More on Angular Momentum

$$\underline{\underline{L_{op}^2}} = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$$L_x = i\hbar\left(\sin\varphi\,{\partial}/{\partial\theta} + \cot\theta\,\cos\varphi\,{\partial}/{\partial\theta}\right)$$

$$L_y = -i\hbar\left(\cos\varphi\,{\partial}/{\partial\theta} - \cot\theta\,\sin\varphi\,{\partial}/{\partial\varphi}\right)$$

$$\underline{\underline{L_z}} = -i\hbar\,{\partial}/{\partial\varphi}$$

Eigenfunctions of L_{op}^2

First, $\left[L_z, L_{op}^2\right] = 0$ so eigs. of L $_z$ are eigs of L_{op}^2.

$$L_z\Phi_m(\varphi) = \lambda\Phi_m(\varphi) \qquad \Phi_n(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}}$$

$$-\frac{i\hbar\partial\Phi_m}{\partial\varphi} = -i\hbar(im)\Phi_m(\varphi)$$

$$L_2\Phi_m = m\hbar\Phi_m \qquad \Phi_m(\varphi + 2\pi) = \Phi_m(\varphi)$$

So eigenvalues of L_z are $m\hbar$, m=0, ±1, ±2,…

(recall plane rotor-- ${L_z^2}/{2\mu r_e^2}$)

$\Upsilon_{\ell m}(\theta,\varphi) = \bar{P}_\ell^{|m|}(\cos\theta)\dfrac{e^{im\varphi}}{\sqrt{2\pi}}$ --<u>Spherical Harmonic</u>

where the eigenvalue equation for $\Upsilon_{\ell m}$ is

$$L_{op}^2\Upsilon_{\ell m} = \Lambda\Upsilon_{\ell m}\left[-\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + cot\,\theta\frac{\partial}{\partial\theta}\right) + \frac{\hbar^2 m^2}{sin^2\theta} - \Lambda\right]\bar{P}_\ell^{|m|}(cos\,\theta) = 0$$

Solutions are known—<u>Associated Legendre Polynomials</u>

And $\Lambda = \hbar^2\ell(\ell+1)$, $\ell = 0,1,2,...$ and $-\ell \le m \le \ell$.

Summary so far:

$$L_z Y_{\ell m}(\theta,\varphi) = L_z \bar{P}_\ell^{|m|}(\cos\theta)\frac{e^{im\varphi}}{\sqrt{2\pi}} = \bar{P}_\ell^{|m|}(\cos\theta)\, m\hbar \frac{e^{im\varphi}}{\sqrt{2\pi}}$$

$$L_z Y_{\ell m} = m\hbar Y_{\ell m}(\theta,\varphi)$$

$$L_{op}^2 Y_{\ell m} = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta,\varphi) \qquad \ell = 0,1,2,\ldots \text{ and } -\ell \le m \le \ell$$

Orthonormality

$$\langle Y_{l'm'} | Y_{\ell m}\rangle = \delta_{\ell'\ell}\delta_{m'm}.$$

$$\int_0^{2\pi} d\varphi \int_{-1}^{1} d(\cos\theta)\, Y_{\ell'm'}^* Y_{\ell m} = \delta_{\ell'\ell}\delta_{m'm}$$

(spherical polar coordinates: $dxdydz=r^2 dr d(\cos\theta) d\varphi$)

Integral over φ is straightforward.

$$\bar{P}_\ell^{|m|}(\cos\theta) = \frac{2\ell+1}{2}\left[\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta)$$

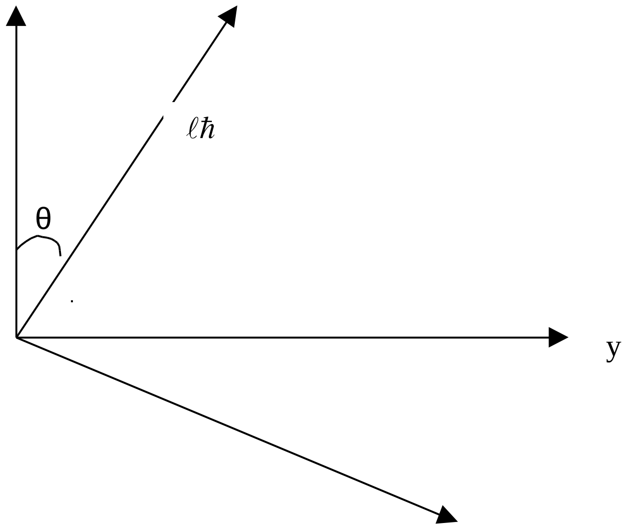
and $P_\ell^{|m|}(x) = \frac{1}{2^\ell \ell!}\left(1-x^2\right)^{|m|/2} \frac{d^{\ell+|m|}}{dx^{\ell+|m|}}\left(x^2-1\right)^\ell \qquad \ell = 0,1,2,\ldots$

Examples

$\bar{P}_0^0 = \frac{1}{2}\sqrt{2}$, $\qquad \bar{P}_1^0 = \frac{1}{2}\sqrt{6}\cos\theta \qquad \bar{P}_2^0 = \frac{1}{4}\sqrt{10}(3\cos^2\theta - 1)$

$\bar{P}_1^1 = \frac{1}{2}\sqrt{3}\sin\theta \qquad \bar{P}_2^1 = \frac{1}{2}\sqrt{15}\sin\theta\cos\theta \qquad \bar{P}_2^2 = \frac{1}{4}\sqrt{15}\sin^2\theta$

Physical rationale for inequality $-m \le \ell \le m$



Vector of magnitude $\ell\hbar$ has a z-component given by $\ell\hbar\sin\theta$ which has a range classically of $-\ell\hbar$ to $\ell\hbar$ $(0 \le \theta \le \pi)$.

<u>Remarks</u>: For each value of ℓ there are $2\ell+1$ values of m; there are $2\ell+1$ spherical harmonics.

$\ell = 1$ in detail:

$$Y_{10}(\theta,\varphi) = \bar{P}_1(\cos\theta) = \tfrac{1}{2}\sqrt{6}\,\cos\theta$$

$$Y_{1,+1}(\theta,\varphi) = \bar{P}_1^1(\cos\theta)\frac{e^{i\varphi}}{\sqrt{2\pi}}, \qquad Y_{1,-1} = \bar{P}_1^1(\cos\theta)\frac{e^{-i\varphi}}{\sqrt{2\pi}}$$

$$\alpha\sin\theta e^{i\varphi} \qquad\qquad \alpha\sin\theta e^{-i\varphi}$$

$$L^2\left(Y_{1,+1} + Y_{1,-1}\right) = \partial\hbar^2\left(Y_{1,+1} + Y_{1,-1}\right)$$

Normalization factor

So, $\dfrac{\left(Y_{1,+1} + Y_{1,-1}\right)}{\sqrt{2}}$ is still an eigenfunction of L_{op}^2 but *not* of L_z.

Why consider this lenear combination? It's real, i.e., $\alpha\sin\theta\cos\varphi \equiv P_x$
$(x = r\sin\theta\cos\varphi)$

$$\frac{\left(Y_{1,+1} - Y_{1,-1}\right)}{\sqrt{2}} \alpha \sin\theta\cos\varphi \equiv P_y \quad (\,y = r\sin\theta\cos\varphi)$$

These <u>orbitals</u> are used in discussions of bonding.