Homework 1

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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 $E_1, E_2, \ldots$ 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,

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

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 perfom some algebraic manipulation,

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

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

$$\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2} = -k_x^2X(x) \to X(x) = A_x\sin[k_xx]+B_x\cos[k_xx],$$
$$\frac{\mathrm{d}^2Y(y)}{\mathrm{d}y^2} = -k_y^2Y(y) \to Y(y) = A_y\sin[k_yy]+B_y\cos[k_yy],$$
$$\frac{\mathrm{d}^2Z(z)}{\mathrm{d}z^2} = -k_z^2Z(z) \to Z(z) = A_z\sin[k_zz]+B_z\cos[k_zz].$$

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,

$$X(x) = A_x\sin[k_xx], \quad Y(y) = A_y\sin[k_yy], \quad Z(z) = A_z\sin[k_zz].$$

Now we recall the fact that x, y and z have units of distance and that the argument of the sin function must be dimensonless, 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,

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

with

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

Finally, in order to get the expression for A_x, A_y and A_z we apply the normalization restiction 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,

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

Solution 2: Energy analysis

Solution 3: Energy 14

2 Problem 4.3

Use

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

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

Solution 4: Spherical harmonic

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

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

and

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

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 $\phi \in (0,2\pi)$,

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

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

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

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

and

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

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

Now we check if the function is normalize,

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

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 stat of hydrogen. *Hint:* this requires no noew integration-note that $r^2 = x^2 + y^2 + z^2$, and explot 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 ypu 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.

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