1. Use separation of variables in cartesian coordinates to solve the infinite cubical well. The potential of the infinite cubical well is

$$V(x, y, z) = \begin{cases} 0, & \text{if } x, y, z \text{ are all between 0 and } a, \\ \infty, & \text{otherwise.} \end{cases}$$

(a.) Find the stationary states and their corresponding energies. Apply boundary conditions at the boundaries of the well. Note that solutions should depend on three distinct quantum numbers.

We begin with the time-independent Schrödinger equation (TISE),

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi,$$

where by our choice of cartesian coordinates we define ∇ as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

We have two regions: (i.) outside the box, and (ii.) inside the box. Outside the box, $V(x, y, z) = \infty$, we have the wavefunction

$$\psi_i(x, y, z) = 0.$$

Inside the box, $V(x, y, z) = 0$, the TISE can be expressed as

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi.$$

We assume that ψ has separable solutions in all three dimensions; that is,

$$\psi(x, y, z) = X(x)Y(y)Z(z).$$

Substituting this expression for ψ, dividing both sides by XYZ, replacing our partial derivatives with ordinary derivatives, and rearranging the $\hbar$ term yields

$$-\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} - \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} - \frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = \frac{2m}{\hbar^2}E.$$

Each term on the left is a function of only one variable and is independent of each other. Therefore, each term on the left side must be constant. We use our typical k^2 constant and define one for each term: k_x^2, k_y^2, k_z^2. Looking into the x-term we say

$$-\frac{1}{X}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} = k_x^2$$

which is a simple differential equation solved with exponential functions or equivalently sine and cosine functions. Since we are dealing with a trapt particle, sine and cosine functions are a natural choice. Notice that each of these terms has the same structure and boundary conditions so we need only solve one. Continuing with the x-term we have a general solution,

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x).$$

Our boundary conditions are (1.) $X(0) = 0$, and (2.) $X(a) = 0$. Our first condition requires that $B_x = 0$. Our second condition then requires that

$$k_x = \frac{n_x \pi}{a},\ n_x \in \mathbb{N}.$$

Thus, our solution for the x-term can be written as

$$X(x) = A_x \sin\left(\frac{n_x \pi}{a} x\right),\ n_x \in \mathbb{N}.$$

The y and z terms have the same structure:

$$Y(y) = A_y \sin\left(\frac{n_y \pi}{a} y\right),\ n_y \in \mathbb{N};$$
$$Z(z) = A_z \sin\left(\frac{n_z \pi}{a} z\right),\ n_z \in \mathbb{N}.$$

Then our wavefunction inside the box, ψ_{ii}, can be written as

$$\psi_{ii}(x,y,z) = A_x A_y A_z \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right).$$

Since each wavefunction resembles a one-dimensional oscillator we can simply take the normalization constants from that system for each term:

$$A_x A_y A_z = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{a}}\sqrt{\frac{2}{a}} = \left(\frac{2}{a}\right)^{3/2}.$$

Thus,

$$\psi_{ii}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right).$$

Finally, we recognize that since each term was equal to some constant, so too was the right hand side of our equation. Expressed with some rearrangement and substitution we find

$$E = \frac{1}{2m}\left(\frac{\hbar \pi}{a}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right),\ n_x, n_y, n_z \in \mathbb{N}.$$

(b.) Call the distinct energies E_1, E_2, E_3, etc., in order of increasing energy. Note that the subscripted integer is not a quantum number here; instead, these number simply represent the lowest energy, E_1, second lowest energy, E_2, etc. Determine what E_1, E_2, E_3, E_4, E_5, and E_6 are in terms of $\hbar, m, \pi$, and a. Determine the degeneracy of each of these energies.

Since $\hbar, m, \pi$, and a are constant we see that the energy level is only changed by the three quantum numbers n_x, n_y, and n_z. Specifically, the energy is determined by the sum of the quantum numbers and the number of ways to sum the quantum numbers equivalently determines the degeneracy.

(c.) What is the degeneracy of E_{14}, and what is unusual about this case?

2. Construct the spherical harmonics $Y_0^0(\theta, \phi)$ and $Y_2^1(\theta, \phi)$ using the formula for spherical harmonics,

$$Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{(2\ell + 1)}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!}} \exp(im\phi) P_\ell^m(\cos(\theta)),$$

where the constant ϵ is defined to be

$$\epsilon = \begin{cases} (-1)^m, & m \geq 0, \\ 1, & m \leq 0, \end{cases}$$

the Rodrigues formula for the Legendre polynomial,

$$P_\ell^m(x) \equiv \left(1 - x^2\right)^{|m|/2} \frac{\mathrm{d}^{|m|}}{\mathrm{d}x^{|m|}} P_\ell(x).$$

Check that solutions for $Y_0^0(\theta, \phi)$ and $Y_2^1(\theta, \phi)$ are normalized and orthogonal.