Chem 442
Fall 2016

Hour Exam 2

1. (10 pts) Consider a particle in a 3D cubic box, at an energy level given by $E = \frac{19\, h^2}{8mL^2}$, where L is the length of each side and m is the mass of the particle. **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?

2. (10 pts) Consider the ∞-dimensional Hilbert space formed by the solutions of the Schrödinger equation for a molecule rotating in the plane: $\varphi_M(\phi) \sim e^{iM\phi}$ where M= ..., -2, -1, 0, 1, 2....

ANY normalizable function $y(\phi)$ over the angle ϕ=0⋯2π should be expressible in terms of this basis. **Show** that $y=\cos^2\phi$ can be expressed as a sum over these basis functions. [Hint: express the function in terms of complex exponentials.]

3. (5+5+5+5 pts) The technique of finding the eigenvalues and eigenvectors of an operator in matrix form is called "diagonalization." In this problem, you will diagonalize the matrix

$$M = \begin{pmatrix} 3 & -2 \\ -2 & 3 \end{pmatrix}.$$

The starting point is the equation $(M - \lambda \cdot I) \cdot \mathbf{v} = 0$, where M is your non-diagonal matrix, λ is any of the eigenvalues, **v** is one of the eigenvectors, and I is the identity matrix.

a. To obtain a non-trivial solution, we impose the condition $\det\|M - \lambda \cdot I\| = 0$; solve the determinant to **find the eigenvalues** of M.
b. Using the answers derived from part a, **find** the eigenvectors of M.
c. **Normalize** these eigenvectors.
d. **What property** of the matrix makes sure that the eigenvalues are real?

4. [5+10 pts] The rotational Hamiltonian in spherical co-ordinates is given by

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

a. **Show** that you can also express the Hamiltonian as:

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

b. **Operate** with the Hamiltonian on the function $Y_{1,-1}(\phi,\theta) = \frac{1}{2}\sqrt{3/(2\pi)}e^{-i\phi}sin\theta$ to verify that this is an eigenfunction of $\hat{H}_{rot}$, and **find** its eigenvalue. [Hint: some trig simplification is needed, such as $cos^2\theta - 1 = -sin^2\theta$ or $cot\theta = \frac{cos\theta}{sin\theta}$.]

5. (10+5+5) Consider a function y whose average value is $\langle y\rangle = 0$. The standard deviation Δy of such a function is given by $\Delta y = \sqrt{\langle y^2\rangle}$ in terms of its variance $\langle y^2\rangle$. Let's use this basic statistics formula and Dirac bracket notation to prove a familiar formula for the ground state |0> of the harmonic oscillator.

Recall the raising operators $a^\dagger$ and lowering operators a, such that $a^\dagger|0\rangle = |1\rangle$ and $a|1\rangle = |0\rangle$ moves you up or down one vibrational state, to the next higher (or lower) energy level. Also recall that for an oscillator of mass m=1 and force constant k=1 (for simplicity), we have that $x = \sqrt{\hbar/2}(a^\dagger + a)$ and $p = i\sqrt{\hbar/2}(a^\dagger - a)$.

a. **Show that** $\langle 0|x^2|0\rangle = \hbar/2$ by multiplying out $(a^\dagger + a)^2$. [Hint: two of the 4 terms give zero. **Why**?]

b. **Show that** $\langle 0|p^2|0\rangle = \hbar/2$ by multiplying out $(a^\dagger - a)^2$.

c. Based on your result in a. and b., **what is** $\Delta x\Delta$p =? **What is** the name of this familiar formula?

Congrats: Werner Heisenberg won the Nobel prize in 1932 for your derivation!