Chem 442: Homework for lecture L15

(only turn in **BOLD** assignment first lecture next week; do all assignments)

1. Using the formulas for x, y, and z show that $\varphi = \tan^{-1}\left(\frac{y}{x}\right)$ and $\theta = \cos^{-1}\left(\frac{z}{R}\right)$

Turn in 2.

a. Prove that the $\widehat{H}_{rot}$ presented in lecture,

$$\widehat{H}_{rot} = \frac{-\hbar^2}{2mr^2}\left\{\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\theta^2} + cot\theta\frac{\partial}{\partial\theta}\right\}$$

is the same as the one on page 87 of the textbook (equations A5.1 and A5.2). **Hint:** Use the chain rule.

Gruebele said that this equation should be solvable by a product wavefunction, so if the solution is called $Y_{\ell M}(\theta,\varphi)$, it can be written as a product $Y_{\ell M}(\theta,\varphi) = P_{\ell M}(\theta)\frac{1}{\sqrt{2\pi}}e^{iM\varphi}$. The last part of the wavefunction is just the solution we previously found for rotation on a surface.

b. Insert this $P_{\ell M}(\theta)\frac{1}{\sqrt{2\pi}}e^{iM\varphi}$ wavefunction into $\widehat{H}_{rot}$ to prove that it solves the rotational eigenvalue equation $\widehat{H}_{rot}Y_{\ell M}(\theta,\varphi) = E_{\ell M}Y_{\ell M}(\theta,\varphi)$. Thus prove that $P_{\ell M}(\theta)$ satisfies the one-dimensional Schrödinger equation

$$\frac{-\hbar^2}{2mr^2}\left\{\frac{\partial^2}{\partial\theta^2} + cot\theta\frac{\partial}{\partial\theta} - \frac{M^2}{sin^2\theta}\right\}P_{\ell M}(\theta) = E_{\ell M}P_{\ell M}(\theta)$$

The solutions of this equations are the functions like P_{10}~cosθ or P_{20}~3cosθ-1 in the table in the N15 lecture notes. Multiply them together with the $e^{iM\varphi}$ part, and you get the whole rotational wavefunctions. As always, these wavefunctions have high probability in the same places where a classical particle would, as we'll discuss on Monday.