Chem 442: Homework for lecture L14

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

1. Write the normalized wavefunction of a particle in the ground state of a 1D box. Call it Ψ. Now consider a 3D box, with the particle in the ground state. [There is just one ground state]. You can write this wavefunction as a product of the particle-in-1D-box wavefunctions, that is $\Psi(x).\Psi(y).\Psi(z)$. Call this $\psi(x,y,z)$. Show that, if $\Psi(x), \Psi(y)$ and $\Psi(z)$ are separately normalized, $\psi(x,y,z)$ is also normalized.

2. Consider a particle in a 3D cubic box, at an energy level given by $E = \frac{17\,h^2}{8mL^2}$, where L is the length of each side. What is the degeneracy of this state, that is, how many different combinations of the n_x, n_y, n_z quantum numbers can you have, that all lie at this exact energy?

Turn in 3. A rotating-vibrating molecule adsorbed on a surface has two coordinates: bond distance r and orientation angle φ. In lecture, Gruebele proved that the wavefunctions are a product $\psi(x,y,\ldots) = \psi_x(x)\psi_y(y)\ldots$ when $\hat{H} = \hat{H}_x + \hat{H}_y + \cdots$ is a sum of completely separate pieces for each coordinate. But he also claimed that the Hamiltonian for the rotating-vibrating molecule

$$\hat{H} = \hat{H}_{rot} + \hat{H}_{vib} = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\varphi^2} - \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + V(r)$$

can be solved by a product wavefunction $\psi_r(r)\psi_\varphi(\varphi)$, even though a $1/r^2$ is mixed into the rotational kinetic energy term. He claimed it's because a product wavefunction can yield a Schrödinger equation that depends only on r (in this special case), so $\psi_r(r)$ can be solved for separately from $\psi_\varphi(\varphi)$.

a. Apply $\hat{H}$ to the wavefunction $\psi_r(r)\psi_\varphi(\varphi)$, and in each of the three terms move any wavefunctions you can to the left hand side.

b. Now assume that $\psi_\varphi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{iM\varphi}$ (the solution if we had <u>only</u> the first term). Do the second derivative in the first term, and show that you can pull $\psi_\varphi(\varphi)$ to the left side in that term also. Does the resulting Schrödinger equation depend on φ anywhere, except in the wavefunction $\psi_\varphi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{iM\varphi}$ itself?

c. Based on you answer in (b), you can cancel out $\psi_\varphi = \frac{1}{\sqrt{2\pi}}e^{iM\varphi}$ and then write down a 'new' Schrödinger equation that must be satisfied by $\psi_r(r)$. Note that even though φ is no longer a variable, the equation does depend on M, or the rotational angular momentum of the molecule. One could solve the 'new' equation for $\psi(r,\varphi) = \psi_r(r)$ (you don't have to!).

d. This proves that $\psi(r,\varphi) = \psi_r(r)\frac{1}{\sqrt{2\pi}}e^{iM\varphi}$ solves the original Schrödinger equation by breaking the solution into two steps: $\psi_\varphi(\varphi)$ first, and then $\psi_r(r)$, but with a 'new' potential energy (not just $V(r)$!) What are the two terms in the 'new' potential energy?