Chapter 1

The hydrogen atom

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The hydrogen atom is a three-dimensional system so crucial to our understanding of physical reality, that it deserves a special place in all annals of quantum mechanics. First, it's simple. It's just an electron bound by the pull of a proton. Second, other atoms and molecules can be build upwards from the lessons taught by hydrogen. Atomic and molecular physics thus start with an understanding of hydrogen. Third, one can begin to decipher the intricacies of spectroscopy by mastering the quantum structure of hydrogen.

The time independent Schrodinger equation is defined by the Hamiltonian $\hat{\mathcal{H}}$ acting on an eigenstate $|\psi\rangle_n$ yielding an eigenvalue E_n,

$$\hat{\mathcal{H}} |\psi_n\rangle = E_n |\psi_n\rangle . \tag{1.1}$$

Solving the Schrodinger equation means finding the eigenenergies and eigenstates. That's what we set to do for the hydrogen atom. In Cartesian space, it is useful to describe a quantum state in either the position or the momentum basis, for example by expressing the eigenstate in position basis,

$$\langle \vec{r} | \psi_n \rangle = \psi_n(\vec{r}). \tag{1.2}$$

yields the wavefunction where it is also customary to express the position vector in terms of polar coordinates

$$|\vec{r}\rangle \triangleq |r, \theta, \phi\rangle . \tag{1.3}$$

Don't forget that the full Schrodinger equation is

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{\mathcal{H}} |\psi(t)\rangle , \tag{1.4}$$

and includes a time dependent part too. We will deal with time dependence as well.

The hydrogen atom as we all know has a proton with charge $+e$ and an electron with charge $-e$ separated by distance $\vec{r}$. But truly so, in the quantum mechanical world it is uncalled for to think of the electron as a particle located at some position, since the electron is best described by a wavefunction that is spread everywhere in space. The most one can do is to write the quantum state for the electron, perhaps write a wavefunction and it is only the modulus square of the wavefunction that provides probability densities informing the inquirer where the electron can probably be found when an attempt to is made to find where it is! So let's stop thinking of the location of the electron, rather consider where we can catch it to be, during a particular measurement run.

If an electron sees a proton, as it does in the hydrogen atom, what kind of eigenstates does it possess and what are the corresponding eigenenergies? The eigenenergies have a "normalness" to the hydrogen atom. The analogy is quite straightforward. When a mass m is attached to a spring with spring constant k it has a normal mode with a normal or natural frequency $\omega_o = \sqrt{k/m}$ which provides a measure of the natural energy. It is exactly in this sense that the hydrogen atom has some natural energies. The eigenstates associated with these natural energies will be stationary states. Let's for now call these stationary states "orbits". An electron in orbit remains there, neither absorbing nor emitting energy; unless some disturbance to the Hamiltonian takes place.

However if the electron is in a superposition of orbits, say

$$|\psi\rangle = a\,|\psi_1\rangle + b\,|\psi_2\rangle \tag{1.5}$$

then $|\psi\rangle$ will in general not be a stationary state, except when $|\psi_1\rangle$ and $|\psi_2\rangle$ are degenerate with identical eigenvalues. Suppose $|\psi_1\rangle$ and $|\psi_2\rangle$ have eigenenergies λ_1 and λ_2, i.e

$$\begin{aligned} \hat{\mathcal{H}}\,|\psi_1\rangle &= \lambda_1\,|\psi_1\rangle\,, \text{ and} \qquad (1.6)\\ \hat{\mathcal{H}}\,|\psi_2\rangle &= \lambda_2\,|\psi_2\rangle \qquad (1.7)\end{aligned}$$

allowing us to write the action of the Hamiltonian, on Eq. (1.5)

$$\begin{aligned} \hat{\mathcal{H}}\,|\psi\rangle &= \hat{\mathcal{H}}\big(a\,|\psi_1\rangle + b\,|\psi_2\rangle\big) \qquad (1.8)\\ &= a\lambda_1\,|\psi_1\rangle + b\lambda_2\,|\psi_2\rangle \qquad (1.9)\\ &\neq c\big(a\,|\psi_1\rangle + b\,|\psi_2\rangle\big) \qquad (1.10)\end{aligned}$$

indicating that the superposition of eigenstates will be an eigenstate only when we can write Eq. (1.9) as Eq. (1.10) which happens only when $\lambda_1 = \lambda_2 = c$. A superposition of orbits, is therefore another orbit only if the component orbits possess identical energies. In the next section, we begin the process of determining these orbits. This requires us to solve the Schrodinger equation Eq. (1.1).

1.1 Solving the Schrodinger equation for the hydrogen atom

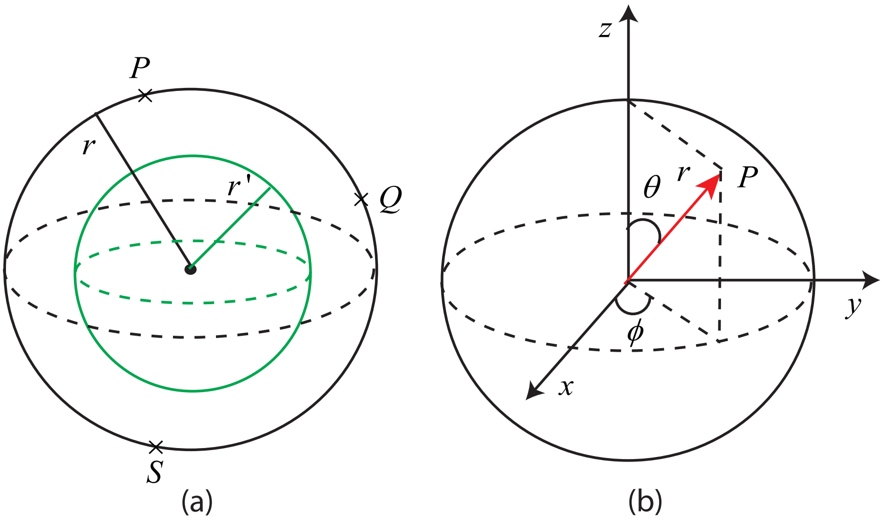

Figure 1.1: (a) Spherical symmetry of the electronic potential inside the hydrogen atom. The potential energy is uniform on a radius r and on any other radius r'. (b) Since there is spherical symmetry it is worthwhile using polar coordinates (r, θ, ϕ). Point P is at distance r from the origin. When P is projected on the xy plane the azimuthal angle ϕ varies from 0 to 2π. The angle θ between the positive z-axis and P is the angle of colatitude or polar angle and varies from 0 to π.

We begin by proposing the Hamiltonian for the hydrogen atom. First of all, think about the forces acting on the electron? The Coulombic interaction between the electron and the proton is the force which causes potential energy,

$$V(r) = -\frac{e^2}{4\pi\varepsilon_o r}, \tag{1.11}$$

where ε_o is the permittivity of free space and r is the distance from the proton. The potential energy drops as $1/r$. The electron also possesses momentum which has the three components $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$. Therefore we can write the total Hamiltonian as,

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \hat{V}(\vec{r}) = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} - \frac{e^2}{4\pi\varepsilon_o r} \tag{1.12}$$

where m is the mass of electron. The momentum tells how fast the electron is moving, while the potential energy tells where the electron can be found with respect to the nucleus in some measurement, but remember that really we should

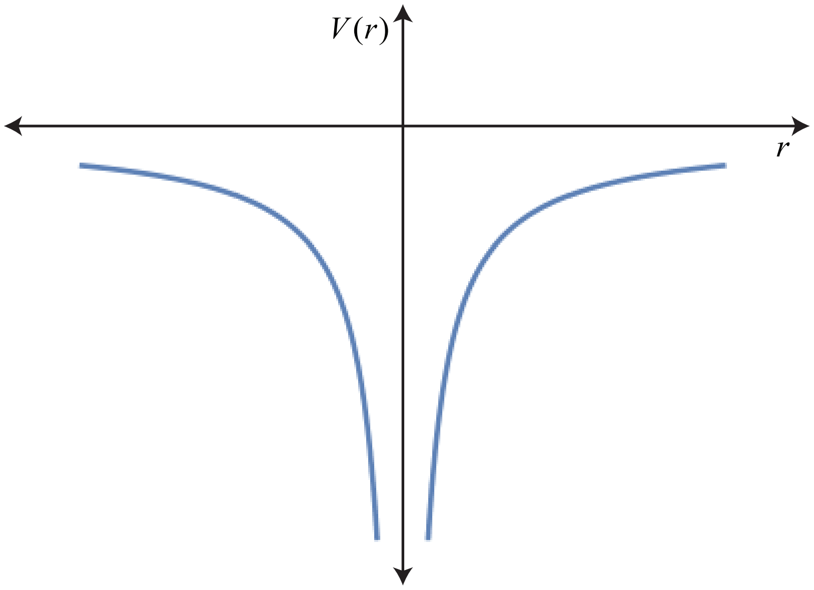

Figure 1.2: Central potential for the hydrogen atom.

rest aside our conventional notation of a “moving” electron or an electron that is “located somewhere”. The potential term does not depend on the precise location on a sphere of fixed radius r, therefore points P, Q and S in Figure 1.1 (a) have the same potential energy. However if we take another sphere with radius r' concentric to sphere of radius r, the potential energy does change across the spheres. This means the potential energy is spherically symmetric independent of angular orientation (θ, ϕ) and dependent exclusively on radius r.

In these situations, it is useful to employ a coordinate system that respects this spherical symmetry. Instead of Cartesian coordinates x, y and z, one uses the polar coordinates r, θ and ϕ, which are defined in Figure 1.1 (b). The spherically symmetric potential is called a central potential since the strength of interaction depends only on the electron-nucleus distance. As shown in Figure 1.2 the energy gets lower as the electron gets closer to the nucleus. It is natural to ask why doesn’t the electron fall right into the nucleus, squishing the atom to dimensions of the nucleus? In fact, the uncertainty principle doesn’t let that happen. If one were to confine the electron to a small region of space, Δr, the uncertainty in momentum, Δp, becomes really large. According to the uncertainty principle,

$$\Delta r \Delta p \geq \hbar \tag{1.13}$$

$$\Delta p \geq \frac{\hbar}{\Delta r} = \frac{\hbar}{a_o}, \tag{1.14}$$

where we have chosen the Bohr radius[1] a_o as a measure of Δr. Since uncertainty in momentum is large, the momentum must also be large and at least as big as the uncertainty in momentum,

$$p_{\min} \geq \Delta p = \frac{\hbar}{a_o} \tag{1.15}$$

indicating that the minimum energy must be

$$E_{\min} = \frac{(\Delta p)^2}{2m} \geq \frac{\hbar^2}{2ma_o^2} \approx 13.6 \text{ eV}. \tag{1.16}$$

This puts a lower limit on the energy. This phenomenon can be imagined as an outward pressure due to the uncertainty principle. A similar effect also manifests in neutron stars wherein due to the extreme density of the star, the neutrons are confined to a very small space, which results in a large uncertainty in their momentum imparting an outward degeneracy pressure that may also result in a supernova explosion.

We now attempt to write the Hamiltonian in Eq. (1.12) in the position basis, while being represented in polar coordinates. The momentum in the position basis is

$$\langle\vec{r}|\,\hat{p}_x = -i\hbar\frac{\partial}{\partial x}; \quad \langle\vec{r}|\,\hat{p}_y = -i\hbar\frac{\partial}{\partial y}; \quad \langle\vec{r}|\,\hat{p}_z = -i\hbar\frac{\partial}{\partial z}. \tag{1.17}$$

whose square becomes

$$\langle r|\,\hat{p}^2 = -(i\hbar)^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\hbar^2\vec{\nabla}^2, \tag{1.18}$$

with $\vec{\nabla}^2$ being the Laplacian operator which in itself is a scalar,

$$\vec{\nabla}^2 = \vec{\nabla}.\vec{\nabla} = \left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right).\left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right) \tag{1.19}$$

since it is the dot product of the gradient operator $\vec{\nabla}$ with itself. The time independent three-dimensional Schrodinger equation therefore becomes

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right)\psi_i(\vec{r}) = E_i\psi_i(\vec{r}). \tag{1.20}$$

The subscript i is introduced to allow for labeling of the various eigenfunctions. We notice later that these indexes are a quantum number. We write the operator

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[1] The value of a_o is 5.29×10^{-11} m and can be determined by applying methods described later in this chapter.

$\vec{\nabla}^2$, in term of polar coordinates,

$$\left[-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}-\frac{e^2}{4\pi\varepsilon_o r}\right]\psi_i(\vec{r})=E_i\psi_i(\vec{r}). \tag{1.21}$$

All terms in curly brackets are merely the Laplacian operator in spherical coordinates. All terms in square brackets acting on $\psi_i(\vec{r})$ produce the energy when they act on the eigenfunction. For a moment we are going to suppress the index i in $\psi_i(\vec{r})$, reintroducing it later. Eq. (1.21) is a partial differential equation and we assume a trial solution,

$$\Psi(\vec{r})=\psi(r,\theta,\phi)\triangleq R(r)\Theta(\theta)\Phi(\phi)=R\Theta\Phi \tag{1.22}$$

which is the product of a function R that depends only on r, a function Θ that depends only on θ and a function Φ that depends only on ϕ. Inserting the ansatz into the Schrodinger equation,

$$\begin{aligned}&-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R\Theta\Phi+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)R\Theta\Phi+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}R\Theta\Phi\right\}\\&+VR\Theta\Phi=ER\Theta\Phi,\end{aligned} \tag{1.23}$$

and dividing both sides by $R\Theta\Phi$,

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{Rr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right\}+(V-E)=0, \tag{1.24}$$

followed by multiplying both sides of the equation with $2mr^2\sin^2\theta/\hbar^2$

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}\right\}+r^2\sin^2\theta\frac{2m}{\hbar^2}(V-E)=0 \tag{1.25}$$

The first term and the fourth term above depend on r and θ, the second term depends only on θ and the third terms depends only on ϕ.

1.1.1 Solving the azimuthal part

The azimuthal term $-(1/\Phi)\partial^2\Phi/\partial\phi^2$ is really simple to handle since it is completely independent of r and θ, and so we tackle it first. We move it to the R.H.S. of Eq. (1.25) yielding,

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-\frac{2mr^2\sin^2\theta}{\hbar^2}(V-E)=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}. \tag{1.26}$$

Since the R.H.S now depends exclusively on ϕ and the L.H.S. exclusively on distinct variables, r and θ, each side must be equal to an identical constant, say C. Therefore

$$-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} = C \tag{1.27}$$

which upon rearrangement gives the differential equation

$$\frac{d^2\Phi(\phi)}{d\phi^2} + C\Phi(\phi) = 0$$

whose solution is proportional to,

$$\Phi(\phi) = Ae^{i\sqrt{C}\phi} + \cancel{Be^{-i\sqrt{C}\phi}}, \tag{1.28}$$

where A and B are normalization constants. Wait a minute as we prove that the B containing term is not really needed. This is a 3D problem, so it is inconvenient to normalize each function separately. It suffices to normalize the angular part $\Theta(\theta)\Phi(\phi)$ separately and R separately and multiply these parts together in the end. Therefore the unnormalized azimuthal part of the wavefunction is

$$\Phi(\phi) = e^{i\sqrt{C}\phi}, \tag{1.29}$$

and has the property that if one rotates ϕ by 2π or multiples thereof, the wave function does not change,

$$\Phi(\phi + 2\pi n) = e^{i\sqrt{C}(\phi+2\pi n)} = e^{i\sqrt{C}\phi}e^{i\sqrt{C}2\pi n} = e^{i\sqrt{C}\phi} \tag{1.30}$$

indicating that $e^{i\sqrt{C}2\pi n}$ must be equal to 1.

$$\begin{aligned} e^{i\sqrt{C}2\pi n} &= e^{i2\pi k} = 1, \text{ or that} \\ C &= \left(\frac{k}{n}\right)^2 \end{aligned} \tag{1.31}$$

where k and n are integers and since this must hold true for $n = 1$, we have

$$C = k^2 = m_l^2. \tag{1.32}$$

The variable k is an integer and we have denoted it by m_l. Therefore the azimuthal solution (unnormalized is)

$$\Phi(\phi) = e^{im_l\phi}, \qquad m_l \in \mathbb{Z}. \tag{1.33}$$

We were justified in ignoring the $Be^{-i\sqrt{C}\phi}$ term in Eq. (1.28) because it is subsummed in Eq. (1.33) when m_l is a negative integer; so Eq. (1.33) is a sufficient solution when m_l is allowed to take both positive and negative integer values. We notice that we constrained the value of m_l by evoking the property of uniqueness of the wave function. The consequence is that m_l is an integer $0, \pm 1, \pm 2, \ldots$. Additional constraints on m_l will emerge as we explore further. If m_l changes, the wavefunction changes, hence we denote the wavefunction as $\Phi_{m_l}(\phi)$. The number m_l is called the magnetic quantum number. The index i that we suppressed in $\psi_i(r)$ is a combination in fact, of three quantum numbers, not just m_l, as we show shortly. We have now solved the azimuthal part and move onto the polar part.

1.1.2 Solving the polar part

We start by Eq. (1.26), divide both sides by $\sin^2\theta$ and take all the angular terms to the R.H.S, leaving us with

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left(V - E\right) = -\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}. \tag{1.34}$$

where from Eqs.(1.27) and (1.33) we also have

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left(V - E\right) = -\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{m_l^2}{\sin^2\theta}. \tag{1.35}$$

Furthermore, using an argument similar to what preceded Eq. (1.27), each side of the equation must be equal to a constant that we call $l(l+1)$. Therefore, we obtain

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left(V - E\right) = -\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{m_l^2}{\sin^2\theta} = l(l+1). \tag{1.36}$$

It will become clear later why we write this constant in this rather unusual form of a number multiplied by that number +1.

Eq. (1.36) is a differential equation for the polar part. Multiplying Eq. (1.36) by Θ, and putting a minus sign on both sides gives us an equation for polar part,

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m_l^2\Theta}{\sin^2\theta} = -l(l+1)\Theta, \tag{1.37}$$

which is then slightly rearranged to produce

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta = 0. \tag{1.38}$$

Using the chain rule for differentiation,

$$\frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta} + \frac{d^2\Theta}{d\theta^2} + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta = 0. \tag{1.39}$$

Multiplying by $\sin^2\theta$ we obtain

$$\sin\theta\cos\theta\frac{d\Theta}{d\theta}+\sin^2\theta\frac{d^2\Theta}{d\theta^2}+\left(l(l+1)\sin^2\theta-m_l^2\right)\Theta=0. \tag{1.40}$$

In order to solve Eq. (1.40), we implement a series of substitutions, the first being $\Theta(\theta)=P(z)$ where

$$z=\cos\theta \tag{1.41}$$

which leads to the relations,

$$\begin{aligned}\sin\theta &= \sqrt{1-z^2} && (1.42)\\ \frac{dz}{d\theta} &= -\sin\theta && (1.43)\\ \frac{d\sin\theta}{dz} &= -\frac{z}{1-z^2}. && (1.44)\end{aligned}$$

These identification will come in handy in subsequent steps. Next, we use the chain rule to compute,

$$\begin{aligned}\frac{d\Theta}{d\theta} &= \frac{d\Theta}{dz}\frac{dz}{d\theta}=-\frac{dP}{dz}\sin\theta, \quad \text{yielding} && (1.45)\\ \frac{dP}{dz} &= -\frac{1}{\sin\theta}\frac{d\Theta}{d\theta}. && (1.46)\end{aligned}$$

In the next step, let's find the second derivative of $\Theta(\theta)$ with respect to θ expressing it in terms of $P(z)$ and z,

$$\begin{aligned}\frac{d^2\Theta}{d\theta} &= \frac{d}{d\theta}\left(\frac{d\Theta}{d\theta}\right) && (1.47)\\ &= \frac{d}{d\theta}\left(-\frac{dP}{dz}\sin\theta\right) && (1.48)\\ &= \frac{d}{dz}\left(-\frac{dP}{dz}\sin\theta\right)\frac{dz}{d\theta} && (1.49)\\ &= \sin\theta\frac{d}{dz}\left(\frac{dP}{dz}\sin\theta\right) && (1.50)\end{aligned}$$

where we have used Eq. (1.43) in writing the last step above. From this we obtain

$$\frac{d^2\Theta}{d\theta}=\sin^2\theta\frac{d^2P}{dz^2}+\sin\theta\frac{dP}{dz}\frac{d}{dz}\sin\theta, \tag{1.51}$$

and upon inserting results from Eq. (1.42) and (1.44), we arrive at,

$$\frac{d^2\Theta}{d\theta}=\left(1-z^2\right)\frac{d^2P}{dz^2}-z\frac{dp}{dz}. \tag{1.52}$$

From Eqs.(1.41), (1.43) and (1.52) the polar equation Eq. (1.40) has been fully recast in terms of P and z,

$$\big(1-z^2\big)^2\frac{d^2P}{dz^2}-2\big(1-z^2\big)z\frac{dP}{dz}+\Big(\big(1-z^2\big)l\big(l+1\big)-m_l^2\Big)P=0, \tag{1.53}$$

which upon division by $(1-z^2)$ becomes

$$\big(1-z^2\big)\frac{d^2P}{dz^2}-2z\frac{dP}{dz}+\left(l\big(l+1\big)-\frac{m_l^2}{\big(1-z^2\big)}\right)P=0. \tag{1.54}$$

This is the historically famous Legendre equation and can be written in the compact form,

$$\frac{d}{dz}\left(\big(1-z^2\big)\frac{dP}{dz}\right)+\left(l\big(l+1\big)-\frac{m_l^2}{\big(1-z^2\big)}\right)P=0 \tag{1.55}$$

and can be solved by a standard power series method. At this juncture, we throw in another function $G(z)$ to the mix, which is defined by

$$P(z)=(1-z^2)^{|m_l|/2}G(z). \tag{1.56}$$

Differentiating this by parts gives,

$$\begin{align}
\frac{dP}{dz} &= \frac{|m_l|}{2}\big(1-z^2\big)^{\left(\frac{|m_l|}{2}-1\right)}(-2z)G(z)+(1-z^2)^{\frac{|m_l|}{2}}G'(z) \tag{1.57}\\
&= -|m_l|z\big(1-z^2\big)^{\left(\frac{|m_l|}{2}-1\right)}G(z)+(1-z^2)^{\frac{|m_l|}{2}}G'(z), \tag{1.58}
\end{align}$$

where $G'(z)$ is the first derivative of $G(z)$. Multiplying both sides by $(1-z^2)$,

$$\big(1-z^2\big)\frac{dP}{dz}=-|m_l|z\big(1-z^2\big)^{\frac{|m_l|}{2}}G(z)+(1-z^2)^{\left(\frac{|m_l|}{2}+1\right)}G'(z). \tag{1.59}$$

Now differentiating both sides with respect to z finally results in

$$\begin{align}
\frac{d}{dz}\left(\big(1-z^2\big)\frac{dP}{dz}\right) &= -|m_l|\big(1-z^2\big)^{\frac{|m_l|}{2}}G(z)+|m_l|^2z^2\big(1-z^2\big)^{\left(\frac{|m_l|}{2}-1\right)}G(z)\\
&\quad -|m_l|z\big(1-z^2\big)^{\frac{|m_l|}{2}}G'(z)-2z\left(\frac{|m_l|}{2}+1\right)(1-z^2)^{\frac{|m_l|}{2}}G'(z)\\
&\quad +(1-z^2)^{\left(\frac{|m_l|}{2}+1\right)}G''(z), \tag{1.60}
\end{align}$$

where double and triple primes show the order of differentiation. Inserting the value of $P(z)$ and Eq. (1.60) into Eq. (1.55) (which is written here again for convenience) presents us with the form

$$\begin{aligned} & \frac{d}{dz}\left(\left(1-z^2\right)\frac{dP}{dz}\right)+\left(l\left(l+1\right)-\frac{m_l^2}{\left(1-z^2\right)}\right)P(z) \\ = \; & (1-z^2)^{\left(\frac{|m_l|}{2}+1\right)}G''(z) \\ & +\left(-|m_l|z\left(1-z^2\right)^{\frac{|m_l|}{2}}-2z\left(\frac{|m_l|}{2}+1\right)(1-z^2)^{\frac{|m_l|}{2}}\right)G'(z) \\ & +\left(|m_l|^2z^2\left(1-z^2\right)^{\left(\frac{|m_l|}{2}-1\right)}-|m_l|\left(1-z^2\right)^{\frac{|m_l|}{2}}\right)G(z) \\ & +\left(l\left(l+1\right)-\frac{m_l^2}{\left(1-z^2\right)}\right)(1-z^2)^{|m_l|/2}\right)G(z)=0, \qquad (1.61) \end{aligned}$$

which is divided by $(1-z^2)^{\frac{|m_l|}{2}}$ producing the result

$$(1-z^2)G''(z)-\left(2|m_l|z+2z\right)G'(z)+\left(l\left(l+1\right)-|m_l|-|m_l|^2\right)G(z)=0. \qquad (1.62)$$

This is finally the new equation we set to solve. We find a $G(z)$ that solves Eq. (1.62) and back substitute it to find $P(z)$ through Eq. (1.56) and ultimately $\Theta(\theta)$.

Suppose $G(z)$ is a power series (a polynomial in z),

$$G(z)=\sum_{n=0}^{\infty}a_z z^n \qquad (1.63)$$

thus we have the derivatives,

$$\begin{aligned} G'(z) &= \sum_{n=0}^{\infty}na_z z^{n-1} && (1.64) \\ G''(z) &= \sum_{n=0}^{\infty}n\left(n-1\right)a_z z^{n-2}. && (1.65) \end{aligned}$$

Substitution of these values into Eq. (1.62) needs a bit of patience but is relatively straightforward,

$$(1-z^2)\sum_{n=0}^{\infty}n\left(n-1\right)a_z z^{n-2}-\left(2|m_l|z+2z\right)\sum_{n=0}^{\infty}na_z z^{n-1}+\left(l\left(l+1\right)-|m_l|-|m_l|^2\right)\sum_{n=0}^{\infty}a_z z^n=0 \qquad (1.66)$$

$$(1-z^2)\sum_{n=0}^{\infty} n\big(n-1\big)a_z z^{n-2} - 2\left(|m_l|+1\right)\sum_{n=0}^{\infty} n a_z z^{(n)} + \left(l\big(l+1\big)-|m_l|-|m_l^2|\right)\sum_{n=0}^{\infty} a_z z^n = 0. \tag{1.67}$$

Carefully opening the terms in the series, one by one, yields

$$\begin{aligned}
&+\big((2)(1)a_2 + (3)(2)a_3 z + (4)(3)a_4 z^2 + (5)(4)a_5 z^3 + \ldots\big) \\
&-\big((2)a_2 z^2 + (3)(2)a_3 z^3 + (4)(3)a_4 z^4 + (5)(4)a_5 z^5 + \ldots\big) \\
&-2\left(|m_l| + 1\right)\big(a_1 z + 2a_2 z^2 + 3a_3 z^3 + \ldots\big) \\
&+\left(l\big(l+1\big) - |m_l|^2 - |m_l|\right)\big(a_o + a_1 z + a_2 z^2 + a_3 z^2 + \ldots\big) = 0.
\end{aligned} \tag{1.68}$$

The terms in parentheses can be recast in series form to be

$$\big((2)(1)a_2 + (3)(2)a_3 z + (4)(3)a_4 z^2 + \ldots\big) = \sum_{n=0}^{\infty}(n+2)(n+1)a_{n+2}z^n \tag{1.69}$$

$$\big((2)(1)a_2 z^2 + (3)(2)a_3 z^3 + (4)(3)a_4 z^4 + \ldots\big) = \sum_{n=0}^{\infty} n(n-1)a_n z^n \tag{1.70}$$

$$\big(a_1 z + 2a_2 z^2 + 3a_3 z^3 + \ldots\big) = \sum_{n=0}^{\infty} n a_n z^n \tag{1.71}$$

$$\big(a_o + a_1 z + a_2 z^2 + a_3 z^2 + \ldots\big) = \sum_{n=0}^{\infty} a_n z^n \tag{1.72}$$

Therefore Eq. (1.68) can also be written as

$$\sum_{n=0}^{\infty}\left[(n+2)(n+1)a_{n+2} - n(n-1)a_n - 2\big(|m_l|+1\big)n a_n + \left(l\big(l+1\big)-|m_l|-|m_l|^2\right)a_n\right]z^n = 0. \tag{1.73}$$

Since each of the coefficients of z_n must be zero, each term in the square brackets must also be zero,

$$(n+2)(n+1)a_{n+2} - n(n-1)a_n - 2\big(|m_l|+1\big)n a_n + \left(l\big(l+1\big)-|m_l|-|m_l|^2\right)a_n = 0, \tag{1.74}$$

which results in the recursive formula,

$$a_{n+2} = \left(\frac{n(n-1) + 2\big(|m_l|+1\big)n - \big(l\big(l+1\big) + |m_l| + |m_l|^2\big)}{(n+2)(n+1)}\right)a_n \tag{1.75}$$

$$= \left(\frac{\big(n+|m_l|\big)\big(n+|m_l|+1\big) - l\big(l+1\big)}{(n+2)(n+1)}\right)a_n, \tag{1.76}$$

where both n and m_l are integers.

At the moment, we do not know what is the allowed form of the number l. So let's figure it out! We know that $z = \cos\theta$ whose unconstrained range is $[-1 \leq z \leq 1]$ including $z = \pm 1$ but $G(z) = \sum_{n=0}^{\infty} a_n z^n$ is an infinite series, so the endpoints $z = \pm 1$ will yield an unconstrained infinity when $n \to \infty$. Therefore we cannot allow the index n in the power series Eq. (1.63) go all the way to infinity. This series must be truncated at an upper bound $n_{\max}$. If we want the series to converge then the numerator in Eq. (1.76) must also successively get smaller and smaller and finally $a_{n_{\max}}$ diminishes to zero. Thus we can find $n_{\max}$ by setting the numerator as zero,[2]

$$\big(n_{\max} + |m_l|\big)\big(n_{\max} + |m_l| + 1\big) = l\big(l + 1\big), \tag{1.77}$$

from which we observe that

$$l = \big(n_{\max} + |m_l|\big). \tag{1.78}$$

What pops out from this analysis is that first, l is a positive integer, since $n_{\max}$ and $|m_l|$ both are positive integers themselves. Secondly $|m_l| \leq l$ indicating m_l is a positive or negative integer whose magnitude is less than or equal to l and is given by $|m_l| = l - n_{\max}$. Solving the polar part of the Schrodinger equation has imposed one more constraint on the integer m_l.

Let's summarize our results as this has become quite a lengthy argument. We choose a positive integer l and some m_l such that $|m_l| \leq l$. For this combination of l and m_l, we determine $n_{\max} = l - |m_l|$. We then find the coefficients a_n from Eq. (1.76) from $n = 0$ to $n = n_{\max}$. This helps us determine the series $G(z) = \sum_{n=0}^{n_{\max}} a_n z^n$. Once $G(z)$ is available, we obtain $P(z) = (1 - z^2)^{|m_l|/2} G(z)$ which is Eq. (1.56) and finally replacing z by $\cos\theta$, yields $\Theta(\theta) = P(z)$. Bingo, we have the solution to the polar part of the Schrodinger equation of hydrogen atom.

We need a few examples to bring together some of these calculations. Let's just take the plunge and try out a few test cases. The simplest of course is $l = 0$ for which only $m_l = 0$ is allowed and hence $n_{\max} = 0$. Dot simple! This means that $G(z) = a_o$ is just a constant with no z-dependence. Hence $\Theta(\theta)$ is also a constant stripped of on any angular dependence. We learn later how to find that constant. So $\Theta(\theta)$ for $l = 0$, $m_l = 0$ is for practical purposes proportional to 1, i.e., no angular dependence.

Next, consider $l = 1$ for which we allow m_l to take the values 0, +1 and −1. Begin by $m_l = 0$, which gives $n_{\max} = l - |m_l| = 1$, allowing us to write $G(z) = a_o + a_1 z$ and that's it, just two terms in the series. Now $a_2 = 0$, so from the recursive formula, Eq. (1.76), $a_o = 0$ and we are left with $G(z) = a_1 z$ and $\Theta(\theta)$ is just proportional to $\cos\theta$. Repeating a similar line of reasoning for $m_l = +1$, we have $n_{\max} = l - |m_l| = 0$, giving us $G(z) = a_o$ and $P(z) = (1 - z^2)^{1/2} G(z) = (1 - z^2)^{1/2} a_o$ or $\Theta(\theta)$ proportional to $\sin\theta$. We also obtain $\Theta(\theta) = \sin\theta$ for $m_l = -1$.

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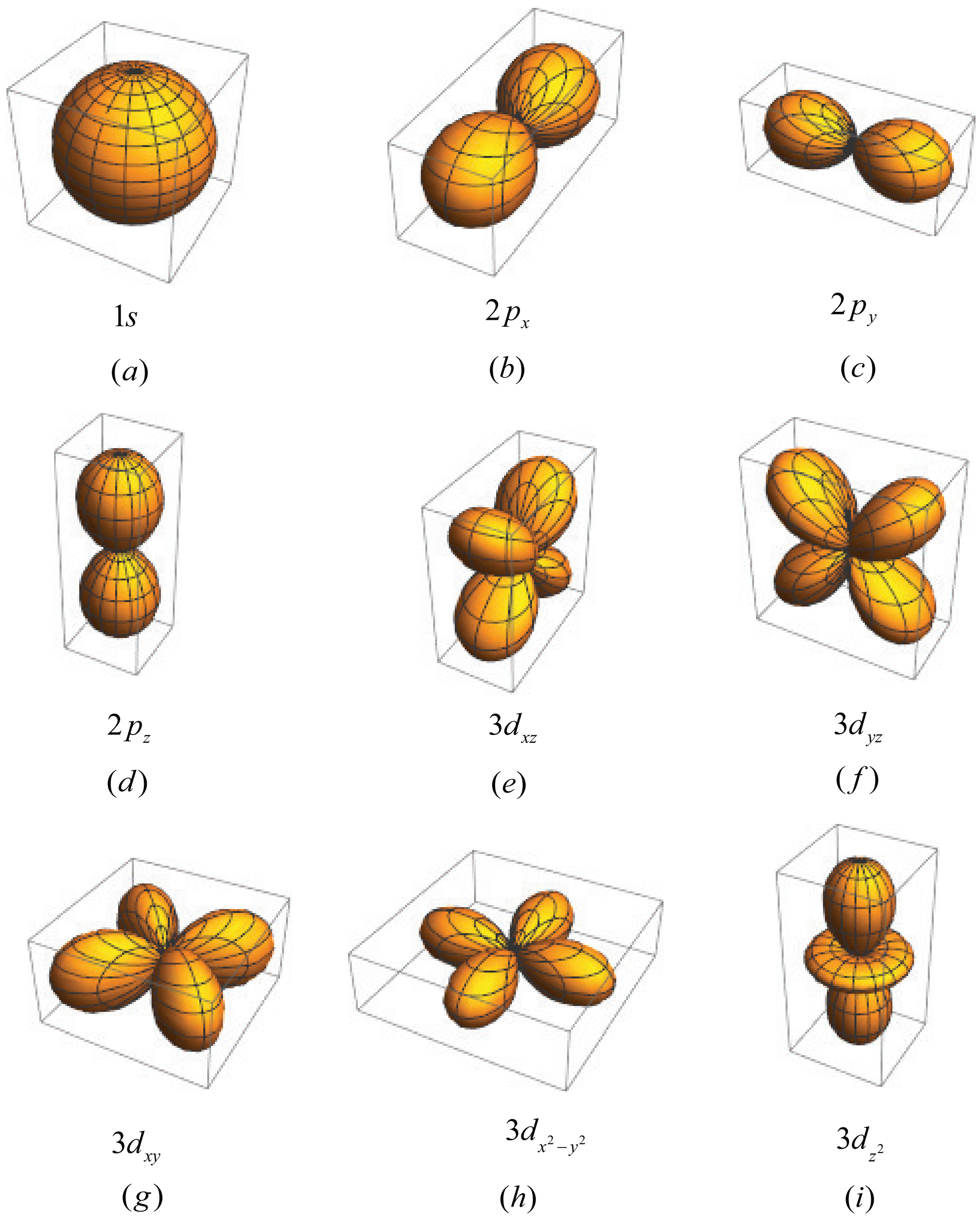
[2] Don't confuse $n_{\max}$ with the principal quantum number.



$1s$ (a)

$2p_x$ (b)

$2p_y$ (c)

$2p_z$ (d)

$3d_{xz}$ (e)

$3d_{yz}$ (f)

$3d_{xy}$ (g)

$3d_{x^2-y^2}$ (h)

$3d_{z^2}$ (i)

Figure 1.3: Orbitals of hydrogen atom.

Just another example to give you a feel for higher values. Consider $l = 3$ and while $m_l = \pm 3, \pm 2, \pm 1, 0$, we consider the example of only $m_l = 2$. This gives us $n_{\max} = l - |m_l| = 1$ and therefore $G(z) = a_o + a_1 z$. But $a_2 = 0$ gives $a_o = 0$, hence $G(z) = a_1 z$ and $P(z) = (1 - z^2)^{|m_l|/2} G(z) = a_1 z(1 - z^2)$ which produces a $\Theta(\theta)$ proportional to $\cos\theta \sin^2\theta$, which is the solution for this particular combination of l and m_l, of course up to a yet to be determined proportionality factor.

Table 1.1.2 is a compilation of some of these calculations for $l = 3$. Pick in one or two instances from this Table and confirm if $\Theta(\theta)'s$ provided can be derived. Since we already determined the azimuthal solutions in section 1.1.1 we now have a method to determine the complete angular solution to the Schrodinger equation for the hydrogen atom.

l	m_l	$n_{\max}$	$G(z)$	$P(z)$	$\Theta(\theta) \propto$
3	3	0	a_o	$a_o(1 - z^2)^{3/2}$	$\sin^3\theta$
3	2	1	$a_1 z$	$a_1 z(1 - z^2)$	$\cos\theta \sin^2\theta$
3	1	2	$a_0(1 - 5z^2)$	$a_o(1 - z^2)^{1/2}(1 - 5z^2)$	$\sin\theta(1 - 5\cos^2\theta)$
3	0	3	$a_1 z(1 - (5/3)z^2)$	$a_1 z(1 - (5/3)z^2)$	$\cos\theta(3 - 5\cos^2\theta)$
3	−1	2	$a_0(1 - 5z^2)$	$a_o(1 - z^2)^{1/2}(1 - 5z^2)$	$\sin\theta(1 - 5\cos^2\theta)$
3	−2	1	$a_1 z$	$a_1 z(1 - z^2)$	$\cos\theta \sin^2\theta$
3	−3	0	a_o	$a_o(1 - z^2)^{3/2}$	$\sin^3\theta$

Table 1.1: This table shows the list of combinations for the $l = 3$ state, including the non-zero terms in the series expansion $G(z)$ and $P(z)$ and finally the polar solution $\Theta(\theta)$. See if you are able to reproduce some of these expressions.

1.1.3 Normalizing the angular part

At this stage, we try to wrap everything together and get an idea of some of the implications of what we have achieved so far. We know that the angular part of wavefunction in Eq. (1.22) is

$$\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi). \tag{1.79}$$

The azimuthal part will change with m_l, hence it is written with this very subscript, called the magnetic quantum number because it is in the presence of a magnetic field, that the different $m_l's$ acquire different energies, otherwise they remain degenerate. This is the Zeeman effect and will be discussed later. The polar part $\Theta(\theta)$ clearly depends on both l and m_l which are quantum numbers that have popped out from the formalism of quantum mechanics due to conditions imposed on the wavefunction —uniqueness, finitude, and the requirement that the modulus square when integrated must be 1. The allowed values of these quantum numbers are

$$l = 0, 1, 2, 3, \dots \tag{1.80}$$

$$\text{and for any } l, \quad |m_l| \leq l, \text{where} \quad m_l \in \mathbb{Z}. \tag{1.81}$$

The product of $\Theta(\theta)$ and $\Phi(\phi)$ is a new function that is well known in mathematical physics and is denoted by $Y^l_{m_l}(\theta, \phi)$. It depends on θ and ϕ and parametrized by the two quantum numbers l and m_l. It is called a spherical harmonic function. These functions have well known properties and are commonly used in many areas of mathematical physics. The spherical harmonics which combine $\Theta_{l,m_l}(\theta)$ and $\Phi_{m_l}(\phi)$ are given in Table 1.2. Figure 1.3 depicts some of the spherical harmonic functions in a 3D enviroment.

The arbitrariness of the constant of proportionality which was left unattended in sections 1.1.1 and 1.1.2 is still coming back to us. We know that as we integrate the modulus square over the entire volume, the answer should be one,

$$\int d\mathcal{V} \left| Y^l_{m_l}(\theta, \phi) \right|^2 = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} d\theta \, d\phi \, \sin\theta \left| Y^l_{m_l}(\theta, \phi) \right|^2 = 1. \tag{1.82}$$

The normalization condition helps determine the constant. So far we are only looking the normalization for the angular coordinates, ignoring the radial parts. Both $R_{n,l}(r)$ and $Y^l_{m_l}(\theta, \phi)$ will be independently normalized and subsequently multiplied together. When we are talking about the spherical harmonic functions, they tell us how the electronic wavefunction looks in three dimensional space as one goes around the nucleus subsequently at a fixed radius. These wavefunctions are called "orbitals".

Here are some examples showing the protocol of determining the normalizations in Table 1.2 and hence complete the story. The lowest value possible is $l = 0$ and $m_l = 0$, for which

$$Y^0_0(\theta, \phi) \propto \text{constant} = C. \tag{1.83}$$

With this mere constant, the normalization constant in Eq. (1.82) yields

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} d\theta d\phi \sin\theta \left| Y^l_{m_l}(\theta, \phi) \right|^2 = C^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} d\theta d\phi \sin\theta = C^2(4\pi) = 1 \tag{1.84}$$

giving us $C = (1/2)\sqrt{1/\pi}$ and hence $Y^0_0(\theta, \phi) = (1/2)\sqrt{1/\pi}$. This is the s orbital. If the electron is in this quantum state, irrespective of the radial part, it will have no

$l = 0$	$Y_0^0(\theta, \phi)$	$= \frac{1}{2}\sqrt{\frac{1}{\pi}}$	
$l = 1$	$Y_{-1}^1(\theta, \phi)$	$= \frac{1}{2}\sqrt{\frac{3}{2\pi}} e^{-i\phi} \sin\theta$	$= \frac{1}{2}\sqrt{\frac{3}{2\pi}} \frac{(x - iy)}{r}$
	$Y_0^1(\theta, \phi)$	$= \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$	$= \frac{1}{2}\sqrt{\frac{3}{\pi}} \frac{z}{r}$
	$Y_1^1(\theta, \phi)$	$= -\frac{1}{2}\sqrt{\frac{3}{2\pi}} e^{i\phi} \sin\theta$	$= -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \frac{(x + iy)}{r}$
$l = 2$	$Y_{-2}^2(\theta, \phi)$	$= \frac{1}{4}\sqrt{\frac{15}{2\pi}} e^{-2i\phi} \sin^2\theta$	$= \frac{1}{4}\sqrt{\frac{15}{2\pi}} \frac{(x - iy)^2}{r^2}$
	$Y_{-1}^2(\theta, \phi)$	$= \frac{1}{2}\sqrt{\frac{15}{2\pi}} e^{-i\phi} \sin\theta\cos\theta$	$= \frac{1}{2}\sqrt{\frac{15}{2\pi}} \frac{(x - iy)z}{r^2}$
	$Y_0^2(\theta, \phi)$	$= \frac{1}{4}\sqrt{\frac{5}{\pi}} (3\cos^2\theta - 1)$	$= \frac{1}{4}\sqrt{\frac{5}{\pi}} \frac{(3z^2 - r^2)}{r^2}$
	$Y_1^2(\theta, \phi)$	$= -\frac{1}{2}\sqrt{\frac{15}{2\pi}} e^{i\phi} \sin\theta\cos\theta$	$= -\frac{1}{2}\sqrt{\frac{15}{2\pi}} \frac{(x + iy)z}{r^2}$
	$Y_2^2(\theta, \phi)$	$= \frac{1}{4}\sqrt{\frac{15}{2\pi}} e^{2i\phi} \sin^2\theta$	$= \frac{1}{4}\sqrt{\frac{15}{2\pi}} \frac{(x + iy)^2}{r^2}$
$l = 3$	$Y_{-3}^3(\theta, \phi)$	$= \frac{1}{8}\sqrt{\frac{35}{\pi}} e^{-3i\phi} \sin^3\theta$	$= \frac{1}{8}\sqrt{\frac{35}{\pi}} \frac{(x - iy)^3}{r^3}$
	$Y_{-2}^3(\theta, \phi)$	$= \frac{1}{4}\sqrt{\frac{105}{2\pi}} e^{-2i\phi} \sin^2\theta\cos\theta$	$= \frac{1}{4}\sqrt{\frac{105}{2\pi}} \frac{(x - iy)^2 z}{r^3}$
	$Y_{-1}^3(\theta, \phi)$	$= \frac{1}{8}\sqrt{\frac{21}{\pi}} e^{-i\phi} \sin\theta(5\cos^2\theta - 1)$	$= \frac{1}{8}\sqrt{\frac{21}{\pi}} \frac{(x - iy)(5z^2 - r^2)}{r^3}$
	$Y_0^3(\theta, \phi)$	$= \frac{1}{4}\sqrt{\frac{7}{\pi}} (5\cos^3\theta - 3\cos\theta)$	$= \frac{1}{4}\sqrt{\frac{7}{\pi}} \frac{(5z^3 - 3zr^2)}{r^3}$
	$Y_1^3(\theta, \phi)$	$= -\frac{1}{8}\sqrt{\frac{21}{\pi}} e^{i\phi} \sin\theta(5\cos^2\theta - 1)$	$= -\frac{1}{8}\sqrt{\frac{21}{\pi}} \frac{(x + iy)(5z^2 - r^2)}{r^3}$
	$Y_2^3(\theta, \phi)$	$= \frac{1}{4}\sqrt{\frac{105}{2\pi}} e^{2i\phi} \sin^2\theta\cos\theta$	$= \frac{1}{4}\sqrt{\frac{105}{2\pi}} \frac{(x + iy)^2 z}{r^3}$
	$Y_3^3(\theta, \phi)$	$= -\frac{1}{8}\sqrt{\frac{35}{\pi}} e^{3i\phi} \sin^3\theta$	$= -\frac{1}{8}\sqrt{\frac{35}{\pi}} \frac{(x + iy)^3}{r^3}$

Table 1.2: Listing of spherical harmonic functions.

dependence on θ and ϕ. Hence, it is best drawn as sphere! A pictorial depiction of the spherical harmonic is presented in Figure 1.3. Shortly we describe how to draw some of these orbitals through a systematic procedure.

Similarly for $l = 1$, we have three possibilities $m_l = 0, \pm 1$. Let's consider $m_l = 0$, then $\Theta(\theta) \propto \cos\theta$, $\Phi(\phi) \propto 1$ and $Y_0^1(\theta, \phi) \propto \cos\theta$. The normalization constant is straightforward to compute.

$$C^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} d\theta d\phi \sin\theta \cos^2\theta = C^2 (2\pi) \frac{2}{3} = 1 \tag{1.85}$$

yielding,

$$C = \frac{1}{2} \sqrt{\frac{3}{\pi}} \tag{1.86}$$

which is identical to the entry in third row in Table 1.2.

1.1.4 Drawing orbitals

It would be really interesting to make an attempt to draw some orbitals, at least on paper or your digital screen. We draw what are called polar diagrams. A polar diagram plots a value of the function evaluated at some θ and ϕ, at a distance from the origin proportional to the value of that function, at the θ and ϕ specified.

Let's exemplify by plotting the orbital $Y_0^1(\theta, \phi) = (1/2)\sqrt{3/\pi} \cos\theta$. We set aside the normalization factor for the visualization process. First of all, Figure 1.4 (a) shows a plot of the function $\cos\theta$, indicating how the function varies from $\theta = 0$ to $\theta = \pi$. From this we generate one cut of the lobe shown in Figure 1.4 (b) which is the cross section of the 3D space drawn at the plane $\phi = 0$. For the point a $(\theta = 0)$, we have the value of the function = 1. This creates a point a' on the polar diagram in Figure 1.4 (b). The distance of a' from the origin is 1 unit and it lies squarely on the z axis (since $\theta = 0$). The lobe in Figure 1.4 (b) is just a plane cut in the xz plane. We convert this to 3D later. Now, the function needs to be traversed point to another point. Consider point b at $\theta = \pi/6$ $(= 30°)$. The function has a value $\cos(\pi/6) = 0.866$, so we draw a point b' in Figure 1.4 (b) at an angle of $30°$ from the z axis, at a distance of 0.866 units from the origin. We repeat the mapping c (at $\theta = \pi/3$, value = 0.5) to c'. For d, we have $\theta = \pi/2$, value = 0 which generates the point d' in the cut lobe. Though we have shown only the mappings $a \to a'$, $b \to b'$, $c \to c'$ and $d \to d'$, this is in fact a continuous process, negotiating the entire domain of the function from $\theta = 0$ to $\theta = \pi$. Going continuously from a to d generates the top right half of the cut lobe shown in Figure 1.4 (b). The function is positive everywhere, we just place a $\boxed{+}$ symbol next to the top half.

As we continue our journey onward beyond $\theta = \pi/2$, upto $\theta = \pi$, which is point e, we continue the same mapping process. Points are mapped onto the polar

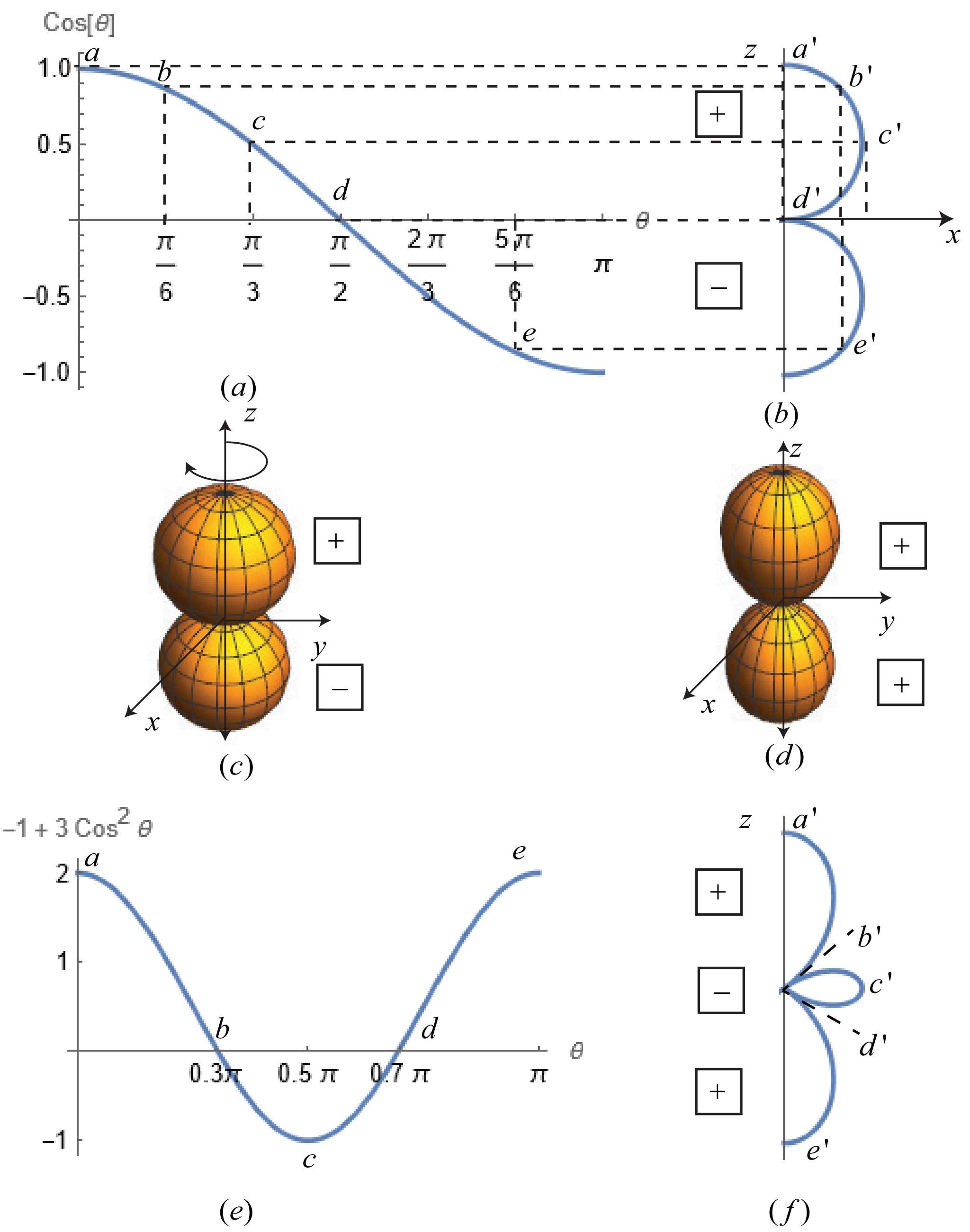


Figure 1.4: (a)Plot of $Y_0^1(\theta,\phi) = \cos\theta$ from 0 to π. (b)Visualizing the p_z orbital with θ from 0 to π at a fixed ϕ drawn by mapping points $a \to a'$, $b \to b'$, $c \to c'$, $d \to d'$,$e \to e'$ and all points in between. A half-cut lobe appears in the polar diagram. (c) The orbital p_z is cylindrically symmetric and obtained by twisting (b) around the z-axis. (d) Probability density function for the p_z orbital. (e)$3\cos^2\theta - 1$ (f)d_{z^2} orbital,

diagram by distances from the origin reflective of the magnitude of the function, synthesizing the lower half of the lobe in Figure 1.4 (b). This locus from d' to e' has a negative connotation, thus is indicated by the $\boxed{-}$ symbol. So we have successfully created the lobe of the $Y_1^1(\theta, \phi)$ orbital called a p_z orbital at least in the $(+x, +z)$ half plane. This half lobe is at $\phi = 0$. Since the orbital has no ϕ dependence, m_l being zero, the 3D pattern of the lobe will be cylindrically symmetric and can be generated by smoothly twisting the lobe structure as shown in Figure 1.4 (c). If I were to plot the probability density function which is the square of probability amplitude, then both lobes well change shape a little bit and both of them will be positive. This is shown in Figure 1.4 (d).

The case of the orbital $Y_0^2(\theta, \phi)$ in three dimensions is also rather interesting. The functional form of this spherical harmonic is $3\cos^2\theta - 1$ shown in Figure 1.4 (e). This function is not symmetric about the horizontal axis which imparts an interesting bimodal feature to the half-cut lobe. The function starts at $\theta = 0^\circ$ with a negative value and becomes 0 at $b = \cos^{-1}(1/\sqrt{3}) = 54.7^\circ$, the so called magic angle. The mapping from $a \to a'$ to $b \to b'$ synthesis the bigger loop in the $(+x, +z)$ quarter plane. This quarter lobe has a $\boxed{-}$ character. Then it rises in the positive range to c, to a maximum and falls back to zero at $d = 135^\circ$, creating another lobe. The point c is not as high as a is below zero, so this secondary loop formed from $b \to c \to d$ is smaller in size. Repeating the continuous process, we generate the lobe in the whole $(+x, \pm z)$ plane which is finally twisted around z in three dimensions showing the picture of the $Y_0^2(\theta, \phi)$ orbital called the d_{z^2} half plane orbital. If we plot $Y_0^2(\theta, \phi)$ in 3 dimensions we obtain donut in the center with an upper central lobe and a lower central lobe. The upper and lower lobes are $\boxed{-}$ in character while the donut is $\boxed{+}$. See Figure 1.4 (f). The angular wavefunction vanishes when $3\cos^2\theta - 1 = 0$ at angles of $\cos^{-1}(1/\sqrt{3})$ and $\pi - \cos^{-1}(1/\sqrt{3})$. The other four d-orbitals are also clover leaf shaped, identical to one another but with different orientations in space. d-orbitals are illustrated in Figure 1.3 (e), (f), (g), (h) and (i).

1.1.5 Superpositions of orbitals

We also have spherical harmonics such as

$$Y_1^1(\theta, \phi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi} \tag{1.87}$$

$$Y_{-1}^1(\theta, \phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\phi}, \tag{1.88}$$

which are complex functions. Plotting these is not straightforward. One possibility is to draw the real and imaginary parts one by one, but we can also fashion linear combinations so that the resultants become real, easy to plot and visualize. Consider the equal superpositions,

$$\frac{Y_1^1(\theta,\phi)+Y_{-1}^1(\theta,\phi)}{\sqrt{2}} = Y_x^1(\theta,\phi)=\frac{1}{\sqrt{2}}\sqrt{\frac{3}{2\pi}}\sin\theta\cos\phi \tag{1.89}$$

$$\frac{Y_1^1(\theta,\phi)-Y_{-1}^1(\theta,\phi)}{i\sqrt{2}} = Y_y^1(\theta,\phi)=-\frac{1}{\sqrt{2}}\sqrt{\frac{3}{2\pi}}\sin\theta\sin\phi \tag{1.90}$$

In fact, it is these orbitals that are conventionally drawn in textbooks and are called, respectively, p_x and p_y orbitals. See Figure 1.3 (b) and(c). The $\sin\theta$ factor in Eqs.(1.89) and (1.90) indicates that the lobe has maximal strength around $\theta = \pi/2$ which is the equatorial plane. However these orbitals don't possess the cylindrical symmetry that we've seen for some of the $m_l = 0$ orbitals. The $Y_x^1(\theta,\phi)$ has $\cos\phi$ dependence showing that even in the equatorial plane, not all $\phi's$ are the same. The lobe will exist primarily around $\phi = 0$ which is the x-axis. Therefore we get the lobe predominately along the $\pm x$ axis, hence the name p_x orbital. Similarly the p_y orbital, being proportional to $\sin\theta\sin\phi$ has maximum alignment along y.

1.2 Radial part of the Schrodinger equation

1.2.1 Deriving the radial solution

We know how the wavefunction looks like in three dimension at a fixed distance but we don't know how it varies with distance. For this purpose, we turn attention to the radial part $R(r)$, which also depends on some yet to be determined quantum number. At the onset, let's call the that is principal quantum number(s) denoted by n. It transpires that $R(r)$ will also depend on l.

The Schrodinger equation in spherical coordinates is given by Eq. (1.24) and reproduced here,

$$-\frac{\hbar^2}{2mr^2}\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\hbar^2}{2mr^2}\left\{-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right\}+(V-E)=0 \tag{1.91}$$

The terms in curly bracket is identical to Eq. (1.36) and we equated it to a constant denoted by $l(l+1)$ where l is an integer and at the moment we conceive this number as going from 0 to ∞. There is no further constraint on it for the time being. Therefore we have

$$-\frac{\hbar^2}{2mr^2}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\hbar^2}{2mr^2}\left(l(l+1)\right)+(V-E)=0 \tag{1.92}$$

which is cast into the form,

$$-\frac{\hbar^2}{2mr^2}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\left\{V(r)+\frac{\hbar^2}{2mr^2}\Big(l(l+1)\Big)\right\}-E\right]=0 \tag{1.93}$$

where we have lumped the terms $V(r)$ and $\hbar^2(l(l+1))/2mr^2$ together. We call this the effective potential,

$$V_{\text{eff}}=-\frac{e^2}{4\pi\varepsilon_o r}+\frac{\hbar^2}{2mr^2}\big(l(l+1)\big). \tag{1.94}$$

Eq. (1.93) is a purely radial equation whose solution will provide the radial part of the wavefunction. Notice that the bare nuclear potential is

$$V(r)=-\frac{e^2}{4\pi\varepsilon_o r} \tag{1.95}$$

but as a result of angular energy (second term on R.H.S. of Eq. (1.94)), the potential energy is modified. In fact the potential energy increases for $l \neq 0$ while for $l = 0$, the potential energy is just the bare value in Eq. (1.95). The physical implication is that higher l states[3] evade the nucleus, suggest that the angular term with $l = 0$ is acting as a barrier against the electron approaching the nucleus. This barrier $\hbar^2(l(l+1))/2mr^2$ is called the centrifugal barrier. As l increases, the centrifugal barrier increases and the electron tend to be pushed further out.

With this background, we can begin the solution of the time-independent radial wave equation. In order to solve the radial equation we need to do a sequence of substitutions. We first define $u(r)$,

$$u(r)=rR(r) \tag{1.96}$$

which leads to the derivatives,

$$\begin{aligned}\frac{du(r)}{dr} &= R+r\frac{dR}{dr}, && (1.97)\\ \text{and}\quad \frac{d^2u(r)}{dr^2} &= 2\frac{dR}{dr}+r\frac{d^2R}{dr^2} && (1.98)\end{aligned}$$

Analyzing the Schrodinger equation Eq. (1.93) again,

$$-\frac{\hbar^2}{2mr^2}\frac{1}{R}\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right]+V_{\text{eff}}=E, \tag{1.99}$$

---

[3] We will see in the next chapter that higher l means larger angular momentum.

the term in the square bracket really is (using Eq. (1.98)),

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = 2r\frac{dR}{dr} + r^2\frac{d^2R}{dr^2} = r\frac{d^2u(r)}{dr^2}, \tag{1.100}$$

and so Eq. (1.93) becomes,

$$-\frac{\hbar^2}{2mu(r)}\frac{d^2u(r)}{dr^2} + V_{\text{eff}} = E \tag{1.101}$$

which is appointed as

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + V_{\text{eff}}u(r) = Eu(r). \tag{1.102}$$

Curiously, this looks very similar to a one dimensional Schrodinger equation albeit with the modified potential given in Eq. (1.94). We open up the potential term and divide by E,

$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} + \left[\frac{\hbar^2 l(l+1)}{2mr^2E} - \frac{e^2}{4\pi\varepsilon_o rE}\right]u = u. \tag{1.103}$$

We define the dimensionless variable,

$$\rho = \frac{\sqrt{-2mE}}{\hbar}r, \tag{1.104}$$

Since the bound electron has negative energy, the radical is a positive number and so ρ remains real. We want to express all derivatives in Eqs.(1.97) and (1.98) in term of ρ. Let's try to perform these substitutions. Using the chain rule,

$$\begin{aligned} \frac{dF}{dr} &= \frac{dF}{d\rho}\frac{d\rho}{dr} && (1.105)\\ &= \frac{\sqrt{-2mE}}{\hbar}\frac{dF}{d\rho}. && (1.106) \end{aligned}$$

Therefore writing d/dr in terms of $d/d\rho$ we have

$$\frac{d}{dr} = \frac{\sqrt{-2mE}}{\hbar}\frac{d}{d\rho}, \tag{1.107}$$

and the second order derivative becomes

$$\frac{d^2}{dr^2} = \frac{-2mE}{\hbar^2}\frac{d^2}{d\rho^2}. \tag{1.108}$$

With these substitutions the Schrodinger equation Eq. (1.103) transforms to,

$$\frac{d^2u}{d\rho^2} + \left[\frac{\hbar^2 l(l+1)}{2mr^2E} - \frac{e^2}{4\pi\varepsilon_o rE}\right]u = u \tag{1.109}$$

Expressing $1/r^2$ and $1/r$ in terms of ρ using Eq. (1.104), we can rewrite Eq. (1.109) as

$$\frac{d^2u}{d\rho^2} = \left[1 + \frac{l(l+1)}{\rho^2} - \frac{\rho_o}{\rho}\right]u, \tag{1.110}$$

where we have also defined

$$\rho_o = \frac{e^2}{4\pi\varepsilon_o\hbar}\sqrt{\frac{-2m}{E}}. \tag{1.111}$$

After all, Eq. (1.110) looks much simpler. The elegance comes out of substitutions, one after another! Next, we use physical intuition and historical baggage to solve this differential equation. Furthermore, the solutions should hold true at all boundaries, whether close or far away from the nucleus. These boundary conditions narrow down or help discard certain solutions.

Let's look at the asymptotic expression of Eq. (1.110), when we are close to and far from the nucleus. As ρ is proportional to r, $\rho \to \infty$ means that one is very far from the nucleus. In this case, the second and third terms approach zero, leading to

$$\frac{d^2u}{d\rho^2} \approx u \tag{1.112}$$

predicting a general solution

$$u(\rho) = Ae^{-\rho} + \cancel{Be^{\rho}}. \tag{1.113}$$

This is our first guess for $u(\rho)$. However, ρ is always positive, so when ρ approaches infinity, the Be^{ρ} terms blows up giving us an unphysical wavefunction, thus $B = 0$. So for any ρ, we propose that one component of the of solution be,

$$u_1(\rho) = Ae^{-\rho}. \tag{1.114}$$

which is a decaying function of ρ which makes sense, for at large ρ, u_ρ diminishes. We want the electron to, after all, be bound to the nuclear influence! On the other hand when $rho = 0$ Eq. (1.110) becomes

$$\frac{d^2u}{d\rho^2} \approx \frac{l(l+1)}{\rho^2}u, \tag{1.115}$$

as the middle term on the R.H.S. of Eq. (1.110)f overwhelms the first and third terms. A guess for the solution in this regime is,

$$u_2(\rho) = C\rho^{l+1} + \cancel{D\rho^{-l}}. \tag{1.116}$$

Try inserting this ansatz into Eq. (1.115) verifying that this is indeed a prospective solution. However, as $\rho \to 0$, ρ^{-l} explodes and hence D must be zero, leading to another component,

$$u_2(\rho) \approx C\rho^{l+1} \tag{1.117}$$

which suggests an increasing function. The two solutions u_1 and u_2 from Eqs.(1.114) and (1.117) represent respectively a decaying function and an increasing function. The decaying function u_1 however dominates because it is an exponential function whereas the increasing function is a mere polynomial. Hence everything will remain finite when combined together. Therefore, we juxtapose the two solutions, by multiplying them together and allow the possibility of another polynomial function $\nu(\rho)$ to serve as a pre-multiplier, hence

$$u(\rho) = u_1(\rho)u_2(\rho)\nu(\rho) = \rho^{l+1}e^{-\rho}\nu(\rho), \tag{1.118}$$

which adequately satisfies boundary condition: $e^{-\rho}$ will be zero when $\rho \to \infty$ and ρ^{l+1} will remain finite when $\rho \to 0$.

The task at hand is now to find the premultiplying polynomial $\nu(\rho)$. You may appreciate that in this drawn out argument, we are introducing functions that are easier to compute through new and newer substitutions. If we substitute Eq. (1.118) into Eq. (1.110), this lead to the modified equation,

$$\rho\frac{d^2\nu}{d\rho^2} + 2(l+1-\rho)\frac{d\nu}{d\rho} + (\rho_o - 2(l+1))\,\nu = 0 \tag{1.119}$$

The amenable observation about this equation is that we don't have a ρ in the denominator. To solve it, we use the power series approach. Assume the polynomial $\nu(\rho)$ is power series in ρ with some index j,

$$\nu(\rho) = \sum_{j=0}^{\infty} C_j\rho^j. \tag{1.120}$$

For inserting this into Eq. (1.119) we need to find the derivative and double derivative of $\nu(\rho)$. Lets take the first derivative of the series,

$$\frac{d\nu(\rho)}{d\rho} = \sum_{j=0}^{\infty} C_j j\rho^{(j-1)} = \sum_{j=1}^{\infty} C_j j\rho^{(j-1)}, \tag{1.121}$$

followed by the substitution,

$$j' = j - 1, \tag{1.122}$$

giving us

$$\frac{d\nu(\rho)}{d\rho} = \sum_{j'=0}^{\infty} C_{j'+1}(j'+1)\rho^{j'} = \sum_{j=0}^{\infty} C_{j+1}(j+1)\rho^{j}. \tag{1.123}$$

The reason for doing the substitution in Eq. (1.122) was to get a series of terms ρ^j. Let's now take the second derivative of the power series

$$\frac{d^2\nu(\rho)}{d\rho^2} = \sum_{j=0}^{\infty} C_{j+1}(j+1)(j)\rho^{(j-1)} \tag{1.124}$$

Inserting the expression from Eqs.(1.120), (1.121), (1.123) and (1.124) into Eq. (1.119), we finally obtain

$$\rho\left(\sum_{j=0}^{\infty} C_{j+1}(j+1)(j)\rho^{(j-1)}\right) + 2(l+1)\left(\sum_{j=0}^{\infty} C_{j+1}(j+1)\rho^{j}\right) - 2\rho\left(\sum_{j=1}^{\infty} C_j j\rho^{(j-1)}\right)$$
$$+\left(\rho_o - 2(l+1)\right)\left(\sum_{j=0}^{\infty} C_j\rho^{j}\right) = 0.$$

In order for the equality to hold each coefficient in the polynomial expansion must be zero, hence

$$C_{j+1}j(j+1) + 2(l+1)C_{j+1}(j+1) = \left[2j - \rho_o + 2l + 2\right]C_j. \tag{1.125}$$

yielding a recursive equation,

$$C_{j+1} = \frac{2(j+l+1) - \rho_o}{(j+1)(j+2l+2)}C_j. \tag{1.126}$$

These coefficients determine C_j and thus $\nu(\rho)$ and $u(\rho)$ through Eqs.(1.120) and (1.118) and henceforth the radial function $R(r)$. This is highly satisfying, but before we consider the matter closed, we still need a third quantum number that arises out of some additional physicality constraints. Of course we must also normalize.

At the moment j is an arbitrary non zero integer in Eq. (1.120), but what happens for large j? We assume j is much larger than both $l+1$ and ρ_o. In this case, the recursive relation in Eq. (1.126) simplifies to

$$C_{j+1} = \frac{2}{j}C_j. \tag{1.127}$$

This shows that at large j, the ratio of two successive coefficients $C_{j+1}/C_j = 2/j$. In parallel, if we consider the MacLaurin series expansion of e^{2x}

$$e^{2x} = \sum_{j=0}^{\infty} \frac{(2x)^j}{j!} = \sum_{j=0}^{\infty} \frac{2^j}{j!}x^j, \tag{1.128}$$

we observe that the ratio of two successive term in the expansion of e^{2x} is,

$$\frac{2^{j+1}}{(j+1)!}\frac{j!}{2^j} = \frac{2}{(j+1)} \tag{1.129}$$

which for large j, is also equal to $2/j$. Hence this comparison with e^{2x} allows us to write Eq. (1.120) as an exponent,

$$\nu(\rho) = \sum_{j=0}^{\infty} C_j \rho^j \approx \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!} = e^{2\rho}. \tag{1.130}$$

Finally, substituting $\nu(\rho)$ into Equation Eq. (1.118), we obtain

$$u(\rho) \approx \rho^{l+1} e^{-\rho} e^{2\rho} = \rho^{l+1} e^{\rho} \tag{1.131}$$

but this blows up as $\rho \to \infty$. In order to prevent this infinity, we truncate the series in Eq. (1.120) at $j = j_{max}$, such that $C_{j_{\text{max}+1}} = 0$, which allows us to write, with the help of Eq. (1.126),

$$C_{j_{\text{max}+1}} = \frac{2(j_{\text{max}} + l + 1) - \rho_o}{(j_{\text{max}+1})(j_{\text{max}} + 2l + 2)} C_{j_{\text{max}}} = 0, \tag{1.132}$$

whose numerator becomes zero for this choice of $j = j_{\text{max}}$, *i.e.*,

$$2(j_{max} + l + 1) = \rho_o. \tag{1.133}$$

If we were to define

$$n = j_{max} + l + 1, \tag{1.134}$$

ρ_o would become

$$\rho_o = 2n \tag{1.135}$$

and with the ρ_o defined in Equation (1.111), we obtain,

$$\rho_o^2 = \frac{e^4}{(4\pi\varepsilon_o\hbar)^2}\frac{-2m}{E} = 4n^2 \tag{1.136}$$

Therefore the energy turns out as,

$$E_n = \frac{-m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2 \frac{1}{n^2} = \frac{E_1}{n^2}, \qquad n = 1, 2, 3, \ldots \tag{1.137}$$

where E_1 is the ground state energy of hydrogen atom and has a value of -13.6 eV. Hence, we obtain the quantum number n which defines j_{max} for computing $\nu(\rho)$ and as a result the energy also becomes quantized. The number n, which is called the principal quantum number.

At some point in your life, you may have derived Bohr formula by a brute force approach. The approach outlined here is systematic and reproduces what Bohr derived in his old quantum theory. Every time, we try keeping the wavefunction finite or unique, we create a new quantum number and impose a constraint on it. Hence by determining the radial and angular solutions, we have extracted three quantum numbers n, l and m_l. Furthermore, the number n is any nonzero integer; from Eq. (1.134) we have,

$$j_{max} = n - l - 1 \geq 0 \tag{1.138}$$

which imposes another constraint on l itself

$$l \leq n - 1. \tag{1.139}$$

this is an upper bound on the integer l.

These three quantum numbers define the state of the electron in the hydrogen atom. They are called the principal quantum number n, orbital quantum number l and the azimuthal or magnetic quantum number m_l. Each l has $(2l+1)$ values of m_l. There is also a fourth quantum number m_s which deals with spin but that cannot be derived by the Schrodinger equation. If we consider spin as well with its two possibilities $m_s = \pm 1/2$, the total degeneracy which is defined as the number of quantum states all with identical energy, for a given n is

$$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2. \tag{1.140}$$

Before our mind digresses into other avocations, let's turn back to the radial wavefunctions. We have already found them. We know $\nu(\rho)$, $u(\rho)$ and hence can write $R(r)$ and eventually $\psi_{n,l,m_l}(r,\theta,\phi)$. Using Eq. (1.137) we can write

$$\rho = \frac{\sqrt{-2mE}}{\hbar} r = \frac{\sqrt{-2m}}{\hbar}\sqrt{\frac{-m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2 \frac{1}{n^2}} = \frac{me^2}{4\pi\varepsilon_o\hbar^2}\frac{r}{n} = \frac{1}{n}\left(\frac{r}{a_o}\right) \tag{1.141}$$

where

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{me^2} \tag{1.142}$$

is the Bohr radius, depends upon fundamental constants and hence is a constant. The rescaled radius ρ tells how big the radius is compared to the Bohr radius; r is terms of meters (or Angstroms) and ρ is units of the Bohr radius. Finally the radial wavefunction that is given by two quantum number n and l, can be composed using the result derived in Eqs.(1.96), (1.118), and (1.141) and is given by

$$R_{n,l}(r) = \frac{\rho^{l+1}e^{-\rho}\nu(\rho)}{r} = \frac{1}{n}\frac{\rho^l e^{-\rho}\nu(\rho)}{a_o}. \tag{1.143}$$

We can tabulate the functional form $\nu(\rho)$ for different combination of n and l. For example for $n = 1$, $l = 0$, so from Eq. (1.134) $j_{max} = n - l - 1 = 0$. This makes $\nu(\rho) =$ constant. Say the constant is C_o. Therefore, from Eq. (1.143), we obtain

$$R_{10}(r) \propto \frac{1}{a_o n}\rho^l e^{-\rho}\nu(\rho) = \frac{1}{a_o}\rho^0 e^{-\rho} C_o \propto \frac{e^{-r/a_o}}{a_o} \tag{1.144}$$

We can similarly obtain the forms for $R_{n,l}(r)$ for various combinations. Some values are tabulated in Table 1.3. See the rightmost column and don't worry, we will sort the normalization (and the form in the second column of Table 1.3) shortly. Figure 1.5 illustrates the radial wavefunctions for various n and l. Note in the left column of the figure, the absolute amplitude decreases for higher values of n. All radial wavefunctions remain finite. The $l = 0$ radial function (corresponding to s orbitals) all have a maximum at $r = 0$ which is the apparent position of the nucleus. This paradoxical scenario will be addressed shortly.

n	l	$L_{n+l}^{2l+1}(\rho)$	$R_{n,l}(r)$
1	0	$L_1^1(\rho) = -1$	$2\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$
2	0	$L_2^1(\rho) = -2!(2-\rho)$	$\left(\frac{1}{\sqrt{8}}\right)\left(\frac{1}{a_o}\right)^{3/2}\left(2 - \frac{r}{a_o}\right)e^{-r/(2a_o)}$
2	1	$L_3^3(\rho) = -3!$	$\left(\frac{1}{\sqrt{24}}\right)\left(\frac{1}{a_o}\right)^{3/2}\frac{r}{a_o}e^{-r/(2a_o)}$
3	0	$L_3^1(\rho) = -3!(3 - 3\rho + \frac{1}{2}\rho^2)$	$\left(\frac{2}{81\sqrt{3}}\right)\left(\frac{1}{a_o}\right)^{3/2}\left(27 - 18\frac{r}{a_o} + 2\frac{r^2}{a_o^2}\right)e^{-r/(3a_o)}$
3	1	$L_4^3(\rho) = -4!(4-\rho)$	$\left(\frac{4}{81\sqrt{6}}\right)\left(\frac{1}{a_o}\right)^{3/2}\left(6\frac{r}{a_o} - \frac{r^2}{a_o^2}\right)e^{-r/(3a_o)}$
3	2	$L_5^5(\rho) = -5!$	$\left(\frac{4}{81\sqrt{30}}\right)\left(\frac{1}{a_o}\right)^{3/2}\frac{r^2}{a_o^2}e^{-r/(3a_o)}$

Table 1.3: Listing of some elementary radial wavefunctions.

1.2.2 Compact forms of radial wavefunctions

Pre-quantum classical physics gives us some really compact relationship for the radial wavefunction. We use a particularly neat form proposed by Laguerre. In

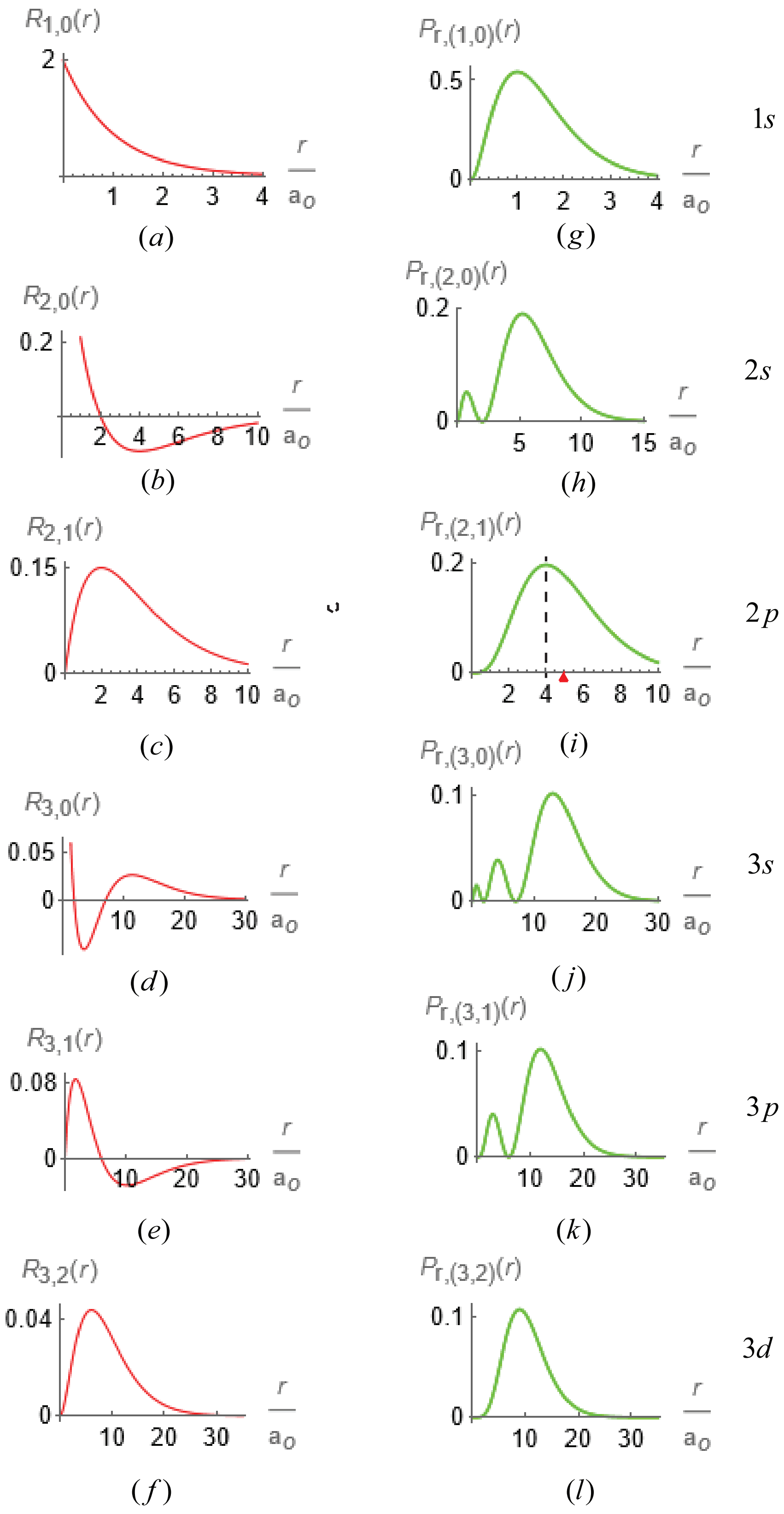


Figure 1.5: Radial wavefunctions and corresponding radial probability densities, shown in the left and right columns respectively.

general,

$$\begin{aligned} \nu(\rho) &= L^{2l+1}_{n-l-1}(2\rho) && (1.145) \\ \text{where } L^{p}_{q-p}(x) &= (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) && (1.146) \end{aligned}$$

is the associated Laguerre polynomial, that is connected to the Laguerre polynomial

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q) \tag{1.147}$$

One can verify in Table 1.3 that the tabulated values of $L^{2l+1}_{n+l}(\rho)$ for a particular value of n and l are also consistent with the following formula,

$$L^{2l+1}_{n+l}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \frac{((n+l)!)^2}{(n-l-1-k)!(2l+1+k)!k!}\rho^k. \tag{1.148}$$

Finally we can assemble everything together and using Eq. (1.145) write,

$$R_{n,l}(r) = A\rho^{l+1} e^{-\rho} L^{2l+1}_{n-l-1}(2\rho) \tag{1.149}$$

which upon the respective substitution finally becomes

$$R_{n,l} = A\left(\frac{2r}{na_o}\right)^l e^{-r/na_o} \left[L^{2l+1}_{n-l-1}\left(\frac{2r}{na_o}\right)\right] \tag{1.150}$$

1.3 Putting everything together

Hence the wavefunction is the product of the radial part and angular part,

$$\begin{aligned} \psi_{n,l,m}(r,\theta,\phi) &= R_{n,l}(r) Y^l_{m_l}(\theta,\phi) \\ &= \sqrt{\left(\frac{2}{na_o}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na_o} \left(\frac{2r}{na_o}\right)^l \left[L^{2l+1}_{n-l-1}\left(\frac{2r}{na_o}\right)\right] Y^l_{m_l}(\theta,\phi) \end{aligned}$$

The square root coefficient is the normalization constant that no one in the world remembers and can be easily determined through a familiar normalization routine. Table 1.4 provides a few wavefunctions of the hydrogen atom.

1.3.1 Finding probabilities of locating the electron in some region of space

The Born postulate states that the wavefunction's modulus square tells where one can find the quantum object in a measurement shot. We know that $|\psi(r,\theta,\phi)|^2$ is

n	l	m_l	$\psi_{n,l,m_l}(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{\pi}a_o^{3/2}}e^{-r/a_o}$
2	0	0	$\frac{1}{4\sqrt{2\pi}a_o^{3/2}}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$
2	1	0	$\frac{1}{4\sqrt{2\pi}a_o^{3/2}}\frac{r}{a_o}e^{-r/2a_o}\cos\theta$
2	1	±1	$\frac{1}{8\sqrt{3\pi}a_o^{3/2}}\frac{r}{a_o}e^{-r/2a_o}\sin\theta e^{\pm i\phi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}a_o^{3/2}}\left(27-18\frac{r}{a_o}+2\frac{r^2}{a_o^2}\right)e^{-r/3a_o}$
3	1	0	$\frac{1}{81\sqrt{3\pi}a_o^{3/2}}\frac{r}{a_o}\left(6-\frac{r}{a_o}\right)e^{-r/3a_o}\cos\theta$
3	1	±1	$\frac{1}{81\sqrt{3\pi}a_o^{3/2}}\frac{r}{a_o}\left(6-\frac{r}{a_o}\right)e^{-r/3a_o}\sin\theta e^{\pm i\phi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}a_o^{3/2}}\frac{r^2}{a_o^2}e^{-r/3a_o}\left(3\cos^2\theta-1\right)$
3	2	±1	$\frac{1}{81\sqrt{\pi}a_o^{3/2}}\frac{r^2}{a_o^2}e^{-r/3a_o}\sin\theta\cos\theta e^{\pm i\phi}$
3	2	±2	$\frac{1}{162\sqrt{\pi}a_o^{3/2}}\frac{r^2}{a_o^2}e^{-r/3a_o}\sin^2\theta e^{\pm 2i\phi}$

Table 1.4: Some of hydrogen wavefunctions

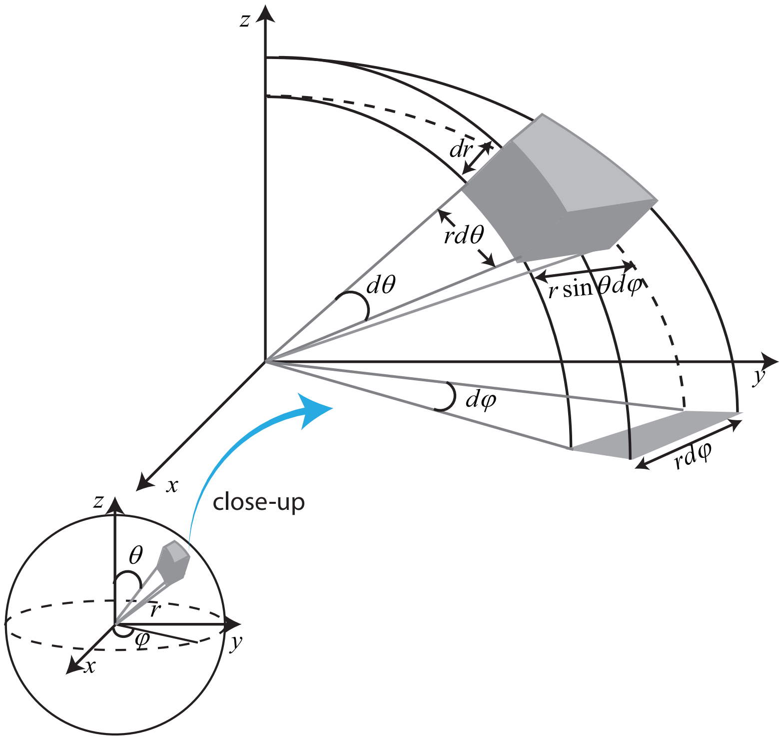


Figure 1.6: Volume element $\mathcal{V}$ on a sphere shown as a shaded grey element. Here dr is the radial length, $r\,d\theta$ is the arc length going from θ to $\theta+d\theta$ and $(r\sin\theta d\phi)$ is the arc length moving parallel to the equatorial plane. The bounded region shown in the equatorial plane is highly exaggerated.

the probability density function. Before making the measurement we don't know where the electron is. When we perform a measurement using a Heisenberg or a tunneling microscope, the image obtained does not tell us where the electron was, only that it was captured at the precise location revealed in the image. This is only one of the numerous a priori potentiates of where it could be found. The electron was "everywhere" but we found it only "somewhere". Only by repeated measurements we can create a probability histogram of potentiates.

The probability of locating the electron in the hydrogen atom inside a small volume element $d\mathcal{V}$ at r, θ and ϕ is given by

$$|\psi(r,\theta,\phi)|^2 d\mathcal{V} = |\psi|^2 r^2 \sin\theta\, d\theta\, d\phi\, dr. \tag{1.151}$$

The small volume element $d\mathcal{V}$ and its dimensions with respect to the spherical coordinate system are shown in Figure 1.6. In order to find the probability of locating a particle inside a macroscopic region in space, we then need to integrate between the appropriate limits, $\phi \in [\phi_1, \phi_2]$, $\theta \in [\theta_1, \theta_2]$ and $r \in [r_1, r_2]$ which bound the region,

$$\int_{r_1}^{r_2}\int_{\theta_1}^{\theta_2}\int_{\phi_1}^{\phi_2} dr\, d\theta\, d\phi\, r^2 \sin\theta |R_{n,l}(r)|^2 |Y_{m_l}^l(\theta,\phi)|^2 \tag{1.152}$$

The radial part and the angular part are independent so one can break this integral into two parts

$$\int_{r_1}^{r_2} dr\, r^2 |R_{n,l}(r)|^2 \int_{\theta_1}^{\theta_2}\int_{\phi_1}^{\phi_2} d\theta\, d\phi\, \sin\theta |Y_{m_l}^l(\theta,\phi)|^2. \tag{1.153}$$

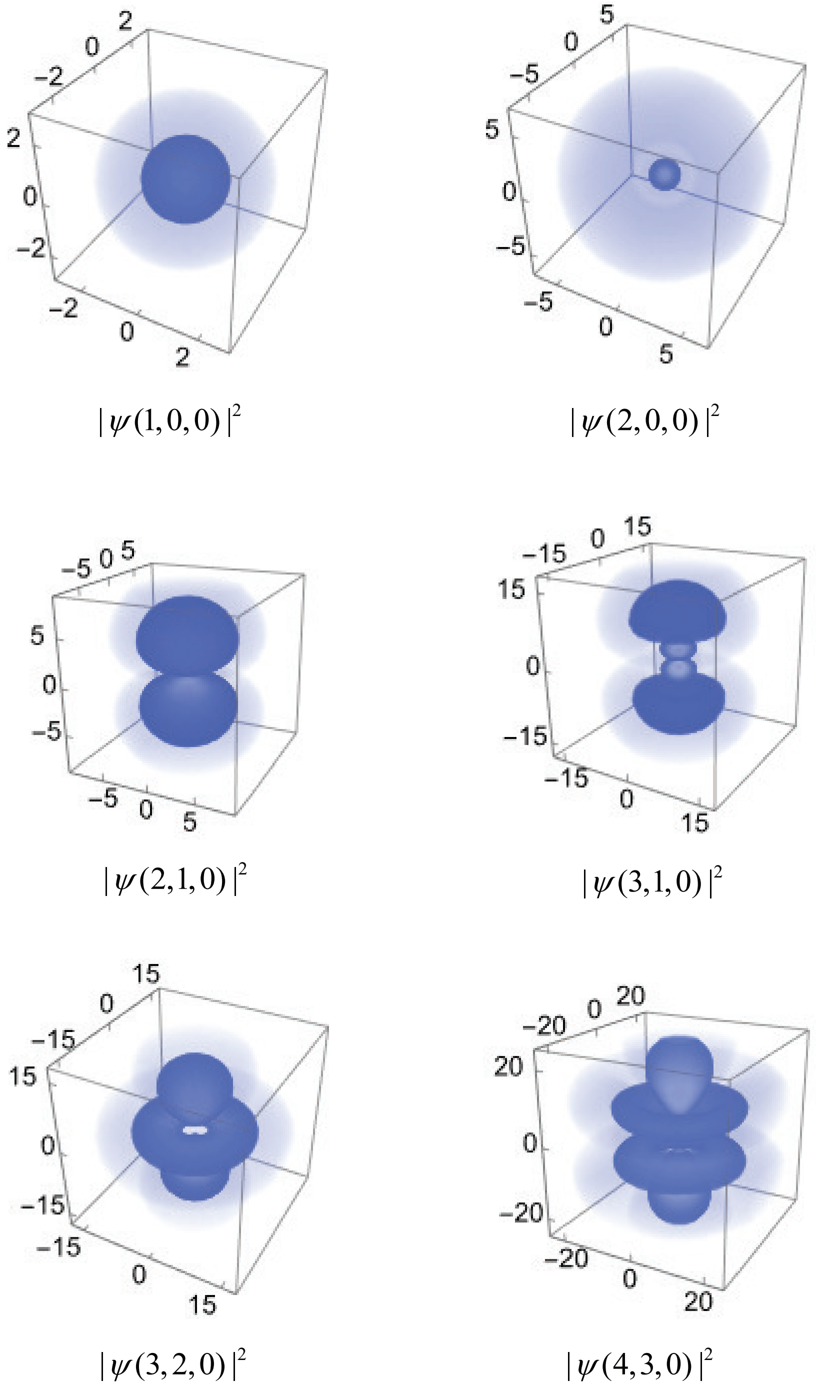
1.3.2 Radial probability density

To calculate the probability of locating the electron just between the radii r_o and $r_o + \Delta r$ which is the the probability of locating the electron in a thin veneer of space, shaped like a thin hollow ring of radius r_o. For this purpose, we need to consider all the θ and ϕ and the second integral in Eq. (1.153) becomes

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} d\theta\, d\phi\, \sin\theta |Y_{m_l}^l(\theta,\phi)|^2 = 1, \tag{1.154}$$

as spherical harmonic functions enumerated in Table 1.2 are already normalized. Therefore the radial probability becomes

$$\begin{aligned} \mathrm{P}(r_o, r_o + \Delta r) &= \int_{r_o}^{r_o+\Delta r} dr\, P_r(R) & (1.155)\\ \text{where } P_r(r) &= r^2 |R_{n,l}(r)|^2. & (1.156) \end{aligned}$$



$|\psi(1,0,0)|^2$ $|\psi(2,0,0)|^2$

$|\psi(2,1,0)|^2$ $|\psi(3,1,0)|^2$

$|\psi(3,2,0)|^2$ $|\psi(4,3,0)|^2$

Figure 1.7: Probability density functions of the hydrogen atom.

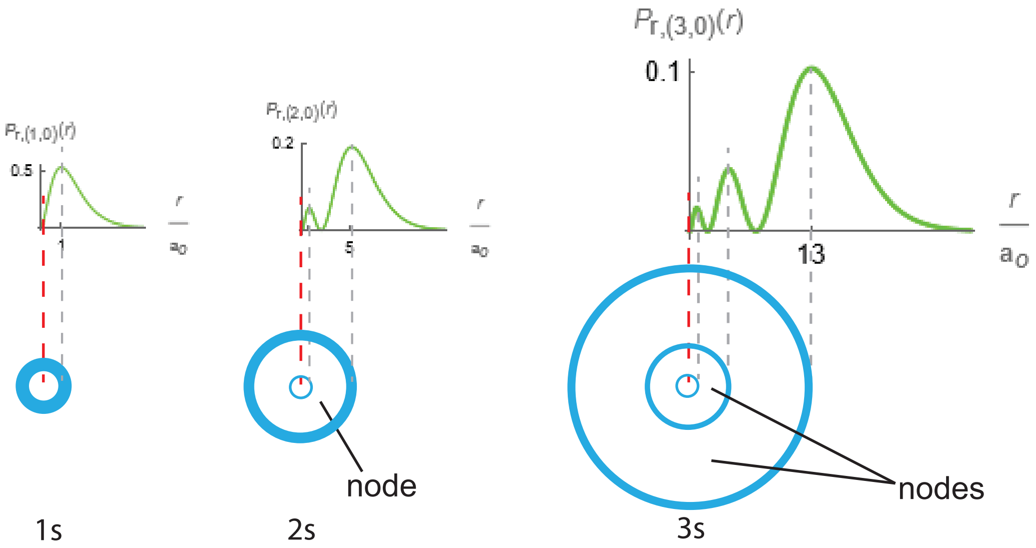


Figure 1.8: 1s, 2s and 3s radial probability distribution functions. The location of the antinodal rings are highlighted. In between the antinodal are the nodal region.

Here is one wholesome example that lets us look at different aspects of the radial structure of the electron state. Consider a $2p$ state given by

$$R_{2,1}(r) = Are^{-r/2a_o}$$

where A is a normalization constant and a_o is the Bohr radius. The radial probability density will be

$$P(r)_{r,(2,1)} = r^2|R_{2,1}(r)|^2 = |A|^2 r^4 e^{-r/a_o} dr$$

First of all we first find the constant A by imposing the normalization condition on just the radial function,

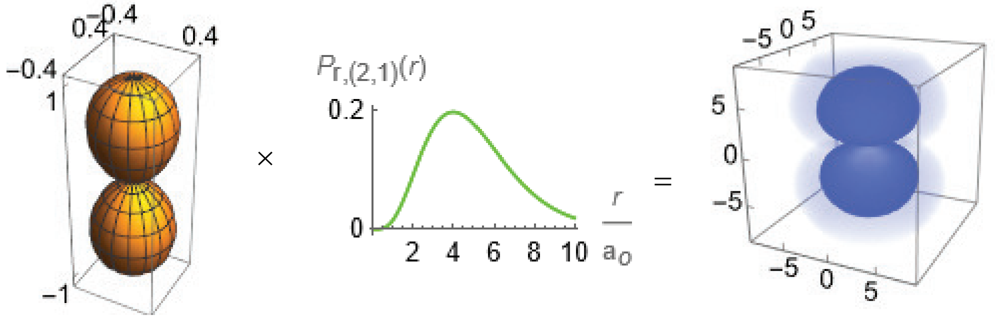
$$\begin{aligned} \int_{r=0}^{\infty} P(r)dr &= |A|^2 \int_{r=0}^{\infty} r^2 r^4 e^{-r/a_o} dr = 1 \\ &= A^2 a_o^5 4! \end{aligned}$$

and using the standard result, $\int_{z=0}^{\infty} z^n e^{-z} dz = n!$, we obtain

$$|A| = \frac{1}{a_o^{5/2} 2\sqrt{6}}$$

which is identical to the third entry in Table 1.3. In the next step, we We may like to calculate the average distance,

$$\langle r \rangle = \int dr\, r\, P_r(r) = A^2 \int dr\, r^5 e^{-r/a_o} = 5a_o,$$



$|Y_0^1|^2$ $|R_{2,1}|^2$ $|\psi_{2,1,0}|^2$

Figure 1.9: Modulus square of the angular part of the wavefunction for $n = 2$, $l = 1$ and $m_l = 0$ is multiplied with the associated radial probability density to yield a pobability density cloud in three dimensions.

which shows that the average (mean) density is five times the Bohr radius. In order to find the maxima, we compute

$$\frac{dP_r(r)}{dr} = |A|^2 \left(4r^3 e^{-r/a_o} - \frac{1}{a_o} r^4 e^{-r/a_o} \right)$$

and set it to zero, yielding $r_{max} = 4a_o$ This is where there is maximum probability of situating the electron, a so called antinode. The position of the average ($\langle r \rangle = 5a_o$) and maximum ($r_{max} = 4a_o$) are shown as a red triangle and dashed line in Figure 1.5 (i).

The definition of the radial density Eq. (1.156) is satisfying on another count as well. The maxima of the radial wavefunction at $r = 0$ (nuclear point) for $l = 0$ orbitals do not pose a problem since the pre-multiplication by r^2 ensures that the probability densities always vanish at the nuclear site. This fully matches our prediction from the uncertainty principle as elucidated in the argument that followed Eqs. (1.15) and (1.16). We cannot squish the atom to nothingness.

The right column of Figure 1.5 shows the radial probability densities for the few wavefunctions. They all start at $P_r(r = 0) = 0$. A node is a radius where $P_r(r) = 0$. It's possible to situate an electron in the vicinity of the node and very likely to be situated near some peak of $P_r(r)$. The peaks can be determined by setting $dP_r(r)/dr = 0$ and choosing where $d^2P_r(r)/dr^2 < 0$ (condition for a maximum that you learn in calculus). The number of nodes is $n-l-1$. This can be easily inspected from the plots of $P_r(r)$ in Figure 1.5.

1.3.3 Drawing the combined probability density emerging from radial and angular parts

In order to visualize the probability density of the overall function, it is quickest and simplest to use some 3D visualization software. For example, we depict a few probability density function for the hydrogenic wavefunction in Figure 1.7 using the popular software Mathematica. Some probability densities can also be visualized through one's mental faculties. For example consider $1s$, $2s$ and $3s$ orbitals where $P_r(r)$ are shown respectively in Figure 1.5 (g), (h) and (j) and reproduced in Figure 1.8. The angular wave function and hence $|Y^l_{m_l}(\theta,\phi)|^2$ are spherically symmetric. So the spherically uniform probability density is modulated along the radial direction by the function $P_r(r)$ whose undulating behavior creates a striated (or layered) structure which can be visualized as a sequence of rings centered at nucleus. This structure is shown in Figure 1.8.

For $n = 2$, $l = 1$ and $m_l = 0$ the wave function is

$$\psi_{2,1,0}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}a_o^{3/2}}\frac{r}{a_o}e^{-r/2a_o}\cos\theta. \tag{1.157}$$

The angular dependence is embodied through the p_z orbital but this is being modulated in the radial dimension by the radial wavefunction. The radial part is an exponentially decaying function $e^{-r/2a_o}$ multiplied by linear function r/a_o. The radial density is therefore proportional to r^4e^{-r/a_o}, whose form is also plotted in Figure 1.5 (e). We now combine the radial density $P_{r,(2,1)}$ with $Y^l_{m_l}|(\theta,\phi)|$ and obtain the result that looks similar to Figure 1.9.

1.3.4 Hydrogenic energy levels

In a hydrogen atom the energy levels are quantized and are given by Eq. (1.137) with the degeneracy $2n^2$ (Eq. (1.140)). These energy levels are not evenly spaced; instead, they come closer together as n increases. Hydrogen's emission spectrum shows bright lines at specific wavelengths, while its absorption spectrum displays dark lines at the same wavelengths. These spectrums are a finger print of the hydrogen atom. for example, the Lyman series refers to the group of spectral lines produced when an electron in a hydrogen atom transitions from a higher energy level $n \geq 2$ to the lowest energy level $n = 1$, resulting in ultraviolet emission. Refer to Figure 1.10. Similarly, the Balmer series is due to electron transitions from higher energy levels $n \geq 3$ to the $n = 2$ energy level, resulting in mostly visible light. The Paschen series, which falls in the near-infrared region, comprises spectral lines resulting from $n \geq 4$ down to $n = 3$. The Rydberg formula helps

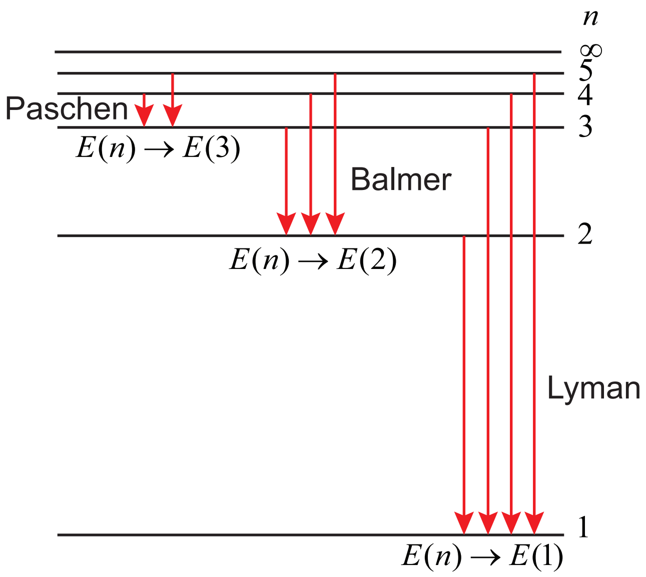


Figure 1.10: Transitions between the energy levels inside the hydrogen atom.

calculate the wavelengths corresponding to these transitions,

$$\frac{1}{\lambda} = \frac{E_i - E_f}{hc} = \frac{E_1}{hc}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] = R\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] \tag{1.158}$$

where R is the Rydberg constant with a value of $1.097 \times 10^7 m^{-1}$ and E_1 is defined in Eq. (1.137).