

Homework 1

Professor: Dr. Jaimes

Francisco Javier Vázquez Tavares A00827546

Contents

1	Problem 4.2	1
2	Problem 4.3	3
3	Problem 4.13	5
4	Problem 4.14	5
5	Problem 4.23	6

1 Problem 4.2

Use separation of variable in *cartesian* coordinates to solve the infinite *cubical* well (or particle in a box):

$$V(x, y, z) = \begin{cases} 0, & \forall x, y, z \in [0, a] \\ \infty, & \forall x, y, z \notin [0, a] \end{cases}$$

1. Find the stationary states, and the corresponding energies.
2. Call the distinct energies E_1, E_2, \dots in order of increasing energy. Find E_1, E_2, E_3, E_4, E_5 and E_6 . Determine their degeneracies (that is, the number of different states that share the same energy).
3. What is the degeneracy of E_{14} , and why is this case interesting?

Solution 1: Stationary states

To find the stationary states of the infinite cubical well, we are going to solve the time independent Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi, \quad \forall x, y, z \in [0, a],$$

with the following boundary conditions $\psi(0, 0, 0) = \psi(a, a, a) = 0$. To solve the equation we are going to use the method of separation of variables, that is, that we assume that the solution of the differential equation has the following form $\psi(x, y, z) = X(x)Y(y)Z(z)$. Substituting this solution to the differential equation, we can perform

some algebraic manipulation,

$$\begin{aligned}
-\frac{\hbar^2}{2m}\nabla^2\psi &= E\psi \\
\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)X(x)Y(y)Z(z) &= -\frac{2m}{\hbar^2}EX(x)Y(y)Z(z) \\
Y(y)Z(z)\frac{\partial^2}{\partial x^2}X(x) + X(x)Z(z)\frac{\partial^2}{\partial y^2}Y(y) + X(x)Y(y)\frac{\partial^2}{\partial z^2}Z(z) &= -\frac{2m}{\hbar^2}EX(x)Y(y)Z(z) \\
\frac{1}{X(x)}\frac{\partial^2}{\partial x^2}X(x) + \frac{1}{Y(y)}\frac{\partial^2}{\partial y^2}Y(y) + \frac{1}{Z(z)}\frac{\partial^2}{\partial z^2}Z(z) &= -\frac{2m}{\hbar^2}E.
\end{aligned}$$

Now we can re-write this partial differential equation into three differential equations assuming that $E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$,

$$\begin{aligned}
\frac{d^2X(x)}{dx^2} &= -k_x^2X(x) \rightarrow X(x) = A_x \sin[k_x x] + B_x \cos[k_x x], \\
\frac{d^2Y(y)}{dy^2} &= -k_y^2Y(y) \rightarrow Y(y) = A_y \sin[k_y y] + B_y \cos[k_y y], \\
\frac{d^2Z(z)}{dz^2} &= -k_z^2Z(z) \rightarrow Z(z) = A_z \sin[k_z z] + B_z \cos[k_z z].
\end{aligned}$$

In order to find the expression for the coefficients A_n , B_n and k_n , we start by applying the boundary conditions. Since sin and cos are periodic functions, they satisfy $f(0) = f(a)$, however only the sin function satisfy the condition $f(0) = f(a) = 0$, hence, we set $B_x = B_y = B_z = 0$ leading to,

$$X(x) = A_x \sin[k_x x], \quad Y(y) = A_y \sin[k_y y], \quad Z(z) = A_z \sin[k_z z].$$

Now we recall the fact that x, y and z have units of distance and that the argument of the sin function must be dimensionless, combining this restriction with the property of periodicity we can define the constants k_n as, $k_x = n_x\pi/a$, $k_y = n_y\pi/a$, $k_z = n_z\pi/a$, where $(n_x, n_y, n_z) \in \mathbb{Z}^+$. With this information we can re-write the solution as,

$$\psi(x, y, z) = A_x A_y A_z \sin\left[\frac{n_x\pi}{a}x\right] \sin\left[\frac{n_y\pi}{a}y\right] \sin\left[\frac{n_z\pi}{a}z\right],$$

with

$$E = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2), \quad (n_x, n_y, n_z) \in \mathbb{Z}^+.$$

Finally, in order to get the expression for A_x, A_y and A_z we apply the normalization restriction to each spatial dimension,

$$\int_0^a A_l^2 \sin^2\left[\frac{n_l\pi}{a}s\right] ds = A_l^2 \frac{a}{4} \left(2 - \frac{1}{\pi n} \sin[2\pi n]\right) = 1,$$

since $n \in \mathbb{Z}^+$ we get that $A_l = \sqrt{2/a}$, therefore,

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left[\frac{n_x\pi}{a}x\right] \sin\left[\frac{n_y\pi}{a}y\right] \sin\left[\frac{n_z\pi}{a}z\right], \quad (n_x, n_y, n_z) \in \mathbb{Z}^+$$

Solution 2: Energy analysis**Solution 3: Energy 14****2 Problem 4.3**

Use

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x)$$

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2-1)^l$$

$$Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos[\theta])$$

to construct Y_0^0 and Y_2^1 . Check that they are normalized and orthogonal.

Solution 4: Spherical harmonic

We start with $Y_0^0(\theta, \phi)$, $m = l = 0$ substituting those values into the associate Legendre polynomials,

$$P_0(x) \equiv \frac{1}{2^0 0!} \left(\frac{d}{dx} \right)^0 (x^2-1)^0 = 1,$$

and

$$P_0^0(x) \equiv (1-x^2)^{|0|/2} \left(\frac{d}{dx} \right)^{|0|} P_0(x) = 1,$$

hence,

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}.$$

Now, to check if it is normalize we integrate in spherical coordinates from $\theta \in (0, \pi)$ and $\phi \in (0, 2\pi)$,

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} |Y_0^0(\theta, \phi)|^2 \sin \theta d\theta d\phi &= \int_0^\pi \int_0^{2\pi} \frac{1}{4\pi} \sin \theta d\theta d\phi \\ &= \frac{1}{4\pi} \left[\int_0^\pi \sin \theta d\theta \right] \left[\int_0^{2\pi} d\phi \right] \\ &= \frac{1}{4\pi} [2] [2\pi] \\ &= 1 \end{aligned}$$

$$\boxed{\int_0^\pi \int_0^{2\pi} |Y_0^0(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1}$$

Now we do the same procedure with Y_2^1 , $m = 1$ and $l = 2$, which gives that $P_2^1(x) = \sqrt{1-x^2} \frac{d}{dx} P_2(x)$ and $P_2(x) = 1/2(3x^2 - 1)$, hence,

$$P_2(x) \equiv \frac{1}{2^2 2!} \left(\frac{d}{dx} \right)^2 (x^2 - 1)^2 = \frac{1}{2} (3x^2 - 1)$$

and

$$P_2^1(x) \equiv (1-x^2)^{|1|/2} \left(\frac{d}{dx} \right)^{|1|} P_2(x) = 3x\sqrt{1-x^2}$$

$$\begin{aligned} Y_2^1(\theta, \phi) &= -\sqrt{\frac{(2(2)+1)(2-|1|)!}{4\pi(2+|1|)!}} e^{im\phi} P_2^1(\cos[\theta]) \\ &= -\sqrt{\frac{5}{4\pi} \frac{1}{6}} e^{i\phi} 3 \cos[\theta] \sqrt{1-\cos^2[\theta]} = -\sqrt{\frac{5}{24\pi}} e^{i\phi} \sqrt{9} \cos[\theta] \sin[\theta] \\ &= -\sqrt{\frac{15}{8\pi}} e^{i\phi} \cos[\theta] \sin[\theta] \end{aligned}$$

Now we check if the function is normalize,

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} |Y_2^1(\theta, \phi)|^2 \sin \theta d\theta d\phi &= \int_0^\pi \int_0^{2\pi} \frac{15}{8\pi} \cos^2[\theta] \sin^2[\theta] \sin \theta d\theta d\phi \\ &= \frac{15}{8\pi} \left[\int_0^\pi \cos^2[\theta] \sin^2[\theta] \sin \theta d\theta \right] \left[\int_0^{2\pi} d\phi \right] \\ &= \frac{15}{8\pi} \left[\frac{4}{15} \right] [2\pi] \\ &= 1 \end{aligned}$$

$$\int_0^\pi \int_0^{2\pi} |Y_2^1(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1$$

Finally, to check orthogonality we perform the following procedure,

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} [Y_0^0(\theta, \phi)]^* Y_2^1(\theta, \phi) \sin \theta d\theta d\phi &= \int_0^\pi \int_0^{2\pi} \left(\frac{1}{\sqrt{4\pi}} \right)^* \left(-\sqrt{\frac{15}{8\pi}} e^{i\phi} \cos [\theta] \sin [\theta] \right) \sin \theta d\theta d\phi \\ &= -\frac{1}{\sqrt{4\pi}} \sqrt{\frac{15}{8\pi}} \left[\int_0^\pi \cos [\theta] \sin [\theta] \sin \theta d\theta \right] \left[\int_0^{2\pi} e^{i\phi} d\phi \right] \\ &= -\sqrt{\frac{15}{32\pi^2}} [0][0] \\ &= 0 \end{aligned}$$

$$\int_0^\pi \int_0^{2\pi} [Y_0^0(\theta, \phi)]^* Y_2^1(\theta, \phi) \sin \theta d\theta d\phi = 0$$

3 Problem 4.13

- Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius.
- Find $\langle x \rangle$ and $\langle x^2 \rangle$ for an electron in the ground state of hydrogen. *Hint:* this requires no new integration-note that $r^2 = x^2 + y^2 + z^2$, and exploit the symmetry of the ground state.
- Find $\langle x^2 \rangle$ in the state $n = 2, l = 1, m = 1$. *Warning:* This state is not symmetrical in x, y, z . Use $x = r \sin \theta \cos \phi$.

Solution 5

4 Problem 4.14

What is the *most probable* value of r , in the ground state of hydrogen? (The answer is not zero!) *Hint:* First you must figure out the probability that the electron would be found between r and $r + dr$.

5 Problem 4.23

In problem 4.3 you showed that

$$Y_2^l(\theta, \phi) = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}.$$

Apply the raising operator to find $Y_2^2(\theta, \phi)$. Use equation $A_l^m = \hbar\sqrt{l(l+1) - m(m \pm 1)} = \hbar\sqrt{(l \mp m)(l \pm m + 1)}$ to get the normalization.

[heading=bibintoc,title=References]