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?

Solution:
The energy for a cubic box is given by

$$E = E_x + E_y + E_z = \frac{(n_x^2+n_y^2+n_z^2)h^2}{8mL^2}$$

So we need to find out how many different combinations of n_x, n_y, n_z satisfy

$$(n_x^2+n_y^2+n_z^2) = 19$$

The most expedient way to do this is by simple logic and guess/check. To get an odd sum of three squares, 2 n's must be even and one must be odd, or all three must be odd. Two of the n's must at least equal 1, in which case the third has to be <√17 or ≤4. 16+1+1=18 only, so 4 is out. That leaves only combinations of 1,2,3 such as (1,2,2) or (1,3,3) or (2,2,3). The only one that works is

$$(1^2 + 3^2 + 3^2) = 19$$

There are 3 different combinations of n_x, n_y, n_z that satisfy the above condition. They are listed below:

$$n_x = 1, n_y = 3, n_z = 3$$
$$n_x = 3, n_y = 3, n_z = 1$$
$$n_x = 3, n_y = 1, n_z = 3$$

Thus the degeneracy is 3.

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.]

Solution:
Recall that $e^{i\phi} = \cos(\phi) + isin(\phi)$ so $\cos(\phi) = \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right)$
Thus,

$$\cos^2\phi = \frac{1}{4}\left(e^{i\phi} + e^{-i\phi}\right)^2 = \frac{1}{4}\left(e^{2i\phi} + 2e^0 + e^{-2i\phi}\right) = \frac{1}{4}\varphi_2(\phi) + \frac{1}{2}\varphi_0(\phi) + \frac{1}{4}\varphi_{-2}(\phi)$$

Thus $\cos^2\phi$ is expressible in terms of eigenfunctions of the rotational Hamiltonian.

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?

Solution:

a. Start by determining the determinant:

$$\begin{vmatrix} 3-\lambda & -2 \\ -2 & 3-\lambda \end{vmatrix} = 0$$

$$(3-\lambda)^2 - 4 = \lambda^2 - 6\lambda + 5 = (\lambda - 5)(\lambda - 1) = 0$$

So we can determine:

$$\lambda = 1, 5$$

b. To find the eigenvectors, we simply impose the condition from the eigenvalue problem:

$$(M - \lambda \cdot I) \cdot \mathbf{v} = 0$$

(Note that any multiple of **v** still satisfy the above condition.)
Now we can plug each eigenvalue into this equation and solve for **v**:

$\boldsymbol{\lambda = 1}$ **:**

$$\begin{pmatrix} 3-1 & -2 \\ -2 & 3-1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

We get two equations:

$$c_1 - c_2 = 0$$
$$-c_1 + c_2 = 0$$

The equation only determines c_1 *in terms of* c_2 *or vice-versa*, not both. To get both, we also need to invoke normalization, or $c_1^2+c_2^2=1$. A simple trick is to *assign* a value to either c_1 or c_2, and then solve for the other. It is by far the easiest course of action to set one of the constants equal to unity and solve for the other, and that is what shall be done here. Setting $c_1 = 1$ we have

$$1 - c_2 = 0$$

and

$$-1 + c_2 = 0$$

Both equations confirm that c_2 must equal 1 (BECAUSE we set $c_1 = 1$). Thus the eigenvector corresponding to $\lambda = 1$ is given by

$$\mathbf{v_1} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Now we determine the other eigenvector:

$\boldsymbol{\lambda = 5}$ **:**

$$\begin{pmatrix} -2 & -2 \\ -2 & -2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

The two equations are:

$$c_1 + c_2 = 0$$
$$c_1 + c_2 = 0$$

Which is a somewhat boring system of equations. Setting c_1 equal to 1, we find:

$$1 + c_2 = 0$$

and

$$1 + c_2 = 0$$

Both equations confirm (we'll call the eigenvector for $\lambda = 5$ "$\mathbf{v}_5$."

$$\mathbf{v_5} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

c. Normalizing $\mathbf{v_1}$ we write

$$\mathbf{v_1}^\dagger \cdot \mathbf{v_1} = (1 \quad 1) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = 1 + 1 = 2$$

Dividing $\mathbf{v_1}$ by $\sqrt{2}$ gives the normalized eigenvector

$$\mathbf{v_1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Normalizing $\mathbf{v_5}$ we write

$$\mathbf{v_5}^\dagger \cdot \mathbf{v_5} = (1 \quad -1) \begin{pmatrix} 1 \\ -1 \end{pmatrix} = 1 + 1 = 2$$

Dividing $\mathbf{v_5}$ by $\sqrt{2}$ gives the normalized eigenvector

$$\mathbf{v_5} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

d. Real eigenvalues are guaranteed by the fact that the matrix is symmetric.

Done!

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.

Solution:
a. We consider,

$$\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) = \frac{1}{sin\theta}\frac{\partial(sin\theta)}{\partial\theta}\left(\frac{\partial}{\partial\theta}\right) + \frac{1}{sin\theta}sin\theta\frac{\partial}{\partial\theta}\left(\frac{\partial}{\partial\theta}\right) = \frac{cos\theta}{sin\theta}\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2}$$

$$\Rightarrow \frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2} = cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

This suggests that the two forms are equivalent.
b. $\hat{H}_{rot}Y_{lM}(\theta,\phi) = -\frac{\hbar^2}{2mr^2}\left\{\frac{\partial^2}{\partial\theta^2} + cot\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}e^{-i\phi}sin\theta$

Note that we can leave out the normalization constant $\frac{1}{2}\sqrt{3/(2\pi)}$ because it will simply show up on both sides. Taking the derivatives,

$$\begin{aligned}\hat{H}_{rot}Y_{lM}(\theta,\phi) &= -\frac{\hbar^2}{2mr^2}\left\{-e^{-i\phi}sin\theta + cot\theta e^{-i\phi}cos\theta + \frac{-1}{sin^2\theta}e^{-i\phi}sin\theta\right\}\\ &= -\frac{\hbar^2}{2mr^2}\left\{-sin\theta + \frac{cos^2\theta}{sin\theta} + \frac{-1}{sin\theta}\right\}e^{-i\phi}\\ &= -\frac{\hbar^2}{2mr^2}\{-sin\theta - sin\theta\}e^{-i\phi}\\ &= \frac{\hbar^2}{mr^2}e^{-i\phi}sin\theta\end{aligned}$$

Thus the eigenvalue is $\frac{\hbar^2}{mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2}$ for l =1, as expected for the $Y_{1,-1}$ eigenfunction.

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?

Chem 442
Fall 2016

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

Solution:

a. Recall that $a|1>=|0>$ and $a^{\dagger}|0>=|1>$ with the limitation that $a|0>=0$.
Thus,

$$\langle x^2\rangle = \langle 0|x^2|0\rangle = \left(\frac{\hbar}{2}\right)\langle 0|(a^{\dagger}+a)^2|0\rangle = \left(\frac{\hbar}{2}\right)\langle 0|({a^{\dagger}}^2 + a^{\dagger}a + aa^{\dagger} + a^2)|0\rangle$$

$$= \frac{\hbar}{2}\left(\langle 0\left|{a^{\dagger}}^2\right|0\rangle + \langle 0\left|aa^{\dagger}\right|0\rangle + \langle 0\left|a^{\dagger}a\right|0\rangle + \langle 0|a^2|0\rangle\right)$$

In this expression, the first term is zero because ${a^{\dagger}}^2$ raises $|0\rangle$ to $|2\rangle$, which is orthogonal to $\langle 0|$. The second term equals 1 because $a^{\dagger}|0\rangle = |1\rangle$ and $a|1\rangle = |0\rangle$ and $\langle 0|0\rangle = 1$. The third term is again zero because $a|0\rangle = 0$. Finally the last term is zero again because lowering $|0\rangle$ just gives 0.

Thus $$\langle x^2\rangle = \frac{\hbar}{2}$$

b.

$$\langle p^2\rangle = \langle 0|p^2|0\rangle = \left(-\frac{\hbar}{2}\right)\langle 0|(a^{\dagger}-a)^2|0\rangle = \left(-\frac{\hbar}{2}\right)\langle 0|({a^{\dagger}}^2 - a^{\dagger}a - aa^{\dagger} + a^2)|0\rangle$$

$$= -\frac{\hbar}{2}\left(\langle 0\left|{a^{\dagger}}^2\right|0\rangle - \langle 0\left|aa^{\dagger}\right|0\rangle - \langle 0\left|a^{\dagger}a\right|0\rangle + \langle 0|a^2|0\rangle\right) = \frac{\hbar}{2}$$

again, for the same reasons already given for *x*.

c. $\Delta x\Delta p = \sqrt{\langle x^2\rangle}\sqrt{\langle p^2\rangle} = \sqrt{\frac{\hbar}{2}}\sqrt{\frac{\hbar}{2}} = \frac{\hbar}{2}$ or $\Delta x\,\Delta p = \frac{\hbar}{2}$.

Yet again, we find the equation for the "uncertainty principle": the ground state of the harmonic oscillator, or $|0\rangle$, satifies the uncertainty principle and is a "minimum uncertainty wavepacket."