1 Problem 8.1

A particle with mass $m$ moves in a 3D box with edges $L_1 = L$, $L_2 = 2L$, and $L_3 = 2L$. Find the energies of the six lowest states. Which ones are degenerate?

1.1 Solution

We get the wavenumbers the usual way, using the boundary conditions.

$$k_1 = \frac{n_1 \pi}{L} = \sqrt{\frac{2mE_1}{\hbar^2}}$$

$$k_2 = \frac{n_2 \pi}{2L} = \sqrt{\frac{2mE_2}{\hbar^2}}$$

$$k_3 = \frac{n_3 \pi}{2L} = \sqrt{\frac{2mE_3}{\hbar^2}}$$

Solving for the energies gives

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2$$

$$E_2 = \frac{\hbar^2 \pi^2}{2mL^2} \frac{n_2^2}{4}$$

$$E_3 = \frac{\hbar^2 \pi^2}{2mL^2} \frac{n_3^2}{4}$$

Or

$$E = E_1 + E_2 + E_3 = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_1^2 + \frac{n_2^2}{4} + \frac{n_3^2}{4}\right)$$

The ground state is when $n_1 = n_2 = n_3 = 1$ leading to

$$E = \frac{\hbar^2 \pi^2}{2mL^2} \left(1^2 + \frac{1}{4} + \frac{1}{4}\right) = \frac{3\hbar^2 \pi^2}{4mL^2}$$

There is a twofold degeneracy in the first excited state: $n_1 = n_2 = 1; n_3 = 2$

or $n_1 = n_3 = 1; n_2 = 2$

$$E = \frac{\hbar^2 \pi^2}{2mL^2} \left(1^2 + \frac{2^2}{4} + \frac{1^2}{4}\right) = \frac{\hbar^2 \pi^2}{2mL^2} \left(1^2 + \frac{1}{4} + \frac{2^2}{4}\right) = \frac{9\hbar^2 \pi^2}{8mL^2}$$

The second excited state is unique and will be $n_1 = 1; n_2 = n_3 = 2$.

$$E = \frac{\hbar^2 \pi^2}{2mL^2} \left(1^2 + \frac{2^2}{4} + \frac{2^2}{4}\right) = \frac{3\hbar^2 \pi^2}{mL^2}$$
Again, there is a twofold degeneracy in the third excited state \( n_1 = 1; n_2 = 2; n_3 = 3 \) or \( n_1 = 1; n_2 = 3; n_3 = 2 \)

\[
E = \frac{\hbar^2 \pi^2}{2mL^2} \left( 1^2 + \frac{2^2}{4} + \frac{3^2}{4} \right) = \frac{\hbar^2 \pi^2}{2mL^2} \left( 1^2 + \frac{3^2}{4} + \frac{2^2}{4} \right) = \frac{17\hbar^2 \pi^2}{8mL^2}
\]

These are the lowest six states. 1 ground + 2 first excited + 1 second excited + 2 third excited = 6.

2 Problem 8.3

A particle of mass \( m \) is in a 3D cube with sides \( L \). It is in the third excited state, corresponding to \( n^2 = 11 \).

(a) Calculate the energy of the particle.
(b) The possible combinations of \( n_1, n_2, \) and \( n_3 \)
(c) The wavefunctions for these states.

2.1 Solution

2.1.1 Part (a)

Just plug in \( n^2 = 11 \) to the 3D box’s energy.

\[
E = \frac{11\hbar^2 \pi^2}{2mL^2}
\]

2.1.2 Part (b) and Part (c)

We’ll need

\[
n^2 = n_1^2 + n_2^2 + n_3^2
\]

There are three ways to do this

\[
11 = (3^2 + 1^2 + 1^2) = (1^2 + 3^2 + 1^2) = (1^2 + 1^2 + 3^2)
\]

Corresponding to the three states and their wavefunctions

\[
n_1 = 3; n_2 = 1; n_3 = 1 \quad \rightarrow \quad \psi(x, y, z) = \left( \frac{2}{L} \right)^{3/2} \sin \left( \frac{3\pi x}{L} \right) \sin \left( \frac{\pi y}{L} \right) \sin \left( \frac{\pi z}{L} \right)
\]

\[
n_1 = 1; n_2 = 3; n_3 = 1 \quad \rightarrow \quad \psi(x, y, z) = \left( \frac{2}{L} \right)^{3/2} \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{3\pi y}{L} \right) \sin \left( \frac{\pi z}{L} \right)
\]

\[
n_1 = 1; n_2 = 1; n_3 = 3 \quad \rightarrow \quad \psi(x, y, z) = \left( \frac{2}{L} \right)^{3/2} \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{\pi y}{L} \right) \sin \left( \frac{3\pi z}{L} \right)
\]
3 Problem 8.4

A particle of mass $m$ is stuck in a 2D box of length $L$.

(a) What are the wavefunctions?
(b) What are the energies of the ground state and the first excited state?

3.1 Solution

3.2 Part (a)

We start with a general wavefunction see if separation of variables works.

$$\psi(x, y) = \psi_1(x) \psi_2(y)$$

Plugging this into the Schrodinger Equation and mixing around a few terms around we get

$$-\frac{\hbar^2}{2m} \left( \frac{1}{\psi_1(x)} \frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{1}{\psi_2(y)} \frac{\partial^2 \psi_2(y)}{\partial y^2} \right) = E$$

This separates into two equations

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_1(x)}{\partial x^2} = E_1 \psi_1(x)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_2(y)}{\partial y^2} = E_2 \psi_2(y)$$

This will have solutions and energies of

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n_1 \pi x}{L} \right) \quad E_1 = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2$$

$$\psi_2(y) = \sqrt{\frac{2}{L}} \sin \left( \frac{n_2 \pi y}{L} \right) \quad E_2 = \frac{\hbar^2 \pi^2}{2mL^2} n_2^2$$

3.3 Part (b)

We can see that the total energy will be

$$E = E_1 + E_2 = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2)$$

The ground state will be at $n_1 = n_2 = 1$ and will have energy

$$E = \frac{\hbar^2 \pi^2}{mL^2}$$

There will be a degeneracy in the first excited state between $n_1 = 2; n_2 = 1$ and $n_1 = 1; n_2 = 2$ which will have energy
\[ E = \frac{\hbar^2 \pi^2}{2mL^2} (2^2 + 1^2) = \frac{\hbar^2 \pi^2}{2mL^2} (1^2 + 2^2) = \frac{5\hbar^2 \pi^2}{2mL^2} \]

4 Problem 8.7

(a) Normalize the wavefunction for a particle in a cube of length L.
(b) What if it is a rectangular prism with sides \( L_1 \neq L_2 \neq L_3 \)

4.1 Solution

4.1.1 Part (a)

We know that the wavefunction will be

\[ \psi(x, y, z) = A \sin \left( \frac{n_1 \pi x}{L} \right) \sin \left( \frac{n_2 \pi y}{L} \right) \sin \left( \frac{n_3 \pi z}{L} \right) \]

We apply the normalization rule

\[ 1 = \int_{-\infty}^{+\infty} \psi^* (\vec{r}) \psi (\vec{r}) dV \]

\[ 1 = \frac{A^2}{L^3} \int_{x=0}^{L} \sin^2 \left( \frac{n_1 \pi x}{L} \right) dx \int_{y=0}^{L} \sin^2 \left( \frac{n_2 \pi y}{L} \right) dy \int_{z=0}^{L} \sin^2 \left( \frac{n_3 \pi z}{L} \right) dz \]

\[ 1 = A^2 \left( \frac{L}{2} \right)^3 \]

\[ A = \left( \frac{2}{L} \right)^{3/2} \]

4.2 Part (b)

The wavefunction (and its square) will be the same as before but with a minor tweak

\[ 1 = A^2 \int_{x=0}^{L_1} \int_{y=0}^{L_2} \int_{z=0}^{L_3} \sin^2 \left( \frac{n_1 \pi x}{L_1} \right) \sin^2 \left( \frac{n_2 \pi y}{L_2} \right) \sin^2 \left( \frac{n_3 \pi z}{L_3} \right) dx dy dz \]

\[ 1 = A^2 \int_{x=0}^{L_1} \sin^2 \left( \frac{n_1 \pi x}{L_1} \right) dx \int_{y=0}^{L_2} \sin^2 \left( \frac{n_2 \pi y}{L_2} \right) dy \int_{z=0}^{L_3} \sin^2 \left( \frac{n_3 \pi z}{L_3} \right) dz \]
\[ 1 = A^2 \left( \frac{L_1}{2} \right) \left( \frac{L_2}{2} \right) \left( \frac{L_3}{2} \right) \]
\[ A = \sqrt{\frac{8}{L_1 L_2 L_3}} \]

5 Problem 8.11

The orbital angular momentum of the Earth is \(4.83 \times 10^{31} \text{ kg} \cdot \text{m}^2/\text{s}\). Calculate \(l\) and the fractional change in \(\|\vec{L}\|\) when \(l \to l + 1\)

5.1 Solution

The quantization rule for \(\|\vec{L}\|\) is

\[ \|\vec{L}\| = \sqrt{l(l+1)} \hbar \]

It will be proven in the second part of this problem that \(l \approx l + 1\). Using this we get

\[ l = \frac{\|\vec{L}\|}{\hbar} \]

Since \(\hbar = 1.05 \times 10^{-34} \text{kg} \cdot \text{m}^2/\text{s}\) we see

\[ l = \frac{4.83 \times 10^{31} \text{ kg} \cdot \text{m}^2/\text{s}}{1.05 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}} \approx 4.6 \times 10^{65} \]

That is a HUGE quantum number! To get a sense of how big this is, look at the second part of the problem

\[ \frac{\|\vec{L}_{l+1}\| - \|\vec{L}_l\|}{\|\vec{L}_l\|} = \frac{\sqrt{(l+1)(l+2)} \hbar - \sqrt{l(l+1)} \hbar}{\sqrt{l(l+1)} \hbar} = \frac{\sqrt{l+2} - \sqrt{l}}{\sqrt{l}} \approx \frac{2}{10^{65}} \approx 10^{-65} \approx 0 \]

This is essentially zero! This is why quantum mechanics isn’t necessary for examining macroscopic objects and the natural world “feels” continuous. When you work with numbers that are so big, the quantization of nature isn’t noticeable.

6 Problem 8.18

A hydrogen atom is in the \(6g\) state.
(a) What is the principle quantum number?
(b) What is the energy of the atom?
(c) What are the possible values for \(l\) and \(\|\vec{L}\|\)?
(d) What are the possible values of \(m_l\)? (e) What are the possible values of \(L_z\) and for each of these what angle will \(\vec{L}\) make with the \(z\)-axis?
6.1 Solution

6.1.1 Part (a)

\( n = 6 \)

6.1.2 Part (b)

In general, the energy for a hydrogen-like atom in the \( n \)-th energy state is

\[
E_n = -\frac{k e^2 Z^2}{2a_0 n^2}
\]

In this case \( Z = 1 \) and \( n = 6 \) so

\[
E_6 = -\frac{k e^2}{72a_0}
\]

6.1.3 Part (c)

The rule for \( l \) is that it must be an integer between

\[ 0 \leq l < n \]

This makes the allowed values 0, 1, 2, 3, 4, and 5.

6.1.4 Part (d)

The rule for \( m_l \) is that it must be an integer between

\[ -l \leq m_l \leq l \]

This makes the allowed values 0, ±1, ±2, ±3, ±4, and ±5. The \( z \) component of the angular momentum is given by

\[
L_z = m_l \hbar
\]

So the allowed values will be 0, ±\( \hbar \), ±2\( \hbar \), ±3\( \hbar \), ±4\( \hbar \), and ±5\( \hbar \). The values of \( \| \mathbf{L} \| \) are given by

\[
\| \mathbf{L} \| = \sqrt{l(l+1)} \hbar
\]

In general we will have

\[
\theta_{lm} = \pm \sin^{-1} \left( \frac{\|L_z\|}{\|L\|} \right) = \pm \sin^{-1} \left( \frac{\|m_l\|}{\sqrt{l(l+1)}} \right)
\]

All possible values of \( \theta_{lm} \) are listed below

\[
\theta_{00} = 90^\circ
\]
\[ \theta_{10} = 90^\circ \quad \theta_{1 \pm 1} = \pm \sin^{-1} \left( \frac{1}{\sqrt{1 \cdot 2}} \right) = \pm 45^\circ \]

\[ \theta_{20} = 90^\circ \quad \theta_{2 \pm 1} = \pm \sin^{-1} \left( \frac{1}{\sqrt{2 \cdot 3}} \right) \approx \pm 24^\circ \quad \theta_{2 \pm 2} = \pm \sin^{-1} \left( \frac{2}{\sqrt{2 \cdot 3}} \right) \approx \pm 55^\circ \]

\[ \theta_{30} = 90^\circ \quad \theta_{3 \pm 1} = \pm \sin^{-1} \left( \frac{1}{\sqrt{3 \cdot 4}} \right) \approx \pm 17^\circ \]

\[ \theta_{3 \pm 2} = \pm \sin^{-1} \left( \frac{2}{\sqrt{3 \cdot 4}} \right) \approx \pm 35^\circ \quad \theta_{3 \pm 3} = \pm \sin^{-1} \left( \frac{3}{\sqrt{3 \cdot 4}} \right) = \pm 60^\circ \]

\[ \theta_{40} = 90^\circ \quad \theta_{4 \pm 1} = \pm \sin^{-1} \left( \frac{1}{\sqrt{4 \cdot 5}} \right) \approx \pm 13^\circ \quad \theta_{4 \pm 2} = \pm \sin^{-1} \left( \frac{2}{\sqrt{4 \cdot 5}} \right) \approx \pm 27^\circ \]

\[ \theta_{4 \pm 3} = \pm \sin^{-1} \left( \frac{3}{\sqrt{4 \cdot 5}} \right) = \pm 42^\circ \quad \theta_{4 \pm 4} = \pm \sin^{-1} \left( \frac{4}{\sqrt{4 \cdot 5}} \right) = \pm 63^\circ \]

\[ \theta_{50} = 90^\circ \quad \theta_{5 \pm 1} = \pm \sin^{-1} \left( \frac{1}{\sqrt{5 \cdot 6}} \right) \approx \pm 11^\circ \quad \theta_{5 \pm 2} = \pm \sin^{-1} \left( \frac{2}{\sqrt{5 \cdot 6}} \right) \approx \pm 21^\circ \]

\[ \theta_{5 \pm 3} = \pm \sin^{-1} \left( \frac{3}{\sqrt{5 \cdot 6}} \right) = \pm 33^\circ \quad \theta_{5 \pm 4} = \pm \sin^{-1} \left( \frac{4}{\sqrt{5 \cdot 6}} \right) = \pm 47^\circ \]

\[ \theta_{5 \pm 5} = \pm \sin^{-1} \left( \frac{5}{\sqrt{5 \cdot 6}} \right) = \pm 66^\circ \]

One cool thing to notice is that \( \theta_l \) increases as \( l \) increases. This agrees with our prediction that in the limit \( l \gg 1 \) we will be able to have \( L_z = ||\vec{L}|| \), which is usually what we deal with classically.

### 7 Problem 8.20

Using a semiclassical approximation, the energy of a circular orbit becomes

\[ E = \frac{\hat{L}^2}{2mr^2} - \frac{kZe^2}{r} \tag{1} \]

Use this to show that we must have \( l \leq n - 1 \)
7.1 Solution

The formula for energy is

$$E_n = -\frac{ke^2 Z^2}{2a_0 n^2}$$

The formula for angular momentum is

$$\|\vec{L}\| = \sqrt{l(l+1)}\hbar$$

According to Bohr, the allowed values of $r$ for an atom with $Z$ protons is

$$r = \frac{a_0 n^2}{Z}$$

Plugging these into Equation 1 we get:

$$-\frac{ke^2 Z^2}{2a_0 n^2} = \frac{l(l+1)\hbar^2 Z^2}{2m (a_0 n^2)^2} - kZ e^2 \frac{Z}{a_0 n^2}$$

Shuffling a few terms around will yield

$$\frac{-ke^2 n^2}{2} = \frac{l(l+1)\hbar^2}{2ma_0} - ke^2 n^2$$

Remember that

$$a_0 = \frac{\hbar^2}{mk e^2}$$

Using this will simplify our equation to

$$\frac{-n^2}{2} = \frac{l(l+1)}{2} - n^2$$

$$n^2 = l(l + 1)$$

Remember that we were dealing with the largest $l$ possible. With this in mind we can see that we must have

$$l \leq n - 1$$

8 Problem 8.22

Given the radial wavefunction

$$R_{2p}(r) = A e^{-r/2a_0}$$

Calculate $\langle r \rangle$ for an electron in this state.
8.1 Solution

First we need to normalize the wavefunction.

\[ 1 = \int_{-\infty}^{+\infty} \psi_{2p}^*(\vec{r}) \psi_{2p}(\vec{r}) dV \]

The question is only asking about the radial part of the wave equation. In reality, there will be an angular dependence as well, but we can still consider solely the radial portion since \( \hat{r} = r \) and the wavefunction is separable.

\[ 1 = \int_{r=0}^{r=\infty} R_{2p}^*(r) R_{2p}(r) [r^2 dr] \]

\[ 1 = \int_{-\infty}^{+\infty} R_{2p}^*(r) R_{2p}(r) r^2 dr \]

\[ 1 = \int_{0}^{\infty} A^2 r^4 e^{-r/a_0} dr \]

\[ 1 = A^2 (24a_0^5) \]

\[ A^2 = \frac{1}{24a_0^5} \]

Now we can calculate the expectation value for \( r \).

\[ \langle r \rangle = \int_{r=0}^{r=\infty} R_{2p}^*(r) \hat{r} R_{2p}(r) [r^2 dr] \]

\[ \langle r \rangle = \frac{1}{24a_0^5} \int_{0}^{\infty} r^5 e^{-r/a_0} dr \]

\[ \langle r \rangle = \frac{1}{24a_0^5} (120a_0^6) \]

\[ \langle r \rangle = 5a_0 \]