PHY358: Problem Set 1

1. Consider a particle in one-dimensional (1D) potential with $V(x) = 0$ for $|x| < a$ and ∞ otherwise
   (a) Find eigenvalues E_n and normalized eigenfunctions $\psi_n(x)$ of $H = \frac{p^2}{2m} + V(x)$.

Solution: This problem can be viewed as an infinite potential well, where the wave function cannot exist outside of the well. We will come to the ansatz that the solution is separable then focus on the inside of the well.

$$H\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)\Psi(x,t) = E\Psi(x,t) \tag{1}$$

where we made the canonical substitution for the linear momentum.
Let $\Psi(x,t) = \psi(x)u(t)$, then differentiate twice and separate

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x) \tag{2}$$

Notice that the temporal function is cancelled out of the equation, which is expected as the Hamiltonian is time independent. Nonetheless, we can solve a simple 1st order ODE to obtain it and we will include it in the complete eigenfunctions found later.
From hereon, we will focus on the solution inside the well since the wavefunction vanishes outside it.

$$\psi'' = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \implies \psi(x) = A\cos(kx) + B\sin(kx) \tag{3}$$

Applying boundary conditions that arise from the continuity condition on the wavefunction

$$\psi(a) = A\cos(ka) + B\sin(ka) = 0 \tag{4}$$
$$\psi(-a) = A\cos(ka) - B\sin(ka) = 0 \tag{5}$$

Adding and subtracting (4) and (5), we get that

$$\begin{cases} (4)+(5) \quad 2A\cos(ka) = 0 \quad ka = (n+\frac{1}{2})\pi \\ (4)-(5) \quad 2B\sin(ka) = 0 \quad ka = n\pi \end{cases} \tag{6}$$

note, we do not set A or B to 0 to avoid trivial solutions, which do not satisfy normalisation.
In the first expression, we can rewrite

$$ka = (n+\frac{1}{2})\pi;\ k = \frac{\pi}{2a}(2n+1);\ k = \frac{n\pi}{2a} \tag{7}$$

such that n is exclusively an odd natural. In the second, we can rewrite

$$ka = n\pi;\ k = \frac{n\pi}{2a} \tag{8}$$

such that n is exclusively an even natural or 0. This allows us to have a consistent value for k which describes all solutions.

Now we normalise the solution obtained

$$\frac{1}{B^2} = \int_{-\infty}^{\infty} \sin^2\left(\frac{n\pi x}{2a}\right) \mathrm{d}x \tag{9}$$

$$= \frac{1}{2}\int_{-\infty}^{\infty} 1 - \cos\left(\frac{n\pi x}{a}\right) \mathrm{d}x \tag{10}$$

$$= \frac{1}{2}\left[x - \frac{a}{n\pi}\sin\left(\frac{n\pi x}{a}\right)\right]_{-a}^{a} \tag{11}$$

$$B = \sqrt{\frac{1}{a}} \tag{12}$$

$$\frac{1}{A^2} = \int_{-\infty}^{\infty} \cos^2\left(\frac{n\pi x}{2a}\right) \mathrm{d}x \tag{13}$$

$$= \frac{1}{2}\int_{-\infty}^{\infty} 1 + \cos\left(\frac{n\pi x}{a}\right) \mathrm{d}x \tag{14}$$

$$= \frac{1}{2}\left[x + \frac{a}{n\pi}\sin\left(\frac{n\pi x}{a}\right)\right]_{-a}^{a} \tag{15}$$

$$A = \sqrt{\frac{1}{a}} \tag{16}$$

Therefore the eigenfunctions are

$$\psi_n(x) = \begin{cases} \sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right) & n \text{ odd} \\ \sqrt{\frac{1}{a}}\sin\left(\frac{n\pi x}{2a}\right) & n \text{ even} \end{cases} \tag{17}$$

We recover the eigenvalues; previously we set $k^2 = \frac{2mE}{\hbar^2}$ and found that $k = \frac{n\pi}{2a}$. Thus, $E_n = \frac{n^2\pi^2\hbar^2}{8ma^2}$.

(b) Compute $\Psi(x,t)$ at a later time t, $\langle\Psi(x,t)|\, p\, |\Psi(x,t)\rangle$, and $\langle\Psi(x,t)|\, x\, |\Psi(x,t)\rangle$ if the initial state at time t $= 0$, $\Psi(x,0)$, is given by: $\Psi(x,0) \propto (2\psi_1(x) + 3\psi_2(x))$ (first normalize the wavefunction).

Solution:

- We will use the fact that normalising the eigenfunction at time $t_0 = 0$ implies that the state remains normalised $\forall t > t_0$.
- Note also that the wavefunction vanishes outside the well, hence we will consider its inside $x \in [-a; a]$.
- Recall that the full wavefunction is expressed

$$\Psi_n(x,t) = \exp\left(-\frac{\imath E_n t}{\hbar}\right)\psi_n(x)$$

- Last, we will evaluate the energies as necessary. Notably

$$E_1 = \frac{\pi^2\hbar^2}{8ma^2} \quad E_2 = \frac{\pi^2\hbar^2}{2ma^2} \quad E_3 = \frac{9\pi^2\hbar^2}{8ma^2}$$

Normalising

$$1 = N^2 \frac{1}{a} \int_{-a}^{a} \mathrm{d}x (2\psi_1(x) + 3\psi_2(x))(2\psi_1(x) + 3\psi_2(x))^* \tag{18}$$

$$\frac{1}{N^2} = \frac{1}{a} \int_{-a}^{a} \mathrm{d}x \left(2\cos\left(\frac{\pi}{2a}x\right) + 3\sin\left(\frac{\pi}{a}x\right)\right)\left(2\cos\left(\frac{\pi}{2a}x\right) + 3\sin\left(\frac{\pi}{a}x\right)\right)^* \tag{19}$$

$$= \frac{1}{a} \int_{-a}^{a} \mathrm{d}x 4\cos^2\left(\frac{\pi}{2a}x\right) + 12\sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{2a}x\right) + 9\sin^2\left(\frac{\pi}{a}x\right) \tag{20}$$

$$= \frac{1}{2a} \left[4x + 0 + 9x\right]_{-a}^{a} \tag{21}$$

$$= \frac{13}{a} \tag{22}$$

$$\therefore \Psi(x,t) = \frac{1}{\sqrt{13a}} \left(2\exp\left(-\frac{\imath E_1 t}{\hbar}\right)\cos\left(\frac{\pi}{2a}x\right) + 3\exp\left(-\frac{\imath E_2 t}{\hbar}\right)\sin\left(\frac{\pi}{a}x\right)\right) \tag{23}$$

Expectation of position

$$\langle x \rangle = \frac{1}{13a} \int_{-a}^{a} \mathrm{d}x \left(2\exp\left(-\frac{\imath E_1 t}{\hbar}\right)\cos\left(\frac{\pi}{2a}x\right) + 3\exp\left(-\frac{\imath E_2 t}{\hbar}\right)\sin\left(\frac{\pi}{a}x\right)\right) x \tag{24}$$

$$\left(2\exp\left(-\frac{\imath E_1 t}{\hbar}\right)\cos\left(\frac{\pi}{2a}x\right) + 3\exp\left(-\frac{\imath E_2 t}{\hbar}\right)\sin\left(\frac{\pi}{a}x\right)\right)^* \tag{25}$$

$$= \frac{1}{13a} \int_{-a}^{a} \mathrm{d}x \left(4\cos^2\left(\frac{\pi}{2a}x\right) + 9\sin^2\left(\frac{\pi}{a}x\right) + 12\sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{2a}x\right)\right. \tag{26}$$

$$\left.\left(\exp\left(\frac{\imath(E_2 - E_1)t}{\hbar}\right) + \exp\left(-\frac{\imath(E_2 - E_1)t}{\hbar}\right)\right)\right) x \tag{27}$$

$$= \frac{1}{13a} \int_{-a}^{a} \mathrm{d}x \left(4\cos^2\left(\frac{\pi}{2a}x\right) + 9\sin^2\left(\frac{\pi}{a}x\right) + 12\sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{2a}x\right)\right. \tag{28}$$

$$\left.\left(\exp\left(\frac{\imath 3\pi^2\hbar t}{8ma^2}\right) + \exp\left(-\frac{\imath 3\pi^2\hbar t}{8ma^2}\right)\right)\right) x \tag{29}$$

using integral calculator (30)

$$= \frac{64}{39}\frac{a}{\pi^2} \left(\exp\left(\frac{3\imath\pi^2\hbar t}{8ma^2}\right) + \exp\left(\frac{-3\imath\pi^2\hbar t}{8ma^2}\right)\right) \tag{31}$$

Expectation of momentum

Note $\langle\Psi|\, p \,|\Psi\rangle \to \langle\Psi| - \imath\hbar\partial_x \Psi^*\rangle$ where

$$\partial_x \Psi^*(x,t) = \frac{\pi}{a\sqrt{13a}} \left(-\exp\left(\frac{\imath E_1 t}{\hbar}\right)\sin\left(\frac{\pi}{2a}x\right) + 3\exp\left(\frac{\imath E_2 t}{\hbar}\right)\cos\left(\frac{\pi}{a}x\right)\right) \tag{32}$$

$$\langle p \rangle = \frac{\pi}{13a^2} \int_{-a}^{a} \mathrm{d}x \Psi(x,t)\partial_x \Psi^*(x,t) \tag{33}$$

$$= \frac{\pi}{13a^2} \int_{-a}^{a} \mathrm{d}x \left(2\exp\left(-\frac{\imath E_1 t}{\hbar}\right)\cos\left(\frac{\pi}{2a}x\right) + 3\exp\left(-\frac{\imath E_2 t}{\hbar}\right)\sin\left(\frac{\pi}{a}x\right)\right) \tag{34}$$

$$\left(-\exp\left(\frac{\imath E_1 t}{\hbar}\right)\sin\left(\frac{\pi}{2a}x\right) + 3\exp\left(\frac{\imath E_2 t}{\hbar}\right)\cos\left(\frac{\pi}{a}x\right)\right) \tag{35}$$

using integral calculator

$$\langle p \rangle = -\frac{\imath 8\hbar}{13a} \left(\exp\left(-\frac{\imath 3\pi^2\hbar t}{8ma^2}\right) - \exp\left(\frac{\imath 3\pi^2\hbar t}{8ma^2}\right)\right) \tag{36}$$

(c) $\Psi(x, t=0) \propto (\psi_1(x) + \psi_2(x) + \psi_3(x))$ (first normalize the wavefunction).

Solution: Using the same notes as (b).

Normalising:

We have equal contributions from all orthogonal ψ_i, hence we can normalise $\frac{1}{N^2} = 3 \implies N = \frac{1}{\sqrt{3}}$ for each contribution. Therefore

$$\Psi(x,t) = \frac{1}{\sqrt{3a}}\left(e^{\left(-\frac{\imath E_1 t}{\hbar}\right)}\cos\left(\frac{\pi}{2a}x\right) + e^{\left(-\frac{\imath E_2 t}{\hbar}\right)}\sin\left(\frac{\pi}{a}x\right) + e^{\left(-\frac{\imath E_3 t}{\hbar}\right)}\cos\left(\frac{3\pi}{2a}x\right)\right) \tag{37}$$

Expectation of position

$$\langle x\rangle = \frac{1}{3a}\int_{-a}^{a} \mathrm{d}x \Psi(x,t) x \Psi^*(x,t) \tag{38}$$

$$= \frac{1}{3a}\int_{-a}^{a} \mathrm{d}x \left(\left(e^{\left(-\frac{\imath E_1 t}{\hbar}\right)}\cos\left(\frac{\pi}{2a}x\right) + e^{\left(-\frac{\imath E_2 t}{\hbar}\right)}\sin\left(\frac{\pi}{a}x\right) + e^{\left(-\frac{\imath E_3 t}{\hbar}\right)}\cos\left(\frac{3\pi}{2a}x\right)\right)\right. \tag{39}$$

$$\left(e^{\left(\frac{\imath E_1 t}{\hbar}\right)}\cos\left(\frac{\pi}{2a}x\right) + e^{\left(\frac{\imath E_2 t}{\hbar}\right)}\sin\left(\frac{\pi}{a}x\right) + e^{\left(\frac{\imath E_3 t}{\hbar}\right)}\cos\left(\frac{3\pi}{2a}x\right)\right)x \tag{40}$$

using integral calculator (41)

$$=\frac{32a}{27\pi^2}\left(e^{\left(\frac{\imath 3\pi^2\hbar t}{8ma^2}\right)} + e^{\left(-\frac{\imath 3\pi^2\hbar t}{8ma^2}\right)}\right) - \frac{32a}{25\pi^2}\left(e^{\left(\frac{\imath 5\pi^2\hbar t}{8ma^2}\right)} + e^{\left(-\frac{\imath 5\pi^2\hbar t}{8ma^2}\right)}\right) \tag{42}$$

Expectation of momentum

$$\langle p\rangle = (-\imath\hbar)\int_{-a}^{a} \mathrm{d}x \Psi(x,t)\partial_x \Psi^*(x,t) \tag{43}$$

where

$$\partial_x \Psi^*(x,t) = \frac{\pi}{a\sqrt{3a}}\left(-\frac{1}{2}e^{\left(\frac{\imath E_1 t}{\hbar}\right)}\sin\left(\frac{\pi}{2a}x\right) + e^{\left(\frac{\imath E_2 t}{\hbar}\right)}\cos\left(\frac{\pi}{a}x\right) - \frac{3}{2}e^{\left(\frac{\imath E_3 t}{\hbar}\right)}\sin\left(\frac{3\pi}{2a}x\right)\right) \tag{44}$$

$$\langle p\rangle = (-\imath\hbar)\frac{\pi}{3a^2}\int_{-a}^{a} \mathrm{d}x \left(-\frac{1}{2}e^{\left(\frac{\imath E_1 t}{\hbar}\right)}\sin\left(\frac{\pi}{2a}x\right) + e^{\left(\frac{\imath E_2 t}{\hbar}\right)}\cos\left(\frac{\pi}{a}x\right) - \frac{3}{2}e^{\left(\frac{\imath E_3 t}{\hbar}\right)}\sin\left(\frac{3\pi}{2a}x\right)\right) \tag{45}$$

$$\left(e^{\left(-\frac{\imath E_1 t}{\hbar}\right)}\cos\left(\frac{\pi}{2a}x\right) + e^{\left(-\frac{\imath E_2 t}{\hbar}\right)}\sin\left(\frac{\pi}{a}x\right) + e^{\left(-\frac{\imath E_3 t}{\hbar}\right)}\cos\left(\frac{3\pi}{2a}x\right)\right) \tag{46}$$

using integral calculator

$$\langle p\rangle = -\frac{\imath\hbar 4}{a}\left(\frac{1}{9}\left(\exp\left(\frac{\imath 3\pi^2\hbar t}{8ma^2}\right) - \exp\left(-\frac{\imath 3\pi^2\hbar t}{8ma^2}\right)\right) + \frac{1}{5}\left(\exp\left(\frac{\imath 5\pi^2\hbar t}{8ma^2}\right) - \exp\left(-\frac{\imath 5\pi^2\hbar t}{8ma^2}\right)\right)\right) \tag{47}$$

2. Consider a free particle $H = \frac{p^2}{2m}$ in 1D space. The initial state at $t = 0$ is described by $\Psi(x, 0) = A\exp(-\alpha x^2)$, compute the normalization constant A and the wavefunction at a later time t, $\Psi(x, t)$. Discuss the physical implication of $t \to \infty$.

Solution: By normalisation, we have that

$$\int |\Psi(x, 0)|^2 \mathrm{d}x = 1 \tag{1}$$

$$A^2 \int_{-\infty}^{\infty} \exp(-2\alpha x^2)\mathrm{d}x = \tag{2}$$

Using the Gaussian trick by setting I equal to the above integral, squaring it and employing a polar coordinate transform we obtain

$$I^2 = \int_{-\infty}^{\infty} e^{(-2\alpha x^2)}\mathrm{d}x \int_{-\infty}^{\infty} e^{(-2\alpha y^2)}\mathrm{d}y = \int_0^{2\pi}\int_0^{\infty} e^{(-2\alpha r^2)} r\mathrm{d}r\mathrm{d}\theta = 2\pi \cdot \frac{1}{2}\left[-\frac{1}{2\alpha}e^{(-2\alpha r^2)}\right]_0^{\infty} \tag{3}$$

$$\implies I = \sqrt{\frac{\pi}{2\alpha}} \tag{4}$$

Thus

$$A = \sqrt[4]{\frac{2\alpha}{\pi}} \tag{5}$$

Now we have a function normalised at time $t = 0$. Notice that the initial state given is not an eigenfunction of the SE equation. We can convert it into a momentum representation using the Fourier transform

$$\overline{\psi} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \sqrt[4]{\frac{2\alpha}{\pi}} \exp(-\alpha x^2 - \imath kx)\mathrm{d}x \tag{6}$$

which we can massage

$$= \frac{1}{\sqrt{2\pi}} \sqrt[4]{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} \exp(-\alpha(x^2 + \imath kx/\alpha))\mathrm{d}x \tag{7}$$

$$= \frac{1}{\sqrt{2\pi}} \sqrt[4]{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} \exp(-\alpha((x + \imath kx/2\alpha)^2 - (\imath k/2\alpha)^2))\mathrm{d}x \tag{8}$$

$$= \frac{1}{\sqrt{2\pi}} \sqrt[4]{\frac{2\alpha}{\pi}} \exp(\alpha(\imath k/2\alpha)^2) \int_{-\infty}^{\infty} \exp(-\alpha((x + \imath kx/2\alpha)^2)\mathrm{d}x \tag{9}$$

$$\text{let } u = (x + \frac{\imath k}{2\alpha}) \text{ then use the afore Gaussian trick} \tag{10}$$

$$\overline{\psi} = \sqrt[4]{\frac{1}{2\pi\alpha}} \exp\left(-\frac{k^2}{4\alpha}\right) \tag{11}$$

Recall that the free particle eigenvalues are given as

$$E_k = \frac{\hbar^2 k^2}{2m} \tag{12}$$

We can propagate this wavefunction in time while it's in the momentum basis

$$\overline{\Psi} = \overline{\psi}\exp(-\imath E_k t/\hbar). \tag{13}$$

Now we can return the wavefunction to the position representation, now with time evolution

$$\Psi = \frac{1}{\sqrt{2\pi}} \int \overline{\Psi}\exp(\imath kx)\mathrm{d}k = \frac{1}{\sqrt{2\pi}} \sqrt[4]{\frac{1}{2\pi a}} \int_{-\infty}^{\infty} \mathrm{d}k \exp\left(-\frac{k^2}{4\alpha}\right) \exp\left(-\frac{\imath E_k t}{\hbar}\right) \exp(\imath kx) \tag{14}$$

Letting

$$b = \frac{1}{2\alpha}\left(1 + \frac{\imath 2\hbar\alpha t}{m}\right) \tag{15}$$

We obtain a familiar integral

$$\Psi = \frac{1}{\sqrt{2\pi}} \sqrt[4]{\frac{1}{2\pi a}} \int_{-\infty}^{\infty} \mathrm{d}k \exp\left(-\frac{bk^2}{2} + ikx\right) \tag{16}$$

which we solve similarly

$$\therefore \Psi(r,t) = \sqrt{\frac{2a}{1 + \frac{\imath 2\hbar\alpha t}{m}}} \sqrt[4]{\frac{1}{2\pi a}} \exp\left(-\frac{\alpha x^2}{1 + \frac{\imath 2\hbar\alpha t}{m}}\right) \tag{17}$$

We can see from the time evolution applied on the solution that the Gaussian wave will disperse and spread out over time. We say that, as $t \to \infty$, the wave will be everywhere since the Gaussian peak will have flattened out completely.

3. Consider a particle in two-dimensional (2D) central potential, $V(r) = \frac{1}{2}m\omega^2 r^2$

(a) Find the eigenvalues and eigenfunctions of the lowest and second lowest state(s) $\psi(r)$ of $H = \frac{p^2}{2m} + V(r)$.

Solution: We write

$$V(r) = \frac{1}{2}m\omega^2 r^2 = \frac{1}{2}m\omega^2(x^2+y^2) \tag{1}$$

and

$$H = \frac{p^2}{2m} + V(r) = \underbrace{-\frac{\hbar^2}{2m}\partial_{xx} + \frac{1}{2}m\omega^2 x^2}_{H_x} + \underbrace{-\frac{\hbar^2}{2m}\partial_{yy} + \frac{1}{2}m\omega^2 y^2}_{H_y} \tag{2}$$

which is a simplification of the tensor state space that allows us to treat the problem in each direction individually.

The eigenproblem then becomes, with separable solution

$$(H\psi = H_x\psi_x + H_y\psi_y) = (E\psi = E_x\psi_x + E_y\psi_y) \longrightarrow \psi(r) = \psi_x\psi_y; \quad E = E_x + E_y \tag{3}$$

We will solve the 1D harmonic oscillator in the x direction and use symmetry to argue in the y direction.

Consider the x-direction eigenproblem. We obtain solutions using the Hermite polynomials

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(x\sqrt{m\omega/\hbar})\exp(-x^2 m\omega/2\hbar) \tag{4}$$

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp(-x^2 m\omega/2\hbar) \tag{5}$$

$$\psi_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} x\sqrt{\frac{m\omega}{\hbar}}\exp(-x^2 m\omega/2\hbar) \tag{6}$$

$$\tag{7}$$

with eigenvalue energies

$$E_n = \left(\frac{1}{2}+n\right)\hbar\omega \quad E_0 = \frac{\hbar\omega}{2} \quad E_1 = \frac{3}{2}\hbar\omega \tag{8}$$

By symmetry, we find the lowest state to be

$$\psi_{n_x=0,n_y=0} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\exp(-(x^2+y^2)m\omega/2\hbar) \quad E_{n_x=0,n_y=0} = \hbar\omega \tag{9}$$

and the second lowest, having 2-fold degeneracy

$$\begin{cases}\psi_{n_x=0,n_y=1} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} y\sqrt{\frac{m\omega}{\hbar}}\exp(-(x^2+y^2)m\omega/2\hbar) \\ \psi_{n_x=1,n_y=0} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} x\sqrt{\frac{m\omega}{\hbar}}\exp(-(x^2+y^2)m\omega/2\hbar)\end{cases} ; E_{\{(0,1),(1,0)\}} = 2\hbar\omega \tag{10}$$

(b) Imagine that the initial state at time $t=0$, $\Psi(r,t=0)$ is an equal combination of the ground state and 1st excited state(s). Compute $\Psi(r,t)$ at later time t.

Solution: We will interpret the problem statement to mean that we have an equal contribution from each state regardless of degeneracy, hence the sum of all 3 previously found states. The complete solution to the harmonic oscillator problem include a time propagation denoted

$$\exp\left(-\frac{\imath E_n t}{\hbar}\right) \tag{11}$$

The complete solution is then

$$\Psi(r,t) = \frac{1}{\sqrt{3}}\bigg(\exp(-\imath\omega t)\psi_{0,0} + \exp(-2\imath\omega t)(\psi_{1,0} + \psi_{0,1})\bigg) \tag{12}$$

Note that the standard solutions to the harmonic oscillator are orthonormal, hence individually normalised a priori.

(c) Discuss any degeneracy of the 1st excited state(s) and find a way to break the degeneracy; discuss why such a change would break the degeneracy (use the symmetry of H).

Solution: The first excited state has energy $E_1 = 2\hbar\omega$ which can be obtained from $(n_x, n_y) = (0, 1)$ or $(1, 0)$. This is due to the symmetry of the problem, and specifically the isotropicity of the potential. We can break the degeneracy by introducing a perturbation in only 1 direction or by changing the oscillation frequency such that $\omega_x \neq \omega_y$. Hence the eigenvalues will not be the same for a given n and the degeneracy will be broken.

4. Consider an electron in Hydrogen atom under three-dimensional (3D) spherical potential $V(r) = -\frac{e^2}{r}$. When a small quadrupole field is applied, the Hamiltonian is given by $H = \frac{p^2}{2m} + V(r) - g(L_x^2 + L_y^2)$, where g is a positive constant and L is angular momentum operator. Assume that g is small enough that the energy associated with the second term is small compared to the energy differences between different eigenvalues E_n.

   (a) Determine the first four lowest energies(indicate degeneracy, if any) and corresponding eigenfunctions of H.

Solution: Firstly, observe that we can write the Hamiltonian as

$$H = \frac{-\hbar^2}{2m}\nabla^2 + \frac{e^2}{r} - g(L^2 - L_z^2), \tag{1}$$

where

$$H_0 = \frac{-\hbar^2}{2m}\nabla^2 + \frac{e^2}{r}$$

is the original spherical central force hydrogen problem and $L_x^2 + L_y^2 + L_z^2 = L^2$ is rearranged. Notice the TISE becomes

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + \frac{e^2}{r} - g(L^2 - L_z^2)\right)\psi = E\psi. \tag{2}$$

Recall that the L^2 and L_z operators commute with the Hamiltonian (and with each other) have eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$ respectively. Therefore, we can denote ψ_{nlm} the common eigenfunction shared across all components of the Hamiltonian. By matching to the spherical central potential problem, we separate the solution into a radial function and a spherical harmonic. The eigenproblem is developed as follows

$$\begin{aligned} H\psi_{nlm} &= \left(\frac{-\hbar^2}{2m}\nabla^2 + \frac{e^2}{r} - g(L^2 - L_z^2)\right)\psi_{nlm} && (3)\\ &= \left(-\frac{e^2 Z^2}{2a_0 n^2} - g(\hbar^2 l(l+1) - \hbar^2 m^2)\right)\psi_{nlm} && (4)\\ &= E_{nlm}\psi_{nlm} && (5) \end{aligned}$$

where $a_0 = \frac{\hbar^2}{m_e e^2}$ is the Bohr radius.
Thus we compute the energy of a state as

$$E_{nlm} = -\frac{m_e e^4}{2n^2\hbar^2} - g\hbar^2(l(l+1) - m^2) \tag{6}$$

Recall that $l < n, m \in [-l; l]$. Thus we seek to characterise the four lowest energy states with the following indices $\{(1,0,0), (2,0,-1), (2,0,1), , (2,0,0)\}$ (in order of increasing energy):

1. State $(1,0,0)$
   - Energy $E_{100} = 13.6\text{eV}$
   - Eigenfunctions

$$\psi_{100} = 2a_0^{-3/2}\exp(-r/a_0)\frac{1}{\sqrt{4\pi}} \tag{7}$$

   - Degeneracy none (only 1 state)

2. State $(2,1,0)$

- Energy $E_{210} = -3.4\text{eV} - 2g\hbar^2$.
- Eigenfunctions

$$\psi_{210} = (2a_0)^{-3/2} \frac{r}{a_0\sqrt{3}} \exp(-r/2a_0) \sqrt{\frac{3}{4\pi}} \cos(\theta) \tag{8}$$

- Degeneracy none (only 1 state)

3. State $(2, 1, -1), (2, 1, 1)$
   - Energy $E_{21\pm1} = -3.4\text{eV} - g\hbar^2$
   - Eigenfunctions

$$\psi_{21-1} = (2a_0)^{-3/2} \frac{r}{a_0\sqrt{3}} \exp(-r/2a_0) \sqrt{\frac{3}{8\pi}} \sin(\theta) \exp(-\imath\phi) \tag{9}$$

$$\psi_{211} = -(2a_0)^{-3/2} \frac{r}{a_0\sqrt{3}} \exp(-r/2a_0) \sqrt{\frac{3}{8\pi}} \sin(\theta) \exp(\imath\phi) \tag{10}$$

   - Degeneracy 2 fold

4. State $(2, 0, 0)$
   - Energy $E_{200} = -3.4\text{eV}$
   - Eigenfunction

$$\psi_{200} = (2a_0)^{-3/2} \frac{r}{a_0\sqrt{3}} (2 - \frac{r}{a_0}) \sqrt{\frac{1}{4\pi}} \exp(-r/(2a_0)) \tag{11}$$

   - Degeneracy none (only 1 state)

Since g is stated to be small, we see that the energies in $n = 2$ are split into 3 distinct values and we expect that the shift in energy be much smaller than the original energy spacing in the hydrogen atom.

(b) Using the second lowest energy eigenstate(s), compute $\langle r^2 \rangle$ and $\langle L_z^2 \rangle$.

Solution:

$$\begin{aligned}
\langle r^2\rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{210} \cdot r^2 \psi_{210}^* \cdot r^2 \sin(\theta) \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r && (12)\\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} (2a_0)^{-3/2} \frac{r}{a_0\sqrt{3}} \exp(-r/2a_0) \sqrt{\frac{3}{4\pi}} \cos(\theta)\cdot && (13)\\
&\quad r^2 (2a_0)^{-3/2} \frac{r}{a_0\sqrt{3}} \exp(-r/2a_0) \sqrt{\frac{3}{4\pi}} \cos(\theta) \cdot r^2 \sin(\theta) \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r && (14)\\
&= (2a_0)^{-3} \frac{1}{a_0^2 3} \frac{3}{4\pi} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^6 \exp(-r/a_0) \cos^2(\theta) \sin(\theta) \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r && (15)\\
&= (2a_0)^{-3} \frac{1}{2a_0^2} \int_0^\infty r^6 \exp(-r/a_0) \mathrm{d}r \int_0^\pi \cos^2(\theta) \sin(\theta) \mathrm{d}\theta \text{ using integral calculator} && (16)\\
&= (2a_0)^{-3} \frac{1}{2a_0^2} (720 a_0^7)(\frac{2}{3}) && (17)\\
&= 30 a_0^2 && (18)
\end{aligned}$$

Since ψ_{210} is an eigenfunction of the Hamiltonian, we can immediately recognise that

$$\langle L_z^2\rangle = \langle \psi_{210} | L_z^2 | \psi_{210}\rangle = 0 \qquad (19)$$

since ψ_{210} has $m = 0$.

(c) Discuss the physical implication of your results of (d). Discuss how the answers should be modified (or not modified), if you consider the lowest energy state (qualitative description is sufficient).

Solution: From part(b), we found $\langle r^2\rangle = 30a_0^2$ which we can interpret as the average distance between the electron to the hydrogen proton is $r = \sqrt{30}a_0$.
$\langle L_z^2\rangle = 0$ is also found, from which $m^2 = 0 \implies m = 0$ follows meaning that the spin in the z-axis is 0.

Griffiths sections 4.1 and 4.3 problems also.