Problem Set 6

P18.2) In this problem you will derive the commutator $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$.

a. The angular momentum vector in three dimensions has the form $\mathbf{l} = \mathbf{i}l_x + \mathbf{j}l_y + \mathbf{k}l_z$ where the unit vectors in the *x*, *y*, and *z* directions are denoted by $\mathbf{i}, \mathbf{j}$, and $\mathbf{k}$. Determine l_x, l_y, and l_z by expanding the 3 × 3 cross product $\mathbf{l} = \mathbf{r} \times \mathbf{p}$. The vectors $\mathbf{r}$ and $\mathbf{p}$ are given by $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$ and $\mathbf{p} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z$.

b. Substitute the operators for position and momentum in your expressions for l_x and l_y. Always write the position operator to the left of the momentum operator in a simple product of the two.

c. Show that $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$

a)

$$\mathbf{l} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \mathbf{i}\begin{vmatrix} y & z \\ p_y & p_z \end{vmatrix} - \mathbf{j}\begin{vmatrix} x & z \\ p_x & p_z \end{vmatrix} + \mathbf{k}\begin{vmatrix} x & y \\ p_x & p_y \end{vmatrix}$$

$$= \mathbf{i}\left(y\,p_z - z\,p_y\right) - \mathbf{j}\left(x\,p_z - z\,p_x\right) + \mathbf{k}\left(x\,p_y - y\,p_x\right)$$

$$= \mathbf{i}\left(y\,p_z - z\,p_y\right) + \mathbf{j}\left(z\,p_x - x\,p_z\right) + \mathbf{k}\left(x\,p_y - y\,p_x\right)$$

b)

$$\hat{l} = \mathbf{i}\left(-i\hbar\, y\frac{\partial}{\partial z} + i\hbar\; z\frac{\partial}{\partial y}\right) + \mathbf{j}\left(-i\hbar\; z\frac{\partial}{\partial x} + i\hbar x\frac{\partial}{\partial z}\right) + \mathbf{k}\left(-i\hbar\; x\frac{\partial}{\partial y} + i\hbar\; y\frac{\partial}{\partial x}\right)$$

$$\hat{l}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad \hat{l}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad \hat{l}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

c)

$$\left[\hat{l}_x, \hat{l}_y\right] = \hat{l}_x\hat{l}_y - \hat{l}_y\hat{l}_x =$$

$$-\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial x}\right) + \hbar^2\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right)\left(y\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial y}\right)$$

$$= -\hbar^2\, y\frac{\partial}{\partial z}\left(x\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial x}\right) + \hbar^2 z\frac{\partial}{\partial y}\left(x\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial x}\right) + \hbar^2\, x\frac{\partial}{\partial z}\left(y\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial y}\right) - \hbar^2\, z\frac{\partial}{\partial x}\left(y\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial y}\right)$$

$$= -\hbar^2\, y\,x\frac{\partial^2 f}{\partial z^2} + \hbar^2\, y\frac{\partial f}{\partial x} + \hbar^2 yz\frac{\partial^2 f}{\partial z\partial x} + \hbar^2 zx\frac{\partial^2 f}{\partial y\partial z} - \hbar^2 z^2\frac{\partial^2 f}{\partial y\partial x}$$

$$+\,\hbar^2 xy\frac{\partial^2 f}{\partial z^2} - \hbar^2 xz\frac{\partial^2 f}{\partial y\partial z} - \hbar^2 x\frac{\partial f}{\partial y} - \hbar^2 yz\frac{\partial^2 f}{\partial z\partial x} + \hbar^2 z^2\frac{\partial^2 f}{\partial y\partial x} =$$

$$\hbar^2\, y\frac{\partial f}{\partial x} - \hbar^2 x\frac{\partial f}{\partial y}$$

$$\left[\hat{l}_x, \hat{l}_y\right] = -\hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = i\hbar \times i\hbar\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) = i\hbar\hat{l}_z$$

P18.5) $^1H^{127}I$ has a force constant of 314 N m^{-1} and a bond length of 160.92 pm. Calculate the frequency of the light corresponding to the lowest energy pure vibrational and pure rotational transitions. In what regions of the electromagnetic spectrum do the transitions lie?

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{314 \text{ kg s}^{-2}}{\frac{1.008 \text{ amu}\times 126.9045 \text{ amu}}{1.008 \text{ amu} + 126.9045 \text{ amu}}\times\frac{1.661\times 10^{-27}\text{ kg}}{\text{amu}}}}$$

$$= 6.92\times 10^{13}\text{ s}^{-1}$$

This frequency lies in the infrared region of the eletromagnetic spectrum.

The lowest energy transition is $J = 0 \rightarrow J = 1$.

$$I = \mu r_0^2 = \frac{1.008 \text{ amu}\times 126.9045 \text{ amu}}{1.008 \text{ amu} + 126.9045 \text{ amu}}\times\frac{1.661\times 10^{-27}\text{ kg}}{\text{amu}}\times\left(160.92\times 10^{-12}\text{ m}\right)^2$$

$$= 4.30\times 10^{-47}\text{ kg m}^2$$

$$\Delta E_{rot} = 2(J+1)\frac{\hbar^2}{2\mu r_0^2} = \frac{\hbar^2}{\mu r_0^2} = \frac{\left(1.055\times 10^{-34}\text{ J s}\right)^2}{4.30\times 10^{-47}\text{ kg m}^2} = 2.59\times 10^{-22}\text{ J}$$

$$\nu = \frac{\Delta E_{rot}}{h} = 3.91\times 10^{11}\text{ s}^{-1}$$

This frequency lies in the microwave region of the eletromagnetic spectrum.

P18.6) The wave functions p_x and d_{xz} are linear combinations of the spherical harmonic functions, which are eigenfunctions of the operators $\hat{H}$, $\hat{l}^2$, and $\hat{l}_z$ for rotation in three dimensions. The combinations have been chosen to yield real functions. Are these functions still eigenfunctions of $\hat{l}_z$? Answer this question by applying the operator to the functions.

$\hat{l}_z p_x = -i\hbar\frac{\partial}{\partial\theta}\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi = i\hbar\sqrt{\frac{3}{4\pi}}\cos\theta\cos\phi$. This shows that p_x is not an eigenfunction of $\hat{l}_z$.

$\hat{l}_z d_{xz} = -i\hbar\frac{\partial}{\partial\theta}\sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi = -i\hbar\sqrt{\frac{15}{4\pi}}\cos\theta\cos\theta\cos\phi$. This shows that d_{xz} is not an eigenfunction of $\hat{L}_z$.

P18.7) At what values of θ does $Y_2^0(\theta,\phi) = (5/16\pi)^{1/2}(3\cos^2\theta - 1)$ have nodes? Are the nodes points, lines, planes, or other surfaces?

$Y_2^0(\theta,\phi)$ has nodes when $\left(3\cos^2\theta - 1\right)$ has nodes. This occurs for

$\theta = 0.955$ and $\pi - 0.955$ radians or 54.7 and 125.3 degrees. These surfaces are cones.

P18.10) Show by carrying out the necessary integration that the eigenfunctions of the Schrödinger equation for rotation in two dimensions, $\frac{1}{\sqrt{2\pi}}e^{im_l\phi}$ and $\frac{1}{\sqrt{2\pi}}e^{-in_l\phi}$, $m_l \neq n_l$

are orthogonal

$$\left(\frac{1}{\sqrt{2\pi}}\right)^2 \int_0^{2\pi} e^{im_l\phi}e^{-in_l\phi}d\phi = \frac{1}{2\pi}\int_0^{2\pi}\left(\cos(m_l - n_l)\phi + i\sin(m_l - n_l)\phi\right)d\phi$$

$$= \frac{1}{2\pi}\left(\cos 2\pi(m_l - n_l) - 1 + i\sin 2\pi(m_l - n_l)\right) = 0$$

because $(m_l - n_l)$ is an integer

P18.15) Evaluate the average kinetic and potential energies, $\langle E_{kinetic}\rangle$ and $\langle E_{potential}\rangle$, for the ground state ($n = 0$) of the harmonic oscillator by carrying out the appropriate integrations.

We use the standard integrals $\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$ and

$$\int_0^\infty e^{-ax^2}dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\langle E_{potential}\rangle = \int \psi_0^*(x)\left(\frac{1}{2}kx^2\right)\psi_0(x)dx$$

$$= \frac{1}{2}k\left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^2e^{-\alpha x^2}dx = k\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^\infty x^2e^{-\alpha x^2}dx$$

$$= k\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}} = k\frac{1}{4\alpha} = \frac{\hbar}{4}\sqrt{\frac{k}{\mu}}$$

$$\langle E_{kinetic}\rangle = \int \psi_0^*(x)\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}\right)\psi_0(x)dx$$

$$= \int_{-\infty}^{\infty}\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\frac{1}{2}\alpha x^2}\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}\right)\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\frac{1}{2}\alpha x^2}dx$$

$$= -\frac{\hbar^2}{\mu}\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^\infty e^{-\alpha x^2}\left(\alpha x^2 - \alpha\right)dx$$

$$= -\frac{\hbar^2}{\mu}\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\alpha}{4}\sqrt{\frac{\pi}{\alpha}} - \frac{\alpha}{2}\sqrt{\frac{\pi}{\alpha}}\right) = \frac{\hbar^2}{\mu}\frac{\alpha}{4}$$

$$= \frac{\hbar^2}{4\mu}\sqrt{\frac{k\mu}{\hbar^2}} = \frac{\hbar}{4}\sqrt{\frac{k}{\mu}}$$

P18.22) The force constant for the D_2 molecule is 577 N m^{-1}. Calculate the vibrational zero point energy of this molecule. If this amount of energy were converted to translational energy, how fast would the molecule be moving? Compare this speed to the root mean square speed from the kinetic gas theory, $|v|_{rms} = \sqrt{3kT/m}$ for T = 300. K.

$$E = \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{1}{2}\times 1.055\times 10^{-34}\ \text{J s}\times\sqrt{\frac{577\ \text{N m}^{-1}}{\frac{2.014\ \text{amu}\times 2.014\ \text{amu}}{2.014\ \text{amu}+2.014\ \text{amu}}\times 1.66\times 10^{-27}\ \text{kg amu}^{-1}}}$$

$$= 3.10\times 10^{-20}\ \text{J}$$

The speed if converted to translational energy would be

$$|v| = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2\times 3.10\times 10^{-20}\ \text{J}}{(2.014+2.014)\ \text{amu}\times 1.66\text{x}10^{-27}\ \text{kg amu}^{-1}}} = 3.04\times 10^{3}\ \text{m s}^{-1}$$

The average speed from the kinetic gas theory is

$$|v_{rms}| = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3\times 1.381\times 10^{-23}\ \text{J K}^{-1}\times 300.\ \text{K}}{(2.014+2.014)\ \text{amu}\times 1.66\times 10^{-27}\ \text{kg amu}^{-1}}} = 1.36\times 10^{3}\ \text{m s}^{-1}$$

$$\frac{|v|}{|v_{rms}|} = \frac{3.04\times 10^{3}\ \text{ms}^{-1}}{1.36\times 10^{3}\ \text{ms}^{-1}} = 2.23$$

P18.26) Using your results for Problems P18.11, 29, 31, and 32, calculate the uncertainties in the position and momentum $\sigma_p^2 = \langle p^2\rangle - \langle p\rangle^2$ and $\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2$ for the ground state (n = 0) and first two excited states (n = 1 and n = 2) of the quantum harmonic oscillator. Compare your results with the predictions of the Heisenberg uncertainty principle.

$$\sigma_p^2 = \left\langle p^2 \right\rangle - \left\langle p \right\rangle^2 \text{ and } \sigma_x^2 = \left\langle x^2 \right\rangle - \left\langle x \right\rangle^2$$

For $n = 0$, $\sigma_p^2 = \frac{1}{2}\hbar\sqrt{k\,\mu} - 0 = \frac{1}{2}\hbar\sqrt{k\,\mu}$

$$\sigma_x^2 = \frac{\hbar}{2\sqrt{k\,\mu}} - 0 = \frac{\hbar}{2\sqrt{k\,\mu}}$$

$$\Delta p \Delta x = \sqrt{\sigma_p^2 \sigma_x^2} = \frac{1}{2}\hbar \geq \frac{1}{2}\hbar$$

For $n = 1$, $\sigma_p^2 = \frac{3}{2}\hbar\sqrt{k\,\mu} - 0 = \frac{3}{2}\hbar\sqrt{k\,\mu}$

$$\sigma_x^2 = \frac{3\hbar}{2\sqrt{k\,\mu}} - 0 = \frac{3\hbar}{2\sqrt{k\,\mu}}$$

$$\Delta p \Delta x = \sqrt{\sigma_p^2 \sigma_x^2} = \frac{3}{2}\hbar \geq \frac{1}{2}\hbar$$

For $n = 2$, $\sigma_p^2 = \frac{5}{2}\hbar\sqrt{k\,\mu} - 0 = \frac{5}{2}\hbar\sqrt{k\,\mu}$

$$\sigma_x^2 = \frac{5\hbar}{2\sqrt{k\,\mu}} - 0 = \frac{5\hbar}{2\sqrt{k\,\mu}}$$

$$\Delta p \Delta x = \sqrt{\sigma_p^2 \sigma_x^2} = \frac{5}{2}\hbar \geq \frac{1}{2}\hbar$$

P18.31) Evaluate the average of the square of the vibrational amplitude of the quantum harmonic oscillator about its equilibrium value, $\langle x^2 \rangle$, for the ground state (n = 0) and first two excited states (n = 1 and n = 2). Use the hint about evaluating integrals in Problem P18.12.

We use the standard integrals $\int_0^\infty x^{2n} e^{-ax^2} d\,x = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n}\sqrt{\frac{\pi}{a}}$ and

$$\int_0^\infty e^{-ax^2}dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\langle x^2\rangle = \int_{-\infty}^{\infty}\psi_n^*(x)(x^2)\psi_n dx$$

for $n = 0$, $\langle x^2\rangle = \int_{-\infty}^{\infty}\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2}(x^2)\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} dx$

$$\langle x^2\rangle = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = 2\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} x^2 e^{-\alpha x^2} dx$$

$$\langle x^2\rangle = 2\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^2\alpha}\sqrt{\frac{\pi}{\alpha}} = \frac{1}{2\alpha} = \frac{\hbar}{2\sqrt{k\mu}}$$

for $n = 1$, $\langle x^2\rangle = \int_{-\infty}^{\infty}\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\frac{1}{2}\alpha x^2}(x^2)\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} dx$

$$\langle x^2\rangle = \left(\frac{4\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = 2\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\int_0^{\infty} x^4 e^{-\alpha x^2} dx$$

$$\langle x^2\rangle = 2\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\frac{3}{2^3\alpha^2}\sqrt{\frac{\pi}{\alpha}} = \frac{3}{2\alpha} = \frac{3\hbar}{2\sqrt{k\mu}}$$

for $n = 2$, $\langle x^2\rangle = \int_{-\infty}^{\infty}\left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\frac{1}{2}\alpha x^2}(x^2)\left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\frac{1}{2}\alpha x^2} dx$

$$\langle x^2\rangle = \left(\frac{\alpha}{4\pi}\right)^{1/2}\int_{-\infty}^{\infty}(4\alpha^2x^6 - 4\alpha x^4 + x^2)e^{-\alpha x^2} dx = 2\left(\frac{\alpha}{4\pi}\right)^{1/2}\int_0^{\infty}(4\alpha^2x^6 - 4\alpha x^4 + x^2)e^{-\alpha x^2} dx$$

$$\langle x^2\rangle = 2\left(\frac{\alpha}{4\pi}\right)^{1/2}\left(4\alpha^2\frac{15}{2^4\alpha^3}\sqrt{\frac{\pi}{\alpha}} - 4\alpha\frac{3}{2^3\alpha^2}\sqrt{\frac{\pi}{\alpha}} + \frac{1}{2^2}\sqrt{\frac{\pi}{\alpha}}\right) = \frac{5}{2\alpha} = \frac{5\hbar}{2\sqrt{k\mu}}$$

P18.32) Evaluate the average vibrational amplitude of the quantum harmonic oscillator about its equilibrium value, $\langle x\rangle$, for the ground state ($n = 0$) and first two excited states ($n = 1$ and $n = 2$). Use the hint about evaluating integrals given in Problem P18.12.

$\langle x\rangle = \int_{-\infty}^{\infty}\psi_n^*(x)\,x\,\psi_n dx = \int_{-\infty}^{\infty} x\,(\psi_n)^2 dx$. Because $(\psi_n)^2$ is an even function of x for all n, the product $x(\psi_n)^2$ is an odd function of x. Therefore, $\langle x\rangle = 0$ for all n.