L37-Spherical Harmonics and Angular Momentum

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* Angular Momentum – recall 3 nested S.-L. problems

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m}\nabla^2 = \frac{-\hbar^2}{2m}\cdot\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}\right)\right)$$

$$= \underbrace{\left(-\hbar^2\cdot\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right)/2m}_{\hat{T}_r = \hat{P}_r^2/2m} + \left[\underbrace{\frac{-\hbar^2}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)}_{\hat{L}_\theta^2} + \frac{1}{\sin^2\theta}\underbrace{\left(-\hbar^2\frac{\partial^2}{\partial\phi^2}\right)}_{\hat{L}_\phi^2}\right]\Big/\underbrace{2mr^2}_{I}$$

$$\hat{T}_\Omega = \hat{L}^2/2I$$

* $\hat{L}_z = -i\hbar\partial_\phi \qquad \hat{L}_z e^{im\phi} = \hbar m\, e^{im\phi}$

periodic boundary conditions: $\Phi(0) = \Phi(2\pi) \qquad \Phi'(0) = \Phi'(2\pi)$

$\Rightarrow m = 0, \pm1, \pm2, \ldots \in \mathbb{Z}$

* $$\hat{L}^2 = \hbar^2\cdot\frac{-1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\frac{\sin^2\theta}{\sin\theta}\frac{\partial}{\partial\theta} - \frac{m^2}{\sin\theta}\right)$$

$L^2\,\Theta(\theta) = \hbar^2 \ell(\ell+1)\,\Theta(\theta)$

let $x = \cos\theta \equiv C_\theta$

$dx = -\sin\theta\, d\theta$

$\sqrt{1-x} = \sin\theta \equiv S_\theta$

$$= \hbar^2\left(\frac{-d}{dx}(1-x^2)\frac{d}{dx} + \frac{m^2}{1-x^2}\right)$$

$$\hat{L}^2 P_\ell^{|m|}(x) = \hbar^2\ell(\ell+1)\,\underbrace{P_\ell^{|m|}(x)}$$ Associated Legendre functions

* if $m=0$ (azimuthal symmetry, $L_z=0$) $\quad P_\ell^{|0|}(x) = P_\ell(x)$ Legendre Polynomial

$$P_\ell(x) \equiv \frac{1}{2^\ell\ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$$ Rodrigues' formula $\quad P_0 = 1 \quad P_1 = x$

$$(\ell+1)P_{\ell+1}(x) = (2\ell+1)x\,P_\ell(x) - \ell\,P_{\ell-1}(x)$$ Bonnet's recursion formula

$$\int_{-1}^{1} dx\, P_{\ell'}(x)\,P_\ell(x) = \delta_{\ell\ell'}\frac{2}{2\ell+1}$$ Orthogonality & normalization (S.-L.)

* if $m>0$ $$P_\ell^m(x) \equiv \underbrace{(1-x^2)^{|m|/2}}_{S_\theta^{|m|}}\left(\frac{d}{dx}\right)^{|m|}P_\ell(x)$$ some authors add factor $(-1)^m$ $m>0$ "Condon Shortly phase"

$$(\ell-m+1)P_{\ell+1}^m(x) = (2\ell+1)\,x\,P_\ell^m(x) - (\ell+m)P_{\ell-1}^m(x)$$ Recursion formula

$$P_m^m(x) = \underbrace{(-1)^m}_{\text{Condon-Shortley phase}}(2m-1)!!\,(1-x^2)^{m/2} \qquad P_{m+1}^m(x) = x(2m+1)\,P_m^m(x)$$ first 2 terms to start recursion.

$$\int_{-1}^{1} dx\, P_{\ell'}^{|m|}(x)\,P_\ell^{|m|}(x) = \delta_{\ell\ell'}\frac{2}{2\ell+1}\frac{(\ell+|m|)!}{(\ell-|m|)!}$$ Orthogonality & normalization (S.-L.)

$P_0(x) = 1$ $(m=0)$ $\qquad |m|=1:\ \ell=1,2,3\ldots \qquad |m|=2:\ \ell=2,3,\ldots \qquad |m|=3\ \ \ell=3,4,\ldots$

$P_1(x) = x = C_\theta \qquad P_1^1(x) = (-)\,S_\theta$

$P_0(x) = 1$ $(m=0)$ | $|m|=1:\ \ell=1,2,3\ldots$ | $|m|=2:\ \ell=2,3,\ldots$ | $|m|=3\ \ \ell=3,4,\ldots$

$P_1(x) = x = c_\theta$ $\quad P_1^1(x) = (-)\,s_\theta$

$P_2(x) = \frac{1}{2}(3c_\theta^2-1)$ $\quad P_2^1(x) = (-)3\,s_\theta c_\theta$ $\quad P_2^2(x) = 3s_\theta^2$

$P_3(x) = \frac{1}{2}(5c_\theta^3-3c_\theta)$ $\quad P_3^1(x) = (-)\frac{3}{2}s_\theta(5c_\theta^2-1)$ $\quad P_3^2(x) = 15\,s_\theta^2 c_\theta$ $\quad P_3^3(x) = (-)15\,s_\theta^3$

Group activity: 1) use recursion formulas or derivatives to calculate P_ℓ^m
2) verify that $L^2 P_\ell^{|m|}(c_\theta) = \hbar^2\ell(\ell+1)P_\ell^{|m|}(c_\theta)$

* Spherical harmonics: $Y_{\ell m}(\theta,\phi) \equiv \varepsilon\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\,P_\ell^{|m|}(c_\theta)\,e^{im\phi}$, $\quad \varepsilon = \begin{cases}(-1)^m & m>0\\ 1 & m<0\end{cases}$

They are eigenfunctions of both L^2, L_z: $L^2 Y_{\ell m} = \hbar^2\ell(\ell+1)Y_{\ell m}$ $\quad L_z Y_{\ell m} = \hbar m Y_{\ell m}$

They are normalized: $\langle \ell' m'|\ell m\rangle = \int d\Omega\, Y^*_{\ell' m'}(\Omega)\,Y_{\ell m}(\Omega) = \delta_{\ell\ell'}\delta_{mm'}$

They are complete: $\sum_{\ell,m}|\ell m\rangle\langle \ell m| = I$ $\quad \sum_{\ell,m} Y_{\ell m}(\theta,\phi)Y^*_{\ell m}(\theta',\phi') = \delta(c_\theta - c_{\theta'})\,\delta(\phi-\phi')$

* Application: solution of $\nabla^2 V = 0$ in spherical co-ords: solid harmonics

$$\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\ell(\ell+1)}{r^2}\right]R(r) = 0 \qquad \text{let } rR(r) = u(r)$$

$$u'' = \frac{\ell(\ell+1)}{r^2}u = \frac{(-\ell-1)(-\ell)}{r^2}u \qquad u = \underbrace{r^{\ell+1}}_{\text{nonsingular at } r\to 0} \text{ or } r^{-\ell}$$

$$V(r,\theta,\phi) = \sum_{\ell m} r^\ell P_\ell^{|m|}(c_\theta)\,e^{im\phi}$$

$$= \sum_{\ell m} r^{\ell-|m|}\left(a\,c_\theta^{\ell-|m|} + b\,c_\theta^{\ell-|m|-2}+\ldots\right) r^{|m|} s_\theta^{|m|}(c_\phi + i s_\phi)^m$$

$$= \sum_{\ell m}\left(a z^{\ell-|m|} + b z^{\ell-|m|-2}r^2 + \ldots\right)(x\pm iy)^m$$

$$= \sum_{\substack{i+j=|m|\\ i+j+k=\ell\\ i,j,k\pm 2}} a_{ijk}\,x^i y^j z^k \quad \text{multinomial in } x,y,z\text{! (but not all terms)}$$

$$\nabla^2 V = \sum_{ijk} a_{ijk}(\partial_x^2+\partial_y^2+\partial_z^2)\,x^i y^j z^k$$

$$= \sum_{ijk} a_{i'j'k'}\left[i'(i'-1)x^{i'-2}y^{j'}z^{k'} + \ldots\right] = \sum_{ijk}\underbrace{\begin{pmatrix} + (i+2)\cdot(i+1)\cdot a_{ijk} \\ + (j+2)\cdot(j+1)\cdot a_{i\,j+2\,k} \\ + (k+2)\cdot(k+1)\cdot a_{ijk+2}\end{pmatrix}}_{=0\ \ \forall i,j,k} x^i y^j z^k = 0$$

Example: $a_{200}+a_{020}+a_{002} = 0$ excludes $\ell=0$. $r^2 = x^2+y^2+z^2$, but not

$\ell=2$: [$m=2$: x^2-y^2, $2xy$, $m=1$: $2xz$, $2yz$, $m=0$: $\frac{1}{2}(3z^2-r^2)$]

* Atomic orbitals:

	$\lvert m\rvert=0$	$\lvert m\rvert=1$	$\lvert m\rvert=2$	$\lvert m\rvert=3$
$\ell=0$ (s)harp	$s=1$			
$\ell=1$ (p)rincipal	$p_z=z$	$p_x=x$ $p_y=y$		
$\ell=2$ (d)iffuse	$d_{3z^2-r^2}=z^2-\frac{1}{2}(x^2+y^2)$	$d_{xz}=2xz$ $d_{yz}=2yz$	$d_{xy}=2xy$ $d_{x^2-y^2}=x^2-y^2$	
$\ell=3$ (f)ine	$d_{5z^2-3zr^2}=z^3-\frac{3}{2}(x^2+y^2)z$	$f_{5z^2x-r^2x}=6z^2x-\frac{3}{2}(x^3+xy^2)$ $f_{5z^2y-r^2y}=6z^2y-\frac{3}{2}(y^3+yx^2)$	$f_{xyz}=30xyz$ $f_{x^2z-y^2z}=15(x^2z-y^2z)$	$f_{x^3-3xy^2}=15(x^3-3xy^2)$ $f_{y^3-3yx^2}=15(y^3-3yx^2)$