Chem 3322 homework #6 solutions

Problem 1 – angular momentum

Angular momentum in classical mechanics measures the 'amount of rotation'. It is analogous to linear momentum, which measures the 'amount of motion'. In classical mechanics, angular momentum is conserved. The definition of angular momentum for a point particle is given by

$$\underline{L} = \underline{r} \times \underline{p} \tag{1}$$

namely by the cross product of the position vector with the (linear) momentum vector.

a) From this definition, show that, in quantum mechanics, the z-component of the angular momentum operator is given by

$$\hat{L}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \tag{2}$$

Solution:

From the definition of the cross product,

$$L_z = xp_y - yp_x \tag{3}$$

where $\underline{r} = (x, y, z)$ and $\underline{p} = (p_x, p_y, p_z)$. To convert to a quantum mechanical operator,

$$x \to \hat{x} = x \tag{4}$$

$$y \to \hat{y} = y \tag{5}$$

$$p_x \to \hat{p_x} = -i\hbar\frac{\partial}{\partial x} \tag{6}$$

$$p_y \to \hat{p_y} = -i\hbar\frac{\partial}{\partial y} \tag{7}$$

which yields the desired result.

b) Let us assume that our particle motion is restricted to the x-y plane. In this case, we can transform to plane polar coordinates. The transformations and reverse transformations are

$$\begin{aligned} x &= r\cos\theta & \qquad r &= \sqrt{x^2+y^2} \\ y &= r\sin\theta & \qquad \theta &= \arctan(y/x) \end{aligned} \tag{8}$$

Show that, in plane polar coordinates,

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\theta} \tag{9}$$

Hint: you must use the chain rule

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} \quad \text{and} \quad \frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta} \tag{10}$$

and you will need the derivative of arctan:

$$\frac{\partial \arctan(x)}{\partial x} = \frac{1}{1+x^2} \tag{11}$$

Solution:

First we can work out the four derivatives we need:

$$\frac{\partial r}{\partial x} = \frac{\partial}{\partial x}\sqrt{x^2+y^2} = \left(\frac{1}{2}\right)\left(\frac{1}{r}\right)(2x) = \frac{x}{r} = \frac{r\cos\theta}{r} = \cos\theta \tag{12}$$

$$\frac{\partial r}{\partial y} = \frac{\partial}{\partial y}\sqrt{x^2+y^2} = \left(\frac{1}{2}\right)\left(\frac{1}{r}\right)(2y) = \frac{y}{r} = \frac{r\sin\theta}{r} = \sin\theta \tag{13}$$

$$\frac{\partial\theta}{\partial x} = \frac{\partial}{\partial x}\arctan(y/x) = \frac{1}{1+(y/x)^2}\frac{\partial}{\partial x}\left(\frac{y}{x}\right) = \frac{1}{1+(y/x)^2}\left(-\frac{y}{x^2}\right)$$

$$= \left(-\frac{y}{x^2}\right)\left(\frac{x^2}{x^2+y^2}\right) = -\frac{r\sin\theta}{r^2} = -\frac{\sin\theta}{r} \tag{14}$$

$$\frac{\partial\theta}{\partial y} = \frac{\partial}{\partial y}\arctan(y/x) = \frac{1}{1+(y/x)^2}\frac{\partial}{\partial y}\left(\frac{y}{x}\right) = \frac{1}{1+(y/x)^2}\left(\frac{1}{x}\right)$$

$$= \left(\frac{1}{x}\right)\left(\frac{x^2}{x^2+y^2}\right) = \frac{r\cos\theta}{r^2} = \frac{\cos\theta}{r} \tag{15}$$

Then we can assemble the operator:

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= -i\hbar\left[r\cos\theta\left(\sin\theta\frac{\partial}{\partial r} + \frac{\cos\theta}{r}\frac{\partial}{\partial\theta}\right) - r\sin\theta\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\right]$$

$$-i\hbar\left[\cos^2\theta\frac{\partial}{\partial\theta}+\sin^2\theta\frac{\partial}{\partial\theta}\right]=-i\hbar\frac{\partial}{\partial\theta} \tag{16}$$

c) For the doubly degenerate excited states of the particle-on-a-ring model, we can write the stationary states in real form (as we did in class) as $\psi_{\text{sin}} = A\sin(n\theta)$ and $\psi_{\text{cos}} = A\cos(n\theta)$ or in complex form as $\psi_+ = Ae^{in\theta}$ and $\psi_- = Ae^{-in\theta}$.

Using ψ_+ determine the value of the normalization constant A. (It is the same value for all 4 wavefunctions.)

Solution:

$$1=\int_0^{2\pi}\psi_+^*\psi_+ d\theta=\int_0^{2\pi}Ae^{-in\theta}Ae^{in\theta}d\theta=A^2\int_0^{2\pi}d\theta=2\pi A^2 \tag{17}$$

Thus $A = 1/\sqrt{2\pi}$

d) If we think of the ring as lying in the x-y plane, our transformations from part (b) can be used. Using the transformed $\hat{L}_z$ operator, find the expectation value of the angular momentum for each of the 4 wavefunctions ψ_{sin}, ψ_{cos}, ψ_+, and ψ_-

Solution:

For ψ_{sin},

$$\begin{aligned}\langle L\rangle=\int_0^{2\pi}\psi_{\text{sin}}^*\hat{L}\psi_{\text{sin}}d\theta&=-\frac{i\hbar}{2\pi}\int_0^{2\pi}\sin(n\theta)\frac{\partial}{\partial\theta}\sin(n\theta)d\theta\\&=-\frac{i\hbar n}{2\pi}\int_0^{2\pi}\sin(n\theta)\cos(n\theta)d\theta=0\end{aligned} \tag{18}$$

For ψ_{cos},

$$\begin{aligned}\langle L\rangle=\int_0^{2\pi}\psi_{\text{cos}}^*\hat{L}\psi_{\text{cos}}d\theta&=-\frac{i\hbar}{2\pi}\int_0^{2\pi}\cos(n\theta)\frac{\partial}{\partial\theta}\cos(n\theta)d\theta\\&=\frac{i\hbar n}{2\pi}\int_0^{2\pi}\cos(n\theta)\sin(n\theta)d\theta=0\end{aligned} \tag{19}$$

For ψ_+,

$$\begin{aligned}\langle L\rangle=\int_0^{2\pi}\psi_+^*\hat{L}\psi_+d\theta&=-\frac{i\hbar}{2\pi}\int_0^{2\pi}e^{-in\theta}\frac{\partial}{\partial\theta}e^{in\theta}d\theta\\=-\frac{i^2\hbar n}{2\pi}\int_0^{2\pi}e^{-in\theta}e^{in\theta}d\theta&=\frac{\hbar n}{2\pi}\int_0^{2\pi}d\theta=\hbar n\end{aligned} \tag{20}$$

For ψ_-,

$$\begin{aligned}\langle L\rangle &= \int_0^{2\pi} \psi_-^* \hat{L}\psi_- d\theta = -\frac{i\hbar}{2\pi}\int_0^{2\pi} e^{in\theta}\frac{\partial}{\partial\theta}e^{-in\theta}d\theta \\ &= \frac{i^2\hbar n}{2\pi}\int_0^{2\pi} e^{in\theta}e^{-in\theta}d\theta = -\frac{\hbar n}{2\pi}\int_0^{2\pi} d\theta = -\hbar n\end{aligned} \tag{21}$$

e) Find the standard deviation of the angular momentum for each of the 4 wavefunctions.

Solution:

For ψ_{sin},

$$\langle L^2\rangle = \int_0^{2\pi} \psi_{\text{sin}}^* \hat{L}^2\psi_{\text{sin}} d\theta = -\hbar^2\int_0^{2\pi} \sin(n\theta)\frac{\partial^2}{\partial\theta^2}\sin(n\theta)d\theta \tag{22}$$

Now, since $\psi_{\text{sin}} = A\sin(n\theta)$, $\frac{\partial^2}{\partial\theta^2}\psi_{\text{sin}} = -n^2 A\sin(n\theta) = -n^2\psi_{\text{sin}}$. Thus

$$\langle L^2\rangle = (-\hbar^2)(-n^2)\int_0^{2\pi} \psi_{\text{sin}}^*\psi_{\text{sin}} d\theta = \hbar^2 n^2 \tag{23}$$

since ψ_{sin} is a normalized wavefunction. Thus $\sigma = \sqrt{\hbar^2 n^2 - 0} = \hbar n$.

For ψ_{cos}, the derivation is similar to ψ_{sin} and we get $\sigma = \hbar n$.

For ψ_+,

$$\langle L^2\rangle = \int_0^{2\pi} \psi_+^* \hat{L}^2\psi_+ d\theta = \int_0^{2\pi} \psi_+^* \hat{L}(\hat{L}\psi_+)d\theta \tag{24}$$

Now, $\hat{L}\psi_+ = -i\hbar(in)Ae^{in\theta} = \hbar n\psi_+$. So

$$\langle L^2\rangle = \hbar n\int_0^{2\pi} \psi_+^* \hat{L}\psi_+ d\theta = \hbar^2 n^2\int_0^{2\pi} \psi_+^*\psi_+ d\theta = \hbar^2 n^2 \tag{25}$$

Thus $\sigma = \sqrt{\hbar^2 n^2 - (\hbar n)^2} = 0$.

For ψ_-, the derivation is similar to ψ_+ and we get $\sigma = 0$.

f) Which of the 4 wavefunctions are eigenfunctions of the $\hat{L}_z$ operator? For those that are, give the corresponding eigenvalue. In light of this result, comment on your answers from parts (d) and (e).

Solution: clearly ψ_{cos} and ψ_{sin} are not eigenfunctions of the $\hat{L}$ operator. Also, in the solution to part (e) we actually showed that $\hat{L}\psi_+ = -i\hbar(in)Ae^{in\theta} = \hbar n\psi_+$ so this is an eigenfunction with eigenvalue $\hbar n$. Likewise, $\hat{L}\psi_-$ is an eigenfunction with eigenvalue $-\hbar n$. We can now understand why the standard deviation was zero in part (e) for $\hat{L}\psi_+$ and $\hat{L}\psi_-$.

It is because they are eigenfunctions of $\hat{L}$ and so they have a definite value for their angular momentum.

g) Explain the results (give a physical interpretation) of parts (d), (e), and (f). Remember that the real forms (ψ_{sin}, ψ_{cos}) and the complex forms (ψ_+, ψ_-) are linear combinations of each other through the Euler relation $e^{i\xi} = \cos\xi + i\sin\xi$.

Solution:

From Euler's relation, $\psi_+ = \psi_{\text{cos}} + i\psi_{\text{sin}}$ and $\psi_- = \psi_{\text{cos}} - i\psi_{\text{sin}}$. Also, $\psi_{\text{cos}} = \frac{1}{2}(\psi_+ + \psi_-)$ and $\psi_{\text{sin}} = \frac{i}{2}(\psi_- - \psi_+)$.

Now, ψ_+ is an eigenvector of $\hat{L}$ with eigenvalue $\hbar n$. Here the particle is rotating in the forwards direction around the ring. Also, ψ_- is an eigenvector of $\hat{L}$ with eigenvalue $-\hbar n$. Here the particle is rotating in the backwards direction around the ring.

If we add these together, $\frac{1}{2}(\psi_+ + \psi_-) = \psi_{\text{cos}}$, we have a particle behavior that includes equal forwards and backwards motions, so on average we have zero angular momentum.

ψ_{sin} is also an equal weight linear combination of ψ_+ and ψ_- so on average we would expect zero angular momentum.

Problem 2 – expectation values

For a particle in a 1d box, use the normalized wavefunctions derived in class to compute

$$a)\ \langle x\rangle \qquad b)\ \langle x^2\rangle \qquad c)\ \langle p_x\rangle \qquad d)\ \langle p_x^2\rangle \tag{26}$$

for the ground state. Interpret the results of parts a) and c) physically.

Solution:

$$\langle x\rangle = \frac{2}{L}\int_0^L x\sin^2(\frac{\pi x}{L}) \tag{27}$$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin(2\pi x/L)}{4\pi/L} - \frac{\cos(2\pi x/L)}{8\pi^2/L^2}\right]_0^L \tag{28}$$

$$= \frac{2}{L}\left[\frac{L^2}{4} - \frac{L^2}{8\pi^2} + \frac{L^2}{8\pi^2}\right] = \frac{L}{2} \tag{29}$$

Physically, this makes sense, because the potential energy is symmetric about the middle of the box, so we would not expect to find the particle, on average, in the right hand half of the box: we would expect to find it in the middle, which is another way of saying that we would expect to find the particle as often in the left hand side of the box as in the right hand side of the box.

$$
\begin{aligned}
\langle x^2 \rangle &= \frac{2}{L}\int_0^L x^2 \sin^2(\pi x/L) && (30)\\
&= \frac{2}{L}\left[\frac{x^3}{6} - \left(\frac{x^2}{4\pi/L} - \frac{1}{8\pi^3/L^3}\right)\sin(2\pi x/L) - \frac{x\cos(2\pi x/L)}{4\pi^2/L^2}\right]_0^L && (31)\\
&= \frac{2}{L}\left[\frac{L^3}{6} - \frac{L^3}{4\pi^2}\right] && (32)\\
&= L^2\left(\frac{1}{3} - \frac{1}{2\pi^2}\right) = 0.2827L^2 && (33)
\end{aligned}
$$

$$
\begin{aligned}
\langle p_x \rangle &= \frac{2}{L}(-i\hbar)\frac{\pi}{L}\int_0^L \sin(\pi x/L)\cos(\pi x/L) && (34)\\
&= -i\hbar\frac{2\pi}{L^2}\left[\frac{L}{2\pi}\sin^2(\pi x/L)\right]_0^L = 0 && (35)
\end{aligned}
$$

Physically, this again makes sense because of the symmetry in the potential. On average, we expect to find the particle traveling to the right as often as to the left, making the average velocity zero. Don't forget that velocity is a vector quantity, which in one dimension means that it carries sign information with it.

$$
\begin{aligned}
\langle p_x^2 \rangle &= \frac{2}{L}(-\hbar^2)\int_0^L \sin(\pi x/L)\frac{d^2}{dx^2}\sin(\pi x/L) && (36)\\
&= \frac{2}{L}\hbar^2\frac{\pi^2}{L^2}\int_0^L \sin^2(\pi x/L) && (37)\\
&= \frac{2\pi^2\hbar^2}{L^3}\left[\frac{x}{2} - \frac{1}{4\pi/L}\sin(2\pi x/L)\right]_0^L = \frac{\pi^2\hbar^2}{L^2} && (38)
\end{aligned}
$$

Problem 3 – uncertainty

a) Using the results of Problem 2), determine the standard deviations Δx and Δp_x.

Solution:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = 0.181L \qquad (39)$$

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} = \frac{\pi\hbar}{L} \qquad (40)$$

b) Find the value of the product $\Delta x \, \Delta p_x$. This kind of product of standard deviations is called an uncertainty product. It can be proved that, for any normalized ψ,

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2} \tag{41}$$

known as the Heisenberg Uncertainty Principle. Your result should, of course, be consistent with this inequality. Verify this.

Solution:

$$\Delta x \Delta p_x = 0.569\hbar \tag{42}$$

which is greater than $\hbar/2$.

Problem 4 – particle in a box energies

For the particle in a one dimensional box with quantum number n, work out a) the expected value of the potential energy, b) the expected value of the kinetic energy, and c) compare the sum of these two expected values to the energy value E_n which we calculated in class.

Solution:

a) $< V >= 0$

b)

$$< K >= -\frac{\hbar^2}{2m} \int_0^L \psi_n \frac{d^2}{dx^2} \psi_n \tag{43}$$

$$= -\frac{\hbar^2}{2m} \int_0^L \psi_n^2 \left(-\frac{n\pi}{L} \right)^2 \tag{44}$$

$$= \left(\frac{n\pi}{L} \right)^2 \frac{\hbar^2}{2m} \tag{45}$$

since the probability density integrates to one over the box.

c)

$$< V > + < K >= \frac{n^2 \pi^2 \hbar^2}{2mL^2} = E_n \tag{46}$$

Problem 5 – **harmonic oscillator energies**

Recall the harmonic oscillator model has potential energy $V(x) = m\omega^2 x^2/2$. For the ground state,

$$\psi_0(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2} \tag{47}$$

where $\alpha = m\omega/2\hbar$. First, prove (by integrating) that $\psi_0(x)$ is normalized. Next, work out a) the expected value of the potential energy, b) the expected value of the kinetic energy, and c) compare the sum of these two expected values to the energy E_0 which we calculated in class. For the integrals in this question you will need to use integral tables or online resources to help you, for example https://www.wolframalpha.com/

Solution:

First we need to show that $\psi_0(x)$ is normalized.

$$\left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-2\alpha x^2} \tag{48}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} = 1 \tag{49}$$

a)

$$< V > = < m\omega^2 x^2/2 > = \frac{1}{2} m\omega^2 \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx \tag{50}$$

$$= \frac{1}{2} m\omega^2 \frac{2^{1/2}\alpha^{1/2}}{\pi^{1/2}} \frac{\pi^{1/2}}{2(2\alpha)^{3/2}} = \frac{1}{4}\hbar\omega \tag{51}$$

b)

$$< K > = < p^2/2m > = \frac{1}{2m} \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} (-i\hbar \frac{d}{dx})^2 e^{-\alpha x^2} dx \tag{52}$$

$$= -\frac{\hbar^2}{2m} \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} (4\alpha^2 x^2 - 2\alpha) e^{-2\alpha x^2} dx \tag{53}$$

$$= -\frac{\hbar^2}{2m} \left(\frac{2\alpha}{\pi}\right)^{1/2} \left[4\alpha^2 \frac{\pi^{1/2}}{2(2\alpha)^{3/2}} - 2\alpha \frac{\pi^{1/2}}{(2\alpha)^{1/2}}\right] = \frac{1}{4}\hbar\omega \tag{54}$$

c)

$$< V > + < K > = \frac{1}{4}\hbar\omega + \frac{1}{4}\hbar\omega = \frac{1}{2}\hbar\omega = E_0 \tag{55}$$