

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:

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

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

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

We may observe that this gives us $L_z \psi_{321} = \hbar \psi_{321}$, and, therefore, ψ_{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:

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

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

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

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

Using trigonometric identities, we may simplify to:

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

And finally:

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

We may see that this indicates that ψ_{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:

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

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

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

From here, we proceed to evaluate (note, we simplify the θ and ϕ dependent terms as Θ and Φ):

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

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

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

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

$$H\psi_{321} = -\frac{Z^2}{9}R_{nl}\psi_{321}$$

Thus, we see that the energy eigenvalue is $-Z^2R_{nl}/9$, 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 $n = 2, 3, 4$:

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

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

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

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

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

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

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

Thus, we obtain the following histogram:

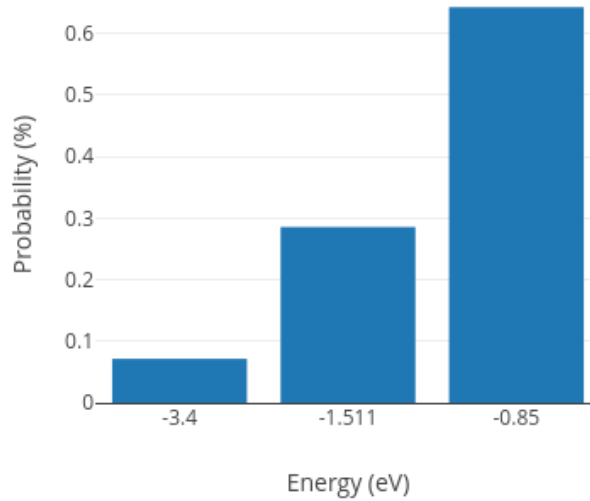


Figure 1: Histogram of Energy Probabilities

We proceed to calculate the expectation value of energy as:

$$\begin{aligned}\langle E \rangle &= \langle \psi | H | \psi \rangle \\ \langle \psi | H | \psi \rangle &= -13.6 \sum_{n=1}^{\infty} \frac{P_{E_n}}{n^2} \\ -13.6 \sum_{n=1}^{\infty} \frac{P_{E_n}}{n^2} &= -13.6 \left(\frac{1/14}{4} + \frac{4/14}{9} + \frac{9/14}{16} \right) \\ \langle E \rangle &= -1.221[\text{eV}]\end{aligned}$$

- (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 $l = 2\hbar^2, 6\hbar^2$. The probabilities can then be calculated as:

$$\begin{aligned}P_{l=1} &= \left(\frac{1}{\sqrt{14}} \right)^2 = \frac{1}{14} \\ P_{l=2} &= \left(\frac{-2}{\sqrt{14}} \right)^2 + \left| \frac{3i}{\sqrt{14}} \right|^2 = \frac{13}{14}\end{aligned}$$

Accordingly, we may plot the histogram as:

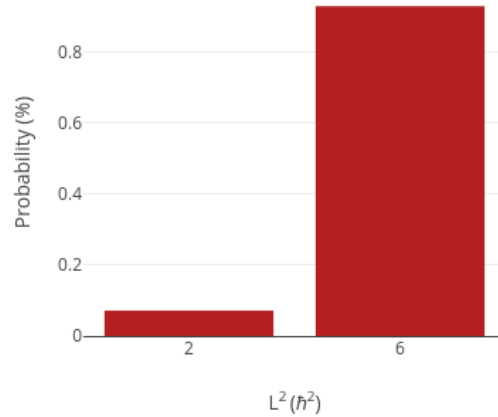


Figure 2: Histogram of Spin Vector Probabilities

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

$$\begin{aligned}\langle \vec{L}^2 \rangle &= \hbar^2 \left(\frac{2}{14} + \frac{6(13)}{14} \right) \\ \langle \vec{L}^2 \rangle &= 5.7143\hbar^2\end{aligned}$$

- (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:

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

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

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

We can then plot the histogram as:

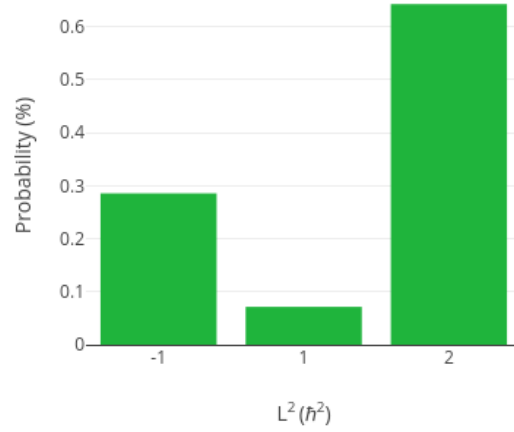


Figure 3: Histogram of L_z Probabilities

Finally, we calculate the expectation value as:

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

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

- (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