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,

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

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

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

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,

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

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,

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

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,

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

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

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 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.