Homework 1

Professor: Dr. Jaimes

Francisco Javier Vázquez Tavares A00827546

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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,

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

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

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

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,

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

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

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

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

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

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

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

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

Now we check if the function is normalize,

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

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

Finally, to check orthogonality we perform th following procedure,

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

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

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 (ρ).
- 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: Expected value of position.

By solving the Schrodinger equation in spherical coordinates with the Coulomb's law as the potential energy, the stationary states are in terms of the Bohr's radius,

$$\psi_{(n,m,l)}(r,\theta,\phi) = \frac{1}{r}\rho^{l+1}e^{-\rho}\upsilon(\rho)Y_l^m(\theta,\phi),$$

with $\upsilon(\rho)$ being a polynimial of degree $j_{\max} = n - l - 1$ with coefficients,

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j.$$

For the ground state of the Hydrogen atom we set the parameters to

$(n = 1, l = 0, m = 0)$, which gives,

$$\psi_{1,0,0}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}.$$

To compute the expected value we perform the following operation,

$$\begin{aligned}
\langle r \rangle &= \int_V r |\psi_{1,0,0}(r, \theta, \phi)|^2 dV \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} r \frac{1}{\pi a^3} e^{-2r/a} r^2 \sin\theta d\theta d\phi dr \\
&= \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^3 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{\pi a^3} \left(\frac{3}{8} a^4\right) (2)(2\pi) \\
&= \frac{3}{2} a.
\end{aligned}$$

Now, for $\langle r^2 \rangle$,

$$\begin{aligned}
\left\langle r^2 \right\rangle &= \int_V r^2 |\psi_{1,0,0}(r, \theta, \phi)|^2 dV \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \frac{1}{\pi a^3} e^{-2r/a} r^2 \sin\theta d\theta d\phi dr \\
&= \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^4 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{\pi a^3} \left(\frac{3}{4} a^5\right) (2)(2\pi) \\
&= 3a^2.
\end{aligned}$$

Therefore,

$$\boxed{\langle r \rangle = \frac{3}{2} a, \quad \left\langle r^2 \right\rangle = 3a^2}$$

Solution 6: Expected values and standard deviation of the x component.

Recalling the hint, $r^2 = x^2 + y^2 + z^2$ and using the symmetry of the ground state we can conclude that,

$$\begin{aligned}
\left\langle x^2 \right\rangle &= \frac{1}{3} \left\langle r^2 \right\rangle \\
&= a^2.
\end{aligned}$$

On the other hand, for $\langle x \rangle$ we can write the integrals considering that $x = r\sin\theta\cos\phi$,

$$\begin{aligned}\langle x \rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} (r\sin\theta\cos\phi)\frac{1}{\pi a^3}e^{-2r/a}r^2\sin\theta d\theta d\phi dr \\ &= \frac{1}{\pi a^3}\int_0^\infty e^{-2r/a}r^3 dr \int_0^\pi \sin^2\theta d\theta \int_0^{2\pi}\cos\phi \\ &= \frac{1}{\pi a^3}\left(\frac{3}{8}a^4\right)\left(\frac{\pi}{2}\right)(0) \\ &= 0\end{aligned}$$

Hence,

$$\boxed{\langle x \rangle = 0, \quad \left\langle x^2 \right\rangle = a^2}$$

Solution 7: Stationary state $(n = 2, l = 1, m = 1)$

For this case we recall the stationay state of the hydrogen atom,

$$\psi_{(n,m,l)}(r,\theta,\phi) = \frac{1}{r}\rho^{l+1}e^{-\rho}\upsilon(\rho)Y_l^m(\theta,\phi),$$

with $\upsilon(\rho)$ being a polynimial of degree $j_{\max} = n - l - 1$ with coefficients,

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j.$$

Applying the values of the parameters,

$$\psi_{(2,1,1)}(r,\theta,\phi) = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-r/2a}e^{i\phi}\sin\theta.$$

Now we can perform the previous procedures to compute $\langle x^2 \rangle$,

$$\begin{aligned}\left\langle x^2 \right\rangle &= \int_V r^2|\psi_{1,0,0}(r,\theta,\phi)|^2 dV \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} (r\sin\theta\cos\phi)^2 \frac{1}{64\pi a^5}r^2 e^{-r/a}\sin^2\theta r^2\sin\theta d\theta d\phi dr \\ &= \frac{1}{64\pi a^5}\int_0^\infty r^6 e^{-r/a}dr \int_0^\pi \sin^5\theta d\theta \int_0^{2\pi}\cos^2\phi d\phi \\ &= \frac{1}{64\pi a^5}\left(720a^7\right)\left(\frac{16}{15}\right)(\pi) \\ &= 12a^2\end{aligned}$$

Therefore,

$$\boxed{\left\langle x^2 \right\rangle = 12a^2}$$

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 $r + dr$.

Solution 8: Most probable value of the position in the ground state.

To compute the most probable value of r we integrate thru space $|\psi_{1,0,0}(r,\theta,\phi)|^2$ to get the probability density function.

$$\begin{aligned} p(r) &= \int_0^r \int_0^\pi \int_0^{2\pi} |\psi_{1,0,0}(r,\theta,\phi)|^2 r^2 \sin\theta d\theta d\phi dr \\ &= \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{\pi a^3}() \end{aligned}$$

need to take into account that the probability density for the ground state is given by $P = 4\pi$, due to normalization restrictions. Now we can compute the mos probable value we perfom the integral thru the radial component, because it has angular symmetry, Since it has angular symmetry we only integrate the radial component,

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.