In this Chapter the one-electron atom will be examined. The simplest one-electron atom is the Hydrogen atom; it has one proton and one electron. Its potential is well known: the Coulomb potential. The Hydrogen atom is the simplest bound system.

In order to describe the properties of the one-electron atom, we must solve the three-dimensional Schrödinger equation. The solutions of the Schrödinger equation will provide us with the following information:

1. Provide us with a "picture" of the electron orbits. Note: we can use the wavefunction to construct a picture of the distributions of the most likely position of the electrons. Our ability to do his does not violate the uncertainty principle.
2. The wavefunctions can be used to introduce the concept of angular momentum. The details differ from the Bohr predictions but agree with the results of experiments.
3. Electron spin.
4. Transition rate.

The one-electron atom is a two-body system, and to find a solution to the Schrödinger equation we need to solve a two-body problem. However, the two-body problem can be converted to a on-body problem by using the reduced mass and the distance between the two bodies in our calculations. The following substitution will be required:

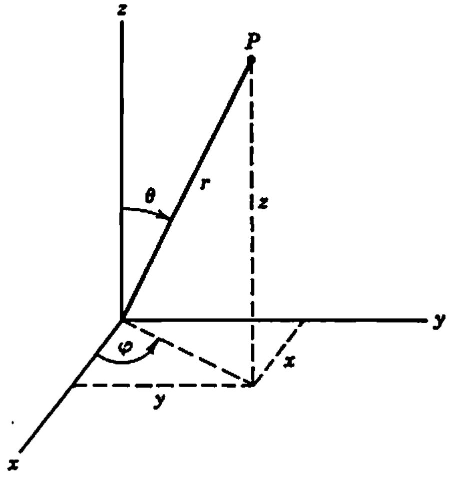
$$m_2 \quad \rightarrow \quad \frac{M_p}{M_p + m_e} m_e$$

The potential of the one-electron atom only depends on the magnitude of r and not on its direction:

$$V(r) = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r}$$

where Z is the number of protons in the atom. For Hydrogen, $Z = 1$.

Since the system has spherical symmetry, due to the fact that the potential only depends on the magnitude of r, we can use spherical coordinates to study this system. The spherical coordinates are related to the Cartesian coordinates:



$$
\begin{aligned}
x &= r\cos\varphi\sin\theta \\
y &= r\sin\varphi\sin\theta \\
z &= r\cos\theta
\end{aligned}
$$

The wavefunction that describes the one-electron atom is a solution of the Schrödinger equation:

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

The **Laplacian operator** ∇^2 is defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For the one-electron atom, the potential does not depend on time t. In this case, we can use separation of variables to separate the time-dependent component of the wavefunction from the space-dependent part:

$$\Psi(x,y,z,t) = \psi(x,y,z)e^{-iEt/\hbar}$$

The space-dependent part of the wavefunction must satisfy the following equation:

$$
\begin{aligned}
&-\frac{\hbar^2}{2\mu}\nabla^2\left(\psi(x,y,z)e^{-iEt/\hbar}\right) + V\left(\psi(x,y,z)e^{-iEt/\hbar}\right) = i\hbar\frac{\partial}{\partial t}\left(\psi(x,y,z)e^{-iEt/\hbar}\right) \quad \Leftrightarrow \\
&\left[-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi\right]e^{-iEt/\hbar} = i\hbar\left(\frac{-iE}{\hbar}\right)\psi e^{-iEt/\hbar} = E\psi e^{-iEt/\hbar} \quad \Rightarrow \quad \boxed{-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi}
\end{aligned}
$$

The potential V depends on x, y, and z and we cannot simplify this equation by considering further separation of variables:

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

However, since the potential depends on the magnitude of r, switching to spherical coordinates may allow us to use separation of variables using spherical coordinates.
The Laplacian operator in terms of spherical coordinates is given by:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Now consider that we can write the wavefunction in the following way:

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

The Schrödinger equation can be rewritten as

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi \quad \Rightarrow \quad -\frac{\hbar^2}{2\mu}\frac{1}{\psi}\nabla^2\psi + V = E$$

With this separation of variables we note that

$$\begin{aligned}
\frac{\partial\psi}{\partial r} &= \Theta(\theta)\Phi(\varphi)\frac{dR}{dr} \\
\frac{\partial\psi}{\partial\theta} &= R(r)\Phi(\varphi)\frac{d\Theta}{d\theta} \\
\frac{\partial\psi}{\partial\varphi} &= R(r)\Theta(\theta)\frac{d\Phi}{d\varphi}
\end{aligned}$$

The Laplacian of this wavefunction can be written as

$$\frac{1}{\psi}\nabla^2\psi = \frac{1}{R(r)}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta(\theta)}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi(\varphi)}\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}$$

The Schrödinger equation now becomes

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{\hbar^2}{2\mu}\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{\hbar^2}{2\mu}\frac{1}{\Phi}\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2} + V(r) = E \quad \Rightarrow$$

$$\underbrace{\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)}_{\text{Depends on } r} + \underbrace{\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)}_{\text{Depends on } r \text{ and } \theta} + \underbrace{\frac{1}{\Phi}\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}}_{\text{Depends on } r,\, \phi, \text{ and } \theta} = \underbrace{-\frac{2\mu}{\hbar^2}\left(E - V(r)\right)}_{\text{Depends on } r} \quad \Rightarrow$$

$$\underbrace{\left[\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{2\mu}{\hbar^2}\left(E - V(r)\right)\right]r^2\sin^2\theta}_{\text{Depends on } r \text{ and } \theta} = -\underbrace{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}}_{\text{Depends on } \phi}$$

The left-hand side of the last equation does not depend on the azimuthal angle and must thus add up to a constant:

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=-m_\ell^2 \quad\Rightarrow\quad \frac{\partial^2\Phi}{\partial\varphi^2}=-m_\ell^2\Phi \quad\Rightarrow\quad \Phi(\varphi)=e^{im_\ell\varphi}$$

Since the solution must be the same when the azimuthal angle changes by 2π, we must require that

$$\Phi(\varphi)=\Phi(\varphi+2\pi)=e^{im_\ell(\varphi+2\pi)}=e^{im_\ell\varphi}e^{i2\pi m_\ell}=\Phi(\varphi)e^{i2\pi m_\ell} \quad\Rightarrow$$

$$e^{i2\pi m_\ell}=\cos(2\pi m_\ell)+i\sin(2\pi m_\ell)=1 \quad\Rightarrow\quad m_\ell=0,\pm1,\pm2,\pm3,...$$

With this solution for the azimuthal component of the wavefunction, the Schrödinger equation becomes

$$\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-\frac{m_\ell^2}{r^2\sin^2\theta}=-\frac{2\mu}{\hbar^2}\left(E-V(r)\right)$$

This equation can be rewritten in the following way:

$$\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}\left(E-V(r)\right)=\frac{m_\ell^2}{r^2\sin^2\theta}-\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) \quad \underset{\text{Multiply by } r^2}{\Rightarrow}$$

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)}_{\text{Depends on } r}=\underbrace{\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)}_{\text{Depends on } \theta}$$

The left-hand and the right-hand sides must thus be equal to a constant; assume the constant is $\ell(\ell+1)$. Let us first look at the right-hand side of this equation:

$$\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)=\ell(\ell+1) \quad\Rightarrow\quad -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{m_\ell^2}{\sin^2\theta}\Theta=\ell(\ell+1)\Theta$$

The solution of this differential equation can be written in the following way:

$$\Theta(\theta)=\sin^{|m_\ell|}\theta\, F_{\ell,|m_\ell|}(\cos\theta)$$

where $F_{\ell,|m_\ell|}(\cos\theta)$ is a polynomial in $\cos\theta$.

The radial component of the wavefunction is a solution of the following differential equation:

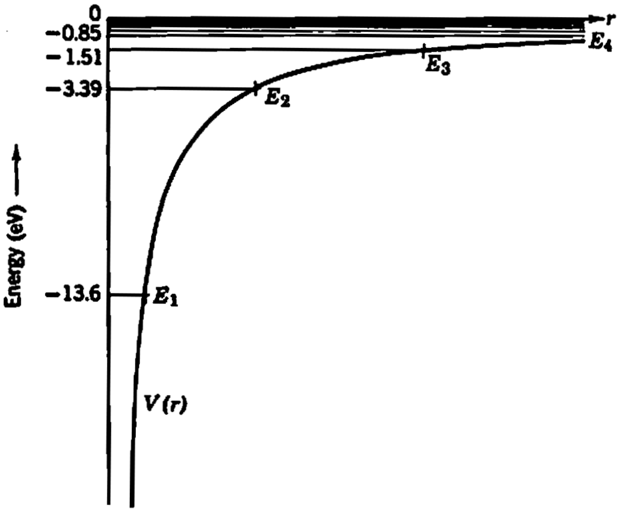
$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)=\ell(\ell+1) \Rightarrow \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}\left(E-V(r)\right)R=\ell(\ell+1)\frac{R}{r^2}$$

The solution of this differential equation is

$$R(r)=e^{-Zr/na_0}\left(\frac{Zr}{a_0}\right)^{\ell}G_{n,\ell}\left(\frac{Zr}{a_0}\right) \quad where \quad a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

where $G_{n,\ell}(Zr/a_0)$ is a polynomial in Zr/a_0. Details on the derivation of this solution can be found in appendix N of the textbook.

The corresponding energy, shown schematically in the Figure on the right, is quantized and determined by the quantum number n:



$$E_n=-\frac{\mu Z^2e^4}{2\left(4\pi\varepsilon_0\right)^2\hbar^2n^2}$$

This energy is the same as the energy obtained with the Bohr model.

The wavefunction of the one-electron atom is thus specified by three quantum numbers: n, m, and ℓ:

1. **Principle quantum number *n***. The principle quantum number can be 1, 2, 3, …. The energy of the system depends on n only.
2. **Azimuthal quantum number ℓ**. The azimuthal quantum number can be 0, 1, 2, …, n-1. The azimuthal quantum number is related to the angular momentum of the system.
3. **Magnetic quantum number *m***. The values of the magnetic quantum number depend on the value of the azimuthal quantum number:

$$m_\ell=-\ell,-\ell+1,....,\ell-1,\ell$$

In an external magnetic field, the energy levels of the atom will have an m dependence.

Since the energy of the wavefunction is determined by the value of n, a number of wavefunctions (with the same principle quantum number but different azimuthal and magnetic quantum numbers) will have the same energy. These wavefunctions are said to be **degenerate**.

The solution of the Schrödinger equation can thus be written as

$$\psi_{n\ell m}(r,\theta,\varphi)=R_{n\ell}(r)\Theta_{\ell m}(\theta)\Phi_m(\varphi)$$

This energy E_n associated with the wavefunction is given by

$$E_n=-\frac{\mu Z^2e^4}{2(4\pi\varepsilon_0)^2\hbar^2n^2}$$

The wavefunction provides us with information about the radial position of the electron. To look at the radial distribution we examine the following probability density distribution:

$$\underbrace{P_{n\ell}(r)dr}_{\substack{\text{Probability to find the electron}\\ \text{between } r \text{ and } r\,+\,dr.}}=R^*(r)R(r)\underbrace{4\pi r^2dr}_{\substack{\text{Volume between a sphere}\\ \text{of radius } r \text{ and radius } r\,+\,dr.}}$$

Examples of the radial probability distributions for several different quantum numbers are shown in the Figure on Page 7.

The average radial position can be calculated in the following way:

$$\bar{r}_{n\ell}=\int_0^\infty rP_{n\ell}\,dr=\frac{n^2a_0}{Z}\left\{1+\frac{1}{2}\left[1-\frac{\ell(\ell+1)}{n^2}\right]\right\}$$

The radial positions consistent with the Bohr model are given by the following expression:

$$\bar{r}_{Bohr}=\frac{n^2a_0}{Z}$$

Expressing the average radial position in terms of the Bohr radius we obtain

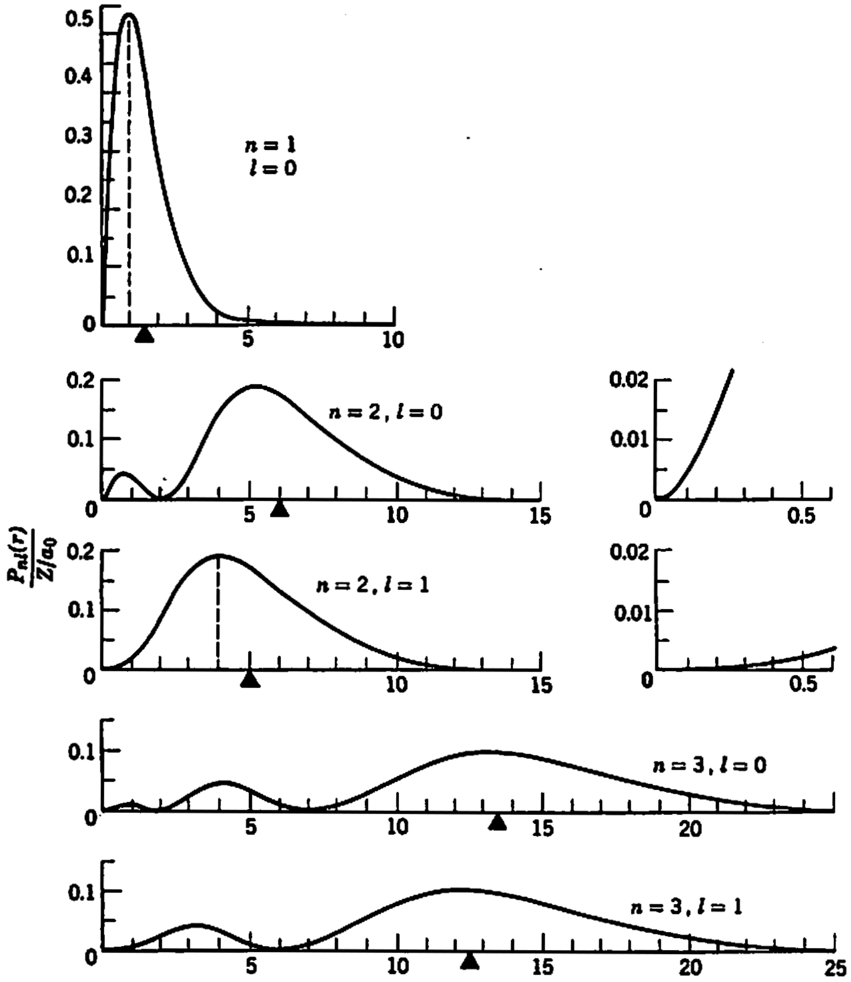
$$\bar{r}_{n\ell}=\bar{r}_{Borh}\left\{1+\frac{1}{2}\left[1-\frac{\ell(\ell+1)}{n^2}\right]\right\}$$

The largest difference occurs for *n* = 0 for which the Bohr radius is 50% larger than the radius obtained from the quantum mechanical model. For larger values of *n* the percentage difference between these radii decreases.

By looking at the radial probability distributions, shown in the Figure below, we conclude:

1. The radial probability distributions are concentrated over a restricted range of radial positions.
2. For a fixed principle quantum number *n*, there are differences in the radial distribution for different values of ℓ.
3. When the principle quantum number *n* increases the average radial position increases.
4. The average radii are similar to the radii that correspond to the classical Bohr orbits.
5. Only for $\ell = 0$ is the probability density significant near $r = 0$.
6. The average position is located at distances larger.

The average radial position obtained for *n* = 1 is taken to be the size of the atom.



At small distances, the exponent of $-Zr/a_0$ is approximately equal to 1 and the wavefunctions close to $r = 0$ are proportional to:

$$\begin{aligned} \ell = 0: &\quad \psi \propto \text{constant} \\ \ell = 1: &\quad \psi \propto r \\ \ell = 2: &\quad \psi \propto r^2 \end{aligned}$$

See Table 7-2 in the textbook. In general we find that close to $r = 0$ the wavefunction $\psi \propto r^{\ell}$.

To examine the angular dependence of the probability density distribution we need to examine the following function:

$$\psi^*\psi = \left(R^*R\right)\left(\Theta^*\Theta\right)\left(\Phi^*\Phi\right)$$

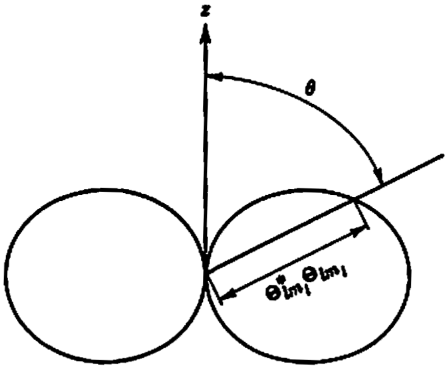
Using the known solution for the azimuthal component of the wavefunction we conclude that

$$\Phi^*\Phi = e^{-im\varphi}e^{im\varphi} = 1$$

and the probability density distribution has thus no azimuthal angular dependence.

To examine the polar angular dependence, we use **polar diagrams**. To construct polar diagrams, we follow the procedure outlined in the Figure on the right:

1. At a given angle θ calculate $\Theta_{\ell m}(\theta)$.
2. The probability density is proportional to $\Theta^*_{\ell m}(\theta)\Theta_{\ell m}(\theta)$.
3. Plot a point at an angle θ with respect to the z axis, a distance $\Theta^*_{\ell m}(\theta)\Theta_{\ell m}(\theta)$ away from the origin.
4. Doing this for all values of θ generates the polar diagram.



Rotating the polar diagram around the z axis can visualize the region in space where the electron is most likely to be found. Examples of polar diagrams for $\ell = 3$ are shown on the next page. We see that when the magnitude of m increase the polar diagram becomes flatter; it is less likely that the electron will be found close to the z axis.

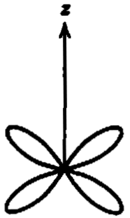
In the Bohr model, the angular momentum of the electron was assumed to be quantized. This assumption was required in order to be able to predict the quantized nature of the energy levels observed in Hydrogen. In our study of the one-electron atom we have not made this assumption, but we can show that the wavefunction we obtained by solving the Schrödinger equation is consistent with this assumption. In order to be able to determine the angular momentum associated with our wavefunction, we must introduce the angular momentum operator.

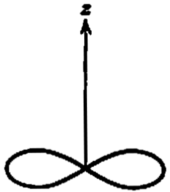
In classical mechanics, the angular momentum of a particle is defined as

$$\vec{L} = \vec{r} \times \vec{p}$$


$l = 3, m_l = 0$


$l = 3, m_l = \pm 1$


$l = 3, m_l = \pm 2$


$l = 3, m_l = \pm 3$

The Cartesian components of the angular momentum are:

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

In order to determine the expectation value of the angular momentum and/or its components we need to determine the expectation values of the products of positions and linear momentum. Let us first consider the *z* component of the angular momentum:

$$L_z = xp_y - yp_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

We note that the position and momentum operator operate on different Cartesian coordinates, and the order of operation thus does not matter.

Since the wavefunction is expressed in terms of spherical coordinates, we also have to express the various angular momentum operators in terms of spherical coordinates. Since we know the relation between Cartesian and spherical coordinates, we can differentiate these expressions to obtained relations between the changes in the Cartesian coordinates and the changes in the spherical coordinates. For example, consider the relations between the changes in x, y, and z and the change in φ:

$$\left.\begin{array}{l} x = r\cos\varphi\sin\theta \quad \Rightarrow \quad \dfrac{\partial x}{\partial\varphi} = -r\sin\varphi\sin\theta = -y \\[2ex] y = r\sin\varphi\sin\theta \quad \Rightarrow \quad \dfrac{\partial y}{\partial\varphi} = r\cos\varphi\sin\theta = x \\[2ex] z = r\cos\theta \quad \Rightarrow \quad \dfrac{\partial z}{\partial\varphi} = 0 \end{array}\right\} \Rightarrow \left\{\begin{array}{l} \dfrac{\partial\psi}{\partial\varphi} = \dfrac{\partial x}{\partial\varphi}\dfrac{\partial\psi}{\partial x} + \dfrac{\partial y}{\partial\varphi}\dfrac{\partial\psi}{\partial y} + \dfrac{\partial z}{\partial\varphi}\dfrac{\partial\psi}{\partial z} \quad \Leftrightarrow \\[2ex] \qquad \dfrac{\partial\psi}{\partial\varphi} = -y\dfrac{\partial\psi}{\partial x} + x\dfrac{\partial\psi}{\partial y} \end{array}\right.$$

Comparing the last expression with the expression for *Lz* in Cartesian coordinates, we conclude that

$$L_z\psi = -i\hbar\left\{x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right\}\psi = -i\hbar\frac{\partial}{\partial\varphi}\psi$$

In a similar fashion we can obtain expressions for the *x* and *y* components of the angular momentum:

$$L_x\psi = -i\hbar\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}\psi = -i\hbar\left\{\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right\}\psi$$

$$L_y\psi = -i\hbar\left\{z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right\}\psi = -i\hbar\left\{-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right\}\psi$$

These relations can also be obtained by using the following relations between the differential operators in the Cartesian and spherical coordinate systems:

$$\frac{\partial}{\partial x} = \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}$$

Using the known solution of the Schrödinger equation we immediately see that this solution is an eigenfunction of the z component of L operator:

$$L_z|\psi\rangle = -i\hbar\frac{\partial}{\partial\varphi}|\psi\rangle = -i\hbar\frac{\partial}{\partial\varphi}(R\Theta\Phi) = -i\hbar R\Theta\frac{\partial}{\partial\varphi}(\Phi) = -i\hbar(im)R\Theta\Phi = m\hbar|\psi\rangle$$

The solution of the Schrödinger equation is not an eigenfunction of the x and y components of the L operator. However, the solutions are eigenfunctions of the operator L^2:

$$\begin{aligned} L^2 &= L_x^2 + L_y^2 + L_z^2 = \\ &= -\hbar^2\left(\left\{\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right\}^2 + \left\{-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right\}^2 + \left\{\frac{\partial}{\partial\varphi}\right\}^2\right) = \\ &= -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}\right\} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) \end{aligned}$$

Applying this operator to the solution of the Schrödinger equation we obtain the following:

$$\begin{aligned} L^2|\psi\rangle &= -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}\right\} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)R\Theta\Phi = \\ &= -\hbar^2\left((R\Phi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}\right\}\Theta + R\Theta\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Phi\right) = \\ &= \hbar^2(R\Phi)\left(-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}\right\}\Theta + \frac{m^2}{\sin^2\theta}\Theta\right) = \hbar^2(R\Phi)\big(\ell(\ell+1)\Theta\big) = \ell(\ell+1)\hbar^2|\psi\rangle \end{aligned}$$

We thus conclude that

$$\langle L_z\rangle = \langle\psi|L_z\psi\rangle = m\hbar\langle\psi|\psi\rangle = m\hbar$$

$$\langle L^2\rangle = \langle\psi|L^2\psi\rangle = \ell(\ell+1)\hbar^2\langle\psi|\psi\rangle = \ell(\ell+1)\hbar^2$$

We thus see that the expectation values of L_z and L^2 are quantized. Any wavefunction that is a solution of the Schrödinger equation thus has a well-defined total angular momentum and a well-defined projection on the z axis.

We must note that the observation that the expectation value of an operator is quantized does not immediately imply that the wavefunction is an eigenfunction of the operator. In order to show that the wavefunction is an eigenfunction of the operator we must also show that the spread in the operator is zero. This implies that

$$\Delta A \equiv \sqrt{\overline{A^2} - \overline{A}^2} = 0$$

We can easily verify that this is relation is satisfied for both L_z and L^2. On the other hand, the operators L_x and L_y operating on the solution of the Schrödinger equation produce a new wavefunction that is not proportional to the original wavefunction. The wavefunctions are thus not eigenfunction of these operators.

In the remainder of these notes, material that is not covered in the book is introduced to describe other important properties of operators related to the angular momentum operator.
The L_x and L_y are commonly combined to create what are called **the raising and lowering operators**:

$$L_\pm = L_x \pm iL_y$$

The product of these two operators is equal to

$$L_+L_- = \left(L_x + iL_y\right)\left(L_x - iL_y\right) = L_x^2 + L_y^2 - i\left(L_xL_y - L_yL_x\right) = L_x^2 + L_y^2 - i\left[L_x, L_y\right]$$

Using the expressions for the Cartesian coordinates of the linear momentum operators we can rewrite $\left[L_x, L_y\right]$, **the commutation relation between L_x and L_y**, as

$$\begin{aligned}
\left[L_x, L_y\right] &= L_xL_y - L_yL_x = \\
&= -\hbar^2\left\{\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right\}\left\{-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right\} + \\
&\qquad -\hbar^2\left\{\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right\}\left\{\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right\} = \\
&= -\hbar^2\left\{-\frac{\sin^2\varphi}{\sin^2\theta}\frac{\partial}{\partial\varphi} + \cot^2\theta\cos^2\varphi\frac{\partial}{\partial\varphi} - \frac{\cos^2\varphi}{\sin^2\theta}\frac{\partial}{\partial\varphi} + \cot^2\theta\sin^2\varphi\frac{\partial}{\partial\varphi}\right\} = \\
&= -\hbar^2\left\{-\frac{1}{\sin^2\theta}\frac{\partial}{\partial\varphi} + \cot^2\theta\frac{\partial}{\partial\varphi}\right\} = \hbar^2\frac{\partial}{\partial\varphi} = i\hbar\left(-i\hbar\frac{\partial}{\partial\varphi}\right) = i\hbar L_z
\end{aligned}$$

In the same way we can confirm the following commutation relations:

$$\left[L_y, L_z\right] = i\hbar L_x$$

$$\left[L_z, L_x\right] = i\hbar L_y$$

When a commutation relation between two operators is not equal to zero, the order of operation matters and when we evaluate expectation values associated with these operators we will have to symmetrized expressions of these operators. Consider for example the one-dimensional linear momentum operator p and the one-dimensional position operator x. The commutation relation between p and x is equal to

$$[p,x] = \left[-i\hbar\frac{\partial}{\partial x}, x\right] = \left\{\left(-i\hbar\frac{\partial}{\partial x}\right)x\right\} - \left\{x\left(-i\hbar\frac{\partial}{\partial x}\right)\right\} = \left(-i\hbar - i\hbar x\frac{\partial}{\partial x}\right) + \left(i\hbar x\frac{\partial}{\partial x}\right) = -i\hbar$$

This tells us that the order of operation matters. In order to calculate the expectation values of various combinations of p and x we have to use expressions that are symmetric in p and x. For example:

$$xp \quad \rightarrow \quad \frac{1}{2}(xp + px)$$

$$x^2 p \quad \rightarrow \quad \frac{1}{4}\left(x^2 p + 2xpx + px^2\right)$$

Using the commutation relation we can rewrite the expression of the product of the raising and the lowering operator:

$$L_+L_- = \left(L_x + iL_y\right)\left(L_x - iL_y\right) = L_x^2 + L_y^2 - i\left(L_xL_y - L_yL_x\right) = L_x^2 + L_y^2 - i\left[L_x, L_y\right] = L^2 - L_z^2 + \hbar L_z$$

In the same way we can calculate the product of the lowering and the raising operator:

$$L_-L_+ = \left(L_x - iL_y\right)\left(L_x + iL_y\right) = L_x^2 + L_y^2 + i\left(L_xL_y - L_yL_x\right) = L_x^2 + L_y^2 + i\left[L_x, L_y\right] = L^2 - L_z^2 - \hbar L_z$$

The commutation relation between the raising and the lowering operator is thus equal to

$$\left[L_+, L_-\right] = L_+L_- - L_-L_+ = \left(L^2 - L_z^2 + \hbar L_z\right) - \left(L^2 - L_z^2 - \hbar L_z\right) = 2\hbar L_z$$

The commutation relation between the raising and lowering operators and L_z can now also be evaluated:

$$\left[L_+,L_z\right]=\left[L_x+iL_y,L_z\right]=\left[L_x,L_z\right]+i\left[L_y,L_z\right]=-i\hbar L_y+i\left(i\hbar L_x\right)=-\hbar\left(L_x+iL_y\right)=-\hbar L_+$$

$$\left[L_-,L_z\right]=\left[L_x-iL_y,L_z\right]=\left[L_x,L_z\right]-i\left[L_y,L_z\right]=-i\hbar L_y-i\left(i\hbar L_x\right)=+\hbar\left(L_x-iL_y\right)=+\hbar L_-$$

Applying these commutation relations to the solution of the Schrödinger equation we make the following observation:

$$\left[L_+,L_z\right]\psi_{n\ell m}=\left(L_+L_z-L_zL_+\right)\psi_{n\ell m}=m\hbar L_+\psi_{n\ell m}-L_zL_+\psi_{n\ell m}=-\hbar L_+\psi_{n\ell m}$$

$$\left[L_-,L_z\right]\psi_{n\ell m}=\left(L_-L_z-L_zL_-\right)\psi_{n\ell m}=m\hbar L_-\psi_{n\ell m}-L_zL_-\psi_{n\ell m}=+\hbar L_-\psi_{n\ell m}$$

We can rewrite these relations in the following way:

$$L_z\left(L_+\psi_{n\ell m}\right)=\left(m+1\right)\hbar\left(L_+\psi_{n\ell m}\right)$$

$$L_z\left(L_-\psi_{n\ell m}\right)=\left(m-1\right)\hbar\left(L_-\psi_{n\ell m}\right)$$

We thus see that when we operate the raising operator on a solution of the Schrödinger equation with a magnetic quantum number m we create another solution that has a magnetic quantum number m+1; ***m* is raised by 1**. When we operate the lowering operator on a solution of the Schrödinger equation with a magnetic quantum number m we create another solution that has a magnetic quantum number m-1; ***m* is lowered by 1**. In order to fully understand how the raising and lowering operators operate on the wavefunctions we need to determine how they change the azimuthal quantum number ℓ. In order to address this question we observe that

$$\left[L^2,L\right]=0$$

From this relation we conclude that

$$\left[L^2,L_\pm\right]=0$$

$$\left[L^2,L_z\right]=0$$

To proof the last commutation relation we observe that:

$$\begin{aligned}\left[L^2,L_z\right] &= \left[L_x^2+L_y^2+L_z^2,L_z\right]=\left[L_x^2,L_z\right]+\left[L_y^2,L_z\right]\\ &= L_x^2L_z-L_zL_x^2+L_y^2L_z-L_zL_y^2=\\ &= L_x\left(L_xL_z-L_zL_x\right)+\left(L_xL_z-L_zL_x\right)L_x+L_y\left(L_yL_z-L_zL_y\right)+\left(L_yL_z-L_zL_y\right)L_y=\\ &= L_x\left[L_x,L_z\right]+\left[L_x,L_z\right]L_x+L_y\left[L_y,L_z\right]+\left[L_y,L_z\right]L_y=\\ &= -i\hbar L_xL_y-i\hbar L_yL_x+i\hbar L_yL_x+i\hbar L_xL_y=0\end{aligned}$$

The relation between L^2 and the raising and lowering operators can be demonstrated in the same manner.

Now consider the following relations:

$$\left[L^2,L_+\right]\psi_{n\ell m}=\left(L^2L_+-L_+L^2\right)\psi_{n\ell m}=L^2\left(L_+\psi_{n\ell m}\right)-\ell(\ell+1)\hbar^2\left(L_+\psi_{n\ell m}\right)=0$$

$$\left[L^2,L_-\right]\psi_{n\ell m}=\left(L^2L_--L_-L^2\right)\psi_{n\ell m}=L^2\left(L_-\psi_{n\ell m}\right)-\ell(\ell+1)\hbar^2\left(L_-\psi_{n\ell m}\right)=0$$

These imply that

$$L^2\left(L_+\psi_{n\ell m}\right)=\ell(\ell+1)\hbar^2\left(L_+\psi_{n\ell m}\right)$$

$$L^2\left(L_-\psi_{n\ell m}\right)=\ell(\ell+1)\hbar^2\left(L_-\psi_{n\ell m}\right)$$

We thus conclude that operating the raising or the lowering operator on a solution of the Schrödinger equation does not change the azimuthal quantum number.

The raising and lowering operators are important operators since they can be part of an operator that is responsible for transitions between atomic states. The solutions of the Schrödinger equation are orthogonal:

$$\left\langle\psi_{n\ell m}\middle|\psi_{n'\ell'm'}\right\rangle=\delta_{n.n'}\delta_{\ell,\ell'}\delta_{m,m'}$$

There is thus no overlap between states with different magnetic quantum numbers and thus no spontaneous transitions between states with different quantum numbers. On the other hand, if an operator operates on the system and the operator contains raising and lowering operators, transitions between states with different magnetic quantum numbers become possible.