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 \( \hat{H}_{\text{rot}} \) presented in lecture,

\[
\hat{H}_{\text{rot}} = \frac{-\hbar^2}{2mr^2} \left\{ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right\}
\]

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 \( \hat{H}_{\text{rot}} \) to prove that it solves the rotational eigenvalue equation \( \hat{H}_{\text{rot}} Y_{\ell M}(\theta, \varphi) = E_{\ell M} Y_{\ell M}(\theta, \varphi) \). 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 \( P_{10} \sim \cos \theta \) or \( P_{20} \sim 3 \cos \theta - 1 \) 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.