Quantum Mechanics I

Week 13 (Solutions)

Spring Semester 2025

1 Coulomb Potential Superposition States

Let $\phi_{nlm}(r)$ denote the properly–normalized energy eigenfunctions of the Coulomb potential with principal quantum number n and angular-momentum quantum numbers l and m. Consider an electron in the state

$$\psi(r) = C\Big(\phi_{100}(r) + 4i\,\phi_{210}(r) - 2\sqrt{2}\,\phi_{21\,-1}(r)\Big). \tag{1.1}$$

For the following questions, do not use the functional form of the eigenstates!

(a) Find the normalization constant C.

Our wavefunction is given by

$$\psi = C\Big(\phi_{100} + 4i\phi_{210} - 2\sqrt{2}\,\phi_{22\,-1}\Big), \tag{1.2}$$

To normalize, we compute $\langle\psi|\psi\rangle$ and set it to 1:

$$\begin{aligned}\langle\psi|\psi\rangle \;&=\; \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C^{*}\Big(\phi_{100} + 4i\phi_{210} - 2\sqrt{2}\,\phi_{22\,-1}\Big)^{*} C\Big(\phi_{100} + 4i\phi_{210} - 2\sqrt{2}\,\phi_{22\,-1}\Big)\,d^3r\\ &= |C|^2\Big(\int \phi_{100}^{*}\phi_{100}\,d^3r + 16\int \phi_{210}^{*}\phi_{210}\,d^3r + 8\int \phi_{22\,-1}^{*}\phi_{22\,-1}\,d^3r\Big)\\ &= |C|^2(1+16+8) = 25|C|^2,\end{aligned} \tag{1.3}$$

where we have used the fact that the energy eigenfunctions are normalized and orthogonal, so "cross-terms" do not appear. Choosing C to be real gives $C = 1/5$.

(b) What is the expectation value of $\hat{H}$?

Finding the expectation value of $\hat{H}$ requires very similar manipulations, except this time we need to "sandwich" the Hamiltonian operator in between the two copies of ψ:

$$\langle\hat{E}\rangle = \langle\psi|\hat{H}|\psi\rangle. \tag{1.4}$$

Note that the cross-terms still do not appear, because the energy eigenstates satisfy the eigenvalue equation. For example

$$\langle\phi_{100}|\hat{H}|\psi_{311}\rangle = E_3\langle\phi_{100}|\psi_{311}\rangle = 0. \tag{1.5}$$

Armed with this, we can immediately say

$$\begin{aligned}
E &= \langle\psi|\hat{H}|\psi\rangle \\
&= |C|^2\Big[\langle\phi_{100}|\hat{H}|\phi_{100}\rangle + 16\langle\phi_{210}|\hat{H}|\phi_{210}\rangle + 8\langle\phi_{22\,-1}|\hat{H}|\phi_{22\,-1}\rangle\Big] \\
&= |C|^2\big[E_1\langle\phi_{100}|\phi_{100}\rangle + 16E_2\langle\phi_{210}|\phi_{210}\rangle + 8E_2\langle\phi_{22\,-1}|\phi_{22\,-1}\rangle\big] \\
&= \frac{1}{51}\big(E_1 + 24E_2\big).
\end{aligned}$$

(c) What is the expectation value of $\hat{L}^2$?

The algebra required to find $\hat{L}^2$ is very similar to what we have already done:

$$\begin{aligned}
\langle\hat{L}^2\rangle &= \langle\psi|\hat{L}^2\psi) \\
&= |C|^2\Big[\langle\phi_{100}|\hat{L}^2|\phi_{100}\rangle + 16\langle\phi_{210}|\hat{L}^2|phi_{210}\rangle + 8\langle\phi_{22\,-1}|\hat{L}^2|\phi_{22\,-1}\rangle\Big] \\
&= |C|^2\big[(0\hbar)^2\langle\phi_{100}|\phi_{100}\rangle + 16(2\hbar)^2\langle\phi_{210}|\phi_{210}\rangle + 8(6\hbar)^2\langle\phi_{22\,-1}|\phi_{22\,-1}\rangle\big] \\
&= \frac{80\hbar^2}{25}.
\end{aligned}$$

(d) What is the expectation value of $\hat{L}_z$?

Finally, for $\hat{L}_z$ we have

$$\begin{aligned}
\langle\hat{L}_z\rangle &= \langle\psi|\hat{L}_z|\psi\rangle \\
&= |C|^2\Big[\langle\phi_{100}|\hat{L}_z|\phi_{100}\rangle + 16\langle\phi_{210}|\hat{L}_z|\phi_{210}\rangle + 8\langle\phi_{22\,-1}|\hat{L}_z|\phi_{22\,-1})\Big] \\
&= |C|^2\big[(0\hbar)\langle\phi_{100}|\phi_{100}\rangle + 16(0\hbar)\langle\phi_{210}|\phi_{210}\rangle + 8(-\hbar)\langle\phi_{22\,-1}|\phi_{22\,-1}\rangle\big] \\
&= -\frac{8\hbar}{25}.
\end{aligned}$$

(e) Write down $\psi(r,t)$ at some later time t.

Each energy eigenstate evolves in time by a phase:

$$\psi_{nlm}(\vec{r},t) = \psi_{nlm}(\vec{r},0)\,e^{-iE_nt/\hbar}. \tag{1.6}$$

where $E_n = -13.6\,\mathrm{eV}/n^2$ are the energies of the Hydrogen atom. Recall that the energy (and therefore the time evolution) depends only on the principal quantum number n. Using the superposition principle, we have

$$\psi(\vec{r},t) = C\big(\phi_{100}(\vec{r})e^{-iE_1t/\hbar} + 4i\phi_{210}(\vec{r})e^{-iE_2t/\hbar} - 2\sqrt{2}\,\phi_{22\,-1}(\vec{r})e^{-iE_2t/\hbar}\big), \tag{1.7}$$

2 Muonic atom

When a slow muon interacts with matter it can get captured by the Coulomb potential of a nucleus, thus entering into a hydrogen-like orbit. By emitting radiation, the muon collapses to the ground level of the Coulomb potential. What is the energy of the ground state and of the first excited state of a muon orbiting around the nucleus of ^{206}Pb (Z= 82)? What is the frequency of the radiation emitted in the transition between the first level and the ground state?

The muon is about 200 times heavier than the electron, so its orbits are confined much closer to the nucleus than those of the electrons. For this reason, we can ignore the effect of the electrons in the lead atom on the muon. at the same time, the muon is much lighter than the nucleus of lead, so we can ignore the motion of the nucleus's center of mass. As a result, we can model the system through the Hamiltonian

$$H = \frac{p^2}{2m_\mu} - \frac{Ze^2}{r} \ , \tag{2.1}$$

where m_μ is the mass of the muon. The energy levels of the bound states are

$$E_{n,\ell,m,s} = -\frac{Z^2 m_\mu e^4}{2n^2\hbar^2} \ . \tag{2.2}$$

The ratio between the muon and the electron masses is $m_\mu/m_e \simeq 207$. As a result, the spectrum has the same form of the hydrogen spectrum, but with all energies multiplied by a factor $m_\mu/m_e Z^2 \simeq 1750000$! In particular, the energy for the transition between the two lowest levels is approximately 17.8 MeV. This corresponds to a frequency 4.3×10^{21} Hz.

3 The 3D Infinite Well

Consider the three-dimensional infinite well, with potential:

$$V(x,y,z) = \begin{cases} 0, & x \in (0, L_x),\ y \in (0, L_y),\ z \in (0, L_z) \\ \infty & \text{otherwise.} \end{cases} \tag{3.1}$$

where L_x, L_y, L_z are the dimensions of the well in each spatial direction.

(a) Write down the Hamiltonian of the system.

This is the generalization of the infinite square well in one dimension, as we examined it in class. The Hamiltonian is defined within the interval $0 < x < L_x$, $0 < y < L_y$, $0 < z < L_z$, as:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m}. \tag{3.2}$$

In the position representation, the momentum operator acts as a derivative on the wavefunction, namely:

$$\hat{p}_x \to -i\hbar\partial_x, \quad \hat{p}_y \to -i\hbar\partial_y, \quad \hat{p}_z \to -i\hbar\partial_z. \tag{3.3}$$

Thus, the Hamiltonian becomes:

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}. \tag{3.4}$$

(b) Find the eigenstates and eigenenergies of the system by imposing the appropriate boundary conditions.

Because there are no coupling terms between spatial coordinates, we opt for a separable solution for the wavefunction of the form:

$$\psi(x,y,z) = X(x)Y(y)Z(z). \tag{3.5}$$

Inserting this into the time-independent Schrödinger equation, we get

$$-\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2}{dx^2}X(x) - \frac{\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2}{dx^2}Y(y) - \frac{\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2}{dx^2}Z(z) = E. \tag{3.6}$$

From the latter result, we obtain three second-order ordinary differential equations, one for each spatial dimension:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) = E_x X(x), \tag{3.7}$$

and likewise for y, z. The quantity E_x (and similarly for y, z) is a number to be determined. We have studied this differential equation in class, and the solution is:

$$R_i(r_i) = \sqrt{\frac{2}{L_i}}\sin\frac{\pi r_i n_i}{L_i}, \quad E_i = \frac{\pi^2\hbar^2 n_i^2}{2mL_i^2}, \quad n_i \in \{1,2,3,...\} \tag{3.8}$$

where $i \in \{x,y,z\}$ and $r_x = x, r_y = y, r_z = z$. To obtain these results, we have imposed the usual boundary conditions for the infinite well problem, namely that the wavefunction is zero at the ends of the well, in all three dimensions. The full wavefunction becomes

$$\psi(x,y,z) = \sqrt{\frac{8}{V}}\sin\frac{\pi x n_x}{L_x}\sin\frac{\pi y n_y}{L_y}\sin\frac{\pi z n_z}{L_z}, \tag{3.9}$$

where $V = L_x L_y L_z$, and we may verify that indeed this is normalized to unity through the condition

$$\int dxdydz\, |\psi(x,y,z)|^2 = 1. \tag{3.10}$$

The energies of the total system are simply:

$$E_{n_x,n_y,n_z} = E_x + E_y + E_z = \frac{\hbar^2\pi^2}{2m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]. \tag{3.11}$$

(c) Comment on the degeneracy in the energies for the cases $L_x \neq L_y \neq L_z$, $L_x = L_y \neq L_z$ and $L_x = L_y = L_z = L$.

In the case $L_x \neq L_y \neq L_z$, there is no degeneracy in the energies. However, when L_i are rationally related (commensurate), then degeneracy may appear. For commensurability, the ratio of two real numbers is a rational number. For instance, if $L_x = L, L_y = 2L, L_z = 3L$, the energies become:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}\left[n_x^2 + \frac{n_y^2}{4} + \frac{n_z^2}{9}\right]. \tag{3.12}$$

Then, the combinations $(n_x, n_y, n_z) = (2, 2, 3)$ and $(n_x, n_y, n_z) = (1, 4, 3)$ give the same energy $E \propto \left[6\right]$, so there could be found degeneracy for commensurate spatial lengths.

In the case of $L = L_x = L_y \neq L_z$, there is partial degeneracy due to partial symmetry between the x and y direction. The energies become:

$$E_{n_x,n_y,n_z} \frac{\hbar^2\pi^2}{2m}\left[\frac{n_x^2 + n_y^2}{L^2} + \frac{n_z^2}{L_z^2}\right]. \tag{3.13}$$

So for example the combinations $(n_x, n_y, n_z) = (1, 2, 1)$ and $(n_x, n_y, n_z) = (2, 1, 1)$ give the same energy.

In the case of $L_x = L_y = L_z = L$, we have degeneracy due to a total symmetry of the system. The potential is the same in each dimension, and thus if we rotate the wave around gives the same energy as before. The energies simply become:

$$E_{n_x,n_y,n_z} \frac{\hbar^2\pi^2}{2m}\frac{n_x^2 + n_y^2 + n_z^2}{L^2}. \tag{3.14}$$

For $n_i = 1$, there is a unique energy and wavefunction. However, for higher-order combinations, multiple wavefunctions will correspond to the same energy (degeneracy).

4 The Large-n, l Limit in the Hydrogen Atom

Consider an electron trapped in a Coulomb potential in the state corresponding to maximum orbital angular momentum $l = n - 1$.

(a) Show that the expectation value of $\hat{r}$ and $\hat{r}^2$ for the eigenstates of the Hydrogen atom are

$$\langle r \rangle = r_0 n\left(n + \frac{1}{2}\right), \quad \langle r^2 \rangle = r_0^2 n^2 (n+1)\left(n + \frac{1}{2}\right). \tag{4.1}$$

where $r_0 = \hbar^2/(m_e e^2)$.

Hint 1: The general eigenfunctions of Hydrogen are:

$$\psi_{nlm}(r,\theta,\phi) = \left[\left(\frac{2}{nr_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}\right]^{1/2} e^{-r/nr_0}\left(\frac{2r}{nr_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{nr_0}\right) Y_{lm}(\theta,\phi), \quad (4.2)$$

where L_p^k are the associated Laguerre polynomials and $Y_{l,m}$ are the spherical harmonics.

Hint 2: You may find the following integral useful:

$$\Gamma(n) = \int_0^\infty t^{n-1} e^{-t} dt = (n-1)!, \quad (4.3)$$

where n is an integer. The function $\Gamma(n)$ is called the gamma function and is defined by the above integral.

The general hydrogen eigenfunctions are given by

$$\psi_{nlm}(r,\theta,\phi) = \left[\left(\frac{2}{nr_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}\right]^{1/2} e^{-r/nr_0}\left(\frac{2r}{nr_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{nr_0}\right) Y_{lm}(\theta,\phi), \quad (4.4)$$

where L_p^k are the associated Laguerre polynomials. For the case when $l = n-1$, the Laguerre polynomial in the above expression becomes $L_0^{2n-1} = 1$, but in general $L_0^k = 1$. In this case, the Hydrogen eigenfunctions simplify to

$$\psi_{n=n-1,m}(r,\theta,\phi) = \left[\left(\frac{2}{nr_0}\right)^3 \frac{1}{2n(2n-1)!}\right]^{1/2} e^{-r/nr_0}\left(\frac{2r}{nr_0}\right)^{n-1} Y_{n-1,m}(\theta,\phi). \quad (4.5)$$

From the expression above, we determine can determine the expectation value of r as

$$\begin{aligned}\langle r\rangle &= \int d^3r\ \psi^*_{n,n-1,m}(r,\theta,\phi) r\ \psi_{n,n-1,m}(r,\theta,\phi)\\ &= \left[\left(\frac{2}{nr_0}\right)^3 \frac{1}{2n(2n-1)!}\right] \times \left[\int_0^\infty r^3 \left(\frac{2r}{nr_0}\right)^{2n-2} e^{-2r/nr_0} dr\right] \times\\ &\quad \times \left[\int d\Omega\ Y^*_{n-1,m}(\theta,\phi) Y_{n-1,m}(\theta,\phi)\right].\end{aligned}$$

The integral contained in the third square brackets evaluated to 1 due to the orthonormality condition of the spherical harmonics. We will now work with the integral in the second square brackets which we will denote as $\mathcal{I}$,

$$\mathcal{I} = \left(\frac{2}{nr_0}\right)^{2n-2} \int_0^\infty r^{2n+1} e^{-2r/nr_0} dr. \quad (4.6)$$

We change variables as follows $2r/nr_0 = t$ and write:

$$\mathcal{I} = \left(\frac{2}{nr_0}\right)^{-4} \int_0^\infty dt\, t^{2n+1} e^{-t}. \tag{4.7}$$

Using the hint provided, the integral evaluates to:

$$\mathcal{I} = \left(\frac{2}{nr_0}\right)^{-4} (2n+1)!. \tag{4.8}$$

Thus, the expectation value of r takes the final form of:

$$\langle r \rangle = nr_0 \left(n + \frac{1}{2}\right). \tag{4.9}$$

In a very similar fashion, we can calculate the expectation value of r^2 in the state $\psi_{n,n-1,m}$ which evaluates to:

$$\langle r^2 \rangle = (nr_0)^2 \left(n + \frac{1}{2}\right)(n+1). \tag{4.10}$$

(b) For large values of n and l, show that the results of part (a), become:

$$\sqrt{\langle r^2 \rangle} \to r_0 n^2, \quad \frac{\Delta r}{\langle r \rangle} \to 0, \quad E_n \to -\frac{1}{2}\frac{e^2}{n^2 r_0}. \tag{4.11}$$

What do these results mean physically? To gain more insights of these limiting cases, compute the energy of an circularly orbiting (classical) electron around the proton. Take the circular orbit to have a radius of $n^2 r_0$.

We first look at the expectation value of r^2 squared, which for large n becomes

$$\sqrt{\langle r^2 \rangle} = n^2 r_0 \sqrt{1 + \frac{3}{2n} + \frac{1}{2n^2}} \xrightarrow{n\to\infty} n^2 r_0. \tag{4.12}$$

By definition, the standard deviation (uncertainty) in r is

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2} = \sqrt{(nr_0)^2\left(n + \frac{1}{2}\right)(n+1) - (nr_0)^2\left(n + \frac{1}{2}\right)^2} = \frac{nr_0}{\sqrt{2}}\sqrt{n + \frac{1}{2}}$$

so the relative uncertainty in position becomes

$$\frac{\Delta r}{\langle r \rangle} = \frac{nr_0\sqrt{n + \frac{1}{2}}}{\sqrt{2}\, nr_0 \left(n + \frac{1}{2}\right)} = \frac{1}{\sqrt{2}\sqrt{n + \frac{1}{2}}} \xrightarrow{n\to\infty} 0. \tag{4.13}$$

In the expression for the energy there are no powers of n that we can neglect for high n, so the energy retains its exact expression. The goal of this question is to demonstrate the correspondence principle: for high quantum numbers, quantum systems start to behave classically. And we show this by further computing the energy of the classical system. A system comprised of a classical electron orbiting in a circular has energy

$$E = \frac{p^2}{2m} - \frac{e^2}{r}. \tag{4.14}$$

Using Newton's second law, we find

$$\frac{e^2}{r^2} = m\frac{v^2}{r} \quad \Rightarrow \quad mv^2 = \frac{e^2}{r} \tag{4.15}$$

and thus the energy becomes:

$$E = \frac{1}{2}\frac{e^2}{r} - \frac{e^2}{r} = -\frac{e^2}{2r}. \tag{4.16}$$

For $r = n^2 r_0$, we obtain the energies of the quantum Hydrogen atom.

For large quantum numbers n, l, the energy levels of the hydrogen atom correspond to orbits at radii $r = n^2 r_0$, consistent with the Bohr model. In this semiclassical limit, the quantum electron is well localized near the surface of a sphere of radius $n^2 r_0$, with minimal uncertainty in position. This reflects the classical picture of an electron in a circular orbit at a fixed distance from the nucleus. Moreover, the energy matches that of a classical electron in such an orbit, reinforcing the correspondence between quantum and classical descriptions in the large-n, large-l limit.

(c) What can you say about the size of a weakly bound state of Hydrogen (when n is large)? Is this an idiosyncrasy of hydrogen, or is it generally true of weakly bound states? *Hint: Discuss the range of interaction and compare to that of the finite well.*

As shown in part (b), the radius of the bound state increases as $n^2 r_0$. This behavior is specific to long-range potentials (actually infinite in the case of the Coulomb potential). For example, in a finite-range potential well the bound state is limited more or less to the width of the well. Look at the discussion on the finite well and its wavefunctions in Chapter 6 of the Lecture notes.

5 3D harmonic oscillator

Consider an electron confined by a harmonic potential. The Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m_e} + \frac{1}{2}m_e\omega^2\mathbf{r}^2 \ . \tag{5.1}$$

(a) Find all energy levels. Find the degeneracy of the ground state and of the first two excited levels.

Although the problem has a radial symmetry, it is most easily solved in Cartesian coordinates, since it breaks into 3 independent oscillators, in the three orthogonal cartesian directions:

$$H = \frac{p_x^2}{2m_e} + \frac{1}{2}m_e\omega^2 x^2 + \frac{p_y^2}{2m_e} + \frac{1}{2}m_e\omega^2 y^2 + \frac{p_z^2}{2m_e} + \frac{1}{2}m_e\omega^2 z^2 \ . \tag{5.2}$$

The eigenstates can be labeled with three quantum numbers $|n_x, n_y, n_z\rangle$, representing the excitation energies along the three direction. Formally, we can say that $H = H_x + H_y + H_z$, where the three operators H_x, H_y, H_z are mutually commuting, and therefore are simultaneously diagonalizable. The energy is $E_{n_x,n_y,n_z} = (3/2 + n_x + n_y + n_z)\hbar\omega$. The ground state is non-degenerate and corresponds to $n_x = n_y = n_z = 0$. The first excited state has degeneracy 3, because *one* among the three quantum numbers n_x, n_y, n_z is one, whereas the other two are 0. The second excited state has degeneracy 6: one can put either two quantum numbers equal to 1 and the other equal to 0 or one quantum number equal to 2 and the other two equal to zero.

(b) Show that the ground state has $\ell = 0$ (s-wave) whereas the first excited states have $\ell = 1$ (p-wave). *Hint: For $l = 1$, consider the relation between the spatial components (x, y, z) and the spherical harmonics $Y_{l,m}$.*

The ground-state wavefunction can be written as the product

$$\psi_0(x, y, z) = \phi_0(x)\phi_0(y)\phi_0(z) \tag{5.3}$$

where

$$\phi_0(u) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega u^2}{2\hbar}} \ . \tag{5.4}$$

Multiplying the three Gaussian functions we find:

$$\psi_0(x, y, z) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} e^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} e^{-\frac{m\omega \mathbf{r}^2}{2\hbar}} \ . \tag{5.5}$$

Since the wavefunction depends only on the radial coordinate $|\mathbf{r}|$ and not on the angle, it has $\ell = 0$ (it has s-wave symmetry).

Consider now the first excited level. The level is composed of three degenerate states which we can choose to denote as

$$\begin{gathered} \psi_{1,0,0}(x, y, z) = \phi_1(x)\phi_0(y)\phi_0(z) \ , \quad \psi_{0,1,0}(x, y, z) = \phi_0(x)\phi_1(y)\phi_0(z) \ , \\ \psi_{0,0,1}(x, y, z) = \phi_0(x)\phi_0(y)\phi_1(z) \ . \end{gathered} \tag{5.6}$$

Here

$$\phi_n(u) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega u^2}{2\hbar}} H_n\left(\sqrt{\frac{m\omega}{\hbar}} u\right) \ , \tag{5.7}$$

with H_n the Hermite polynomials. For $n = 1$,

$$\phi_1(u) \propto u e^{-\frac{m\omega u^2}{2\hbar}} \ . \tag{5.8}$$

As a result, up to a normalization constant,

$$\begin{aligned} &\psi_{1,0,0}(x,y,z) \propto x e^{-\frac{m\omega \mathbf{r}^2}{2\hbar}} , \qquad \psi_{0,1,0}(x,y,z) \propto y e^{-\frac{m\omega \mathbf{r}^2}{2\hbar}} , \\ &\psi_{0,0,1}(x,y,z) \propto z e^{-\frac{m\omega \mathbf{r}^2}{2\hbar}} . \end{aligned} \tag{5.9}$$

In spherical coordinates

$$\begin{aligned} &z = r\cos\theta = rY_{1,0}(\theta,\varphi) , \\ &x = r\sin\theta\cos\varphi = \frac{r}{2}\sin\theta(e^{i\varphi}+e^{-i\varphi}) \propto \frac{r}{2}(Y_{1,1}(\theta,\varphi)+Y_{1,-1}(\theta,\varphi)) \\ &y = r\sin\theta\sin\varphi = \frac{r}{2i}\sin\theta(e^{i\varphi}-e^{-i\varphi}) \propto \frac{r}{2}(Y_{1,1}(\theta,\varphi)-Y_{1,-1}(\theta,\varphi)) . \end{aligned} \tag{5.10}$$

Thus we see that the first excited states have all the form of a function of r only, multiplied by a linear combination of the spherical harmonics with $\ell = 1$ and $m = -1, 0, 1$. (Any linear combination is an eigenstate, as the level is 3-fold degenerate).

These result could have been derived more quickly as follows. The Hamiltonian has radial symmetry so it commutes with $\hat{L}^2$ and $\hat{L}^z$. This implies that we can diagonalize simultaneously $\hat{H}$, $\hat{L}^2$, and $\hat{L}^z$, obtaining a set of eigenstates labeled by quantum numbers $\tilde{n}, \ell, m$. In addition, due to symmetry, the states with different m but the same ℓ and $\tilde{n}$ must have the same energy. Since $m = -\ell, ..., \ell$ this gives a degeneracy of at least $2\ell + 1$ for states with angular momentum ℓ.

Since the ground state is nondegenerate the only option is $\ell = 0$. For the first excited state, with degeneracy 3 we must have $\ell = 1$. In principle, one may consider the option that there are 3 states all having $\ell = 0$. However, the wavefunctions $\psi_{1,0,0}$, $\psi_{0,1,0}$, $\psi_{0,0,1}$ are odd under space inversion, while wavefunctions with $\ell = 0$ are symmetric under space inversion.

6 Particle in a Spherical Well

Consider a particle of mass m subjected to the following potential:

$$V(r) = \begin{cases} 0, & r < R, \\ \infty & \text{otherwise.} \end{cases} \tag{6.1}$$

where $r = \sqrt{x^2+y^2+z^2}$

(a) Write the Hamiltonian of the system using the angular momentum operator $\hat{L}^2$, and the resulting Schrödinger equation.

The Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}^2}{2m}. \tag{6.2}$$

Then, the Schrödinger equation is expressed in the position representation as follows:

$$-\frac{\hbar^2}{2m\,r}\frac{\partial^2}{\partial r^2}\big[r\Psi(x)\big] + \frac{1}{2mr^2}L^2\Psi(x) = E\Psi(x) \tag{6.3}$$

where $L^2\Psi(x) = \langle x|\hat{L}^2|\Psi\rangle$ and

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}\big[r\Psi(x)\big] = \Big(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\Big)\Psi(x). \tag{6.4}$$

(b) The wavefunction can be factorized in the following way:

$$\Psi(r,\theta,\varphi) = \Psi_{lm}(r,\theta,\varphi) = \Phi^l(r)Y^l_m(\theta,\varphi), \tag{6.5}$$

where the functions $Y^l_m(\theta,\varphi)$ are the spherical harmonics and $\Phi^l(r)$ is some function of r, characterized by the angular momentum number l. Justify this factorization, and find the differential equation for $\Phi^l(r)$.

The factorization is justified since we are dealing with a central potential, i.e. the potential depends only on r. In the case of the spherical well, the potential is zero. The Hamiltonian of central potentials commute with L^2 and L_z, and thus they share common eigenstates, i.e. the spherical harmonics. Thus, the angular part of the wavefunction (including the polar angle θ and the azimuthal angle ϕ) is described by the latter functions. A second function $\Phi^l(r)$ depends only on the radial coordinate r. Using this factorization, we obtain for the radial part $\Phi^\ell(r)$ the equation:

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}\big[r\Phi^l(r)\big] + \frac{\hbar^2 l(l+1)}{2mr^2}\,\Phi^l(r) = E\Phi^l(r), \tag{6.6}$$

where we have used $L^2Y^l_m = \hbar^2 l(l+1)Y^l_m$. If we perform the second derivative according to r, we obtain

$$\frac{\partial^2}{\partial r^2}\Phi^l(r) + \frac{2}{r}\frac{\partial}{\partial r}\Phi^l(r) + \Big[k^2 - \frac{l(l+1)}{r^2}\Big]\Phi^l(r) = 0, \qquad \text{with} \quad k^2 = \frac{2mE}{\hbar^2}. \tag{6.7}$$

(c) What are the boundary conditions to be applied to $\Phi^l(r)$?

Since the potential becomes infinite for distance $r > R$, we require that the wave function vanishes at $R = 0$, and specifically the radial part.

(d) For the case $l = 0$, solve the differential equation for $\Phi^l(r)$ by imposing the boundary conditions. What are the energies and their degeneracy?

For $l = 0$, the second term of the third term in the differential equation for $\Phi^0(r)$ vanishes, and thus the DE simplifies to:

$$\frac{\partial^2}{\partial r^2}\Phi^0(r) + \frac{2}{r}\frac{\partial}{\partial r}\Phi^0(r) + k^2\Phi^0(r) = 0 \tag{6.8}$$

We may re-write this equation in the following way:

$$\frac{\partial^2(r\Phi^0)}{\partial r^2} + k^2 r\Phi^0 = 0. \tag{6.9}$$

The solution to this differential equation takes the form:

$$r\Phi^0(r) = A\sin(kr) + B\cos(kr) \quad \Rightarrow \quad \Phi^0(r) = A\,\frac{\sin(kr)}{r} + B\,\frac{\cos(kr)}{r}. \tag{6.10}$$

The wave-function $\Phi^0(r)$ must be continuous at $r = 0$, and thus $B = 0$, since the cosine term diverges when $r \to 0$. Thus:

$$\Phi^0(r) = A\,\frac{\sin(kr)}{r}. \tag{6.11}$$

where A is determined through the normalization condition.

Imposing the boundary condition we found in the previous question, i.e. $\Phi^l(R) = 0$, we find that k is restricted to values such that $kR = n\pi$ with $n \in \{1, 2, 3, ...\}$, since $\sin(kR) = 0$. We therefore find:

$$E_n^{l=0} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{R}\right)^2 \tag{6.12}$$

We notice that only the values $n \in \{1, 2, 3, ...\}$ are considered. Indeed, for negative values of n the wave-function Φ^0 becomes negative, and the minus sign is simply a phase factor. Note that the energy levels for fixed $l = 0$ depend on n only, and not on the eigenvalue m of L_z. Hence, the degeneracy is given by the number of possible values m can take, i.e. $(2l + 1)$. So for $l = 0$ we have only one state, $(2l + 1) = 1$.

(e) Let us, from now on, consider the case of a generic l. For small r, we may use:

$$\Phi^l(r) \sim r^s, \tag{6.13}$$

where s is some parameter. Show that the differential equation for $\Phi^l(r)$ requires $s = l$.

For small r, we can drop the term proportional to k^2 since the term $l(l + 1)/r^2$ dominates. Then,

$$\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right] r^s = 0, \tag{6.14}$$

from which we deduce that

$$s(s-1) + 2s - l(l+1) = 0 \quad \Rightarrow \quad s(s+1) - l(l+1) = 0. \tag{6.15}$$

Therefore, either $s = l$ or $s = -l - 1$ satisfy this algebraic equation. We are forced to select the solution $s = l$ so that the wave function does not diverge.

(f) In order to take the asymptotic behavior of the wavefunction into account, we consider

$$\Phi^l(r) = \lambda_l(r) r^l, \tag{6.16}$$

where $\lambda_l(r)$ is some function of r. Show that the radial equation becomes:

$$\lambda_l'' + 2(l+1)\frac{\lambda_l'}{r} + k^2\lambda_l = 0, \quad \text{where} \quad k^2 = \frac{2mE}{\hbar^2}. \tag{6.17}$$

The prime notation corresponds to the derivative with respect to r.

If we introduce $\lambda_l(r) = r^{-l}\Phi^l(r)$ in order to take into account the asymptotic behavior found in the previous part, we have:

$$\Phi^l = \lambda_l(r)\, r^l \tag{6.18}$$

while for the first derivative we have:

$$(\Phi^l)' = l r^{l-1}\lambda_l(r) + r^l \lambda_l'(r) = r^l \left[\lambda_l' + \frac{l}{r}\lambda_l\right] \tag{6.19}$$

and the second derivative:

$$(\Phi^l)'' = l(l-1)r^{\,l-2}\lambda_l(r) + 2lr^{\,l-1}\lambda_l'(r) + r^l\lambda_l''(r) = r^l\left[\lambda_l'' + \frac{2l}{r}\lambda_l' + \frac{l(l-1)}{r^2}\lambda_l\right] \tag{6.20}$$

Substituting into the equation for $\Phi^\ell(r)$,

$$(\Phi^l)'' + \frac{2}{r}(\Phi^l)' + \left[k^2 - \frac{l(l+1)}{r^2}\right]\Phi^l = 0 \tag{6.21}$$

we immediately find

$$\lambda_\ell'' + \frac{2(\ell+1)}{r}\lambda_\ell' + k^2\lambda_\ell = 0. \tag{6.22}$$

(g) Show that if $\lambda_l(r)$ satisfies Eq. (6.17), then $\lambda_l'(r)/r$ satisfies this equation for $l+1$. In other words, check that

$$\lambda_l \propto \lambda_{l-1}'/r. \tag{6.23}$$

Using this recurrence relation, establish the form for $\Phi^l(r)$. *Hint: Start by dividing the equation for $\lambda^l(r)$, obtained in the previous question, by r.*

If we take the derivative of the previous equation and divide it by r, we find

$$\frac{\lambda_l'''}{r} + 2(l+1)\,\frac{1}{r}\left(\frac{\lambda_l'}{r}\right)' + k^2\,\frac{\lambda_l'}{r} = 0. \tag{6.24}$$

Using the fact that

$$\left(\frac{\lambda_l'}{r}\right)'' = \frac{\lambda_l'''}{r} - \frac{2}{r}\left(\frac{\lambda_l'}{r}\right)', \tag{6.25}$$

the previous equation becomes

$$\left(\frac{\lambda_l'}{r}\right)'' + 2(l+2)\,\frac{1}{r}\left(\frac{\lambda_l'}{r}\right)' + k^2\,\frac{\lambda_l'}{r} = 0. \tag{6.26}$$

By shifting l to $l-1$, the last equation becomes

$$\left(\frac{\lambda_{l-1}'}{r}\right)'' + 2(l+1)\,\frac{1}{r}\left(\frac{\lambda_{l-1}'}{r}\right)' + k^2\,\frac{\lambda_{l-1}'}{r} = 0. \tag{6.27}$$

We notice that the latter equation and Eq. (6.17) represent the same differential equation. The only difference being that Eq. (6.17) is written for λ_l whereas our equation here is written for λ'_{l-1}/r. We can hence conclude that $\lambda_l \propto \lambda'_{l-1}/r$. We obtain a recurrence relation:

$$\lambda_l \;\propto\; \left(\tfrac{1}{r}\tfrac{\partial}{\partial r}\right)\lambda_{l-1} \;\propto\; \cdots \;\propto\; \left(\tfrac{1}{r}\tfrac{\partial}{\partial r}\right)^l \lambda_0. \tag{6.28}$$

Using this recurrence relation, we can determine the radial component of the wavefunction, namely:

$$\Phi^l(r) = r^l \lambda_l(r) = A_l\, r^l \left(\tfrac{1}{r}\tfrac{\partial}{\partial r}\right)^l \Phi^0(r), \tag{6.29}$$

where $\lambda_0 = \Phi^0$. Because $\Phi^l(r)$ must not diverge as $r \to 0$, the cosine term in Φ^0 must be removed. The functions $\Phi^l(r)$ are therefore spherical Bessel functions:

$$\Phi^l(r) = A_l\, r^l \left(\tfrac{1}{r}\tfrac{\partial}{\partial r}\right)^l \frac{\sin(kr)}{r}. \tag{6.30}$$

(h) Confirm that you obtain the correct result for the case $l = 0$.

For $l = 0$, the wavefunction becomes:

$$\Phi^0(r) = A_0 r^0 \left(\frac{1}{r}\frac{\partial}{\partial r}\right)^0 \frac{\sin kr}{r} = A_0 \frac{\sin kr}{r}, \tag{6.31}$$

and reduces to the wavefunction obtained in part (d).

(i) Determine the energies of the states having $l = 1$. What is their degeneracy?

For the case of $l = 1$, we have:

$$\Phi^1(r) \;\propto\; \partial_r \Phi^0(r) \;\propto\; \frac{\cos(kr)\, kr - \sin(kr)}{r^2}. \tag{6.32}$$

We impose the boundary condition at R, i.e. that the radial function becomes zero at that point, and find the condition:

$$\tan(kR) = kR. \tag{6.33}$$

From a graphical solution, the energies are therefore again quantized, and each energy level has degeneracy $2l + 1 = 3$ (again, there is no dependency on m).