Notes follow and parts taken from sources in Bibliography

Formalism

Just as ordinary vectors live in (or span) a vector space, the wave functions we deal with span something called Hilbert space. The wave functions are like vectors with an infinite number of components. The reason linear algebra is so important when studying quantum mechanics is that, while the wave functions are like vectors, operators are like matrices and the result of an operator acting on a wave function can be represented by an infinite-dimensional matrix multiplying an infinite dimensional vector. Because the vectors have to be normalizable, the Hilbert space is restricted to wave functions $\psi$ satisfying

$$\int_{a}^{b} |\psi|^2 \, dx < \infty$$

We’ve already seen the form for expectation values, and it looks similar to what we have above.

$$\langle m | \hat{x} | n \rangle = \int \psi_m^*(x) x \psi_n(x) \, dx$$

Operators that represent physically observable quantities (like position or momentum) have to have a special property. The reason for this restriction on these operators is that physically observable quantities have to be real – we can’t measure a complex position or momentum for some particle. A real expectation value corresponds to the equality below:

$$\langle Q \rangle = \langle Q \rangle^*$$

We can rewrite the previous expression in a more expanded and complete form as

$$\langle \psi | \hat{Q} \psi \rangle = \langle \hat{Q} \psi | \psi \rangle$$

Operators for which the previous equation holds are known as hermitian operators. A matrix representation of a hermitian operator is one that is equal to the complex conjugate of its transpose. In other words, rows and columns are switched and $i \rightarrow -i$. A hermitian operator acting to the right on a wave function $\psi$ is the same as the operator’s complex conjugate acting to the left on the wave function’s conjugate $\psi^*$. 
**Eigenstates & Eigenfunctions**

From the German word meaning “characteristic”, eigenfunctions are like eigenvectors in ordinary finite-dimensional linear algebra. For a given matrix $A$, an eigenvector $x$ satisfies the relationship below:

$$\hat{A} \tilde{x} = a \tilde{x}$$

In this equation, $a$ (which is just a number) is known as the **eigenvalue** corresponding to the eigenvector $x$. For example, if the matrix representation of our operator $A$ is

$$\hat{A} = \begin{pmatrix} 1 & 1 & 3 \\ 1 & 4 & 5 \\ 2 & 1 & 2 \end{pmatrix}$$

the following eigenvectors and eigenvalues satisfy our previous equation:

$$\begin{pmatrix} 1 & 1 & 3 \\ 1 & 4 & 5 \\ 2 & 1 & 2 \end{pmatrix} \begin{pmatrix} 1 \\ \sqrt{6} \\ 1 \end{pmatrix} = 4 + \sqrt{6} \begin{pmatrix} 1 \\ \sqrt{6} \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 1 & 3 \\ 1 & 4 & 5 \\ 2 & 1 & 2 \end{pmatrix} \begin{pmatrix} 1 \\ -\sqrt{6} \\ 1 \end{pmatrix} = 4 - \sqrt{6} \begin{pmatrix} 1 \\ -\sqrt{6} \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 1 & 3 \\ 1 & 4 & 5 \\ 2 & 1 & 2 \end{pmatrix} \begin{pmatrix} -10 \\ -7 \\ 9 \end{pmatrix} = -10 \begin{pmatrix} -10 \\ -7 \\ 9 \end{pmatrix}$$

If a system is in the eigenstate $x$, measuring the observable associated with $A$ will always give the same eigenvalue $a$. Your book has a short proof that the uncertainty in the measurement of $A$ in this eigenstate is zero. We have seen eigenstates of energy in the square well and harmonic oscillator problems. Energy measurements of a particle in an eigenstate will always give the same value for the energy.

There could be a finite set of eigenstates and eigenvalues (true for bound state problems with discrete eigenvalues) or an infinite set (true for continuous eigenvalues). A few interesting properties of these operators are explored in proofs in your book (reproduced here).
In the discrete case, hermitian operators have real eigenvalues; if two eigenvalues are different, their associated eigenfunctions are orthogonal to one another. First:

\[
\langle \psi | \hat{Q} | \psi \rangle \Rightarrow \langle \psi | \hat{Q} \psi \rangle = \langle \hat{Q} \psi | \psi \rangle \quad \text{so}
\]

\[
q < \psi | \psi > = q^* < \psi | \psi >
\]

which requires the eigenvalue q to be real since \( \psi = 0 \) is not allowable as an eigenfunction. For the second proof, consider two different eigenfunctions \( \psi \) and \( \phi \) with eigenvalues q and q’ and notice that

\[
\langle \psi | \hat{Q} \phi \rangle = \langle \hat{Q} \psi | \phi \rangle
\]

\[
q' < \psi | \phi > = q^* < \psi | \phi >
\]

Since we just saw that q is real, q* = q and our initial assumption was that the two eigenvalues q and q’ were distinct. The only remaining conclusion is that \( <\psi|\phi> = 0 \). For a continuous spectrum of eigenvalues, the condition on orthonormality is altered. The eigenfunctions of the momentum operator, for example, are written in the Griffiths book as

\[
f_p(x) = Ae^{ipx/\hbar}
\]

We can kind of normalize this by calculating

\[
\int_{-\infty}^{\infty} f_{p'}(x) * f_p(x) = |A|^2 \int_{-\infty}^{\infty} e^{i(p'-p)x/\hbar} dx = |A|^2 \frac{2\pi}{\hbar} \delta(p-p')
\]

so that, if \( A = 1/\sqrt{2\pi \hbar} \), we can write

\[
\langle f_{p'} | f_p \rangle = \delta(p-p')
\]

and that’s about as close to orthonormal as we can hope for.

**Probabilities and Interpretation**

The non-deterministic nature of quantum mechanics makes it more difficult to interpret the results of the theory than is the case in classical mechanics. We can consider the expectation value to be the average value of a measurement made **not repeatedly on one particle or state**, but rather the average value of some measurement made on a **large number of identically prepared samples**. When measuring the value of some
observable for a particular state $\psi$, the state $\psi$ will collapse to an eigenstate of the operator corresponding to that observable. Because of the completeness (in a linear algebra sense) of the eigenstates, they form a basis in which we can write any general state $\psi$. We can write this as

$$\psi(x,t) = \sum_n c_n f_n(x) \text{ where } c_n = \langle f_n | \psi \rangle = \int f_n(x)^* \psi(x,t) dx$$

The notation shows that we can consider $c_n$ to be very much like the “component” of $\psi$ in the $f_n$ “direction” if we want to think in terms of a regular vector space. It’s not quite the same thing as a probability for a measurement on the state $\psi$ to result in the collapse to $f_n$ because it’s really a probability amplitude; the probability is found from $|c_n|^2$.

Reproducing one of the interesting proofs from your book, we find that the sum of all the probabilities is one (as it must be for orthonormal wave functions): 

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_n c_n f_n \right| \sum_n c_n f_n \right\rangle = \sum_{n'} \sum_n c_{n'}^* c_n \langle f_{n'} | f_n \rangle$$

Notice that the orthonormality of the basis set of eigenfunctions $f_n$ means the bracketed quantity will just be $\delta_{nn'}$ meaning we end up with a single sum over $|c_n|^2$ which must equal one. Similar work verifies the interpretation of expectation value as a weighted average, with the $|c_n|^2$ terms serving as the weighting factors:

$$\langle Q \rangle = \sum_n q_n |c_n|^2$$

For the case of operators with a continuous range of eigenvalues, we would replace the $c_n$ by a function $c(z)$. Also, the probability now only makes sense when integrated over some finite range (since the chance of landing exactly on any particular real number would be zero) so we replace $|c_n|^2$ by $|c(z)|^2 \, dz$.

We can now examine wave functions in momentum space. To do this, we look at the inner product of $\psi$ with the eigenfunctions of momentum (previously found to be

$$f(p) = \frac{1}{\sqrt{2\pi \hbar}} e^{ipx/\hbar}$$

We get
The wave function in momentum space (what we have above) is the Fourier transform of the "regular" wave function in position space that we've been using. We represent it by $\Phi(p,t)$. We can see that the probability of a momentum measurement giving a value in the region from $p$ to $p+dp$ to be $|\Phi(p,t)|^2 dp$. The connection between $\Phi(p,t)$ and $\psi(x,t)$ is

$$
\Psi(x,t) = \frac{1}{\sqrt{2\pi \hbar}} \int_{-\infty}^{\infty} e^{i p x / \hbar} \Phi(p,t) \, dp
$$

### Uncertainty

A more careful look at the uncertainty principle will show us the connection between uncertainty and the **commutator** of two operators. The commutator (of position and momentum, for example) is written as $[x,p]$ and defined to be $xp-px$. If $x$ and $p$ were just ordinary numbers, this would give zero because of the commutativity of multiplication. Because they are operators, however, we get something different. Incidentally, if you have had an upper-level course in mechanics, the commutator is closely related to the **Poisson bracket** that you would have seen in that course. To see the commutator in action, we apply it to a function $\psi(x)$ (since the momentum operator won't really make any sense without a function to its right)

$$
[x, p] \psi(x) = -i \hbar \frac{d\psi(x)}{dx} - (-i \hbar \frac{d}{dx} \psi(x))
= -i \hbar \left[ x \frac{d\psi(x)}{dx} - x \frac{d\psi(x)}{dx} - \psi(x) \frac{d\psi(x)}{dx} \right]
= i \hbar \psi(x)
\Rightarrow
[x, p] = i \hbar
$$

The nonzero commutator is at the root of our inability to precisely measure both momentum and position at the same time. In contrast, if we calculate $[x,y]$ or $[p_x, p_y]$, we will get zero. This means we could (in principle) measure both $x$ and $y$ (or $p_x$ and $p_y$) to arbitrarily high accuracy.

Following your book, we can state the uncertainty in terms of the variance $\sigma^2_A$ for an operator $A$:
\[ \sigma_A^2 = \langle (\hat{A} - \langle A \rangle) \psi \mid (\hat{A} - \langle A \rangle) \psi \rangle \]

where the difference between the actual measurement and the expectation value can be written more compactly as \( f \), leaving us with \( \sigma_A^2 = \langle f \mid f \rangle \). The variance for another observable \( B \) is written similarly as \( \sigma_B^2 = \langle g \mid g \rangle \). Using the Schwarz inequality, we get that

\[ \sigma_A^2 \sigma_B^2 = \langle f \mid f \rangle \langle g \mid g \rangle \geq \langle f \mid g \rangle^2 \]

Now, let the inner product of \( f \) and \( g \) (\( \langle f \mid g \rangle \)) be represented by the (in general complex) number \( z \) and write that complex number in \( x+iy \) format. By the basic properties of triangles, if we have a right triangle (with hypotenuse stretching from the origin to the point \((x,y)\)), the hypotenuse is at least as long as one of the other sides. Here, that means that \( |z|^2 \geq \text{Im}(z)^2 \). We can also write \( \text{Im}(z)^2 \) as

\[ \left( \text{Im}(z) \right)^2 = \left[ \frac{1}{2i} (z - z^*) \right]^2 \]

We then calculate \( \langle f \mid g \rangle - \langle g \mid f \rangle \) to be \( \langle \hat{A}\hat{B} \rangle - \langle \hat{B}\hat{A} \rangle \) or \( \langle [\hat{A},\hat{B}] \rangle \), leading to

\[ \sigma_A^2 \sigma_B^2 \geq \left( \frac{1}{2i} \langle [\hat{A},\hat{B}] \rangle \right)^2 \]

so \( \sigma_A \sigma_B \geq \frac{\hbar}{2} \)

A look at the energy-time uncertainty principle is also worthwhile. Because time isn’t a measurable property of a system, we interpret \( \Delta t \) as being the characteristic time for a significant change in the system. The rate of change of some observable \( Q \) is

\[ \frac{d}{dt} \langle Q \rangle = \frac{d}{dt} \langle \psi \mid \hat{Q} \psi \rangle = \langle \psi \mid \frac{\partial}{\partial t} \hat{Q} \psi \rangle + \langle \psi \mid \hat{Q} \frac{\partial}{\partial t} \psi \rangle \]

Using the time-dependent Schrödinger equation \( (\hat{H}\psi = i\hbar \frac{\partial}{\partial t} \psi) \) we can reduce this down to

\[ \frac{d}{dt} \langle Q \rangle = \frac{i}{\hbar} \langle [\hat{H},\hat{Q}] \rangle + \langle \psi \mid \frac{\partial}{\partial t} \hat{Q} \psi \rangle \]
For operators without explicit time dependence (very common), we get a simple relationship between the rate of change of an operator’s expectation value and the commutator of the operator with the Hamiltonian. We also notice that for these operators without explicit time dependence, if the operator commutes with the Hamiltonian, the observable is a constant of motion (in other words, it’s conserved and does not change over time).

More Dirac Notation

As we’ve discussed before, the Dirac notation can be a very compact and efficient way to describe wave functions. Because the actual concept of interest is the state of the system (call it \( \mathbb{R} \)), it’s worth noticing that we can choose to represent that state as a function in more than one basis. In the position basis, we could say that the wave function \( \psi \) is found by

\[
\psi (x,t) = \langle x | \mathbb{R}(t) \rangle
\]

Note that \( \mathbb{R} \) (the state) is in general a function of time, but the “x” part of the function only appears in the position (x) basis. We could also write this state in the momentum basis as

\[
\Phi (p,t) = \langle p | \mathbb{R}(t) \rangle
\]

or in the energy basis as

\[
c_n(t) = \langle n | \mathbb{R}(t) \rangle
\]

so that the state \( \psi(x,t) \) could be written as combinations of any of these:

\[
\psi (x,t) = \int \psi (y,t) \delta (x - y) dy = \int \Phi (p,t) \frac{1}{\sqrt{2\pi \hbar}} e^{i\frac{p}{\hbar}x} dp
\]

\[
= \sum c_n(t) e^{-iE_n t/\hbar} \psi_n(x)
\]

An operator can be considered to be a matrix in a space which may have an infinite number of dimensions or as few as two. When an operator Q is written in between a bra and a ket (like \( \langle \alpha | Q | \beta \rangle \), for example), it can be thought of as representing the probability (amplitude) for the operator Q to carry the state \( \beta \) into the state \( \alpha \). Remembering that the bras and kets are row and column vectors, sandwiching the matrix representing Q between a row and a column vector will yield an ordinary (but possibly complex) number.

A very useful operator with a simple matrix representation is the projection operator. We can express it as
\[ \hat{\varphi} \equiv |\alpha \rangle < \alpha | \quad \text{so} \quad \hat{\varphi} |\beta \rangle = < \alpha |\beta \rangle |\alpha \rangle \]

and the components of \( \beta \) along \( \alpha \) will be "projected" out.

Example 3.8 in your book provides a simple illustration of these concepts for a two-state system. The two-state system is a useful approximation of the true behavior of a variety of physical systems. If there are only two states, the bras & kets will be 1 x 2 (or 2 x 1) vectors and the Hamiltonian will be 2 x 2. We might call the two states \textbf{up} and \textbf{down} or (as in the book) 1 and 2. We can write them as

\[
|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]

so that any state could be written as a linear combination of these two states. If the Hamiltonian matrix is

\[
H = \begin{pmatrix} h & g \\ g & h \end{pmatrix}
\]

then, as long as \( g \neq 0 \), the system can cycle back and forth between states as time passes. The techniques of linear algebra (or \textit{Mathematica}) allow you to calculate the eigenvectors and eigenvalues of this matrix. They are

\[
(h - g) \begin{pmatrix} -1 \\ 1 \end{pmatrix} = |A\rangle \quad \text{and} \quad (h + g) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = |B\rangle
\]

If you normalize the eigenvectors, you get a factor of \( 1/\sqrt{2} \) in front of each. A general state can now be written in terms of the two eigenvectors found above. We could write

\[
|1\rangle = \frac{1}{\sqrt{2}} (|B\rangle - |A\rangle) \quad |2\rangle = \frac{1}{\sqrt{2}} (|B\rangle + |A\rangle)
\]

We can find out how a system starting in state \( |1\rangle \) will evolve in time by including the exponential factor \(-i \, E \, t / \hbar\) and rewriting each of our initial states in terms of these new ones.

\[
|1\rangle = \frac{1}{\sqrt{2}} (e^{-i(h+g)t/\hbar} |B\rangle - e^{-i(h-g)t/\hbar} |A\rangle)
\]
This means a state starting out as purely $|1\rangle$ will evolve into a state with a higher and higher mixture of $|2\rangle$ until it is entirely $|2\rangle$ on a time scale $\sim \hbar/g$, at which point it will begin evolving back towards $|1\rangle$. If $g$ is extremely small, the results will approximate what would happen if it were zero: there is little chance of a change except on very long time scales. If $g$ is large, the fluctuations between states will happen much more rapidly.

**Schrödinger’s Equation in 3-D**

One dimensional problems are instructive when starting to study quantum mechanics, but most interesting problems are three dimensional. As a starting point, we can solve the problem of a 3-D infinite potential well (which is just an unbreakable box). A complete set of wave functions can be written in the form

$$\psi(x, y, z) = \psi_1(x) \psi_2(y) \psi_3(z)$$

Since we have the same boundary conditions here as we had in the 1-D infinite square well (that is, the wave function must be zero at the boundaries), we will get the same kind of solutions, giving us

$$\psi(x, y, z) = A \sin k_1 x B \sin k_2 y C \sin k_3 z$$

In the most general case, where length, width, and height are all different, we will get an expression for the energy of the particle in the box like

$$E_{n_1n_2n_3} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)$$

Notice that there is only one ground state (where $n_1=n_2=n_3=1$), but if the box is a cube, so that $L_1=L_2=L_3$, there will be three states with energies equal to...
These will arise when two of the \(n_i\) are equal to 1 and the other is equal to two, which can happen three ways. When different states have the same energy, the states are known as **degenerate**. Stretching the sides of the box by different amounts so that all the \(L_i\) are different would bring us back to the more complicated expression for \(E\) so that \((1,1,2)\), \((1,2,1)\) and \((2,1,1)\) would all have different energies. This is known as **lifting the degeneracy**.

For a more common 3-D case with a less artificial potential, we can start with a potential that is only a function of distance \(r\). In that case, it is most sensible to use spherical coordinates. We can rewrite the Schrödinger equation to be

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 \psi \left( r, \theta, \phi \right) + V(r) \psi \left( r, \theta, \phi \right) = E \psi \left( r, \theta, \phi \right)
\]

The typical process is to try to solve this by separation of variables; we assume that the general solution \(\psi(r,\theta,\phi)\) can be written as a product of a radial function \(R(r)\) and an angular term \(Y(\theta,\phi)\). Writing out the Laplacian in spherical coordinates we then get

\[
-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + V(r) \psi = E \psi
\]

Separation of variables proceeds by substituting \(\psi=RY\) and then dividing by \(RY\), while multiplying by \(-2mr^2/\hbar^2\)

\[
\left[ \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2m r^2}{\hbar^2} [V(r) - E] \right] + \frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = 0
\]

Following the same steps as when we separated the time and space parts of the 1-D Schrödinger equation, we realize that the part on the left is only a function of \(r\) and the part on the right is only a function of \(\theta\) and \(\phi\). If they always cancel each other out for any value of these coordinates, they must each be equal to a constant (where one is the negative of the other). We will choose the radial part to be equal to \(\ell (\ell + 1)\) and the angular part to be \(-\ell (\ell + 1)\).
Starting with the angular equation, we again try separation of variables. Multiply by \( \sin^2 \theta \) and look for solutions satisfying \( Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \). We can now write

\[
\frac{1}{\Theta} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d \Theta}{d\theta} \right) + \ell(\ell + 1) \sin^2 \theta \right] + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0
\]

We repeat our earlier steps and realize that we now have a function of \( \theta \) that is always equal to a function of \( \phi \); therefore, they are each equal to a constant. Now we get

\[
\frac{1}{\Theta} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d \Theta}{d\theta} \right) + \ell(\ell + 1) \sin^2 \theta \right] = m^2
\]

\[
\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2
\]

We immediately solve the equation for \( \Phi \) as

\[
\Phi(\phi) = e^{im\phi}
\]

For physical reasons, we will require this equation to be periodic (i.e., \( \Phi(\phi + 2\pi) = \Phi(\phi) \) since there is no real difference in the two angles). That will restrict \( m \) to be an integer (though it can be positive or negative, or zero). The equation for \( \Theta \) is a little more complicated. Our solution here is known as an \textbf{associated Legendre function}.

These functions depend on both constants (\( \ell \) and \( m \)) and can be written

\[
P_{\ell}^m(\cos \theta ) = \frac{(\sin \theta)^{|m|}}{2^l l!} \left[ \frac{d}{d(\cos \theta)} \right]^{l+|m|} \left( \cos^2 \theta - 1 \right)^l
\]

so \( \Theta(\theta) = A P_{\ell}^m(\cos \theta) \). These associated Legendre functions can be obtained from the \textbf{Legendre polynomials} \( P_l(x) \) by

\[
P_{\ell}^m(x) = (1 - x^2)^{|m|/2} \left[ \frac{d}{dx} \right]^{|m|} P_{\ell}(x)
\]

where \( x \) is generally replaced by \( \cos(\theta) \).
Because problems that are spherically symmetric are common in physics, these angular functions are very useful. Typically, both the $\Theta$ and $\Phi$ functions are combined into functions known as **spherical harmonics**. The idea is that sines and cosines are harmonic functions in one dimension and these functions are a kind of 2-D version of them.

Your book writes these functions as

$$Y_{\ell}^m(\theta, \phi) = \varepsilon \sqrt{\frac{(2\ell + 1)(\ell - |m|)!}{4\pi(\ell + |m|)!}} e^{im\phi} P_{\ell}^m(\cos \theta)$$

where the symbol $\varepsilon = (-1)^m$ if $m \geq 0$ and 1 otherwise. In this form, the spherical harmonics are orthonormal:

$$\int_0^{2\pi} \int_0^\pi \left( Y_{\ell}^m(\theta, \phi) \right)^* Y_{\ell'}^{m'}(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'}$$

The numbers $\ell$ and $m$ are known as the **azimuthal quantum number** and the **magnetic quantum number**, respectively.

Returning to the rest of the Schrödinger equation, we have

$$\left[ \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2m}{\hbar^2} (V(r) - E) \right] = \ell(\ell + 1)$$

Rewriting this in terms of $u = r R(r)$, we get

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[ V + \frac{\hbar^2}{2m} \frac{\ell(\ell + 1)}{r^2} \right] u = E u$$

Notice that this looks the same as our previous 1-D Schrödinger equation if the “regular” potential $V$ is replaced by the one in square brackets. This modified potential is called the **effective potential** and it includes the effects of angular momentum. To normalize this function, we need the specific form of $V$. Notice that, since the $r^2$ part of the volume element in spherical coordinates is already present (remember that $u^*u = r^2 R^*R$), the normalization condition is now
\[ \int_0^\infty |u|^2 \, dr = 1 \]

Your book goes on to work the example of the three-dimensional infinite “square” well, where \( V = 0 \) when \( r \leq a \) and \( V = \infty \) for \( r > a \). As in the 1-D case, the wave function will be identically zero where \( r > a \). Inside, we can rewrite the radial part as

\[
\frac{d^2 u}{dr^2} = \left[ \frac{\ell (\ell + 1)}{r^2} - k^2 \right] u \Rightarrow k = \sqrt{\frac{2mE}{\hbar}}
\]

If \( \ell = 0 \), the solutions are quickly seen to be the same as in the 1-D case, replacing \( x \) by \( r \):

\[
u(r) = A \sin(k r) + B \cos(k r)
\]

Since \( R = u/r \), the need to have \( R \) remain finite at the center of the well \( (r=0) \) requires \( B=0 \). Now we have just \( A \sin(k r) \) and we have to have \( A \sin(k a) = 0 \). This puts a restriction on \( k \) of \( k = n \pi/a \). The \( \ell = 0 \) energies are then

\[ E_{n0} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \]

where \( n \) is an integer greater than zero. Normalization shows that \( A = \sqrt{(2/a)} \) and the \( \ell = 0 \) condition means the angular part of the wave function is \( Y_{00} = 1/\sqrt{4\pi} \). Combining them, we get

\[ \psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r} \]

All three quantum numbers \( n, \ell \), and \( m \) appear in the wave function but the energy only depends on \( n \) (because of the spherical symmetry of the potential).

For the case when \( \ell \neq 0 \), the general radial equation is a linear combination of functions

\[ u(r) = A r j_\ell(k r) + B r n_\ell(k r) \]

the \( j \) and \( n \) are known as spherical Bessel functions and spherical Neumann functions. The Neumann functions diverge at \( r \to 0 \), so \( B=0 \) for all solutions to the infinite spherical well problem. The boundary condition \( (\psi=0 \text{ at } r=a) \) means that the only allowed values of \( k \) are those which guarantee \( j_\ell(ka)=0 \). There is no simple formula for the location
of the zeros of the general Bessel functions (i.e., nothing like \( k = n\pi/a \)), so we refer to the \( n^{th} \) zero of the \( \ell^{th} \) Bessel function as \( \beta_{n,\ell} \). This means \( k = \beta_{n,\ell}/a \) and the energy is

\[
E_{n\ell} = \frac{\hbar^2 \beta_{n\ell}^2}{2ma^2}
\]

for a wave function of

\[
\psi_{n\ell m}(r, \theta, \phi) = A_{n\ell} j_{\ell}(\beta_{n\ell} r / a) Y_{m}^{m}(\theta, \phi)
\]

**The Hydrogen Atom**

A single electron moving around the nucleus of an atom is another 3-D problem. When more electrons are present, there is no exact closed-form solution, although the numerical approximations are very good. If we want the atom to be neutral overall, that leaves us with the study of hydrogen.

The most important part of the interaction between the electron and the nucleus is the electrostatic attraction between the positive charge in the nucleus and the negative charge of the electron. The potential looks the same here as it did in 2212:

\[
V(r) = \frac{-e^2}{4\pi \varepsilon_0 r}
\]

The radial equation becomes

\[
\frac{1}{\kappa^2} \frac{d^2u}{dr^2} = \left[ 1 - \frac{me^2}{2\pi \varepsilon_0 \hbar^2 \kappa} \frac{1}{(\kappa r)^2} + \frac{\ell(\ell + 1)}{(\kappa r)^2} \right] u \quad \text{where} \quad \kappa = \sqrt{\frac{-2mE}{\hbar}}
\]

Keep in mind that \( E < 0 \) or we don’t have a hydrogen atom, we have an electron and a proton. Following your book, we make the substitutions

\[
\rho = \kappa r \quad \rho_0 = \frac{me^2}{2\pi \varepsilon_0 \hbar^2 \kappa}
\]

leaving
\[
\frac{d^2 u}{d\rho^2} = \left[ 1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell + 1)}{\rho^2} \right] u
\]

which certainly looks simpler. If we move far from the proton (so \(\rho \to \infty\)), we get the familiar

\[
\frac{d^2 u}{d\rho^2} = u
\]

and we know the solution to that will be \(u(\rho) = A e^{\rho} + B e^{-\rho}\). For this to remain finite at infinity, we choose \(B=0\). Notice that we’ve only found the \textit{limiting} form of \(u\); we can’t expect what we have so far to be a solution to the full equation. As we move closer to the center of the potential (the proton), the equation approaches this:

\[
\frac{d^2 u}{d\rho^2} = \frac{\ell(\ell + 1)}{\rho^2} u
\]

which has a general solution of \(u(\rho) = C \rho^\ell e^{\rho} + D \rho^{-\ell}\). Requiring a solution that remains finite at \(r=0\) means \(D=0\). Your book then rewrites the equation yet again, where the behavior at the extremes is separated from the rest of the function:

\[
u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)
\]

and we try to find the solution for \(v(\rho)\). The modified radial equation is now

\[
\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv}{d\rho} + [\rho_0 - 2(\ell + 1)] v = 0
\]

and we begin by rewriting \(v\) as a power series:

\[
v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j
\]

Now we get
The form of the sums has been manipulated, but nothing has changed. If the left hand side of the equation equals zero, every value of $j$ in the sum must give zero. That leaves the following restriction on the coefficients:

$$j(j+1)c_{j+1} + 2(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(j+1)]c_j = 0$$

allowing us to write

$$c_{j+1} = \left[ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right] c_j$$

As $j \to \infty$, the limiting behavior of the coefficients is

$$c_{j+1} = \frac{2}{j+1} c_j$$

If we instead considered this limiting expression to be exact, we could write $v(\rho) = c_0 e^{2\rho}$. This would give the following form for $u(\rho)$:

$$u(\rho) = c_0 \rho^{\ell+1} e^\rho$$

The problem here is that this solution is not finite at infinity, so the power series has to terminate at some point. The maximum nonzero $j$ value will be called $j_{\text{max}}$, and $c_j = 0$ for all higher values of $j$. Using the recursion relation found earlier for $c_{j+1}$ in terms of $c_j$, we get

$$2(j_{\text{max}} + \ell + 1) - \rho_0 = 0$$

We are then led to define a **principal quantum number** $n$ to be

$$n = j_{\text{max}} + \ell + 1$$
so that $\rho_0 = 2\ n$ and the energy in terms of $\rho$ is

$$E = -\frac{me^4}{8\pi^2\varepsilon_0^2\hbar^2\rho_0^2} = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}\frac{E_n}{n^2} \quad n = 1, 2, 3\ldots$$

If we use some earlier work, we can write

$$\rho = \frac{r}{a_0\ n}$$

where $a_0$ is known as the **Bohr radius** (5.29 x 10^{-11} m) and found from

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

The energy of an electron in the lowest possible energy state (the ground state, which has $n = 1$) is then -13.6 eV. As for the wave functions for the hydrogen atom, it turns out that our polynomials $v(\rho)$ are equal (except for constants) to the associated Laguerre polynomials

$$L_{q-\ell}^p(x) = (-1)^p\left(\frac{d}{dx}\right)^p L_q(x)$$

which are themselves derived from the Laguerre polynomials defined as

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

With the correct normalization, we finally come to the general form for the hydrogen wave functions:

$$\psi_{n\ell m}(r, \theta, \phi) = \sqrt{\frac{2}{n a_0}} L_{n-\ell-1}^{\ell+1}(2r/n a_0) Y_{\ell m}(\theta, \phi)$$

The spherical harmonics ensure that wave functions with different values of $\ell$ and/or $m$ are orthogonal, while the form of the radial part of the wave function guarantees orthogonality between states of different values of $n$. **Important:** this form requires small changes depending on the normalization of the Laguerre polynomials. For example, if you use Mathematica’s definition, you will need to write the wave functions as
Angular Momentum Quantization

As it turns out, just as the energy levels of the electron in a hydrogen atom are quantized, the electron’s possible values of angular momentum are similarly restricted. To see this, we begin with the classical expression for angular momentum:

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

If we write out the components of the angular momentum vector, we get

$$L_x = y p_z - z p_y \quad L_y = z p_x - x p_z \quad L_z = x p_y - y p_x$$

and we can replace the momentum operator with its position-basis representation (\(p_j = -i\hbar \frac{\partial}{\partial x_j}\)). We can then calculate the various commutators of the components of angular momentum and find

$$[L_x, L_y] = i\hbar L_z \quad [L_y, L_z] = i\hbar L_x \quad [L_z, L_x] = i\hbar L_y$$

Because these operators don’t commute, we know that there is no way to find functions that are eigenfunctions of all three of them. In fact, we can’t even have eigenfunctions of any two of these operators. As your book calculates, though, we can examine the square of the total orbital angular momentum \(L^2 = L_x^2 + L_y^2 + L_z^2\) and find that it commutes with each component of the angular momentum. This means that there can be simultaneous eigenstates of \(L^2\) and one of the components (generally chosen to be \(L_z\)).

We therefore look for functions \(f\) that satisfy

$$L^2 f = \lambda \ f \quad \text{and} \quad L_z f = \mu \ f$$

It turns out that the creation and annihilation operators we used earlier for the harmonic oscillator are very useful in this search. We define raising and lowering operators \(L_+\) and \(L_-\) as
\[ L_{\pm} = L_x \pm i L_y \]

and we can then demonstrate new commutation relations:

\[ [L_z, L_{\pm}] = \pm \hbar L_{\pm} \quad \text{and} \quad [L_z^2, L_{\pm}] = 0 \]

As was the case in the harmonic oscillator problem, the \( L_x \) and \( L_y \) operators acting on the eigenfunctions \( f \) produce new eigenfunctions and the new eigenvalues are related to the old eigenvalues by \( \pm \hbar \). This leaves us with

\[ L_z^2 (L_{\pm} f) = \lambda (L_{\pm} f) \quad \text{and} \quad L_z (L_{\pm} f) = (\mu \pm \hbar)(L_{\pm} f) \]

Notice that there is no change in the eigenvalue of the \( L_z^2 \) operator. What the \( L_{\pm} \) operator is changing is the \( z \) component of \( L \) — not the length of the angular momentum vector. These operators \( (L_{\pm}) \) can therefore be thought of as moving the tip of the angular momentum vector higher or lower on the \( z \) axis (notice that it only moves in discrete steps of \( \hbar \)).

There must be some highest (lowest) eigenvalues that represent states that cannot be raised (lowered) and therefore have eigenvalues of zero:

\[ L_+ f_{\text{top}} = 0 \quad L_- f_{\text{bot}} = 0 \]

We start with this top state and define its eigenvalues as

\[ L_z f_{\text{top}} = \hbar \ell f_{\text{top}} \quad L_z^2 f_{\text{top}} = \lambda f_{\text{top}} \]

We then continue much the same way as with the original \( a \) and \( a^\dagger \) operators from the harmonic oscillator and find that we can write

\[ L_z^2 f_{\text{top}} = (L_{\pm} L_{\mp} + L_z^2 \mp \hbar L_z) f_{\text{top}} \]

so

\[ L_z^2 f_{\text{top}} = \hbar^2 \ell (\ell + 1) f_{\text{top}} \quad \Rightarrow \quad \lambda = \hbar^2 \ell (\ell + 1) \]

Therefore, \( L_z^2 \) will always be at least a little larger than \( L_z^2 \) (which would be \( \hbar^2 \ell^2 \)). Classical physics would actually allow \( L_z^2 = L_z^2 \) because the \( L_x \) and \( L_y \) components could be zero.
That's not allowed here because a nonzero commutator not only means that we can't have simultaneous eigenfunctions, but it also means we can't measure two components of angular momentum to arbitrary accuracy at the same time. If we allowed \( L^2 = L_z^2 \), we would immediately know \( L_x = L_y = 0 \), violating the commutation relation between them.

We also will have a lowest state since we have found a highest state. This means a state for which

\[
L_- f_{\text{bot}} = 0
\]

We identify the eigenvalues here as

\[
L_z f_{\text{bot}} = \hbar \ell f_{\text{bot}} \quad L^2 f_{\text{bot}} = \lambda f_{\text{bot}}
\]

Reasoning similar to that we used before gives us two possibilities for \( \ell \), and we reject the larger choice since the eigenvalue for the bottom state should certainly be smaller than the eigenvalue for the top state. We get \( \ell = -\ell \). This means the eigenvalues of \( L_z \) range from \( -\ell \) to \( \ell \) in steps of one. In general, we refer to the eigenvalue of \( L_z \) as \( m \) and the eigenvalue of \( L^2 \) as \( \ell(\ell + 1) \). As it happens, \( \ell \) is restricted to half-integer non-negative values (0, ½, 1, 3/2, ...) and \( m \) is between \(-\ell \) to \( \ell \) in steps of one. The eigenfunctions (which we still haven't found explicitly) must be functions of both \( m \) and \( \ell \):

\[
L_z f^{m}_\ell = \hbar m f^{m}_\ell \quad L^2 f^{m}_\ell = \hbar^2 \ell(\ell + 1) f^{m}_\ell
\]

The process of finding these eigenfunctions is detailed in the book, and we'll review it briefly here. It turns out that the eigenfunctions will be the spherical harmonics we've already seen. To demonstrate it, we realize that classical mechanics has already given us a formula for angular momentum: \( L = r \times p \). The 3-D form of the momentum operator in the position basis is \(-i\hbar \nabla\). Spherical coordinates are a natural choice to express \( r \), and we can look up the form of the gradient operator in spherical coordinates. Calculating the cross product, we get

\[
L = -i\hbar \left( \hat{\phi} \frac{\partial}{\partial \phi} + \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right)
\]

and translate it back into Cartesian coordinates. That gives

\[
L = i\hbar \left[ (\sin \phi \hat{i} + \cos \phi \hat{j}) \frac{\partial}{\partial \theta} - (\cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right]
\]
Grouping the i, j, and k parts, we get that

\[ L_x = -i\hbar \left( -\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right) \]

\[ L_y = -i\hbar \left( \cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right) \]

\[ L_z = -i\hbar \frac{\partial}{\partial \phi} \]

Through some algebra, the ladder operators are found to be

\[ L_z = \pm \hbar e^{\pm i\theta} \left( \frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right) \]

so we can write L\(^2\) as

\[ L^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \]

which is the same equation we solved to lead to the spherical harmonics in the first place. Therefore, we’re left with

\[ L_{op}^2 Y_{lm}(\theta, \phi) = \ell(\ell + 1)\hbar^2 Y_{lm}(\theta, \phi) \]

and

\[ \left( L_z \right)_{op} Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \]

Operating on the spherical harmonics with the raising or lowering operators gives us

\[ L_{\pm} Y_{lm}(\theta, \phi) = \hbar \sqrt{\ell(\ell + 1) - m(m \pm 1)} Y_{lm \pm 1}(\theta, \phi) \]

We can use these results to write a more compact 3-D Schrödinger equation:
\[
\frac{1}{2 m r^2} \left[ -\hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + L^2 \psi \right] + V \psi = E \psi
\]

**Spin**

Even though we gave up on the idea of picturing an electron as orbiting in a tiny circle around an atomic nucleus like a planet orbits the sun, there are some similarities to that picture that provide a bridge between our physical intuition (classical mechanics) and reality (quantum mechanics). We can (sort of) think of the electron’s angular momentum in the previous section as being due to its motion around the nucleus and call it orbital angular momentum. If we keep the planet analogy, we might wonder if there is a kind of **spin angular momentum** that would be like the planet rotating on its axis as it moves around the sun.

It turns out that the electron does have angular momentum which doesn’t depend on its orbital situation, and we call this the electron’s spin. Keep in mind, though, that this is very far from the classical idea of spin angular momentum. First, the electron is a point particle and therefore has no structure. No size = no spin. Also, all electrons everywhere have exactly the same value of spin angular momentum \((\sqrt{3}\hbar/2)\). Therefore, we can say that this spin is an **intrinsic** property of the electron, like its mass and charge.

One of the reasons for considering this odd and nonclassical thing to be a kind of angular momentum is that it behaves the same way as orbital angular momentum. For example, the eigenvalue of the spin operator \(S^2\) acting on an electron’s wave function looks like

\[
S^2 = s(s + 1) \hbar^2
\]

which should certainly remind you of the \(L^2\) operator. In this case, the value of \(s\) is \(1/2\) for all electrons everywhere. The commutation relations for the components of \(S\) are also very similar to those for \(L\):

\[
[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y
\]

and we again find that we can’t have simultaneous eigenfunctions for three (or even two) of these components. We can still have them for \(S^2\) and one of the components (again chosen to be \(S_z\)) and we get the familiar eigenvalue relationships:

\[
S_z \mid s m \rangle = \hbar m \mid s m \rangle \quad S^2 \mid s m \rangle = \hbar^2 s(s + 1) \mid s m \rangle
\]
For the same reasons we found previously, $S_z$ can only change by an integer. For the electron, since $s = \frac{1}{2}$, there are only two possible eigenvalues of $S_z$: $+\frac{1}{2}$ and $-\frac{1}{2}$. Some books add a subscript and write the $S_z$ eigenvalue as $m_s$ to eliminate confusion with the magnetic quantum number. Other books write the two values as an arrow going either up or down. This is unique to the spin $\frac{1}{2}$ case; for spin 1 particles (we haven’t seen any of them yet), there are three possible values of $m_s$: $+1$, 0, -1. Spin 3/2 particles could have $m_s = +3/2$, $+1/2$, $-1/2$, $-3/2$. In general, as was the case with orbital angular momentum, there will be $2s+1$ possible values of $m_s$ for a given $s$.

In the case of particles with spin $\frac{1}{2}$ (which includes all matter – protons, neutrons, the quarks that they are made of, electrons and neutrinos), since there are only two states ($s = \frac{1}{2}$, $m_s = +\frac{1}{2}$ and $s = \frac{1}{2}$, $m_s = -\frac{1}{2}$), the general state is written as a two-component column matrix known as a spinor. The basis spinors are just

$$
\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}
$$

and the general state $\chi$ becomes

$$
\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a \chi_+ + b \chi_-
$$

The spin operators will then be 2 x 2 matrices. The matrix form of the $S^2$ operator can be found from its eigenvalue equation. We know that we have to have

$$
S^2 \chi_\pm = \frac{3}{4} \hbar^2 \chi_\pm
$$

which restricts the value of the four matrix elements to be

$$
S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
$$

The form of the matrix representing $S_z$ is found by the same process:

$$
S_z \chi_\pm = \pm \frac{\hbar}{2} \chi_\pm \quad \Rightarrow \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
$$

23
Forming the raising and lowering operators as in the case of the orbital angular momentum operators, we can look at the effects of $S_\pm$ on the two spin eigenstates. Because there are only 2 possible states of $m_s$, acting on the spin down state with $S_-$ will give the same result as acting on the spin up state with $S_+$: both will give zero. Also, we get

$$S_+ \chi_- = \hbar \chi_+ \quad S_- \chi_+ = \hbar \chi_-$$

Through algebra similar to the orbital angular momentum case, we can find

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

It is customary to write the components of the spin matrices as

$$S = \frac{\hbar}{2} \sigma$$

where the $\sigma$ represents three separate 2 x 2 matrices (known as the Pauli spin matrices):

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

When combined with the identity matrix, these form a complete basis set. Any 2 x 2 matrix can be represented as a linear combination of these four matrices.

Check for yourself that the spinors introduced previously ($\chi_{\pm}$) are simultaneous eigenstates of $S_x$ and $S_z$. If you instead want eigenstates of $S_y$, we know that the $\chi_{\pm}$ can’t work. If they could, we’d have simultaneous eigenstates of $S_x$ and $S_y$, which is ruled out by the commutation relations. The eigenstates of the $S_x$ operator would be

$$\chi_{x+} = \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \\ \sqrt{2} \end{pmatrix} \quad \chi_{x-} = \begin{pmatrix} 1 \\ \sqrt{2} \\ -1 \\ \sqrt{2} \end{pmatrix}$$

In another similarity between orbital angular momentum and spin, each has a magnetic moment associated with it. We can calculate the magnetic moment of a current loop (in this case, the electron moving around in its orbit) to be
\[
\mu = I A = q \left( \frac{\nu}{2\pi r} \right) (\pi r^2) = \frac{1}{2} q \left( \frac{L}{m} \right)
\]

\[
\bar{\mu} = \frac{q}{2m} \bar{L}
\]

We combine this with our earlier expression for angular momentum and get

\[
\mu = \frac{e\hbar}{2m_e} \sqrt{\ell(\ell + 1)}
\]

The projection of the magnetic moment along the z axis is then given by

\[
\mu_z = - \frac{e\hbar}{2m_e} m_l
\]

where \(m_l\) is the magnetic quantum number and \(m_e\) is the electron’s mass. These expressions can be written in a more general form if a fundamental unit of magnetic moment is defined. This is known as the Bohr magneton \(\mu_B\) and is equal to

\[
\mu_B = \frac{e\hbar}{2m_e} = 57.9 \mu eV/Tesla
\]

The more general forms are

\[
\mu = \sqrt{\ell(\ell + 1)} \, g_L \, \mu_B
\]

\[
\mu_z = - m_l \, g_L \, \mu_B
\]

The \(g_L\) term is known as the gyromagnetic ratio or, typically, the g-factor. This can be thought of as a measure of the effectiveness of a particular angular momentum at establishing a magnetic moment. For orbital angular momentum, the g-factor is called \(g_L\) and is equal to one. For spin angular momentum, though, the g-factor is \(g_S\) and is approximately equal to 2. This means that the magnetic moment arising from the electron’s spin is described by

\[
\mu = \sqrt{s(s + 1)} \, g_S \, \mu_B = \sqrt{3/4} \, g_S \, \mu_B
\]

\[
\mu_z = - m_s \, g_S \, \mu_B
\]
Since the proton is also a spin $\frac{1}{2}$ particle, we can look at the way the electron spin interacts with the proton spin in the simplest case (hydrogen atom). Your book uses the notation $|\uparrow\uparrow\rangle$ where the first arrow indicates the $m_s$ value for the electron and the second for the proton. The four possibilities are then $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $|\downarrow\downarrow\rangle$. We can also define operators for this new “compound particle” idea. If the total spin is

$$S = S^{(1)} + S^{(2)}$$

where the superscript indicates which of the two particles the operator acts on, we find the $z$ component of spin from

$$S_z = S^{(1)}_z + S^{(2)}_z$$

The eigenvalue relation is then

$$S_z \chi_1 \chi_2 = \hbar (m_1 + m_2) \chi_1 \chi_2$$

Instead of ordering the states by the spins of the individual particles, we can look at the result of adding the two angular momenta. If both spins are up, the total spin is 1 and the total projection along the $z$ axis is also 1. If they're both down, the total is still 1 and the projection is -1. What if they're in opposite directions? Now there are two possibilities – the $z$ projection of the spin will be zero, but the total spin could either be one or zero.

In terms of the total spin and its projection, we can start writing the possible states as $|s m\rangle$ instead of with the up & down arrows. This is similar to the case of two masses attached to each other and two walls by three springs. We can either describe the motion of the two masses or we can talk about the coupled motions (normal modes) of the system. We’ve already identified $|\uparrow\uparrow\rangle$ with $|1 1\rangle$ and $|\downarrow\downarrow\rangle$ with $|1 -1\rangle$. What about the mixed spin cases? There’s not a direct correspondence like $|\uparrow\downarrow\rangle = |0 0\rangle$. The normal mode idea means that we will use linear combinations of the arrow states to find the remaining two $|s m\rangle$ states.

The total spin lowering operator $S_{-\text{Tot}}$ acting on $|1 1\rangle$ will clearly be $|1 0\rangle$. If we apply the “expanded” version of $S_{-\text{Tot}}$ to the $|\uparrow\uparrow\rangle$ state, we get

$$S_{-\text{Tot}}^{\text{Tot}} = S_{-1} + S_{-2}$$

$$\left( S^{(1)}_{-} + S^{(2)}_{-} \right) |\uparrow\uparrow\rangle = \left( S^{(1)}_{-} |\uparrow\rangle + S^{(2)}_{-} |\uparrow\rangle \right) = \hbar \left( |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle \right)$$

This means that we can identify $|1 0\rangle$ with $(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$. To normalize it, we will have to multiply by $1/\sqrt{2}$. Notice that this state is symmetric because of the sum of the two states. The other possibility is $(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$ (again multiplied by our normalization factor) which is antisymmetric. This state corresponds to $|0 0\rangle$. 

26
To check that the new spin states behave as advertised, we write out the $S^2$ operator for the combination of spins:

$$S^2 = (S^{(1)} + S^{(2)})\left( S^{(1)} + S^{(2)} \right) = \left( S^{(1)} \right)^2 + \left( S^{(2)} \right)^2 + 2S^{(1)} \cdot S^{(2)}$$

and we rewrite the dot product of the electron and proton spin operators at the end in its component form:

$$S^{(1)} \cdot S^{(2)} = S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} + S_z^{(1)} S_z^{(2)}$$

The form of the 2 x 2 spin matrices previously shown gives us

$$S^{(1)} \cdot S^{(2)} \begin{pmatrix} \downarrow \uparrow \\ \uparrow \downarrow \end{pmatrix} = \frac{\hbar^2}{4} \begin{pmatrix} 2\uparrow \downarrow > - \downarrow \uparrow > \end{pmatrix}$$

More algebra (detailed in your book) shows that

$$S^{(1)} \cdot S^{(2)} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar^2}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$S^{(1)} \cdot S^{(2)} \begin{pmatrix} 0 \\ 0 \end{pmatrix} = -\frac{3\hbar^2}{4} \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

leaving us with

$$S^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 2\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$S^2 \begin{pmatrix} 0 \\ 0 \end{pmatrix} = 0$$

The combination of angular momenta is very important in quantum mechanics. Here we are combining the spins of two different particles, but later we will combine the spin and orbital angular momenta of the same particle and we will use the same ideas. First, the total spin will range from the sum of the individual spins to the absolute value of the difference of the spins (although only integer values will be allowed). We can then write

$$s_{total \ possible} = \left\{ s_1 + s_2, \ (s_1 + s_2 - 1), \ (s_1 + s_2 - 2), \ldots \right\} \left| (s_1 - s_2) \right|$$
The $m$ part will still range from $+s$ to $-s$ in integer units. As before, the new states $|s_{\text{tot}} m_{\text{tot}}>$ will be linear combinations of the old product states $|s_1 m_1> |s_2 m_2>$. The coefficients that describe the mixing of these are known as **Clebsch-Gordon coefficients**. In the formula below, they are represented by the “C” which is of course a function of all three spins and their associated $m$ values (one for each particle = 2, plus 1 for the total = 3).

$$| s \ m > = \sum_{m_1 + m_2 = m} C^{s_1 s_2 s}_{m_1 m_2 m} | s_1 m_1 > | s_2 m_2 >$$

If you know the coefficients, they will tell you the probabilities of measuring a particular value for the individual spins if the total spin and its projection are known. Your book uses the example of a spin 2 particle and a spin 1 particle. The total spin could be 3, 2, or 1, meaning the projection along the z axis could be anywhere from -3 to +3 in integer units (of course, if the total spin is 2, $m$ would be restricted to be between +2 and -2, etc.).

Assume that in this case, the total spin is known to be 3 and its projection $m$ is 0. From the table in the book (or from *Mathematica*, where you can type something like ClebschGordan[{2, 1}, {1, -1}, {3, 0}] to find the coefficient for the $m_1 = +1, m_2 = -1$ case), you will find that it is composed of three pieces – a $|+1 -1>$ part, a $|0 0>$ part, and a $|-1 +1>$ part. Those are the only combinations of $m_1$ and $m_2$ that could give a zero total $m$. They don’t appear in equal proportions, though. According to the table, we get

$$| 3 0 > = \frac{1}{\sqrt{5}} | 2 1 > | 1 -1 > + \frac{\sqrt{3}}{5} | 2 0 > | 1 0 > + \frac{1}{\sqrt{5}} | 2 -1 > | 1 1 >$$

Squaring the coefficients gives the probability for finding a particular set of $s_1 s_2 m_1 m_2$ for the given $s m$.

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