# Homework 8

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1. First and foremost, we have the wave function as:

$$\psi_{321}(r,\theta,\phi) = -\frac{\sqrt{3}}{27\sqrt{\pi}}\sqrt[3]{\frac{Z}{3a_o}}\left(\frac{Zr}{a_o}\right)^2 e^{-Zr/3a_o}\sin(\theta)\cos(\theta)e^{i\phi}$$

We can apply the differential form $L_z$ to get:

$$L_z\psi_{321}(r,\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}\left[\frac{\sqrt{3}}{27\sqrt{\pi}}\sqrt[3]{\frac{Z}{3a_o}}\left(\frac{Zr}{a_o}\right)^2 e^{-Zr/3a_o}\sin(\theta)\cos(\theta)e^{i\phi}\right]$$

$$L_z\psi_{321}(r,\theta,\phi) = -i\hbar\frac{\sqrt{3}}{27\sqrt{\pi}}\sqrt[3]{\frac{Z}{3a_o}}\left(\frac{Zr}{a_o}\right)^2 e^{-Zr/3a_o}\sin(\theta)\cos(\theta)\frac{\partial}{\partial\phi}\left[e^{i\phi}\right]$$

$$L_z\psi_{321}(r,\theta,\phi) = \hbar\frac{\sqrt{3}}{27\sqrt{\pi}}\sqrt[3]{\frac{Z}{3a_o}}\left(\frac{Zr}{a_o}\right)^2 e^{-Zr/3a_o}\sin(\theta)\cos(\theta)e^{i\phi}$$

We may observe that this gives us $L_z\psi_{321} = \hbar\psi_{321}$, and, therefore, $\psi_{321}$ is an eigenstate of $L_z$ with eigenvalue $\hbar$ (as expected with $m = 1$). We now proceed to check $\vec{L}^2$:

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right]\psi_{321}(r,\theta,\phi)$$

We pull out $r$-dependent terms as constants (let us express these as $\mathbf{R}$), which gives us:

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = -\hbar^2 R\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\cos(\theta)\right]e^{i\phi} + \cot(\theta)\frac{\partial^2}{\partial\phi^2}e^{i\phi}\right]$$

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = -\hbar^2 Re^{i\phi}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\cos^2(\theta) - \sin^3(\theta)\right] - \cot(\theta)\right]$$

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = -\hbar^2 Re^{i\phi}\left[\frac{1}{\sin(\theta)}\left[\cos^3(\theta) - 5\cos(\theta)\sin^2(\theta)\right] - \cot(\theta)\right]$$

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = -\hbar^2 Re^{i\phi}\left[\cos^2(\theta)\cot(\theta) - 5\cos(\theta)\sin(\theta) - \cot(\theta)\right]$$

Using trigonometric identities, we may simplify to:

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = -\hbar^2 Re^{i\phi}\left[-6\cos(\theta)\sin(\theta)\right]$$

And finally:

$$\vec{L}^2\psi_{321}(r,\theta,\phi) = 6\hbar^2 Re^{i\phi}\left[\cos(\theta)\sin(\theta)\right]$$

We may see that this indicates that $\psi_{321}$ is, indeed, an eigenfunction of $\vec{L}^2$, with eigenvalue $6\hbar^2$ (which would be expected for $l = 2$, since $[2(2+1)]$ gives us 6). Finally, we check the Hamiltonian, which can be expressed as:

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin(\theta)}\frac{\partial^2}{\partial\phi^2}\right)\right] + V(r)$$

Before we evaluate, we can simplify this to:

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{r^2\hbar^2}\right] - \frac{Ze^2}{4\pi\varepsilon_o r}$$

We take $\mu \to m_e$ to give us:

$$H\psi_{321} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{r^2\hbar^2} - \frac{2mZe^2}{4\pi\varepsilon_o r\hbar^2}\right]\psi_{321}$$

From here, we proceed to evaluate (note, we simplify the $\theta$ and $\phi$ dependent terms as $\Theta$ and $\Phi$):

$$H\psi_{321} = -\frac{\hbar^2}{2m}\left[\sqrt{\frac{1}{3\pi}}\left(\frac{Z}{3a_o}\right)^{7/2}\right]\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(2r^3 - \frac{Zr^4}{3a_o}\right) - \left(\frac{6}{r^2} - \frac{mZe^2}{2\pi\varepsilon_o r\hbar^2}\right)r^2\right]e^{-Zr/3a_o}\Theta\Phi$$

$$H\psi_{321} = -\frac{\hbar^2}{2m}\left[\sqrt{\frac{1}{3\pi}}\left(\frac{Z}{3a_o}\right)^{7/2}\right]\left[\left(6 - \frac{2Zr}{a_o} + \frac{Z^2r^2}{9a_o^2}\right) - 6 + \frac{mZe^2r}{2\pi\varepsilon_o\hbar^2}\right]e^{-Zr/3a_o}\Theta\Phi$$

$$H\psi_{321} = -\frac{\hbar^2}{2m}\left[\sqrt{\frac{1}{3\pi}}\left(\frac{Z}{3a_o}\right)^{7/2}\right]\left[\frac{Z^2r^2}{9a_o^2}\right]e^{-Zr/3a_o}\Theta\Phi$$

$$H\psi_{321} = -\frac{1}{9}\frac{\hbar^2 Z^2}{2ma_o^2}\psi_{321}$$

$$\boxed{H\psi_{321} = -\frac{Z^2}{9}\text{Ryd}\psi_{321}}$$

Thus, we see that the energy eigenvalue is $-Z^2\text{Ryd}/9$, as would make sense for $n = 3$.

2. (a) First and foremost, we see that, for this superposition state, the possible energies are given by the $n$ values, or $n = 2, 3, 4$:

$$\boxed{E_2 = -\frac{13.6}{4} = -3.4[\text{eV}]}$$

$$\boxed{E_3 = -\frac{13.6}{9} = -1.511[\text{eV}]}$$

$$\boxed{E_4 = -\frac{13.6}{16} = -.85[\text{eV}]}$$

The probabilities will be given by the squares of the magnitudes of the coefficients such that:

$$\boxed{P_{E_2} = \left(\frac{1}{\sqrt{14}}\right)^2 = \frac{1}{14}}$$

$$\boxed{P_{E_3} = \left(\frac{-2}{\sqrt{14}}\right)^2 = \frac{2}{7}}$$

$$\boxed{P_{E_4} = \left(\left|\frac{3i}{\sqrt{14}}\right|\right)^2 = \frac{9}{14}}$$

Thus, we obtain the following histogram:

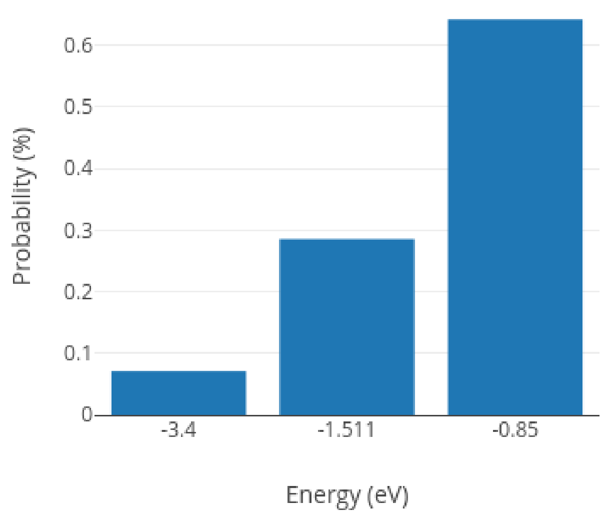


Figure 1: Histogram of Energy Probabilities

We proceed to calculate the expectation value of energy as:

$$\langle E \rangle = \langle \psi | H | \psi \rangle$$

$$\langle \psi | H | \psi \rangle = -13.6 \sum_{n=1}^{\infty} \frac{P_{E_n}}{n^2}$$

$$-13.6 \sum_{n=1}^{\infty} \frac{P_{E_n}}{n^2} = -13.6 \left( \frac{1/14}{4} + \frac{4/14}{9} + \frac{9/14}{16} \right)$$

$$\boxed{\langle E \rangle = -1.221[\text{eV}]}$$

(b) We know that $\vec{L}^2$ is limited to $l(l+1)\hbar^2$, and that $l$ is limited by the superimposed states. Accordingly, we may find that the possible measurements are $\boxed{\vec{L}^2 = 2\hbar^2, 6\hbar^2}$. The probabilities can then be calculated as:

$$\boxed{P_{l=1} = \left( \frac{1}{\sqrt{14}} \right)^2 = \frac{1}{14}}$$

$$\boxed{P_{l=2} = \left( \frac{-2}{\sqrt{14}} \right)^2 + \left| \frac{3i}{\sqrt{14}} \right|^2 = \frac{13}{14}}$$

Accordingly, we may plot the histogram as:

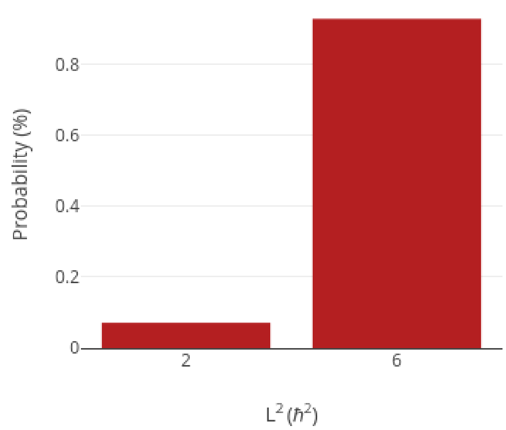


Figure 2: Histogram of Spin Vector Probabilities

We calculate the expectation value in a manner similar to part (a) to get:

$$\langle \vec{L}^2 \rangle = \hbar^2 \left( \frac{2}{14} + \frac{6(13)}{14} \right)$$

$$\boxed{\langle \vec{L}^2 \rangle = 5.7143\hbar^2}$$

(c) By the eigenvalues, we know that $L_z$ can be $m\hbar$. As such, we see that $m = 1, -1, 2$, which gives us measurements of $\pm\hbar, 2\hbar$. We can then find the probabilities as:

$$\boxed{P_{-\hbar} = \left(\frac{-2}{\sqrt{14}}\right)^2 = \frac{2}{7}}$$

$$\boxed{P_{\hbar} = \left(\frac{1}{\sqrt{14}}\right)^2 = \frac{1}{14}}$$

$$\boxed{P_{-\hbar} = \left(\left|\frac{3i}{\sqrt{14}}\right|\right)^2 = \frac{9}{14}}$$

We can then plot the histogram as:

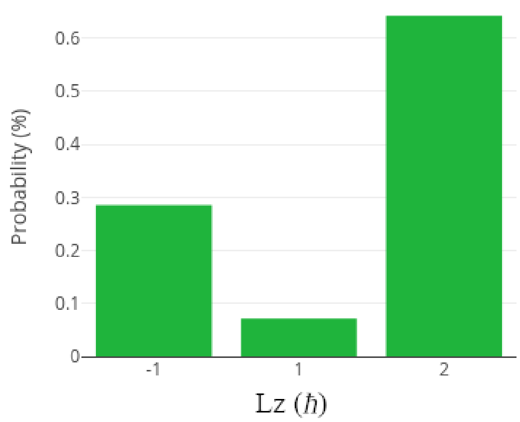


Figure 3: Histogram of $L_z$ Probabilities

Finally, we calculate the expectation value as:

$$\langle L_z \rangle = \frac{-4\hbar}{14} + \frac{\hbar}{14} + \frac{18\hbar}{14}$$

$$\boxed{\langle L_z \rangle = \frac{15\hbar}{14}}$$

(d) We may observe that the answers to (a), (b), and (c) are not dependent on time (*i.e.* they are stationary quantities) since the operators commute with the Hamiltonian