Chem 5314 central force notes

Our goal is to solve the TISE for the central force problem where the potential is a function of r only.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi \tag{1}$$

Try separation of variables: $\psi(r,\theta,\phi) = R(r)P(\theta)Q(\phi)$ This gives, using the spherical polar form of ∇^2 (see, for example, equation 9.51 in Atkins)

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[PQ\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{RQ}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta}) + \frac{RP}{\sin^2\theta}\frac{d^2Q}{d\phi^2}\right] + V(r)RPQ = ERPQ \tag{2}$$

Divide through by $\psi = RPQ$ to get

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{1}{R}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{1}{P\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta}) + \frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2}\right] + V(r) = E \tag{3}$$

The expression in $[\cdots]$ is a function of r only. Why? Solve for it:

$$\left[\frac{1}{R}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{1}{P\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta}) + \frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2}\right] = -\frac{2mr^2(E-V(r))}{\hbar^2} \tag{4}$$

Therefore, the sum of the 2nd and 3rd terms in $[\cdots]$ must be a constant because they have angle dependence only. Call this constant $-\lambda$.

$$\frac{1}{P\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta}) + \frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2} = -\lambda \tag{5}$$

Rearrange Eq. (5) to obtain

$$\frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2} = -\lambda - \frac{1}{P\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta}) \tag{6}$$

and then again to obtain

$$\frac{1}{Q}\frac{d^2Q}{d\phi^2} = \sin^2\theta(-\lambda - \frac{1}{P\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta})) \tag{7}$$

Hence the left hand side of Eq. (7) is a function of θ only, which can only hold if

$$\frac{1}{Q}\frac{d^2Q}{d\phi^2} = -m^2 \tag{8}$$

We have acheived our goal! The three separated equations are:

$$\frac{d^2Q}{d\phi^2} = -m^2Q \tag{9}$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dP}{d\theta}) - \frac{m^2}{\sin^2\theta}P = -\lambda P \tag{10}$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{d}{dr}(r^2\frac{dR}{dr}) - \lambda R\right] + V(r)R = ER \tag{11}$$

A brief table of some of the $P_{\ell m}(\theta)$ (unnormalized)

$\ell = 0$	$P_{00} = 1$
$\ell = 1$	$P_{10} = \cos\theta$
	$P_{11} = \sin\theta$
$\ell = 2$	$P_{20} = 3\cos^2\theta - 1$
	$P_{21} = \sin\theta\cos\theta$
	$P_{22} = \sin^2\theta$
$\ell = 3$	$P_{30} = 5\cos^3\theta - 3\cos\theta$
	$P_{31} = \sin\theta(5\cos^2\theta - 1)$
	$P_{32} = \sin^2\theta\cos\theta$
	$P_{33} = \sin^3\theta$

Spherical harmonics, normalized with respect to the (θ, ϕ) parts of 3d integration in spherical polar coordinates:

$\ell = 0$	$\mathcal{Y}_{00} = \left(\frac{1}{4\pi}\right)^{1/2}$
$\ell = 1$	$\mathcal{Y}_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
	$\mathcal{Y}_{11} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \begin{cases} \sin\phi \\ \cos\phi \end{cases}$
$\ell = 2$	$\mathcal{Y}_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	$\mathcal{Y}_{21} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta \begin{cases} \sin\phi \\ \cos\phi \end{cases}$
	$\mathcal{Y}_{22} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \begin{cases} \sin 2\phi \\ \cos 2\phi \end{cases}$

Notice that, for each ℓ, there are $2\ell + 1$ different spherical harmonics. Using $x = r\sin\theta\cos\phi$, $y = \sin\theta\sin\phi$, $z = r\cos\theta$ and various trig. identities, the spherical harmonics up to $\ell = 2$ can be rewritten as: (normalized)

$\ell = 0$	$\mathcal{Y}_{00} = \left(\frac{1}{4\pi}\right)^{1/2}$	"s" orbital
$\ell = 1$	$\mathcal{Y}_{10} = \left(\frac{3}{4\pi}\right)^{1/2} z/r$	"p_z" orbital
	$\mathcal{Y}_{11}^{\sin} = \left(\frac{3}{4\pi}\right)^{1/2} y/r$	"p_y" orbital
	$\mathcal{Y}_{11}^{\cos} = \left(\frac{3}{4\pi}\right)^{1/2} x/r$	"p_x" orbital
$\ell = 2$	$\mathcal{Y}_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3z^2 - r^2)/r^2$	"d_{z^2}" orbital
	$\mathcal{Y}_{21}^{\sin} = \left(\frac{15}{4\pi}\right)^{1/2} yz/r^2$	"d_{yz}" orbital
	$\mathcal{Y}_{21}^{\cos} = \left(\frac{15}{4\pi}\right)^{1/2} xz/r^2$	"d_{xz}" orbital
	$\mathcal{Y}_{22}^{\sin} = \left(\frac{15}{4\pi}\right)^{1/2} xy/r^2$	"d_{xy}" orbital
	$\mathcal{Y}_{22}^{\cos} = \left(\frac{15}{16\pi}\right)^{1/2} (x^2 - y^2)/r^2$	"$d_{x^2-y^2}$" orbital

You can now understand the origin of the traditional designations of p_x, p_y, p_z, etc.