Homework #10

1. **Griffiths 4.9.** A particle of mass $m$ is placed in a *finite* spherical well:

$$V(r) = \begin{cases} -V_0 & \text{if } r \leq a \\ 0 & \text{if } r > a \end{cases}$$

Find the ground state, by solving the radial equation with $l=0$. Show that there is no bound state if $V_o a^2 < \frac{\pi^2 \hbar^2}{8m}$.

**Solution:**

The radial equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dr^2} + \left[ V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right] u(r) = Eu(r).$$

For $l=0$, we have

$$-\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dr^2} + V(r)u(r) = Eu(r).$$

Thus

$$\begin{cases} -\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dr^2} - V_0 u(r) = Eu(r) & \text{for } r \leq a \\ -\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dr^2} = Eu(r) & \text{if } r > a \end{cases}.$$

For bonding state with the condition of $u(0) = 0$, the solution is

$$u(r) = \begin{cases} A \sin(kr) & \text{for } r \leq a \\ B \exp(-\kappa r) & \text{if } r > a \end{cases}$$

with $E = \frac{\hbar^2 k^2}{2m} - V_0 = -\frac{\hbar^2 \kappa^2}{2m}$, or

$$(k\alpha)^2 + (\kappa \alpha)^2 = \frac{2mV_o a^2}{\hbar^2} \quad (1)$$

From the boundary condition of $\frac{u'(\alpha^-)}{u(\alpha^-)} = \frac{u'(\alpha^+)}{u(\alpha^+)}$, we have

$$k \cot(k\alpha) = -\kappa,$$

or

$$k\alpha = -k \cot(k\alpha). \quad (2)$$

Plotting Eqn (1) and Eqn (2) in the $\kappa \alpha - k\alpha$ plane, the crossing points will be the solutions.
If the radius of the circle $\sqrt{\frac{2mV_0a^2}{\hbar^2}}$ is smaller than $\pi/2$, i.e., if $V_0a^2 < \frac{\pi^2\hbar^2}{8m}$, there will be no solution to the bonding state.

(a) 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.
(b) Find $\langle x \rangle$ and $\langle x^2 \rangle$ for an electron in the ground state of hydrogen. Hint: This requires new integration – note that $r^2 = x^2 + y^2 + z^2$, and exploit the symmetry of the ground state.
(c) 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:
(a) The ground state wavefunction is $\psi = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$.

$$\langle r \rangle = \int \psi^* r \psi d^3r = \int r |\psi|^2 r^2 \sin \theta dr d\theta d\phi = 4\pi \int r^3 \psi^2 dr$$

$$= \frac{4\pi}{\pi a^3} \int_0^\infty r^3 \exp(-2r/a) dr = \frac{4}{a^3} \left(\frac{a}{2}\right)^4 \int_0^\infty z^3 \exp(-z)dz = \frac{4}{a^3} \left(\frac{a}{2}\right)^4 3!$$

$$= \frac{3a}{2}$$
The wavefunction at the ground state is symmetric (independent of $\theta$ and $\phi$).

\[ \langle x \rangle = 0, \quad \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \left( \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \right) = \frac{1}{3} \langle r^2 \rangle = a^2. \]

(c) The wavefunction for $n=2, l=1, m=1$ is $\psi_{211} = \frac{1}{\sqrt{6a^3}} \frac{1}{8a^2} r^2 e^{-r^2/2a^2} \sin \theta e^{i\phi}$.

\[ \langle x^2 \rangle = \int \psi^* x^2 \psi d^3 \vec{r} = \int \psi^* \psi d^3 \vec{r} = \frac{1}{64a^3} \int_0^\infty \int_0^{2\pi} \int_0^\pi r^6 e^{-r^2/2a^2} d\theta d\phi \]
\[ \times \sin^5 \theta \cos^2 \phi \cos^2 \phi e^{r^2/2a^2} d\theta d\phi = \frac{1}{64a^3} a^7 \cdot \frac{16}{15} \cdot \pi \]
\[ = 12a^2. \]

3. **Griffiths 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:**
The probability of finding the electrons within $d^3 \vec{r}$ is $|\psi|^2 d^3 \vec{r} = |\psi|^2 r^2 \sin \theta d\theta d\phi$. Thus the probability of finding the electron between $r$ and $r+dr$ is $|\psi|^2 d^3 \vec{r} = \int_0^\pi d\theta \int_0^{2\pi} d\phi |\psi|^2 r^2 dr$.

For ground state, $\psi = \frac{1}{\sqrt{\pi a^3}} e^{-r^2/a}$. Then the probability of finding the electron between $r$ and $r+dr$ is $4\pi \frac{1}{\pi a^3} e^{-2r^2/a} r^2 dr = \frac{4r^2}{a^3} e^{-2r^2/a} dr$. The most probable value of $r$ satisfy $\frac{d}{dr} \left( \frac{4r^2}{a^3} e^{-2r^2/a} \right) = 0$, or $\frac{8r}{a^3} e^{-2r^2/a} - \frac{8r^3}{a^3} e^{-2r^2/a} = 0$.

This leads to $r=0$ and $r=a$. $r=0$ is the least probable position. $r=a$ is the most probable position.

4. **Griffiths 4.15.** A hydrogen atom starts out in the following linear combination of the stationary states $n=2, l=1, m=1$ and $n=2, l=1, m=-1$:
\[ \psi(\vec{r},0) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) . \]

(a) Construct \( \psi(\vec{r},t) \). Simplify it as much as you can.

(b) Find the expectation value of the potential energy, \( \langle V \rangle \). (Does it depend on time?). Give both the formula and the actual number, in electron volts.

Solution:

(a) From \( \psi(\vec{r},0) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) \), the \( \psi(\vec{r},t) \) is

\[ \psi(\vec{r},t) = \frac{1}{\sqrt{2}} (\psi_{211} e^{-iE_{211}t/\hbar} + \psi_{21-1} e^{-iE_{21-1}t/\hbar}) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) e^{-iE_{211}t/\hbar} . \]

This is still a stationary state because \( |\psi(\vec{r},t)|^2 \) is independent of \( t \).

(b) \( \langle V \rangle \) should be independent of the time.

\[ \langle V \rangle = \frac{1}{2} (\langle 211 | V | 211 \rangle + \langle 21-1 | V | 21-1 \rangle + \langle 211 | V | 21-1 \rangle + \langle 21-1 | V | 211 \rangle) . \]

Because \( V \) depends on \( r \) only, the last two terms involve the inner product of the angular momentum eigen states with different \( L_z \) (\( m=1 \) and \( m=-1 \)), thus should be zero.

Then \( \langle V \rangle = \frac{1}{2} (\langle 211 | V | 211 \rangle + \langle 21-1 | V | 21-1 \rangle) \). The average value of the potential energy should be twice of the total energy for a given state, i.e.,

\[ \langle 211 | V | 211 \rangle = \langle 21-1 | V | 21-1 \rangle = 2E_2 = 2 \frac{E_1}{2^2} = \frac{E_1}{2} . \]

Then \( \langle V \rangle = \frac{1}{2} (\langle 211 | V | 211 \rangle + \langle 21-1 | V | 21-1 \rangle) = \frac{E_1}{2} = \frac{-13.6eV}{2} = -6.8eV . \)