi} \quad (|m| \leq l)$$

$Y_{00} = \sqrt{1/4\pi}$

$Y_{11} = -\sqrt{3/8\pi} \sin\theta\, e^{i\phi}$

$Y_{10} = \sqrt{3/4\pi} \cos\theta$

$Y_{1,-1} = (3/8\pi) \sin\theta\, e^{-i\phi}$

$Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{2i\phi}$

$Y_{21} = -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta\, e^{i\phi}$

$Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$

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

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

$$Y_{33} = -\frac{1}{4}\sqrt{\frac{35}{4\pi}}\,\sin^3\theta\, e^{3i\phi}$$

$$Y_{32} = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\,\sin^2\theta\cos\theta\, e^{2i\phi}$$

$$Y_{31} = -\frac{1}{4}\sqrt{\frac{21}{4\pi}}\,\sin\theta\,(5\cos^2\theta-1)\,e^{i\phi}$$

$$Y_{30} = \sqrt{\frac{7}{4\pi}}\left(\frac{5}{2}\cos^3\theta-\frac{3}{2}\cos\theta\right)$$

$$Y_{l,-m}(\theta,\phi) = (-1)^m\, Y^*_{lm}(\theta,\phi)$$

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}\, P_l^m(\cos\theta)\, e^{im\phi} \qquad (1)$$

donde $$P_l^m(x) = (-1)^m (1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l \qquad (2)$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\; Y^*_{l'm'}(\theta,\phi)\, Y_{lm}(\theta,\phi) = \delta_{l'l}\,\delta_{m'm} \qquad (3)$$

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y^*_{lm}(\theta',\phi')\, Y_{lm}(\theta,\phi) = \delta(\phi-\phi')\,\delta(\cos\theta-\cos\theta')$$

$$g(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{lm}\, Y_{lm}(\theta,\phi)$$

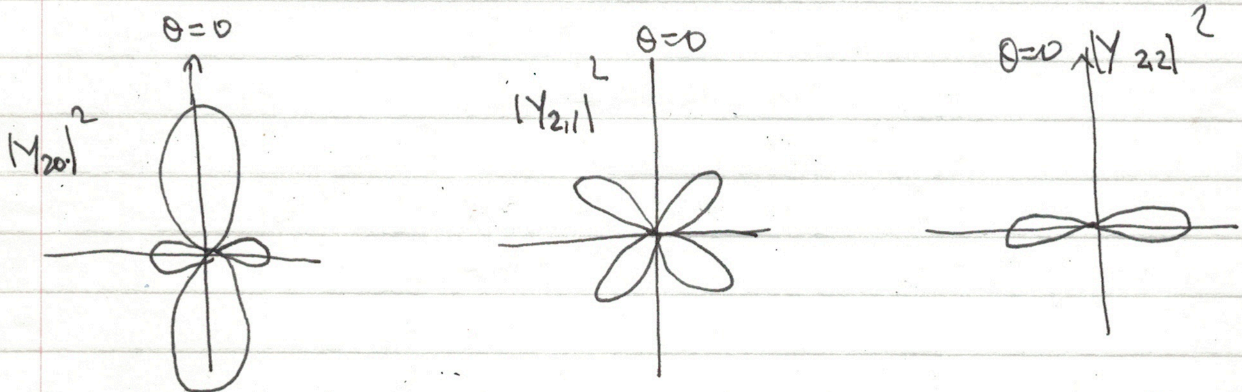
$$\Rightarrow A_{lm} = \int d\Omega\; Y^*_{lm}(\theta,\phi)\, g(\theta,\phi)$$

Notar que $Y_{l,-m} = (-1)^m Y_{lm}^*$

Normalización $\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta |Y_{lm}(\theta,\phi)|^2 = 1$

$|Y_{lm}(\theta,\phi)|^2$ = densidad de probabilidad para las coords. angulares.

$\Rightarrow \int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1}^{\theta_2} d\theta |Y_{lm}|^2 \sin\theta$ = prob. de hallar la partícula en $\phi_1 < \phi < \phi_2$ y $\theta_1 < \theta < \theta_2$



$\frac{5}{16\pi}(3\cos^2\theta-1)^2$ $\frac{15}{8\pi}\sin^2\theta\cos^2\theta$ $\frac{15}{32\pi}\sin^4\theta$