54. Using the final expressions for the internal part of the wavefunction of the hydrogen atom (that is we are not including the center of mass portion here) the lower energy states of the hydrogen atom have the following functional forms:

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \exp\left[-r/a_0\right] \tag{20.64}$$

$$\psi_{2s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{2a_0}\right) \exp\left[-Zr/(2a_0)\right] \tag{20.65}$$

$$\psi_{2p_{m=-1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r \exp\left[-Zr/(2a_0)\right] \sin\theta \exp\left(-\imath\phi\right) \tag{20.66}$$

$$\psi_{2p_{m=0}} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{5/2} r \exp\left[-Zr/(2a_0)\right] \cos\theta \tag{20.67}$$

$$\psi_{2p_{m=1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r \exp\left[-Zr/(2a_0)\right] \sin\theta \exp\left(\imath\phi\right) \tag{20.68}$$

The p-orbitals all have the same energy since the energy of the Hydrogen atom does not depend on the l quantum number. Hence $\psi_{2p_{m=-1}}$, $\psi_{2p_{m=0}}$ and $\psi_{2p_{m=1}}$ are degenerate states. It is $\psi_{2p_{m=0}}$ that is called the ψ_{2p_z} state. The ψ_{2p_x} and ψ_{2p_y} states are actually linear combinations of $\psi_{2p_{m=-1}}$ and $\psi_{2p_{m=1}}$. And since these are degenerate states ψ_{2p_x} and ψ_{2p_y} are eigen-kets that have the same energy as $\psi_{2p_{m=-1}}$ and $\psi_{2p_{m=1}}$. *But notice that* ψ_{2p_x} *and* ψ_{2p_y} *are not eigenstates of* $\mathbf{L_z}$ *anymore.*

55. **Generating functions**: We went through some detail here but did not quite derive everything. Now, if we want to write down the solution to the hydrogen atom for any given state (for example 5p$_{+1}$), how do we do that? Is there a way to directly write down the solution without bothering to do the derivation as we now have a general idea as to how things are derived? Turns out yes. And here we introduce what are known as generating functions for the various polynomials that form the solutions to the hydrogen atom. As the name suggests generating functions are simple functions that may be used to *generate* these solutions.

56. As noted earlier, the solution to the hydrogen atom for the internal degrees of freedom is given by

$$\exp\left[-\rho/2\right]\rho^{l}F(\rho)\mathcal{Y}(\theta,\phi) \tag{20.69}$$

where $F(\rho)$ are proportional to the Laguerre polynomials and

$$\mathcal{Y}(\theta,\phi)\propto\mathcal{P}_{l,m}(\cos\theta)\exp\left\{\imath m\phi\right\} \tag{20.70}$$

where $\mathcal{P}_{l,m}(\cos\theta)$ are the associated Legendre polynomials. Hence if we know how to write down the Legendre polynomials and the Laguerre polynomials for arbitrary n, l, m, we can write down the solution of the hydrogen atom for any orbital!! So how do we do this?

(a) Turns out the following mathematical relations hold and these help us to write down the solutions for any general orbital that we need.

$$\begin{aligned}\mathcal{P}_{l,m}(z) &= \frac{1}{2^l l!}\sqrt{\frac{(2l+1)}{2}\frac{(l-|m|)!}{(l+|m|)!}} \\ &\quad \left(1-z^2\right)^{(|m|/2)} \frac{d^{(l+|m|)}\left(z^2-1\right)^l}{dz^{(l+|m|)}} \qquad (20.71)\\ \mathcal{L}_{n,l}(\rho) &= \frac{d^{2l+1}}{d\rho^{2l+1}}\left[\exp\left(\rho\right)\frac{d^{n+l}\left(\rho^{n+l}\exp\left(-\rho\right)\right)}{d\rho^{n+l}}\right] \qquad (20.72)\end{aligned}$$

and $F(\rho) = \mathcal{L}_{n,l}(\rho)/\rho$.

(b) **Volume Element:** We discussed earlier how we can transform a general Laplacian in Cartesian coordinates to any other coordinate system (for example the spherical coordinate system). In addition to the Laplacian there turns out another quantity that one needs when transforming coordinate systems. This is known as the volume element. Remember that when you perform a one-dimensional integration what you do is multiply the integrand with a quantity, dx. This quantity is dx is a one-dimensional "measure" or *length element* along the x direction. Similarly when you perform the three-dimensional integration what we do is multiply by a three-dimensional *volume element*, $dxdydz$. But this is the volume element in Cartesian coordinates. What does one do if we needed this is spherical coordinates? We need to transform the volume element to the new coordinate system. Using the definitions for the spherical coordinates in Eq. (19.73) it turns out that the volume element in spherical coordinates is given as:

$$r^2 dr \sin\theta d\theta d\phi \tag{20.73}$$

But is there a way we could do this in a general fashion using the definition of the metric tensor we introduced earlier? Turns out yes and the general expression is:

$$dv = \sqrt{g} du_1 du_2 du_3 \tag{20.74}$$

where g is the determinant of the metric tensor as seen earlier. We recall from Eqs. (20.22) that $\sqrt{g} = r^2 \sin\theta$, which proves Eq. (20.73).

(c) As a special case of the volume element in Eq. (20.73) we write what is a spherical shell element. This volume element does not depend on θ and ϕ can be used when the integrand does not have angular dependence. This is for example the case if one were to find the expectation value of position with respect to the 1s orbital:

$$\begin{aligned}
\left\langle \psi_{1s} \left| r \right| \psi_{1s} \right\rangle &= \int r^2 dr \sin\theta d\theta d\phi \left[\frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 \exp\left[-2r/a_0 \right] r \right] \\
&= \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 \left[\int_0^\infty r^3 \exp\left[-2r/a_0 \right] dr \right] \left[\int_0^\pi sin\theta d\theta \right] \left[\int_0^{2\pi} d\phi \right] \\
&= \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 \left[\int_0^\infty r^3 \exp\left[-2r/a_0 \right] dr \right] 4\pi \qquad (20.75)
\end{aligned}$$

This is how you integrate to obtain an expectation value. In general, of course, The integrand may depend on θ and ϕ. But if not the problem can be Simplified as shown above.

(d) **Homework:** Calculate the expectation value of position for the ground electronic state (1s). Compare this expectation value to the Bohr radius. What is the probability of finding the electron inside a sphere $r < a_0$?

(e) **Homework:** Derive relations for $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$ and $\langle p^2 \rangle$ for the 2p$_{+1}$ orbital of the hydrogen atom and use this to obtain the uncertainty product.

(f) **Homework:** Using the energy expression, calculate the ground state energy of the hydrogen atom.