1. Spherical Bessel functions are defined by
$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\sin\rho}{\rho}.$$
Show that these functions satisfy the differential equation
$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + \left(1 - \frac{l(l+1)}{\rho^2}\right)\right] R(\rho) = 0.$$

2. Consider a particle trapped in a spherical box of radius a. Find the eigenvalues and eigenfunctions for angular momentum quantum number $l = 0$.

3. Consider a potential (3D square well)
$$V(\mathbf{r}) = \begin{cases} -V_0, & |\mathbf{r}| < a, \\ 0, & |\mathbf{r}| > a. \end{cases}$$
Assume $E < 0$.
   (a) In both cases, interior ($r < a$) and exterior ($r > a$), obtain the radial differential equation and write down the solutions.
   (b) Write down the BC at $r = a$. Obtain the energy quantization condition.
   (c) For $l = 0$, simplify the energy quantization condition.

4. Starting with the generating function
$$U(\rho, s) = \frac{1}{1-s}\exp\left[-\frac{\rho s}{1-s}\right] = \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q$$
where $|s| < 1$, prove the recurrence relations,
$$L_{q+1}(\rho) + (\rho - 1 - 2q)\, L_q(\rho) + q^2 L_{q-1}(\rho) = 0$$
and
$$\frac{d}{d\rho}L_q(\rho) - q\frac{d}{d\rho}L_{q-1}(\rho) + q\,L_{q-1}(\rho) = 0.$$
Using these, prove
$$\left[\rho\frac{d^2}{d\rho^2} + (1-\rho)\frac{d}{d\rho} + q\right] L_q(\rho) = 0.$$

5. Prove, using generating function, for hydrogen atom
$$\langle r \rangle_{nlm} = a_0 \frac{n^2}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\}.$$

6. Statistically, the probabilty that the hydrogen atom is in a state nlm is $\exp[-E_n/kT]$ where E_n is the energy of the state, k is the Boltzman constant and T is temperature. What is the ratio of the probability of hydrogen being in the ground state to its being in the first excited state?

7. The state of the electron in the hydrogen atom is given by the wave function
$$\Psi(\mathbf{r}) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{3/2} e^{-\alpha^2 r^2/2}.$$
What is the probability that the electron will be found in the ground state? And in state $nlm = 210$?

Tutorial 9.

Q2. If $l=0$, radial Equation becomes (by using $R(r)=\frac{u(r)}{r}$)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+V_{eff}\,u=Eu$$

But $V_{eff}(r)=V(r)+\frac{l(l+1)\hbar^2}{2mr^2}=0$ for $r<a$

Then

$$\frac{d^2u}{dr^2}=-k^2u \qquad k^2=\frac{2mE}{\hbar^2}$$

$$\Rightarrow \quad u(r)=A\sin(kr)+B\cos(kr)$$

$$\Rightarrow \quad R(r)=A\frac{\sin(kr)}{r}+B\cos\left(\frac{kr}{r}\right)$$

Since $R(0)<\infty \Rightarrow B=0$

$R(a)=0 \Rightarrow ka=n\pi \Rightarrow k_n=\frac{n\pi}{a}$, $n=1,2,\cdots$

$\Rightarrow$ Let $E_n=\frac{\hbar^2\pi^2}{2ma^2}n^2$

And

$$\psi_{n,0,0}=A\sin\left(\frac{n\pi r}{a}\right)\frac{1}{r}\frac{1}{\sqrt{4\pi}}=R_n(r)\cdot Y_{00}(\theta,\phi)$$

After normalizing

$$\psi_{n,0,0}=\sqrt{\frac{1}{2\pi a}}\frac{1}{r}\sin\left(\frac{n\pi r}{a}\right)$$

Q3. Given $V(r)=-V_0$, $r<a$

$=0$, $r>a$.

(a) The radial Differential Eq. in R is

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}R+\frac{2}{r}\frac{d}{dr}\right)+\left(V(r)+\frac{l(l+1)}{2mr^2}\right)R=ER$$

Thus for $r<a$.

(a) Interior Solution: $r<a$, $V(r) = \cancel{+}-V_0$.

Let $\alpha^2 = \frac{2m}{\hbar^2}(E+V_0) \geq 0$ if $|E| \leq V_0$. or $0 \geq E \geq -V_0$.

Let $\rho = \alpha r$. The radial Eq.

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2}\right)\right] R(\rho) = 0 \quad \text{———} \quad (1)$$

The sol^{ts} are

$$R_\ell^I(\rho) = A\, j_\ell(\rho) + B\, n_\ell(\rho)$$

since $R_\ell^I(0) < \infty \Rightarrow B = 0. \Rightarrow \boxed{R_\ell^I(\rho) = A\, j_\ell(\rho)}$

(b) Exterior Sol^{tn}: $r > a$, $V(r) = 0$.

Let $\beta^2 = -\frac{2mE}{\hbar^2}$ and $\rho = i\beta r$.

The radial Eq. is same as (1) above. The sol^{n} are

$$R_\ell^E(\rho) = C\, h_\ell^{(1)}(\rho) + D\, h_\ell^{(2)}(\rho)$$

$h_\ell^{(1)} = j_\ell + i n_\ell$ and $h_\ell^{(2)} = j_\ell - i n_\ell$ are called henkel fn

as $\rho \to \infty$ $\quad h_\ell^{(1)} \to e^{+i\rho}$ and $h_\ell^{(2)} \to e^{-i\rho}$

$\Rightarrow$ as $r \to \infty$ $\quad h_\ell^{(1)} \to e^{-\beta r}$ and $h_\ell^{(2)} \to e^{\beta r}$

Thus $D = 0$.

$$\boxed{R_\ell^E(\rho) = C\, h_\ell^{(1)}(\rho)}$$

(c) At Boundary $r = a$,

$$A\, j_\ell(\alpha a) = C\, h_\ell^{(1)}(i\beta a)$$

$$\alpha A\, j_\ell'(\alpha a) = C i\beta\, h_\ell^{(1)\prime}(i\beta a) \qquad \text{: The derivative w.r.t. } \underline{r}$$

$$\Rightarrow \quad \frac{\alpha\, j_\ell'(\alpha a)}{j_\ell(\alpha a)} = \frac{i\beta\, h_\ell^{(1)\prime}(i\beta a)}{h_\ell^{(1)}(i\beta a)}$$

(d) For $\ell = 0$.

$$j_0(\alpha a) = \frac{1}{\alpha a}\cdot \sin(\alpha a) \quad \text{and} \quad h_\ell^{(1)}(\cancel{\ell}\, i\beta a) = -\cancel{i}\frac{e^{-\beta a}}{\cancel{i}\beta a}$$

This gives us

$$\boxed{\alpha \cot(\alpha a) = -\beta}$$

Q4. Given

$$U(\rho,s) = \frac{1}{1-s}\exp\left[-\frac{\rho s}{1-s}\right] = \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q$$

(a) First

$$\frac{dU}{ds} = \frac{(1-s-\rho)}{(1-s)^2} U$$

$$\Rightarrow (1-s)^2 \sum_{q=0}^{\infty} \frac{L_q}{q!} q s^{q-1} = (1-s-\rho)\sum_{q=0}^{\infty} \frac{L_q}{q!} s^q$$

$$\Rightarrow \frac{L_{q+1}(\rho)}{q!} - \frac{2L_q}{(q-1)!} + \frac{L_{q-1}}{(q-2)!} = (1-\rho)\frac{L_q}{q!} - \frac{L_{q-1}}{(q-1)!}$$ Equating co-eff. of s^q.

$$\Rightarrow \boxed{L_{q+1}(\rho) + (\rho-1-2q)L_q(\rho) + q^2 L_{q-1}(\rho) = 0} \quad \text{——} (1)$$

(b) Verify $(1-s)\dfrac{dU}{d\rho} = -sU$

$$\Rightarrow (1-s)\sum_q \frac{1}{q!}\frac{dL_q}{d\rho} s^q = -s\sum_{q} \frac{L_q}{q!} s^q$$

$$\Rightarrow \frac{1}{q!}\frac{dL_q}{d\rho} - \frac{1}{(q-1)!}\frac{dL_{q-1}}{d\rho} = -\frac{L_{q-1}}{(q-1)!}$$

$$\Rightarrow \boxed{\frac{dL_q}{d\rho} - q\frac{d}{d\rho}L_{q-1} + q L_{q-1} = 0} \quad \text{——} (2)$$

(c) To prove DE, we will prove one more identity.

Note : $$\rho\frac{dU}{d\rho} = s\frac{\partial U}{\partial s} - s\frac{\partial}{\partial s}(sU)$$

$$\sum_q \frac{1}{q!}(\rho L_q')s^q = s\sum_q \frac{L_q}{(q-1)!} s^{q-1} - s\sum \frac{L_q}{q!}(q+1)s^q$$

$$\Rightarrow \frac{1}{q!}\rho L_q' = \frac{L_q}{(q-1)!} - \frac{q L_{q-1}}{(q-1)!}$$

$$\Rightarrow \boxed{\rho L_q' = q L_q - q^2 L_{q-1}}$$

(d) Differentiate (1) twice

$$L_{q+1}'' + (\rho - 1 - 2q) L_q'' + 2L_q' + q^2 L_{q-1}'' = 0$$

Replace $q \to q+1$

$$L_{q+2}'' + (\rho - 2q - 3) L_{q+1}'' + 2L_{q+1}' + (q+1)^2 L_q'' = 0 \quad \text{——} (5)$$

From (2)

$$L_{q+2}' = (q+2) L_{q+1}' - (q+2) L_{q+1}$$

$$\Rightarrow L_{q+2}'' = (q+2)\left[L_{q+1}'' - L_{q+1}'\right]$$

put in (5)

$$(\rho - q - 1) L_{q+1}'' - q L_{q+1}' + (q+1)^2 L_q'' = 0 \quad \text{——} (6)$$

From (2) Again

$$\left.\begin{aligned} L_{q+1}' &= (q+1)\left[L_q' - L_q\right] \\ L_{q+1}'' &= (q+1)\left[L_q'' - L_q'\right] \end{aligned}\right\} \text{——} (7)$$

$\Rightarrow$ Thus, by putting (7) into (6)

$$\Rightarrow \left[\rho \frac{d^2}{d\rho^2} + (1-\rho)\frac{d}{d\rho} + q\right] L_q = 0$$

▷ Problem 5:

– Given

$$U_p(x,s) = \frac{(-s)^p}{(1-s)^{p+1}} \exp\left[-x\frac{s}{1-s}\right] = \sum_{q=p}^{\infty} \frac{L_q^p(x)}{q!} s^q$$

– Given

$$\phi_{nlm}(r,\theta,\phi) \quad = \quad N\, R_{nl}(r) Y_{lm}(\theta,\phi)$$

where $R_{nl}(r) = N_{nl} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$. Since Y_{lm} is already normalized.,

$$\begin{aligned} \langle \phi_{nlm}, \phi_{nlm} \rangle &= N_{nl}^2 \int_0^\infty L_{n'+l}^{2l+1}(\rho) L_{n+l}^{2l+1}(\rho) e^{-\rho} \rho^{2l} r^2 dr \\ &= N_{nl}^2 \left(\frac{2Z}{na_0}\right)^{-3} \int_0^\infty L_{n'+l}^{2l+1}(\rho) L_{n+l}^{2l+1}(\rho) e^{-\rho} \rho^{2l} \rho^2 d\rho \end{aligned}$$

– To find the normalization constant, consider (sorry, i have used x in place of ρ below)

$$\begin{aligned} \int_0^\infty U_{2l+1}(x,s) U_{2l+1}(x,t) e^{-x} x^{2l} x^2 dx &= \sum_{q',q=2l+1}^{\infty} \frac{1}{q'!} \frac{1}{q!} s^{q'} t^q \int_0^\infty L_{q'}^{2l+1}(x) L_q^{2l+1}(x) e^{-x} x^{2l} x^2 dx \\ &= \sum_{n',n=l+1}^{\infty} \frac{1}{(n'+l)!} \frac{1}{(n+l)!} s^{n'+l} t^{n+l} \int_0^\infty L_{n'+l}^{2l+1}(x) L_{n+l}^{2l+1}(x) e^{-x} x^{2l} x^2 dx \end{aligned}$$

– Consider the lhs: let $p = 2l+1$.

$$\begin{aligned} & \int_0^\infty U_{2l+1}(x,s) U_{2l+1}(x,t) e^{-x} x^{2l} x^2 dx \\ =\ & \frac{(st)^p}{[(1-s)(1-t)]^{p+1}} \int_0^\infty \exp\left[-x\frac{(1-st)}{(1-s)(1-t)}\right] x^{p+1} dx \\ =\ & \frac{(st)^p (1-s)(1-t)}{[(1-st)]^{p+2}} \int_0^\infty \exp[-y]\, y^{p+1} dy \\ =\ & (st)^p (1-s)(1-t) \sum_{q=0}^{\infty} \frac{(p+1+q)!}{(p+1)!q!} (st)^q (p+1)! \\ =\ & \sum_{q=0}^{\infty} \frac{(p+1+q)!}{q!} (st)^{q+p} + \sum_{q=0}^{\infty} \frac{(p+1+q)!}{q!} (st)^{q+p+1} - (s+t)(\cdots) \\ =\ & \sum_{n=l+1}^{\infty} \frac{(n+l+1)!}{(n-l-1)!} (st)^{n+l} + \sum_{n=l+2}^{\infty} \frac{(n+l)!}{(n-l-2)!} (st)^{n+l} - (s+t)(\cdots) \\ =\ & \frac{(2l+2)!}{1} (st)^{2l+1} + \sum_{n=l+2}^{\infty} \frac{(n+l)!}{(n-l-1)!} [2n] (st)^{n+l} - (s+t)(\cdots) \end{aligned}$$

Now comparing the coefficients of $(st)^{n+l}$ we get,

$$\begin{aligned} \frac{1}{[(n+l)!]^2} \int_0^\infty L_{n'+l}^{2l+1}(x) L_{n+l}^{2l+1}(x) e^{-x} x^{2l} x^2 dx &= \frac{(n+l)!}{(n-l-1)!} [2n] \\ \int_0^\infty L_{n'+l}^{2l+1}(x) L_{n+l}^{2l+1}(x) e^{-x} x^{2l} x^2 dx &= \frac{2n\,[(n+l)!]^3}{(n-l-1)!} \end{aligned}$$

Thus

$$N_{ln} = \left\{ \left(\frac{2Z}{na_0}\right)^{-3} \frac{(n-l-1)!}{2n\,[(n+l)!]^3} \right\}^{1/2}$$

– Now,

$$\int_0^\infty U_{2l+1}(x,s)U_{2l+1}(x,t)e^{-x}x^{2l+1}x^2dx = \sum_{q',q=2l+1}^{\infty}\frac{1}{q'!}\frac{1}{q!}s^{q'}t^q\int_0^\infty L_{q'}^{2l+1}(x)L_q^{2l+1}(x)e^{-x}x^{2l+1}x^2dx$$
$$= \sum_{n',n=l+1}^{\infty}\frac{1}{(n'+l)!}\frac{1}{(n+l)!}s^{n'+l}t^{n+l}\int_0^\infty L_{n'+l}^{2l+1}(x)L_{n+l}^{2l+1}(x)e^{-x}x^{2l+1}$$

– Consider the lhs: let $p = 2l+1$.

$$\begin{aligned}
&\int_0^\infty U_{2l+1}(x,s)U_{2l+1}(x,t)e^{-x}x^{2l+1}x^2dx\\
&= \frac{(st)^p}{[(1-s)(1-t)]^{p+1}}\int_0^\infty \exp\left[-x\frac{(1-st)}{(1-s)(1-t)}\right]x^{p+2}dx\\
&= \frac{(st)^p(1-s)^2(1-t)^2}{[(1-st)]^{p+3}}\int_0^\infty \exp[-y]\,y^{p+2}dy\\
&= (st)^p(1-s)^2(1-t)^2\sum_{q=0}^{\infty}\frac{(p+2+q)!}{(p+2)!q!}(st)^q(p+2)!\\
&= \sum_{q=0}^{\infty}\frac{(p+2+q)!}{q!}(st)^{q+p} + 4\sum_{q=0}^{\infty}\frac{(p+2+q)!}{q!}(st)^{q+p+1}\sum_{q=0}^{\infty}\frac{(p+2+q)!}{q!}(st)^{q+p+2} + (\cdots)\\
&= \sum_{n=l+1}^{\infty}\frac{(n+l+2)!}{(n-l-1)!}(st)^{n+l} + 4\sum_{n=l+2}^{\infty}\frac{(n+l+1)!}{(n-l-2)!}(st)^{n+l} + \sum_{n=l+2}^{\infty}\frac{(n+l)!}{(n-l-3)!}(st)^{n+l} + (\cdots)\\
&= (\cdots) + \sum_{n=l+3}^{\infty}\frac{(n+l)!}{(n-l-1)!}\left(2n^2\right)\left[3-\frac{l(l+1)}{n^2}\right](st)^{n+l} + (\cdots)
\end{aligned}$$

Now comparing the coefficients of $(st)^{n+l}$ we get,

$$\frac{1}{[(n+l)!]^2}\int_0^\infty L_{n'+l}^{2l+1}(x)L_{n+l}^{2l+1}(x)e^{-x}x^{2l+1}x^2dx = \frac{(n+l)!}{(n-l-1)!}\left(2n^2\right)\left[3-\frac{l(l+1)}{n^2}\right]$$
$$\int_0^\infty L_{n'+l}^{2l+1}(x)L_{n+l}^{2l+1}(x)e^{-x}x^{2l+1}x^2dx = \frac{2n^2\left[(n+l)!\right]^3}{(n-l-1)!}\left[3-\frac{l(l+1)}{n^2}\right]$$

– Thus average value of r is

$$\begin{aligned}
\langle r\rangle_{nlm} = \langle\phi_{nlm}, r\phi_{nlm}\rangle &= N_{nl}^2\int_0^\infty L_{n'+l}^{2l+1}(\rho)L_{n+l}^{2l+1}(\rho)e^{-\rho}\rho^{2l}r^3dr\\
&= N_{nl}^2\left(\frac{2Z}{na_0}\right)^{-4}\int_0^\infty L_{n'+l}^{2l+1}(\rho)L_{n+l}^{2l+1}(\rho)e^{-\rho}\rho^{2l+1}\rho^2d\rho\\
&= \frac{n^2a_0}{z}\left[\frac{3}{2}-\frac{l(l+1)}{2n^2}\right]
\end{aligned}$$

▷ Problem 6

– Energy $E_n = -13.6/n^2$.
– Statistical Probability of finding the particle in nth level

$$P_n = g(E_n)e^{-E_n/kT}$$

where $g(E_n)$ is degeneracy of nth level.
– Thus

$$P_2/P_1 = 4\exp\left[-\frac{E_2-E_1}{kT}\right]$$

which at room temperature will be $4e^{-408} \approx 0$.

▷ Problem 7

– Given

$$\Psi = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{3/2} \exp\left[-\frac{\alpha^2 r^2}{2}\right]$$

and

$$\phi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a}\right)^{3/2} \exp\left(-\frac{r}{a}\right)$$

– The required probability

$$\begin{aligned} &= |\langle \phi_{100}, \Psi \rangle|^2 \\ &= \int_0^\infty 4\pi r^2 dr \phi_{100}(r)\Psi(r) \\ &= \frac{1}{\pi^{5/4}(a\alpha)^{7/2}}\left\{-4a\alpha\sqrt{\pi} + 2\pi\sqrt{2}\left(e^{\frac{1}{2a^2\alpha^2}} - 1\right)\right\} \end{aligned}$$