Quantum Mechanics Part 1

Chapter 7

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Chapter 7 **Angular Momentum; 2- and 3-Dimensions**

7.1 **Angular Momentum Eigenvalues and Eigenvectors**

Earlier, we derived the commutation relations that define angular momentum operators

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\varepsilon_{ijk}\hat{J}_k \equiv i\hbar\sum_k \varepsilon_{ijk}\hat{J}_k \tag{7.1}$$

where

$$\epsilon_{ijk} = \begin{cases} +1 & \text{if } ijk = \text{even permutation of } 123 \\ -1 & \text{if } ijk = \text{odd permutation of } 123 \\ 0 & \text{if any two indices are identical} \end{cases} \tag{7.2}$$

and the *Einstein summation convention* over *repeated indices* is understood if the summation sign is left out (unless an explicit override is given).

In addition, these are all Hermitian operators, i.e., $(\hat{J}_i)^\dagger = \hat{J}_i^\dagger = \hat{J}_i$.

Since these three operators form a *closed commutator algebra*, we can solve for the eigenvectors and eigenvalues using only the commutators.

The three operators $\hat{J}_1$, $\hat{J}_2$ and $\hat{J}_3$ do not commute with each other and hence do not share a common set of eigenvectors (called a *representation*).

However, there exists another operator that commutes with each of the angular momentum components separately. If we define

$$\hat{J}^2 = \sum_{i=1}^{3} \hat{J}_i^2 \tag{7.3}$$

which is the square of the total angular momentum vector, we have

$$\left[\hat{J}^2, \hat{J}_i\right] = 0 \text{ for } i = 1, 2, 3 \tag{7.4}$$

In addition, we have $(\hat{J}^2)^\dagger = \hat{J}^2$, so that $\hat{J}^2$ is Hermitian also.

The commutation relations and the Hermitian property say that $\hat{J}^2$ and *any one* of the components *share a complete set of common* eigenvectors. By convention, we choose to use $\hat{J}^2$ and $\hat{J}_3$ as the two operators, whose eigenvalues(good quantum numbers) will characterize the set of common eigenvectors.

As we shall see, $\hat{J}^2$ is a so-called *Casimir invariant operator* that characterizes the representations(set of eigenvectors). In particular, the eigenvalue of $\hat{J}^2$ *characterizes the representation* and the eigenvalues of one of the components of the angular momentum (usually $\hat{J}_3$) will *characterize the eigenvectors within a representation.*

We define the eigenvector/eigenvalue relations by the equations

$$\hat{J}^2 |\lambda m\rangle = \lambda\hbar^2 |\lambda m\rangle \tag{7.5}$$

$$\hat{J}_3 |\lambda m\rangle = m\hbar |\lambda m\rangle \tag{7.6}$$

where the appropriate factors of $\hbar$ that have been explicitly put into the relations make m and λ dimensionless numbers.

We now define some other operators and their associated commutators so that we can use them in our derivations.

$$\hat{J}_\pm = \hat{J}_1 \pm i\hat{J}_2 \tag{7.7}$$

$$\hat{J}_- = \left(\hat{J}_+\right)^+ \to \text{ they are not Hermitian operators} \tag{7.8}$$

We then have

$$\left[\hat{J}^2, \hat{J}_\pm\right] = \left[\hat{J}^2, \hat{J}_1\right] \pm i\left[\hat{J}^2, \hat{J}_2\right] = 0 \tag{7.9}$$

$$\begin{aligned} \left[\hat{J}_3, \hat{J}_\pm\right] &= \left[\hat{J}_3, \hat{J}_1\right] \pm i\left[\hat{J}_3, \hat{J}_2\right] \\ &= i\hbar\hat{J}_2 \mp i\left(i\hbar\hat{J}_1\right) = \pm\hbar\hat{J}_\pm \end{aligned} \tag{7.10}$$

and

$$\begin{aligned} \left[\hat{J}_+, \hat{J}_-\right] &= \left[\hat{J}_1, \hat{J}_1\right] + i\left[\hat{J}_2, \hat{J}_1\right] - i\left[\hat{J}_1, \hat{J}_2\right] - \left[\hat{J}_2, \hat{J}_2\right] \\ &= -2i\left[\hat{J}_1, \hat{J}_2\right] = 2\hbar\hat{J}_3 \end{aligned} \tag{7.11}$$

and

$$\hat{J}_+\hat{J}_- = \left(\hat{J}_1 + i\hat{J}_2\right)\left(\hat{J}_1 - i\hat{J}_2\right)$$
$$= \hat{J}_1^2 + \hat{J}_2^2 - i\left[\hat{J}_1, \hat{J}_2\right] = \hat{J}^2 - \hat{J}_3^2 + \hbar\hat{J}_3 \tag{7.12}$$

and

$$\hat{J}_-\hat{J}_+ = \hat{J}^2 - \hat{J}_3^2 - \hbar\hat{J}_3 \tag{7.13}$$

Finally, we have

$$\hat{J}^2 = \frac{\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+}{2} + \hat{J}_3^2 \tag{7.14}$$

7.1.1 **Derivation of Eigenvalues**

Now the definitions (7.5) and (7.6) tell us that

$$\langle\lambda m|\,\hat{J}^2\,|\lambda m\rangle = \lambda\hbar^2\,\langle\lambda m \mid \lambda m\rangle = \sum_i \langle\lambda m|\,\hat{J}_i^2\,|\lambda m\rangle \tag{7.15}$$

$$\lambda\hbar^2\,\langle\lambda m \mid \lambda m\rangle = \sum_i \langle\lambda m|\,\hat{J}_i\hat{J}_i\,|\lambda m\rangle = \sum_i \langle\lambda m|\,\hat{J}_i^+\hat{J}_i\,|\lambda m\rangle \tag{7.16}$$

Let us define the new vector $|\alpha_i\rangle = \hat{J}_i |\lambda m\rangle$. Remember that the norm of any vector is non-negative, i.e., $\langle a \,|\, a\rangle \geq 0$. Therefore

$$\langle \lambda m \mid \lambda m\rangle \geq 0 \text{ and } \langle \alpha_i \mid \alpha_i\rangle \geq 0 \tag{7.17}$$

Now since $\langle \alpha_i| = \langle \lambda m| \hat{J}_i^\dagger$ we have

$$\lambda\hbar^2 \langle \lambda m \mid \lambda m\rangle = \sum_i \langle \lambda m| \hat{J}_i^+ \hat{J}_i |\lambda m\rangle = \sum_i \langle \alpha_i \mid \alpha_i\rangle \geq 0 \tag{7.18}$$

or we have

$$\lambda \geq 0 \text{ or the eigenvalues of } \hat{J}^2 \text{ are greater than } 0 \tag{7.19}$$

In fact, we can even say more than this using these equations. We have

$$\begin{aligned}
\lambda\hbar^2 \langle \lambda m \mid \lambda m\rangle &= \sum_i \langle \alpha_i \mid \alpha_i\rangle \\
&= \langle \alpha_1 \mid \alpha_1\rangle + \langle \alpha_2 \mid \alpha_2\rangle + \langle \alpha_3 \mid \alpha_3\rangle \\
&= \langle \alpha_1 \mid \alpha_1\rangle + \langle \alpha_2 \mid \alpha_2\rangle + \langle \lambda m| \hat{J}_3^2 |\lambda m\rangle \\
&= \langle \alpha_1 \mid \alpha_1\rangle + \langle \alpha_2 \mid \alpha_2\rangle + m^2\hbar^2 \langle \lambda m \mid \lambda m\rangle \geq 0
\end{aligned}$$

which says that

$$\lambda\hbar^2 \langle \lambda m \mid \lambda m \rangle \geq m^2\hbar^2 \langle \lambda m \mid \lambda m \rangle \Rightarrow \lambda \geq m^2 \tag{7.20}$$

This says that for a *fixed value* of λ (the eigenvalue of $\hat{J}^2$), which characterizes the representation, there must be *maximum and minimum* values of m (the eigenvalue of $\hat{J}_3$), which characterizes the eigenvectors within a representation.

Now we have

$$\begin{aligned}
\hat{J}_3\hat{J}_+ |\lambda m\rangle &= \hat{J}_3(\hat{J}_+ |\lambda m\rangle) \\
&= (\hat{J}_+\hat{J}_3 + \left[\hat{J}_3, \hat{J}_+\right]) |\lambda m\rangle = (\hat{J}_+\hat{J}_3 + \hbar\hat{J}_+) |\lambda m\rangle \\
&= \hbar(m+1)\hat{J}_+ |\lambda m\rangle = \hbar(m+1)(\hat{J}_+ |\lambda m\rangle)
\end{aligned} \tag{7.21}$$

which says that $\hat{J}_+ |\lambda m\rangle$ is an eigenvector of $\hat{J}_3$ with the *raised* eigenvalue $\hbar(m+1)$, i.e., $\hat{J}_+ |\lambda m\rangle \propto |\lambda, m+1\rangle$ (remember the harmonic oscillator discussion).

Since we already showed that for fixed λ, there must be a maximum value of m, say m_{max}, then it must be the case that for that particular m-value we have

$$\hat{J}_+ \left|\lambda m_{\text{max}}\right\rangle = 0 \tag{7.22}$$

If this were not true, then we would have

$$\hat{J}_+ \left|\lambda m_{\text{max}}\right\rangle \propto \left|\lambda, m_{\text{max}} + 1\right\rangle \tag{7.23}$$

but this violates the statement that m_{max} was was the maximum m-value.

Using this result we find

$$\begin{aligned}
&\hat{J}_- \hat{J}_+ \left|\lambda m_{\text{max}}\right\rangle = 0 = \left(\hat{J}^2 - \hat{J}_3^2 - \hbar \hat{J}_3\right) \left|\lambda m_{\text{max}}\right\rangle \\
&\hbar^2 \left(\lambda - m_{\text{max}}^2 - m_{\text{max}}\right) \left|\lambda m_{\text{max}}\right\rangle = 0 \\
&\lambda - m_{\text{max}}^2 - m_{\text{max}} = 0 \rightarrow \lambda = m_{\text{max}}^2 + m_{\text{max}} \\
&\lambda = m_{\text{max}}(m_{\text{max}} + 1)
\end{aligned} \tag{7.24}$$

It is convention to define

$$m_{\max} = j \text{ and hence } \lambda = j(j+1) \tag{7.25}$$

In the same way we can show

$$\begin{aligned}\hat{J}_3\hat{J}_- |\lambda m\rangle &= \hat{J}_3(\hat{J}_- |\lambda m\rangle) \\ &= (\hat{J}_-\hat{J}_3 + \left[\hat{J}_3, \hat{J}_-\right]) |\lambda m\rangle = (\hat{J}_-\hat{J}_3 - \hbar\hat{J}_+) |\lambda m\rangle \\ &= \hbar(m-1)\hat{J}_- |\lambda m\rangle = \hbar(m-1)(\hat{J}_- |\lambda m\rangle)\end{aligned} \tag{7.26}$$

which says that $\hat{J}_- |\lambda m\rangle$ is an eigenvector of $\hat{J}_3$ with the *lowered* eigenvalue $\hbar(m-1)$, i.e., $\hat{J}_- |\lambda m\rangle \propto |\lambda, m-1\rangle$.

If we let the minimum value of m be m_{min}, then as before we must have

$$\hat{J}_- |\lambda m_{\min}\rangle = 0 \tag{7.27}$$

or m_{min} is not the minimum value of m. This says that

$$\begin{aligned}
\hat{J}_+\hat{J}_- \left|\lambda m_{\text{min}}\right\rangle &= 0 = \left(\hat{J}^2 - \hat{J}_3^2 + \hbar\hat{J}_3\right)\left|\lambda m_{\text{min}}\right\rangle \\
\hbar^2\left(\lambda - m_{\text{min}}^2 + m_{\text{min}}\right)\left|\lambda m_{\text{min}}\right\rangle &= 0 \\
\lambda - m_{\text{min}}^2 + m_{\text{min}} = 0 &\to \lambda = m_{\text{min}}^2 - m_{\text{min}} \\
\lambda = m_{\text{min}}(m_{\text{min}} - 1) &= j(j+1)
\end{aligned} \tag{7.28}$$

which says that

$$m_{\text{min}} = -j \tag{7.29}$$

We have thus shown that the pair of operators $\hat{J}^2$ and $\hat{J}_3$ have a common set of eigenvectors $\left|jm\right\rangle$ (we now use the labels j and m), where we have found that

$$-j \leq m \leq j \tag{7.30}$$

and the allowed m-values change by steps of one, i.e., for a given j-value, the allowed m-values are

$$-j, -j+1, -j+2, \ldots\ldots, j-2, j-1, j \tag{7.31}$$

which implies that

$$2j = \text{ integer} \tag{7.32}$$

or

$$j = \frac{\text{integer}}{2} \geq 0 \quad \text{the allowed values} \tag{7.33}$$

Thus, we have the *allowed sets* or *representations of the angular momentum commutation relations* given by

$$\begin{aligned}
j &= 0 \quad , \quad m = 0 \\
j &= \frac{1}{2} \quad , \quad m = \frac{1}{2}, -\frac{1}{2} \\
j &= 1 \quad , \quad m = 1, 0, -1 \\
j &= \frac{3}{2} \quad , \quad m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}
\end{aligned} \tag{7.34}$$

and so on.

For each value of j, there are $2j+1$ allowed m-values in the eigenvalue spectrum(representation) and

$$\hat{J}^2 \left| jm \right\rangle = \hbar^2 j(j+1) \left| jm \right\rangle \tag{7.35}$$

$$\hat{J}_3 \left| jm \right\rangle = m\hbar \left| jm \right\rangle \tag{7.36}$$

Before proceeding, we need a few more relations. We found earlier that

$$\hat{J}_+ |jm\rangle = C_+ |j, m+1\rangle = |\alpha_+\rangle \tag{7.37}$$

$$\hat{J}_- |jm\rangle = C_- |j, m-1\rangle = |\alpha_-\rangle \tag{7.38}$$

and from these we have

$$\langle\alpha_+| = C_+^* \langle j, m+1| \tag{7.39}$$

$$\langle\alpha_-| = C_-^* \langle j, m-1| \tag{7.40}$$

We can then say that

$$\begin{aligned}
\langle\alpha_+ \mid \alpha_+\rangle &= |C_+|^2 \langle j, m+1 \mid j, m+1\rangle = |C_+|^2 \\
&= (\langle jm| (\hat{J}_+)^+)(\hat{J}_+ |jm\rangle) \\
&= \langle jm| \hat{J}_- \hat{J}_+ |jm\rangle \\
&= \langle jm| \left(\hat{J}^2 - \hat{J}_3^2 - \hbar \hat{J}_3\right) |jm\rangle \\
&= \langle jm| \hbar^2 (j(j+1) - m^2 - m) |jm\rangle \\
&= \hbar^2 (j(j+1) - m^2 - m) \langle jm \mid jm\rangle \\
&= \hbar^2 (j(j+1) - m^2 - m)
\end{aligned} \tag{7.41}$$

or

$$C_+ = \hbar\sqrt{j(j+1) - m(m+1)} \tag{7.42}$$

and similarly

$$\begin{aligned}
\langle \alpha_- \mid \alpha_- \rangle &= |C_-|^2 \langle j, m-1 \mid j, m-1 \rangle = |C_-|^2 \\
&= (\langle jm| \, (\hat{J}_-)^+)(\hat{J}_- \, |jm\rangle) \\
&= \langle jm| \, \hat{J}_+ \hat{J}_- \, |jm\rangle \\
&= \langle jm| \left(\hat{J}^2 - \hat{J}_3^2 + \hbar \hat{J}_3 \right) |jm\rangle \\
&= \langle jm| \, \hbar^2 (j(j+1) - m^2 + m) \, |jm\rangle \\
&= \hbar^2 (j(j+1) - m^2 + m) \langle jm \mid jm \rangle \\
&= \hbar^2 (j(j+1) - m^2 + m)
\end{aligned} \tag{7.43}$$

or

$$C_- = \hbar\sqrt{j(j+1) - m(m-1)} \tag{7.44}$$

Therefore, we have the very important relations for the raising/lowering or ladder operators

$$\begin{aligned} \hat{J}_{\pm} |jm\rangle &= \hbar\sqrt{j(j+1) - m(m \pm 1)}\, |j, m \pm 1\rangle \\ &= \hbar\sqrt{(j \pm m + 1)(j \mp m)}\, |j, m \pm 1\rangle \end{aligned} \tag{7.45}$$

7.2 Transformations and Generators; Spherical Harmonics

There are many vector operators and vector component operators in the following discussions. To avoid confusing notation, we will adopt the following conventions:

$$\begin{aligned} \vec{A}_{op} &= \text{ a vector operator} \\ \hat{\mathrm{A}}_j &= \text{ a vector component operator} \\ \hat{B} &= \text{ any non - vector operator or it might be a unit vector} \\ &\qquad\qquad \text{(context will decide)} \\ \vec{q} &= \text{ an ordinary vector} \end{aligned}$$

As we showed earlier, the angular momentum operators are the generators of rotations. The unitary transformation operator for a rotation through an angle θ about an axis along the direction specified by the unit vector $\hat{n}$ is given by

$$\hat{U}_{\hat{n}}(\theta) = e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{J}_{op}} \tag{7.46}$$

where $\vec{J}_{op}$ is the angular momentum operator.

What does the $\hat{J}_3$ operator look like in the position representation?

We will quickly get an idea of the answer and then step back and do things in more detail.

Suppose that we have a position representation wave function $\psi(\vec{r})$. For a rotation about the 3-axis, we showed earlier that for an infinitesimal angle ϵ

$$\hat{U}_3(\varepsilon)\psi(x_1, x_2, x_3) = \psi(x_1\cos\varepsilon + x_2\sin\varepsilon, -x_1\sin\varepsilon + x_2\cos\varepsilon, x_3) \tag{7.47}$$

In general, for infinitesimal shifts(a in this case) in the coordinates, we have, to lowest order in the infinitesimals, for a function of one variable

$$f(x+a) = f(x) + a\frac{\partial f}{\partial x} \tag{7.48}$$

Extending this to two variables, we have, to first order in infinitesimals a and b,

$$f(x+a, y+b) = f(x,y) + a\frac{\partial f}{\partial x} + b\frac{\partial f}{\partial y} \tag{7.49}$$

Therefore, for an infinitesimal angle of rotation ϵ,

$$\begin{aligned}
\hat{U}_3(\varepsilon)\psi(x_1,x_2,x_3) &= \psi(x_1\cos\varepsilon + x_2\sin\varepsilon, -x_1\sin\varepsilon + x_2\cos\varepsilon, x_3) \\
&= \psi(x_1,x_2,x_3) + \varepsilon x_2\frac{\partial\psi}{\partial x_1} - \varepsilon x_1\frac{\partial\psi}{\partial x_2} \\
&= \left(1 + \varepsilon\left(x_2\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_2}\right)\right)\psi(x_1,x_2,x_3)
\end{aligned} \tag{7.50}$$

But we also have (to first order)

$$\hat{U}_3(\varepsilon)\psi(x_1, x_2, x_3) = (1 - \frac{i}{\hbar}\varepsilon\hat{J}_3)\psi(x_1, x_2, x_3) \tag{7.51}$$

Putting these two equations together we have

$$\begin{aligned}\hat{J}_3 &= -i\hbar\left(x_2\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_2}\right) = (\vec{r}_{op} \times (-i\hbar\nabla))_3 \\ &= (\vec{r}_{op} \times \vec{p}_{op})_3 = \left(\vec{L}_{op}\right)_3 = \hat{L}_3 \end{aligned} \tag{7.52}$$

where

$$\begin{aligned}\vec{L}_{op} &= \text{orbital angular momentum operator} \\ \vec{r}_{op} &= (\hat{x}, \hat{y}, \hat{z}) = (\hat{x}_1, \hat{x}_2, \hat{x}_3) \\ \vec{p}_{op} &= (\hat{p}_x, \hat{p}_y, \hat{p}_z) = (\hat{p}_1, \hat{p}_2, \hat{p}_3)\end{aligned}$$

Since $\vec{L}_{op}$ is an angular momentum, it must have the commutation relations

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \tag{7.53}$$

where as we indicated above

$$\hat{L}_1 = \hat{x}_2\hat{p}_3 - \hat{x}_3\hat{p}_2 \tag{7.54}$$

$$\hat{L}_2 = \hat{x}_3\hat{p}_1 - \hat{x}_1\hat{p}_3 \tag{7.55}$$

$$\hat{L}_3 = \hat{x}_1\hat{p}_2 - \hat{x}_2\hat{p}_1 \tag{7.56}$$

and

$$\vec{L}_{op}^{+} = \vec{L}_{op} \tag{7.57}$$

Using

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \tag{7.58}$$

we get

$$\left[\hat{L}_i, x_j\right] = i\hbar\varepsilon_{ijk}x_k \tag{7.59}$$

and for $\hat{n}$ = a unit vector

$$\sum_i \hat{n}_i \left[\hat{L}_i, x_j\right] = i\hbar \sum_i \hat{n}_i \varepsilon_{ijk} x_k \tag{7.60}$$

$$\left[\hat{n} \cdot \vec{L}_{op}, x_j\right] = i\hbar \left(\vec{r}_{op} \times \hat{n}\right)_j \tag{7.61}$$

$$\left[\hat{n} \cdot \vec{L}_{op}, \vec{r}_{op}\right] = \sum_j \left[\hat{n} \cdot \vec{L}_{op}, x_j\right] \hat{e}_j$$

$$= i\hbar \sum_j \left(\vec{r}_{op} \times \hat{n}\right)_j \hat{e}_j = i\hbar \left(\vec{r}_{op} \times \hat{n}\right) \tag{7.62}$$

where we have used

$$\vec{A} \times \vec{B} = \sum_{ijk} \varepsilon_{ijk} A_j B_k \hat{e}_i \tag{7.63}$$

Similarly, we get

$$\left[\hat{n} \cdot \vec{L}_{op}, \vec{p}_{op}\right] = i\hbar \left(\vec{p}_{op} \times \hat{n}\right) \tag{7.64}$$

Now let us step back and consider rotations in 3-dimensional space and try to get a better physical understanding of what is happening.

Consider the operator

$$\vec{r}\,'_{op} = \vec{r}_{op} + \vec{\alpha} \times \vec{r}_{op} \tag{7.65}$$

where $\vec{\alpha}$ = ordinary *infinitesimal* vector.

Now let $|\vec{r}_0\rangle$ = an eigenstate of $\vec{r}_{op}$ with eigenvalue $\vec{r}_0$, i.e.,

$$\vec{r}_{op} \, |\vec{r}_0\rangle = \vec{r}_0 \, |\vec{r}_0\rangle \tag{7.66}$$

We then have

$$\vec{r}\,'_{op} \, |\vec{r}_0\rangle = \vec{r}\,'_0 \, |\vec{r}_0\rangle = (\vec{r}_0 + \vec{\alpha} \times \vec{r}_0) \, |\vec{r}_0\rangle \tag{7.67}$$

which says that $|\vec{r}_0\rangle$ is also an eigenstate of $\vec{r}\,'_{op}$ (different eigenvalue).

Now, for simplicity, let $\vec{\alpha} = \alpha\hat{e}_3$, which says that

$$\vec{\alpha} \times \vec{r}_0 = \alpha\hat{e}_3 \times (x_{01}\hat{e}_1 + x_{02}\hat{e}_2 + x_{03}\hat{e}_3) = \alpha x_{01}\hat{e}_2 - \alpha x_{02}\hat{e}_1 \tag{7.68}$$

$$\vec{r}_0 + \vec{\alpha} \times \vec{r}_0 = (x_{01} - \alpha x_{02})\hat{e}_1 + (x_{02} + \alpha x_{01})\hat{e}_2 + x_{03}\hat{e}_3 \tag{7.69}$$

This last expression is the vector we get if we rotate $\vec{r}_0$ about $\hat{\alpha} = \vec{\alpha}/|\vec{\alpha}|$ ($\hat{e}_3$ in this case) by an infinitesimal angle $\hat{\alpha} = |\vec{\alpha}|$. This result generalizes for $\vec{\alpha}$ in any direction.

Since the eigenvalues of $\vec{r}\,'_{op}$ are those of $\vec{r}_{op}$ rotated by $|\vec{\alpha}|$ about $\vec{\alpha}$, we conclude that $\vec{r}\,'_{op}$ is the position operator rotated by rotated by $|\vec{\alpha}|$ about $\vec{\alpha}$.

Alternatively, $\vec{r}\,'_{op}$ is the position operator in a coordinate frame rotated by $|\vec{\alpha}|$ about $\vec{\alpha}$ (remember our earlier discussions about the active/passive views).

To connect this to generators, unitary transformations, and angular momentum, we proceed as follows. We can rewrite $\vec{r}'_{op}$ as

$$\vec{r}'_{op} = \vec{r}_{op} + \frac{i}{\hbar}\left[\vec{\alpha}\cdot\vec{L}_{op}, \vec{r}_{op}\right] \tag{7.70}$$

which is equivalent (to first order in α) to

$$\vec{r}'_{op} = e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}}\vec{r}_{op}e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} \tag{7.71}$$

i.e.,

$$\begin{aligned}
\vec{r}'_{op} &= e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}}\vec{r}_{op}e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} \\
&= (\hat{I} + \frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op})\vec{r}_{op}(\hat{I} - \frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}) + O(\alpha^2) \\
&= \vec{r}_{op} + \frac{i}{\hbar}\left[\vec{\alpha}\cdot\vec{L}_{op}, \vec{r}_{op}\right] + O(\alpha^2)
\end{aligned} \tag{7.72}$$

Earlier, however, we showed that, if the state vector transforms as

$$\left|\psi'\right\rangle = \hat{U}\left|\psi\right\rangle \tag{7.73}$$

then the operators transform as

$$\hat{U}^{-1}\hat{O}\hat{U} \tag{7.74}$$

which then implies that the rotation operator is

$$\hat{U}(\vec{\alpha}) = e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} \tag{7.75}$$

as we expect.

This result derived for infinitesimal rotation angles holds for finite rotation angles also.

Let us look at the effect on state vectors

$$\vec{r}'_{op} |\vec{r}_0\rangle = \vec{r}'_0 |\vec{r}_0\rangle = e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} \vec{r}_{op} e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} |\vec{r}_0\rangle \tag{7.76}$$

$$\vec{r}_{op} e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} |\vec{r}_0\rangle = \vec{r}'_0 e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} |\vec{r}_0\rangle \tag{7.77}$$

or

$$e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} |\vec{r}_0\rangle \tag{7.78}$$

is an eigenstate of $\vec{r}_{op}$ with eigenvalue $\vec{r}'_0$ or

$$\left|\vec{r}'_0\right\rangle = e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} |\vec{r}_0\rangle \text{ and } \left\langle\vec{r}'_0\right| = \langle\vec{r}_0| e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} \tag{7.79}$$

and thus $\vec{L}_{op}$ is the *generator of ordinary rotations in 3-dimensional space.*

For wave functions we have $\psi(\vec{r}_0) = \langle\vec{r}_0 \,|\, \psi\rangle$. Using this result, the wave function transforms as

$$\begin{aligned} \psi(\vec{r}'_0) &= \left\langle \vec{r}'_0 \,\middle|\, \psi \right\rangle = \langle\vec{r}_0| e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} |\psi\rangle \\ &= \left\langle \vec{r}_0 \,\middle|\, \psi' \right\rangle = \psi'(\vec{r}_0) = \text{ wave function at rotated point } \vec{r}'_0 \end{aligned} \tag{7.80}$$

Now, we have seen that

$$\vec{L}_{op} = \vec{r}_{op} \times \vec{p}_{op} = -i\hbar \vec{r}_{op} \times \nabla \tag{7.81}$$

This can easily be evaluated in different coordinate systems.

Cartesian Coordinates

$$\vec{L}_{op} = -i\hbar \sum_{ijk} \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k} \hat{e}_i \tag{7.82}$$

$$\hat{L}_1 = -i\hbar \left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \tag{7.83}$$

$$\hat{L}_2 = -i\hbar \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) \quad , \quad \hat{L}_3 = -i\hbar \left(x_1 \frac{\partial}{\partial x_2} - x_2 \frac{\partial}{\partial x_1} \right) \tag{7.84}$$

as we saw at the beginning of this discussion.

Spherical-Polar Coordinates

We have

$$\vec{r} = r\hat{e}_r \text{ and } \nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \hat{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi} \tag{7.85}$$

where

$$\hat{e}_r = \sin\theta\cos\varphi\hat{e}_1 + \sin\theta\sin\varphi\hat{e}_2 + \cos\theta\hat{e}_3 \tag{7.86}$$

$$\hat{e}_\theta = \cos\theta\cos\varphi\hat{e}_1 + \cos\theta\sin\varphi\hat{e}_2 + \sin s\theta\hat{e}_3 \tag{7.87}$$

$$\hat{e}_\varphi = -\sin\theta\hat{e}_1 + \cos\theta\hat{e}_2 \tag{7.88}$$

which gives

$$\vec{L}_{op} = -i\hbar\left[\hat{e}_\varphi \frac{\partial}{\partial\theta} - \hat{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right] \tag{7.89}$$

and

$$\hat{L}_3 = \hat{L}_z = \hat{e}_z \cdot \vec{L}_{op} = -i\hbar \frac{\partial}{\partial \varphi} \tag{7.90}$$

$$\vec{L}_{op}^2 = \vec{L}_{op} \cdot \vec{L}_{op} = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] \tag{7.91}$$

Similarly, we have

$$\hat{L}_1 = \hat{L}_x = i\hbar \left[\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right] \tag{7.92}$$

$$\hat{L}_2 = \hat{L}_y = -i\hbar \left[\cos\varphi \frac{\partial}{\partial\theta} - \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right] \tag{7.93}$$

and

$$\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\vec{L}_{op}^2}{\hbar^2 r^2} \tag{7.94}$$

7.2.1 **Eigenfunctions; Eigenvalues; Position Representation**

Since

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \text{and} \left[\hat{L}^2_{op}, \hat{L}_j\right] = 0 \tag{7.95}$$

the derivation of the eigenvalues and eigenvectors follows our earlier work, i.e., the equations

$$\hat{L}^2_{op} |\ell m\rangle = \hbar^2 \ell(\ell+1) |\ell m\rangle \text{ and } \hat{L}_3 |\ell m\rangle = \hbar m |\ell m\rangle \tag{7.96}$$

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \tag{7.97}$$

imply

$$\ell = \frac{\text{integer}}{2} \geq 0 \tag{7.98}$$

and for a given value of ℓ, m takes on the $2\ell+1$ values

$$m = -\ell, -\ell+1, -\ell+2, ..., \ell-2, \ell-1, \ell \tag{7.99}$$

If we move back into 3-dimensional space and define

$$Y_{\ell m}(\theta, \varphi) = \langle \theta\varphi \mid \ell m\rangle = \text{ spherical harmonic} \tag{7.100}$$

then we have the defining equations for the $Y_{\ell m}(\theta, \varphi)$ given by

$$\langle\theta\varphi|\,\vec{L}_{op}^2\,|\ell m\rangle = \vec{L}_{op}^2\,\langle\theta\varphi \mid \ell m\rangle = \vec{L}_{op}^2 Y_{\ell m}(\theta,\varphi)$$
$$= \hbar^2\ell(\ell+1)\,\langle\theta\varphi \mid \ell m\rangle = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\varphi) \tag{7.101}$$

$$\langle\theta\varphi|\,\hat{L}_3\,|\ell m\rangle = \hat{L}_3\,\langle\theta\varphi \mid \ell m\rangle = \hat{L}_3 Y_{\ell m}(\theta,\varphi)$$
$$= \hbar m\,\langle\theta\varphi \mid \ell m\rangle = \hbar m Y_{\ell m}(\theta,\varphi) \tag{7.102}$$

Before determining the functional form of the $Y_{\ell m}{}'s$, we must step back and see if there are any restrictions that need to be imposed on the possible eigenvalues ℓ and m due to the fact that we are in a real 3-dimensional space.

In general, eigenvalue restrictions come about only from the imposition of physical *boundary conditions*. A standard boundary condition that is usually imposed is the following:

In real 3-dimensional space, if we rotate the system (or the axes by 2π, then we get back the *same* world. This means that the $Y_{\ell m}(\theta,\varphi)$ should be *single-valued* under such rotations or that

$$Y_{\ell m}(\theta, \varphi + 2\pi) = Y_{\ell m}(\theta, \varphi) \tag{7.103}$$

Now from the general rules we have developed, this gives

$$\langle \theta, \varphi + 2\pi \mid \ell m \rangle = \langle \theta\varphi |\, e^{2\pi i \hat{L}_3/\hbar}\, |\ell m\rangle = e^{2\pi m i}\, \langle \theta, \varphi \mid \ell m \rangle \tag{7.104}$$

or that single-valuedness of the wave function requires that

$$\langle \theta, \varphi + 2\pi \mid \ell m \rangle = \langle \theta\varphi |\, e^{2\pi i \hat{L}_3/\hbar}\, |\ell m\rangle = e^{2\pi m i}\, \langle \theta, \varphi \mid \ell m \rangle \tag{7.105}$$

This says, that for orbital angular momentum in real 3-dimensional space, no 1/2-integer values are allowed for m and hence that ℓ must be an integer. The allowed sets are:

$$\begin{aligned} \ell &= 0 \quad , \quad m = 0 \\ \ell &= 1 \quad , \quad m = -1, 0, 1 \\ \ell &= 2 \quad , \quad m = -2, -1, 0, 1, 2 \end{aligned}$$

and so on.

It is important to note that we are imposing a much stronger condition than is necessary. In general, as we have stated several times, it is not the state vectors, operators or wave functions that have any physical meaning in quantum mechanics. The only quantities that have physical meaning are those directly related to measurable quantities, namely, the probabilities, and the expectation values. This single-valued condition on m is not needed for the single-valuedness of the expectation values, since the extra phase factors involving m will cancel out during the calculation of the expectation value. Experiment, however, says that ℓ is an integer only, so it seems that the strong condition is valid. We *cannot prove* that this is so, however.

Let us now figure out the $Y_{\ell m}(\theta,\varphi)$. We have

$$\hat{L}_3 Y_{\ell m}(\theta,\varphi) = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} Y_{\ell m}(\theta,\varphi) = \hbar m Y_{\ell m}(\theta,\varphi) \tag{7.106}$$

which tells us the φ-dependence.

$$Y_{\ell m}(\theta,\varphi)=e^{im\varphi}P_{\ell m}(\theta) \tag{7.107}$$

Now we also must have, since $\ell=$ maximum value of m

$$\langle\theta\varphi|\,\hat{L}_+\,|\ell\ell\rangle=0=\hat{L}_+\,\langle\theta\varphi\mid\ell\ell\rangle=\hat{L}_+Y_{\ell\ell}(\theta,\varphi) \tag{7.108}$$

Using the expressions for $\hat{L}_x,\hat{L}_y,\hat{L}_+$ and $\hat{L}_-$ we have

$$\frac{\hbar}{i}e^{i\varphi}\left[i\frac{\partial}{\partial\theta}-\cot\theta\frac{\partial}{\partial\varphi}\right]Y_{\ell\ell}(\theta,\varphi)=0 \tag{7.109}$$

Using

$$\frac{\hbar}{i}\frac{\partial}{\partial\varphi}Y_{\ell\ell}(\theta,\varphi)=\ell\hbar Y_{\ell\ell}(\theta,\varphi) \tag{7.110}$$

we get

$$\left[\frac{\partial}{\partial\theta}-\ell\cot\theta\right]P_{\ell\ell}(\theta)=0 \tag{7.111}$$

or

$$P_{\ell\ell}(\theta)=(\sin\theta)^{\ell} \tag{7.112}$$

Therefore, the final expression is

$$Y_{\ell\ell}(\theta,\varphi)=A_{\ell m}e^{i\ell\varphi}(\sin\theta)^{\ell} \tag{7.113}$$

Now that we have generated the topmost spherical harmonic. We can generate all the others for a given ℓ using the lowering operators, i.e.,

$$\hat{L}_- Y_{\ell m}(\theta,\varphi) = \hbar\sqrt{\ell(\ell+1) - m(m-1)}\,Y_{\ell m-1}(\theta,\varphi) \tag{7.114}$$

where

$$\hat{L}_- = \frac{\hbar}{i} e^{-i\varphi}\left[i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}\right] \tag{7.115}$$

In general, we choose the $A_{\ell m}$ so that the $Y_{\ell m}(\theta,\varphi)$ are normalized, i.e.,

$$1 = \int d\Omega\,|Y_{\ell m}(\theta,\varphi)|^2 = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta\,|Y_{\ell m}(\theta,\varphi)|^2 \tag{7.116}$$

Since the $Y_{\ell m}(\theta,\varphi)$ are eigenfunctions of a Hermitian operators, they form a compete set which we can always make orthogonal so that we also assume that we have

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta Y^*_{\ell' m'}(\theta,\varphi) Y_{\ell m}(\theta,\varphi) = \delta_{\ell'\ell}\delta_{m'm} \tag{7.117}$$

The algebra is complicated. The general result is

$$Y_{\ell m}(\theta,\varphi) - \frac{(-1)\ell}{2^\ell \ell!}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell+m)!}{(\ell-m)!}}\frac{e^{im\varphi}}{(\sin\theta)^m}\left(\frac{d}{d\cos\theta}\right)^{\ell-m}(\sin\theta)^{2\ell} \tag{7.118}$$

Some *examples* are:

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \quad , \quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{7.119}$$

$$Y_{1,\pm 1} = \mp\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\theta \quad , \quad Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \tag{7.120}$$

$$Y_{2,\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi} \quad , \quad Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi} \tag{7.121}$$

Some Properties

$$Y_{\ell,-m}(\theta,\varphi) = (-1)^m Y^*_{\ell,m}(\theta,\varphi) \tag{7.122}$$

Under the parity operation

$$\vec{r} \to -\vec{r} \text{ or } r \to r, \theta \to \pi - \theta, \varphi \to \varphi + \pi \tag{7.123}$$

This says that

$$\begin{aligned} e^{im\varphi} &\to e^{im\varphi} e^{im\pi} = (-1)^m e^{im\varphi} \\ \sin\theta &\to \sin(\pi - \theta) \to \sin\theta \\ \cos\theta &\to \cos(\pi - \theta) \to -\cos\theta \end{aligned}$$

which imply that

$$Y_{\ell,m}(\theta, \varphi) \to (-1)^{\ell} Y_{\ell,m}(\theta, \varphi) \tag{7.124}$$

Therefore,

if ℓ is even, then we have an even parity state
if ℓ is odd, then we have an odd parity state

Since they form a complete set, any function of (θ, φ) can be expanded in terms of the $Y_{\ell m}(\theta, \varphi)$ (the $Y_{\ell m}(\theta, \varphi)$ are a basis), i.e., we can write

$$f(\theta, \varphi) = \sum_{\ell,m} f_{\ell m} Y_{\ell,m}(\theta, \varphi) \tag{7.125}$$

where

$$f_{\ell m} = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta Y^*_{\ell' m'}(\theta, \varphi) f(\theta, \varphi) \tag{7.126}$$

7.3 **Spin**

As we discussed earlier, a second kind of angular momentum exists in quantum mechanics. It is related to *internal degrees of freedom* of particles and is not related in any way to ordinary 3-dimensional space properties.

We designate this new angular momentum by *spin* and represent it by the operator $\vec{S}_{op}$, where since it is an angular momentum, its components must satisfy the commutators.

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\varepsilon_{ijk}\hat{S}_k \tag{7.127}$$

where we have used the Einstein summation convention over repeated indices.

The analysis for the eigenvalues and eigenvectors follows the same path as for earlier discussions. We have

$$\vec{S}^2_{op} \left|s, m_s\right\rangle = \hbar^2 s(s+1) \left|s, m_s\right\rangle \tag{7.128}$$

$$\hat{S}_3 \left|s, m_s\right\rangle = \hbar m_s \left|s, m_s\right\rangle \tag{7.129}$$

which, together with the commutators, gives the following results.

For a given value of s, we have $2s+1$ m_s-values

$$m_s = -s, -s+1, -s+2, ..., s-2, s-1, s \tag{7.130}$$

where

$$s = \frac{\text{integer}}{2} \geq 0 \tag{7.131}$$

There are no boundary conditions restricting the value of s, so we can have both integer and half-integer values.

We now turn our attention to a most important special case and then generalize the details. 7.3.1 **Spin 1/2**

We define a new operator $\vec{\sigma}_{op}$ such that

$$\vec{S}_{op} = \frac{1}{2}\hbar\vec{\sigma}_{op} \tag{7.132}$$

where $\vec{\sigma}_{op} = (\hat{\sigma}_1, \hat{\sigma}_2, \hat{\sigma}_3)$ are called the *Pauli spin operators*.

It is experimentally observed that if one measures the component of this spin angular momentum along any direction, one always obtains either $\pm\hbar/2$.

If we designate the state with spin $= +\hbar/2$ or *spin up* in the $\hat{n}$ direction by the ket vectors $|\hat{n}\uparrow\rangle$ or $|\hat{n}+\rangle$, we then have

$$\vec{S}_{op} \cdot \hat{n} \, |\hat{n} \uparrow\rangle = \frac{\hbar}{2} \, |\hat{n} \uparrow\rangle \text{ and } \vec{S}_{op} \cdot \hat{n} \, |\hat{n} \downarrow\rangle = -\frac{\hbar}{2} \, |\hat{n} \downarrow\rangle \tag{7.133}$$

Any pair of eigenvectors $|\hat{n} \uparrow\rangle$ or $|\hat{n} \downarrow\rangle$ for a given direction $\hat{n}$ form a basis for the vector space associated with spin = 1/2 and we have

$$\begin{aligned} \langle \hat{n} \uparrow | \psi \rangle = & \text{ amplitude for finding spin "up" along } \hat{n} \\ & \text{if we are in the state } |\psi\rangle \\ \langle \hat{n} \downarrow | \psi \rangle = & \text{ amplitude for finding spin "down" along } \hat{n} \\ & \text{if we are in the state } |\psi\rangle \end{aligned}$$

These two amplitudes exhaust all possible measurements for spin = 1/2 in the $\hat{n}$ direction and therefore completely specify the state $|\psi\rangle$. *That is what we mean physically when we say they form a basis set or representation.*

When we build the standard basis from these amplitudes, we choose it to be an eigenstate of the $\hat{S}_3$ or $\hat{S}_z$ operator, i.e., if we write

$$|\psi\rangle = \begin{pmatrix} \langle z\uparrow|\psi\rangle \\ \langle z\downarrow|\psi\rangle \end{pmatrix} = \text{ a 2 - component vector} \tag{7.134}$$

then the appropriate basis is

$$|z\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \rightarrow \text{ spin up in z - direction}$$

$$|z\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \rightarrow \text{spin down in z - direction}$$

Matrix Representations

Using this basis, the matrix representation of

$$\hat{S}_z = \frac{\hbar}{2}\hat{\sigma}_z \tag{7.135}$$

is

$$S_z = \begin{pmatrix} \langle z\uparrow|\hat{S}_z|z\uparrow\rangle & \langle z\uparrow|\hat{S}_z|z\downarrow\rangle \\ \langle z\downarrow|\hat{S}_z|z\uparrow\rangle & \langle z\downarrow|\hat{S}_z|z\downarrow\rangle \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\sigma_z$$

$$\rightarrow \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{7.136}$$

Now

$$\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y \tag{7.137}$$

$$\rightarrow \hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2} \text{ and } \hat{S}_y = \frac{\hat{S}_+ - \hat{S}_-}{2i} \tag{7.138}$$

Therefore, using

$$S_x = \begin{pmatrix} \langle z\uparrow|\hat{S}_x|z\uparrow\rangle & \langle z\uparrow|\hat{S}_x|z\downarrow\rangle \\ \langle z\downarrow|\hat{S}_x|z\uparrow\rangle & \langle z\downarrow|\hat{S}_x|z\downarrow\rangle \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_z$$

$$\rightarrow \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{7.139}$$

and in a similar way

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{7.140}$$

Properties of the $\hat{\sigma}_i$

From

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\varepsilon_{ijk}\hat{S}_k$$

and

$$\vec{S}_{op} = \frac{1}{2}\hbar\vec{\sigma}_{op}$$

we get the commutation relations

$$[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\varepsilon_{ijk}\hat{\sigma}_k \tag{7.141}$$

In addition, we have

$$\hat{\sigma}_i\hat{\sigma}_j = i\varepsilon_{ijk}\hat{\sigma}_k \quad i \neq j \tag{7.142}$$

$$\hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i = \{\hat{\sigma}_i, \hat{\sigma}_j\} = 0 \text{ (called the anticommutator)} \tag{7.143}$$

$$\hat{\sigma}_{\mathrm{i}}^2 = \hat{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{7.144}$$

The fact that the spin = 1/2 operators anticommute is directly linked to the existence of fermions as one can see when the relativistic equation for the electron is studied.

Put all together, these relations give

$$\hat{\sigma}_i\hat{\sigma}_j = \delta_{ij} + i\varepsilon_{ijk}\hat{\sigma}_k \tag{7.145}$$

or going back to the $\hat{S}_i$

$$\hat{S}_i\hat{S}_j = \frac{\hbar^2}{4}\delta_{ij} + i\varepsilon_{ijk}\frac{\hbar}{2}\hat{S}_k \tag{7.146}$$

In the special case of spin = 1/2, we have

$$\begin{aligned} \vec{S}^2_{op} &= \frac{\hbar^2}{4}\left(\hat{\sigma}_x^2 + \hat{\sigma}_y^2 + \hat{\sigma}_z^2\right) = \frac{\hbar^2}{4}\left(\hat{I} + \hat{I} + \hat{I}\right) \\ &= \frac{3\hbar^2}{4}\hat{I} = \hbar^2 s(s+1)\hat{I} \text{ with } s = \frac{1}{2} \end{aligned} \tag{7.147}$$

A very useful property that we will employ many time later on is (using (7.145))

$$\begin{aligned}(\vec{a} \cdot \vec{\sigma}_{op}) \left(\vec{b} \cdot \vec{\sigma}_{op}\right) &= a_i \hat{\sigma}_i b_j \hat{\sigma}_j \\ &= \delta_{ij} a_i b_j + i\varepsilon_{ijk} a_i b_j \hat{\sigma}_k = a_i b_i + i\varepsilon_{ijk} a_i b_j \hat{\sigma}_k \\ &= \vec{a} \cdot \vec{b} + i(\vec{a} \times \vec{b}) \cdot \vec{\sigma}_{op} \end{aligned} \tag{7.148}$$

Rotations in Spin Space

We have said that

$$\vec{S}_{op} \cdot \hat{n} \left|\hat{n}\pm\right\rangle = \pm\frac{\hbar}{2} \left|\hat{n}\pm\right\rangle \tag{7.149}$$

What do the states $|\hat{n}\pm\rangle$ look like in the $|\hat{z}\pm\rangle$ basis? One way to find out is the *direct approach.*

Let us choose a Cartesian basis for the unit vector (we will look at other choices afterwards)

$$\hat{n} = (n_x, n_y, n_z) \quad , \qquad \text{all real} \tag{7.150}$$

We then have

$$
\begin{aligned}
\vec{S}_{op} \cdot \hat{n} &= \frac{\hbar}{2}\vec{\sigma}_{op} \cdot \hat{n} = \frac{\hbar}{2}(n_x\hat{\sigma}_x + n_y\hat{\sigma}_y + n_z\hat{\sigma}_z) \\
&= \frac{\hbar}{2}\left(n_x\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + n_y\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + n_z\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) \\
&= \frac{\hbar}{2}\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix}
\end{aligned}
\tag{7.151}
$$

and

$$
\vec{S}_{op} \cdot \hat{n}\,|\hat{n}+\rangle = +\frac{\hbar}{2}\,|\hat{n}+\rangle \tag{7.152}
$$

$$
\frac{\hbar}{2}\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \tag{7.153}
$$

where we have represented

$$
|\hat{n}+\rangle = \begin{pmatrix} a \\ b \end{pmatrix} \tag{7.154}
$$

This matrix equation gives two homogeneous equations for a and b

$$\begin{aligned}(n_z - 1)a + (n_x - in_y)b = 0 \\ (n_x + in_y)a - (n_z + 1)b = 0\end{aligned}$$

or

$$\frac{a}{b} = -\frac{n_x - in_y}{n_z - 1} = \frac{n_z + 1}{n_x + in_y} \tag{7.155}$$

The homogeneous equations have a non-trivial solution only if the determinant of the coefficients of a and b equals zero or

$$(n_z + 1)(n_z - 1) + (n_x - in_y)(n_x + in_y) = 0 \tag{7.156}$$

We assume that the vector $|\hat{n}+\rangle$ is normalized to one or

$$|a|^2 + |b|^2 = 1 \tag{7.157}$$

Putting all this together we get

$$a = \frac{1}{\sqrt{2}}\sqrt{1+n_z} \text{ and } b = \frac{1}{\sqrt{2}}\sqrt{1-n_z} \tag{7.158}$$

$$|\hat{n}+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} \sqrt{1+n_z} \\ \sqrt{1-n_z} \end{pmatrix} \tag{7.159}$$

We can easily check this by letting $|\hat{n}+\rangle = |\hat{z}+\rangle$ or $n_z = 1, n_x = n_y = 0$ which gives

$$|\hat{z}+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{7.160}$$

as expected. In a similar manner

$$|\hat{n}-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} -\sqrt{1-n_z} \\ \sqrt{1+n_z} \end{pmatrix} \tag{7.161}$$

Note that the two vectors $|\hat{n}+\rangle$ and $|\hat{n}-\rangle$ are orthonormal as we expect.

This calculation can also be carried out in other coordinate bases. For the spherical-polar basis we get

$$\hat{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta) \tag{7.162}$$

$$\vec{S}_{op}\cdot\hat{n} = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & e^{-i\varphi}\sin\theta \\ e^{i\varphi}\sin\theta & -\cos\theta \end{pmatrix} \tag{7.163}$$

$$|\hat{n}+\rangle = \begin{pmatrix} \cos\frac{\theta}{2} \\ e^{i\varphi}\sin\frac{\theta}{2} \end{pmatrix} \text{ and } |\hat{n}-\rangle = \begin{pmatrix} \sin\frac{\theta}{2} \\ -e^{i\varphi}\cos\frac{\theta}{2} \end{pmatrix} \tag{7.164}$$

What can we say about operators in the spin $= 1/2$ vector space?

Any such operator $\hat{B}$ can be expressed as a linear combination of the four linearly independent matrices $\{\hat{I}, \hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\}$ (they are, in fact, a basis for all 2×2 matrices)

$$\hat{B} = a_0\hat{I} + \mathrm{a_x}\hat{\sigma}_x + \mathrm{a_y}\hat{\sigma}_y + \mathrm{a_z}\hat{\sigma}_z = a_0\hat{I} + \tilde{\mathrm{a}}\cdot\vec{\sigma}_{\mathrm{op}} = \begin{pmatrix} a_0 + \mathrm{a_z} & \mathrm{a_x} - i\mathrm{a_y} \\ \mathrm{a_x} + i\mathrm{a_y} & a_0 - \mathrm{a_z} \end{pmatrix} \tag{7.165}$$

In particular, the density operator or the state operator $\hat{W}$ which is the same as any other operator can be written as

$$\hat{W} = \frac{1}{2}(\hat{I} + \vec{a} \cdot \vec{\sigma}_{\text{op}}) \tag{7.166}$$

where the factor of 1/2 has been chosen so that we have the required property

$$Tr\hat{W} = \frac{1}{2}Tr\hat{I} + a_i Tr\sigma_i = 1 \text{ since } Tr\sigma_i = 0 \tag{7.167}$$

Since $\hat{W} = \hat{W}^\dagger$ we must also have all the a_i real. What is the *physical meaning* of the vector $\vec{a}$?

Consider the following

$$\begin{aligned}
\langle \hat{\sigma}_x \rangle = Tr(\hat{W}\hat{\sigma}_x) &= \frac{1}{2}Tr((\hat{I} + a_x\hat{\sigma}_x + a_y\hat{\sigma}_y + a_z\hat{\sigma}_z)\hat{\sigma}_x) \\
&= \frac{1}{2}Tr(\hat{\sigma}_x + a_x\hat{\sigma}_x^2 + a_y\hat{\sigma}_y\hat{\sigma}_x + a_z\hat{\sigma}_z\hat{\sigma}_x) \\
&= \frac{1}{2}Tr(\hat{\sigma}_x + a_x\hat{I} - ia_y\hat{\sigma}_z + ia_z\hat{\sigma}_y) = \frac{a_x}{2}Tr(\hat{I}) = a_x
\end{aligned} \tag{7.168}$$

or, in general,

$$\langle \vec{\sigma}_{op} \rangle = Tr\left(\hat{W}\vec{\sigma}_{op}\right) = \vec{a} = \text{ polarization vector} \tag{7.169}$$

Now the eigenvalues of $\hat{W}$ are equal to

$$\frac{1}{2} + \text{ eigenvalues of } \vec{a}\cdot\vec{\sigma}_{op} \tag{7.170}$$

and from our earlier work the eigenvalues are $\vec{a}\cdot\vec{\sigma}_{op} = \pm 1$. Therefore the eigenvalues of $\hat{W}$ are

$$\frac{1}{2}(1 \pm |\vec{a}|) \tag{7.171}$$

But, as we showed earlier, all eigenvalues of $\hat{W}$ are ≥ 0, which says that polarization vectors have a length $|\vec{a}|$ restricted to $0 \leq |\vec{a}| \leq 1$.

Pure states have $|\vec{a}| = 1$ and this gives eigenvalues 1 and 0 for $\hat{W}$, which corresponds to *maximum* polarization.

Note that for $\vec{a} = a\hat{e}_3 = \hat{e}_3$, we have

$$\hat{W} = \frac{1}{2}(\hat{I} + \hat{\sigma}_3) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = |z+\rangle \langle z+| \tag{7.172}$$

as it should for a pure state. An unpolarized state has $|\vec{a}| = 0$ and this gives eigenvalues $(1/2, 1/2)$ for $\hat{W}$. This represents an *isotropic* state where $\langle \hat{S}_i \rangle = 0$.

In this case we have

$$\hat{W} = \frac{1}{2}\hat{I} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}|z+\rangle \langle z+| + \frac{1}{2}|z-\rangle \langle z-| \tag{7.173}$$

as we expect for a nonpure state or a mixture.

Let us now connect all of this stuff to rotations in spin space. For an infinitesimal rotation through angle $\alpha = |\vec{\alpha}|$ about an axis along $\hat{\alpha} = \vec{\alpha}/\alpha$, a unit vector $\hat{m}$ becomes

$$\hat{n} = \hat{m} + \vec{\alpha} \times \hat{m} \tag{7.174}$$

Following the same steps as earlier, this implies

$$\vec{S}_{op} \cdot \hat{n} = \vec{S}_{op} \cdot \hat{m} + \vec{S}_{op} \cdot (\vec{\alpha} \times \hat{m}) = \vec{S}_{op} \cdot \hat{m} + \varepsilon_{ijk} \alpha_i \hat{m}_j \hat{S}_k \quad (7.175)$$

But we have

$$\varepsilon_{ijk} \hat{S}_k = \frac{1}{i\hbar} \left[\hat{S}_i, \hat{S}_j \right] \quad (7.176)$$

which implies that

$$\begin{aligned} \vec{S}_{op} \cdot \hat{n} &= \vec{S}_{op} \cdot \hat{m} + \frac{1}{i\hbar} \left[\hat{S}_i, \hat{S}_j \right] \alpha_i \hat{m}_j \\ &= \vec{S}_{op} \cdot \hat{m} + \frac{1}{i\hbar} \left[\vec{S}_{op} v \hat{m}, \vec{S}_{op} \cdot \vec{\alpha} \right] \end{aligned} \quad (7.177)$$

Using the same approximations as we did earlier, we can see that this expression, to first order in α, is equivalent to

$$\vec{S}_{op} \cdot \hat{n} = e^{-\frac{i}{\hbar} \vec{S}_{op} \cdot \vec{\alpha}} \vec{S}_{op} \cdot \hat{m} e^{\frac{i}{\hbar} \vec{S}_{op} \cdot \vec{\alpha}} \quad (7.178)$$

This result holds for finite rotation angles also.

Now using this result, we have

$$\vec{S}_{op} \cdot \hat{n} \left[e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} \left| \hat{m}+ \right\rangle \right] = \left[e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} \vec{S}_{op} \cdot \hat{m} \right] \left| \hat{m}+ \right\rangle$$
$$= \frac{\hbar}{2} \left[e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} \left| \hat{m}+ \right\rangle \right] \tag{7.179}$$

This says that

$$e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} \left| \hat{m}+ \right\rangle = \left| \hat{n}+ \right\rangle \text{ and similarly } e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} \left| \hat{m}- \right\rangle = \left| \hat{n}- \right\rangle \tag{7.180}$$

The rotation that takes $\hat{m} \to \hat{n}$ is *not* unique, however. We are free to rotate by an arbitrary amount about $\hat{n}$ after rotating $\hat{m}$ into $\hat{n}$. This freedom corresponds to adding a phase factor.

We say that the unitary operator

$$e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} \tag{7.181}$$

has the effect of *rotating* the eigenstate of $\vec{S}_{op} \cdot \hat{m}$ into the eigenstate of $\vec{S}_{op} \cdot \hat{n}$. The operator performs *rotations* on the spin degrees of freedom. The equations are analogous to those for real rotations in space generated by $\vec{L}_{op}$.

Let us now work out a very useful identity. We can write

$$e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} = e^{-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}} = \sum_{n=0}^{\infty} \frac{\left(-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}\right)^n}{n!} \tag{7.182}$$

Now we have

$$(\vec{\sigma}_{op}\cdot\vec{\alpha})^2 = \vec{\alpha}\cdot\vec{\alpha} + i(\vec{\alpha}\times\vec{\alpha})\cdot\vec{\sigma}_{op} = \vec{\alpha}^2 = \alpha^2 \tag{7.183}$$

Therefore

$$\begin{aligned} e^{-\frac{i}{\hbar}\vec{S}_{op}\cdot\vec{\alpha}} &= \hat{I} + \frac{1}{1!}\left(-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}\right) + \frac{1}{2!}\left(-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}\right)^2 \\ &\qquad + \frac{1}{3!}\left(-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}\right)^3 + \ldots \\ &= \hat{I}\left(1 - \frac{\left(\frac{\alpha}{2}\right)^2}{2!} + \frac{\left(\frac{\alpha}{2}\right)^4}{4!} - \ldots.\right) - i\vec{\sigma}_{op}\cdot\hat{\alpha}\left(\frac{\left(\frac{\alpha}{2}\right)}{1!} - \frac{\left(\frac{\alpha}{2}\right)^3}{3!} + \ldots.\right) \\ &= \hat{I}\cos\frac{\alpha}{2} - i(\vec{\sigma}_{op}\cdot\hat{\alpha})\sin\frac{\alpha}{2} \end{aligned} \tag{7.184}$$

Consider an example. Let $\vec{\alpha} \to -90\,^\circ$ rotation about the x-axis or

$$\vec{\alpha} \to -\frac{\pi}{2}\hat{x} \tag{7.185}$$

Now we have

$$\hat{\sigma}_z(\hat{\sigma}_x)^n = (-\hat{\sigma}_x)^n\hat{\sigma}_z \tag{7.186}$$

which follows from the anticommutation relations. This implies that

$$\begin{aligned}
\hat{\sigma}_z f(\hat{\sigma}_x) &= f(-\hat{\sigma}_x)\hat{\sigma}_z \\
\hat{\sigma}_z f(\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z) &= f(-\hat{\sigma}_x, -\hat{\sigma}_y, \hat{\sigma}_z)\hat{\sigma}_z
\end{aligned}$$

Using these relations we get

$$\begin{aligned}
e^{-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}}\hat{\sigma}_z e^{\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}} &= e^{\frac{i\pi}{4}\hat{\sigma}_x}\hat{\sigma}_z e^{-\frac{i\pi}{4}\hat{\sigma}_x} = e^{\frac{i\pi}{4}\hat{\sigma}_x}e^{\frac{i\pi}{4}\hat{\sigma}_x}\hat{\sigma}_z = e^{\frac{i\pi}{2}\hat{\sigma}_x}\hat{\sigma}_z \\
&= (\cos\frac{\pi}{2} + i\hat{\sigma}_x\sin\frac{\pi}{2})\hat{\sigma}_z = i\hat{\sigma}_x\hat{\sigma}_z = \hat{\sigma}_y
\end{aligned} \tag{7.187}$$

as expected for this particular rotation.

Now the spin degrees of freedom are simply additional degrees of freedom for the system. The spin degrees of freedom are independent of the spatial degrees of freedom, however. This means that we can specify them independently or that $\vec{S}_{op}$ commutes with *all* operators that depend on 3-dimensional space

$$\left[\vec{S}_{op}, \vec{r}_{op}\right] = 0 \quad , \quad \left[\vec{S}_{op}, \vec{p}_{op}\right] = 0 \quad , \quad \left[\vec{S}_{op}, \vec{L}_{op}\right] = 0 \tag{7.188}$$

To specify completely the state of a *spinning* particle or a system with internal degrees of freedom of any kind we must know

1. the amplitudes for finding the particle at points in space
2. the amplitudes for different spin orientations

By convention, we choose $\hat{z}$ as the spin quantization direction for describing state vectors. The total state vector is then a direct-product state of the form

$$|\psi\rangle = |\text{external}\rangle \otimes |\text{internal}\rangle \tag{7.189}$$

and the amplitudes are

$$\begin{aligned}\langle \vec{r}, \hat{z}+ \mid \psi\rangle = &\text{ probability amplitude for finding the particle at} \\ &\ \vec{r} \text{ with spin up in the } \hat{z} \text{ direction} \\ \langle \vec{r}, \hat{z}- \mid \psi\rangle = &\text{ probability amplitude for finding the particle at} \\ &\ \vec{r} \text{ with spin down in the } \hat{z} \text{ direction}\end{aligned}$$

where

$$\langle \vec{r}, \hat{z}+ \mid \psi\rangle = \langle \vec{r} \mid \psi_{external}\rangle \langle \hat{z}+ \mid \psi_{\text{int}ernal}\rangle \tag{7.190}$$

and so on.

The total probability density for finding a particle at $\vec{r}$ is then the sum of two terms

$$|\langle \vec{r}, \hat{z}+ \mid \psi\rangle|^2 + |\langle \vec{r}, \hat{z}- \mid \psi\rangle|^2 \tag{7.191}$$

which represents a sum over all the ways of doing it.

The total angular momentum of such a *spinning* particle is the sum of its orbital and spin angular momenta

$$\vec{J}_{op} = \vec{L}_{op} + S_{op} \tag{7.192}$$

$\vec{J}_{op}$ is now the generator of rotations in 3-dimensional space *and* in spin space or it affects *both* external *and* internal degrees of freedom.

If we operate with $e^{-i\vec{\alpha}\cdot\vec{J}_{op}/\hbar}$ on the basis state $|\vec{r}_0, \hat{m}+\rangle$, where the particle is definitely at $\vec{r}_0$ with spin up $(+\hbar/2)$ in the $\hat{m}$ direction, then we get a new state $|\vec{r}\,'_0, \hat{n}+\rangle$ where

$$\vec{r}\,'_0 = \vec{r}_0 + \vec{\alpha} \times \vec{r}_0 \text{ and } \hat{n} = \hat{m} + \vec{\alpha} \times \hat{m} \tag{7.193}$$

Since $[\vec{S}_{op}, \vec{L}_{op}] = 0$ we have

$$\begin{aligned} e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{J}_{op}} &= e^{-\frac{i}{\hbar}(\vec{\alpha}\cdot\vec{L}_{op}+\vec{\alpha}\cdot\vec{S}_{op})} \\ &= e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{S}_{op}} e^{-\frac{i}{\hbar}\vec{\alpha}\cdot[\vec{S}_{op},\vec{L}_{op}]} \\ &= e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}} e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{S}_{op}} \end{aligned} \tag{7.194}$$

This implies that

$$e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{J}_{op}}\left|\vec{r}_0,\hat{m}+\right\rangle = e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{L}_{op}}e^{-\frac{i}{\hbar}\vec{\alpha}\cdot\vec{S}_{op}}\left|\vec{r}_0,\hat{m}+\right\rangle = \left|\vec{r}\,'_0,\hat{n}+\right\rangle \tag{7.195}$$

and that $e^{-i\vec{\alpha}\cdot\vec{L}_{op}/\hbar}$ carries out the rotation of the spatial degrees of freedom, while $e^{-i\vec{\alpha}\cdot\vec{S}_{op}/\hbar}$ carries out the rotation of the spin degrees of freedom.

If

$$\left|\psi\,'\right\rangle = e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{J}_{op}}\left|\psi\right\rangle \tag{7.196}$$

then the wave function of $\left|\psi\,'\right\rangle$ is

$$\left\langle\vec{r}_0,\hat{m}+\,\middle|\,\psi\,'\right\rangle = \left\langle\vec{r}_0,\hat{m}+\right|e^{\frac{i}{\hbar}\vec{\alpha}\cdot\vec{J}_{op}}\left|\psi\right\rangle = \left\langle\vec{r}\,'_0,\hat{n}+\,\middle|\,\psi\right\rangle \tag{7.197}$$

This is the wavefunction of $\left|\psi\right\rangle$ evaluated at the rotated point with a rotated spin quantization direction.

The *spin representation* of rotations has a feature which is strikingly different from that of rotations in 3-dimensional space.

Consider a rotation by 2π in spin space. This implies that

$$e^{-i\pi\vec{\sigma}_{op}\cdot\vec{\alpha}} = \cos\pi - i\vec{\sigma}_{op}\cdot\vec{\alpha}\sin\pi = -\hat{I} \tag{7.198}$$

A 2π rotation in spin space is represented by $-\hat{I}$. Since the rotations $\vec{\alpha}$ and $\vec{\alpha}+2\pi\vec{\alpha}$ are physically equivalent, we must say that the spin representation of rotations is *double-valued*, i.e.,

$$e^{-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}} \text{ and } e^{-\frac{i}{2}\vec{\sigma}_{op}\cdot(\vec{\alpha}+2\pi\hat{\alpha})} = -e^{-\frac{i}{2}\vec{\sigma}_{op}\cdot\vec{\alpha}} \tag{7.199}$$

represent the same rotation.

7.3.2 **Superselection Rules**

Let us expand on this important point. The 2π rotation transformation operator is given by

$$\hat{U}_{\hat{n}}(2\pi) = e^{-\frac{2\pi i}{\hbar}\hat{n}\cdot\vec{J}_{op}} \tag{7.200}$$

When operating on the angular momentum state vectors we have

$$\hat{U}_{\hat{n}}(2\pi)\left|j,m\right\rangle = e^{-\frac{2\pi i}{\hbar}\hat{n}\cdot\vec{J}_{op}}\left|j,m\right\rangle = e^{-2\pi ij}\left|j,m\right\rangle = (-1)^{2j}\left|j,m\right\rangle \tag{7.201}$$

This says that it has no effect if $j =$ integer and multiplies by -1 if $j =$ half-integer.

We usually think of a rotation through 2π as a trivial operation that changes nothing in a physical system. This belief implies that we are assuming all dynamical variables are invariant under 2π rotations or that

$$\hat{U}_{\hat{n}}(2\pi)\left|j,m\right\rangle = e^{-\frac{2\pi i}{\hbar}\hat{n}\cdot\vec{J}_{op}}\left|j,m\right\rangle = e^{-2\pi ij}\left|j,m\right\rangle = (-1)^{2j}\left|j,m\right\rangle \tag{7.202}$$

where $\hat{A}$ is any physical observable.

But, as we have seen above, $\hat{U}_{\hat{n}}(2\pi)$ is not equal to a trivial operator (not equal to the identity operator for all physical states and operators). This says that invariance under $\hat{U}_{\hat{n}}(2\pi)$ may lead to nontrivial consequences.

The consequences that arise from invariance of an observable are not identical to those that arise from invariance of a state.

Let $\hat{U}$ = a unitary operator that leaves the observable $\hat{F}$ invariant or that we have

$$\left[\hat{U}, \hat{F}\right] = 0 \tag{7.203}$$

Now consider a state that is not invariant under the transformation $\hat{U}$. If it is a pure state represented by $|\psi\rangle$, then $|\psi'\rangle = \hat{U}\,|\psi\rangle \neq |\psi\rangle$. The expectation value of $\hat{F}$ in the state $|\psi\rangle$ is

$$\left\langle \hat{F} \right\rangle = \langle \psi' |\, \hat{F}\, | \psi' \rangle = \langle \psi |\, \hat{U}^{+} \hat{F} \hat{U}\, | \psi \rangle = \langle \psi |\, \hat{U}^{+} \hat{U} \hat{F}\, | \psi \rangle = \langle \psi |\, \hat{F}\, | \psi \rangle \tag{7.204}$$

which implies that the *observable statistical properties* of $\hat{F}$ are the same in the two states $|\psi\rangle$ and $|\psi'\rangle$. This conclusion certainly holds for $\hat{U}(2\pi)$. Does anything else hold? Is there something peculiar to $\hat{U}(2\pi)$?

It turns out that $\hat{U}(2\pi)$ divides the vector space into two subspaces:

1. integer angular momentum - has states $|+\rangle$ where

$$\hat{U}(2\pi)|+\rangle = |+\rangle \tag{7.205}$$

2. half-integer angular momentum - has states $|-\rangle$ where

$$\hat{U}(2\pi)|-\rangle = -|-\rangle \tag{7.206}$$

Now for any invariant physical observable $\hat{B}$ (where $\left[\hat{U}, \hat{B}\right] = 0$), we have

$$\begin{aligned} \langle +| \hat{U}(2\pi)\hat{B} |-\rangle &= \langle +| \hat{B}\hat{U}(2\pi) |-\rangle \\ \langle +| \hat{B} |-\rangle &= -\langle +| \hat{B} |-\rangle \\ \rightarrow \langle +| \hat{B} |-\rangle &= 0 \end{aligned} \tag{7.207}$$

This says that *all* physical observable have *vanishing matrix elements* between states with integer angular momentum and states with half-integer angular momentum (states in the two subspaces). This is called a *superselection rule*.

A superselection rule says that there is *no observable distinction* among vectors of the form

$$|\psi_\varphi\rangle = |+\rangle + e^{i\varphi} |-\rangle \tag{7.208}$$

for different values of the phase φ. This is so because

$$\langle\psi_\varphi| \hat{B} |\psi_\varphi\rangle = \langle+| \hat{B} |+\rangle + \langle-| \hat{B} |-\rangle \tag{7.209}$$

and this is independent of φ.

What about a more general state represented by the state operator

$$\hat{W} = \sum_{i,j} w_{ij} |i\rangle \langle j| \tag{7.210}$$

If we break up the basis for the space into + and − subspaces, i.e.,

$$\text{basis set } = \{\{+ \text{ states}\}, \{- \text{ states}\}\}$$

then the matrix representation of $\hat{W}$ partitions into four blocks

$$\hat{W} = \begin{pmatrix} \hat{W}_{++} & \hat{W}_{+-} \\ \hat{W}_{-+} & \hat{W}_{--} \end{pmatrix} \tag{7.211}$$

While, for any physical observable, the same partitioning scheme produces

$$\hat{B} = \begin{pmatrix} \hat{B}_{++} & 0 \\ 0 & \hat{B}_{--} \end{pmatrix} \tag{7.212}$$

i.e., there is no mixing between the subspaces. This gives

$$\left\langle \hat{B} \right\rangle = Tr\left(\hat{W}\hat{B}\right) = Tr_{+}\left(\hat{W}_{++}\hat{B}_{++}\right) + Tr_{-}\left(\hat{W}_{--}\hat{B}_{--}\right) \tag{7.213}$$

where $Tr_{\pm}$ implies a trace only over the particular subspace. The cross matrix elements $\hat{W}_{+-}$ and $\hat{W}_{-+}$ do not contribute to the expectation value of the observables, or *interference between vectors of the* $|+\rangle$ *and* $|-\rangle$ *types is not observable.*

All equations of motion decouple into two separate equations in each of the two subspaces and no cross-matrix elements of $\hat{W}$ between the two subspaces ever contribute.

If we assume that the cross matrix elements are zero initially, then they will never develop(become nonzero) in time.

What is the difference between a generator $\hat{U}(2\pi)$ of a superselection rule and a symmetry operation that is generated by a universally conserved quantity such as the displacement operator

$$e^{-\frac{i}{\hbar}\vec{a}\cdot\vec{P}_{op}}$$

which is generated by the total momentum $\vec{P}_{op}$?

The Hamiltonian of any closed system is invariant under both transformations. Both give rise to a quantum number that must be conserved in any transition. In these examples the quantum numbers are

± 1 for $\hat{U}(2\pi)$ and the total momentum

The difference is that there exist observables that do not commute with $\vec{P}_{op}$ and $\vec{Q}_{op}$, but there are *no observables* that do not commute with $\hat{U}(2\pi)$.

By measuring the position one can distinguish states that differ only by a displacement, but there is no way to distinguish between states that differ only by a 2π rotation.

The superselection rules from $\hat{U}(2\pi)$, which separates the integer and half-integer angular momentum states, is the only such rule in the quantum mechanics of stable particles (non-relativistic quantum mechanics).

In Quantum Field Theory(relativistic quantum mechanics), where particles can be created and annihilated, the total electric charge operator generates another superselection rule, provided that one assumes all observables are invariant under gauge transformations.

This says that no interference can be observed between states of different total charge because there are no observables that do not commute with the charge operator.

In a theory of stable particles, the charge of each particle and hence the total charge is an invariant. Thus, the total charge operator is simply a multiple of $\hat{I}$. Every operator commutes with $\hat{I}$ implying that the charge superselection rule is trivial in non-relativistic quantum mechanics.

Now back to the normal world.

The techniques that we have developed for the spin $= 1/2$ system can be applied to any two-state system. Here is an example of a two-sided box solved using both the Schrodinger and Heisenberg pictures.

7.3.3 A Box with 2 Sides

Let us consider a box containing a particle in a state $|\psi\rangle$. The box is divided into two halves (**R**ight and **L**eft) by a thin partition. The only property that we will assign to the particle is whether it is on the **R**ight or **L**eft side of the box.

This means that the system has only two states, namely, $|R\rangle$ and $|L\rangle$ that must have the properties

$$\begin{aligned}\langle R \mid \psi\rangle &= \text{ amplitude to find the particle on right side if in state } |\psi\rangle \\ \langle L \mid \psi\rangle &= \text{ amplitude to find the particle on leftt side if in state } |\psi\rangle\end{aligned}$$

We also suppose that the particle can tunnel through the thin partition and that

$$\frac{d}{dt}\langle R \mid \psi\rangle = \frac{K}{i\hbar}\langle L \mid \psi\rangle \quad , \quad K \text{ real} \tag{7.214}$$

How does this system develop in time?

We solve this problem in two ways, namely, using the Schrodinger and Heisenberg pictures.

Schrodinger Picture

We define the general system state vector

$$
\begin{aligned}
|\psi\rangle = \begin{pmatrix} \psi_R \\ \psi_L \end{pmatrix} &= \begin{pmatrix} \langle R \mid \psi\rangle \\ \langle L \mid \psi\rangle \end{pmatrix} \\
&= \psi_R \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_L \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\
&= \psi_R \,|R\rangle + \psi_L \,|L\rangle
\end{aligned} \tag{7.215}
$$

The time-dependent Schrodinger equation is

$$
i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = i\hbar \begin{pmatrix} \frac{\partial \psi_R}{\partial t} \\ \frac{\partial \psi_L}{\partial t} \end{pmatrix} = \hat{H} \begin{pmatrix} \psi_R \\ \psi_L \end{pmatrix} \tag{7.216}
$$

Now we are given that

$$\frac{d\psi_R}{dt} = \frac{K}{i\hbar}\psi_L \rightarrow \frac{d\psi_R^*}{dt} = -\frac{K}{i\hbar}\psi_L^* \tag{7.217}$$

The state vector must remain normalized as it develops in time so that

$$\begin{aligned}
&\langle\psi \mid \psi\rangle = |\psi_R|^2 + |\psi_L|^2 = 1 \\
&\frac{\partial \langle\psi \mid \psi\rangle}{\partial t} = 0 = \frac{\partial\psi_R^*}{\partial t}\psi_R + \psi_R^*\frac{\partial\psi_R}{\partial t} + \frac{\partial\psi_L^*}{\partial t}\psi_L + \psi_L^*\frac{\partial\psi_L}{\partial t} \\
&0 = -\frac{K}{i\hbar}\psi_L^*\psi_R + \psi_R^*\frac{K}{i\hbar}\psi_L + \frac{\partial\psi_L^*}{\partial t}\psi_L + \psi_L^*\frac{\partial\psi_L}{\partial t} \\
&0 = \psi_L\left(\frac{\partial\psi_L^*}{\partial t} + \frac{K}{i\hbar}\psi_R^*\right) + \psi_L^*\left(\frac{\partial\psi_L}{\partial t} - \frac{K}{i\hbar}\psi_R\right)
\end{aligned}$$

which says that

$$\frac{d\psi_L}{dt} = \frac{K}{i\hbar}\psi_R \rightarrow \frac{d\psi_L^*}{dt} = -\frac{K}{i\hbar}\psi_R^* \tag{7.218}$$

Therefore we have

$$K \begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = \hat{H} \begin{pmatrix} \psi_R \\ \psi_L \end{pmatrix} \tag{7.219}$$

which says that

$$\hat{H} = K \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{7.220}$$

The eigenvalues of $\hat{H}$ are $\pm K$ and its eigenvectors are

$$|\pm K\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \tag{7.221}$$

Note that for $\hat{\wp}$ = parity operator (switches right and left) we have

$$\hat{\wp}\, |\pm K\rangle = \pm\, |\pm K\rangle \tag{7.222}$$

so these are also states of definite parity.

If the initial state of the system is

$$|\psi(0)\rangle = \begin{pmatrix} \psi_R(0) \\ \psi_L(0) \end{pmatrix} \tag{7.223}$$

then we can write this state in terms of energy eigenstates as

$$\begin{aligned} |\psi(0)\rangle &= \begin{pmatrix} \psi_R(0) \\ \psi_L(0) \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} (\psi_R(0) + \psi_L(0)) |{+K}\rangle + \frac{1}{\sqrt{2}} (\psi_R(0) - \psi_L(0)) |{-K}\rangle \end{aligned} \tag{7.224}$$

Since we know the time dependence of energy eigenstates

$$|\pm K\rangle_t = e^{\mp \frac{i}{\hbar} K t} |\pm K\rangle \tag{7.225}$$

the time dependence of $|\psi(t)\rangle$ is given by

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} \left(\psi_R(0) + \psi_L(0)\right) e^{-\frac{i}{\hbar}Kt} \left|+K\right\rangle + \frac{1}{\sqrt{2}} \left(\psi_R(0) - \psi_L(0)\right) e^{+\frac{i}{\hbar}Kt} \left|-K\right\rangle \tag{7.226}$$

or

$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{2} \begin{pmatrix} \left(\psi_R(0) + \psi_L(0)\right) e^{-\frac{i}{\hbar}Kt} + \left(\psi_R(0) - \psi_L(0)\right) e^{+\frac{i}{\hbar}Kt} \\ \left(\psi_R(0) + \psi_L(0)\right) e^{-\frac{i}{\hbar}Kt} - \left(\psi_R(0) - \psi_L(0)\right) e^{+\frac{i}{\hbar}Kt} \end{pmatrix} \\ &= \left(\psi_R(0) \cos \frac{Kt}{\hbar} - i\psi_L(0) \sin \frac{Kt}{\hbar}\right) |R\rangle \\ &\quad + \left(-i\psi_R(0) \sin \frac{Kt}{\hbar} + \psi_L(0) \cos \frac{Kt}{\hbar}\right) |L\rangle \end{aligned} \tag{7.227}$$

Therefore, the probability that the particle is on the **R**ight side at time t is

$$P_R = |\langle R \mid \psi(t)\rangle|^2 = \left|\psi_R(0) \cos \frac{Kt}{\hbar} - i\psi_L(0) \sin \frac{Kt}{\hbar}\right|^2 \tag{7.228}$$

Now suppose that

$$\psi_R(0) = \frac{1}{\sqrt{2}} \text{ and } \psi_L(0) = e^{i\delta}\psi_R(0) \tag{7.229}$$

This says that the particle was equally probable to be on either side at $t = 0$, but that the amplitudes differed by a phase factor. In this case, we get

$$P_R = \frac{1}{2}\left(1 + \sin\delta \sin\frac{2Kt}{\hbar}\right) \tag{7.230}$$

Heisenberg Picture

Let us define an operator $\hat{Q}$ such that for a state vector

$$|\psi\rangle = \psi_R |R\rangle + \psi_L |L\rangle$$

we have

$$\langle\psi| \hat{Q} |\psi\rangle = |\psi_R|^2 = \text{ probability that particle is on right side} \tag{7.231}$$

This says that

$$\langle\psi| \hat{Q} |\psi\rangle = |\psi_R|^2 = \langle\psi \mid R\rangle \langle R \mid \psi\rangle \tag{7.232}$$

or

$$\hat{Q} = |R\rangle \langle R| = \text{ pure state projection operator } = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \hat{I} + \hat{\sigma}_z \tag{7.233}$$

and that the expectation value of the pure state projection operator is equal to the probability of being in that state. This agrees with our earlier discussions.

Now we have

$$\hat{H} = K \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = K\hat{\sigma}_x \tag{7.234}$$

Therefore,

$$\hat{Q}(t) = e^{\frac{i}{\hbar}\hat{H}t}\hat{Q}e^{-\frac{i}{\hbar}\hat{H}t} \tag{7.235}$$

Now as we saw earlier

$$e^{\frac{i}{\hbar}\hat{H}t} = e^{\frac{i}{\hbar}K\hat{\sigma}_x t} = \cos\frac{Kt}{\hbar}\hat{I} + i\sin\frac{Kt}{\hbar}\hat{\sigma}_x \tag{7.236}$$

Thus,

$$\begin{aligned}
\hat{Q}(t) &= \left(\cos\frac{Kt}{\hbar}\hat{I} + i\sin\frac{Kt}{\hbar}\hat{\sigma}_x\right)\left(\hat{I}+\hat{\sigma}_z\right)\left(\cos\frac{Kt}{\hbar}\hat{I} - i\sin\frac{Kt}{\hbar}\hat{\sigma}_x\right) \\
&= \cos^2\frac{Kt}{\hbar} + \sin^2\frac{Kt}{\hbar} + \cos^2\frac{Kt}{\hbar}\hat{\sigma}_z - i\sin\frac{Kt}{\hbar}\cos\frac{Kt}{\hbar}\left[\hat{\sigma}_z,\hat{\sigma}_x\right] \\
&\qquad + \sin^2\frac{Kt}{\hbar}\hat{\sigma}_x\hat{\sigma}_z\hat{\sigma}_x \\
&= 1 + \cos^2\frac{Kt}{\hbar}\hat{\sigma}_z + 2\sin\frac{Kt}{\hbar}\cos\frac{Kt}{\hbar}\hat{\sigma}_y - \sin^2\frac{Kt}{\hbar}\hat{\sigma}_z \\
&= 1 + \cos\frac{2Kt}{\hbar}\hat{\sigma}_z + \sin\frac{2Kt}{\hbar}\hat{\sigma}_y
\end{aligned} \tag{7.237}$$

Then

$$P_R(t) = \langle\psi(0)|\,\hat{Q}(t)\,|\psi(0)\rangle \tag{7.238}$$

where

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}|R\rangle + \frac{e^{i\delta}}{\sqrt{2}}|L\rangle \tag{7.239}$$

Now

$$\begin{aligned} \hat{\sigma}_z|R\rangle &= |R\rangle \quad , \quad \hat{\sigma}_z|L\rangle = -|L\rangle \\ \hat{\sigma}_y|R\rangle &= -i|L\rangle \quad , \quad \hat{\sigma}_y|L\rangle = i|R\rangle \end{aligned}$$

and we get

$$P_R = \frac{1}{2}(1 + \sin\delta \sin\frac{2Kt}{\hbar}) \tag{7.240}$$

as before.

7.4 **Magnetic Resonance**

How does an experimentalist observe the spin of a particle?

Classically, a spinning charge distribution will have an associated magnetic moment.

In non-relativistic quantum mechanics particles with internal spin degrees of freedom also have magnetic moments which are connected to their angular momentum. We write for the magnetic moment operator

$$\begin{aligned}\vec{M}_{op} &= \vec{M}_{op}^{orbital} + \vec{M}_{op}^{spin} \\ &= g_\ell \frac{q}{2mc}\vec{L}_{op} + g_s \frac{q}{2mc}\vec{S}_{op} = \frac{q}{2mc}\left(g_\ell \vec{L}_{op} + g_s \vec{S}_{op}\right) \quad (7.241)\end{aligned}$$

where, as we shall derive later,

$$g_{j\ell s} = 1 + \frac{j(j+1) - \ell(\ell+1) + s(s+1)}{2j(j+1)} \quad (7.242)$$

$$g_\ell = g_{jj0} = 1 \text{ and } g_s = g_{j0j} = 2 \quad (7.243)$$

Therefore we have

$$\vec{M}_{op} = \frac{q}{2mc}\left(\vec{L}_{op} + 2\vec{S}_{op}\right) = \frac{q}{2mc}\left(\vec{J}_{op} + \vec{S}_{op}\right) \quad (7.244)$$

which says that $\vec{M}_{op}$ is *not parallel* to $\vec{J}_{op}$. The energy operator or contribution to the Hamiltonian operator from the magnetic moment in a magnetic field $\vec{B}(\vec{r},t)$ is

$$\hat{H}_M = -\vec{M}_{op} \cdot \vec{B}(\vec{r},t) \tag{7.245}$$

Spin measurement experiments are designed to detect the effects of this extra contribution to the system energy and thus detect the effects of spin angular momentum.

We will return to a full discussion of the effect of $\hat{H}_M$ on the energy levels of atoms, etc in a later chapter. For now we will restrict our attention to spin space and investigate the effect of the spin contribution to $\hat{H}_M$ on the states of a particle.

We will use

$$\hat{H}_{spin} = -\frac{g}{2}\frac{q}{mc}\vec{B} \cdot \bar{S}_{op} \tag{7.246}$$

where we have replaced g_s by g. We have not set $g = 2$ since it turns out that it is not exactly that value(due to relativistic effects).

In the Schrodinger picture we have

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = \hat{H}_{spin}\left|\psi(t)\right\rangle \tag{7.247}$$

If we ignore spatial dependences (worry only about spin effects), we have

$$\left|\psi(t)\right\rangle = \begin{pmatrix} \langle \hat{n}+ \mid \psi(t)\rangle \\ \langle \hat{n}- \mid \psi(t)\rangle \end{pmatrix} \tag{7.248}$$

$$\begin{aligned} i\hbar\frac{d}{dt}\begin{pmatrix} \langle \hat{n}+ \mid \psi(t)\rangle \\ \langle \hat{n}- \mid \psi(t)\rangle \end{pmatrix} &= -\frac{g}{2}\frac{q}{mc}\vec{B}\cdot\bar{S}_{op}\begin{pmatrix} \langle \hat{n}+ \mid \psi(t)\rangle \\ \langle \hat{n}- \mid \psi(t)\rangle \end{pmatrix} \\ &= -\frac{g}{4}\frac{q\hbar}{mc}\vec{B}\cdot\vec{\sigma}_{op}\begin{pmatrix} \langle \hat{n}+ \mid \psi(t)\rangle \\ \langle \hat{n}- \mid \psi(t)\rangle \end{pmatrix} \\ &= -\frac{g}{4}\frac{q\hbar}{mc}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}\begin{pmatrix} \langle \hat{n}+ \mid \psi(t)\rangle \\ \langle \hat{n}- \mid \psi(t)\rangle \end{pmatrix} \end{aligned} \tag{7.249}$$

This represents two coupled differential equations for the time dependence of the amplitudes $\langle + \mid \psi\rangle$ and $\langle - \mid \psi\rangle$. When solved, the solution tells us the time dependence of the measurable probabilities.

We can see the physics of the motion best in the Heisenberg picture, where the operators, instead of the states, move in time. In this case, we have

$$i\hbar\frac{d\hat{S}_i(t)}{dt} = \left[\hat{S}_i(t), \hat{H}_{spin}(t)\right]$$
$$= -\frac{gq}{2mc}\left[\hat{S}_i(t), \hat{S}_j(t)\right] B_j(t) = -i\frac{gq\hbar}{2mc}\varepsilon_{ijk}\hat{S}_k(t)B_j(t) \tag{7.250}$$

for each component. The operators are all time-dependent Heisenberg picture operators. This gives

$$\frac{d\vec{S}_{op}(t)}{dt} = \frac{gq}{2mc}\vec{S}_{op}(t)\times\vec{B}(t) = \vec{M}_{spin}(t)\times\vec{B}(t) \tag{7.251}$$

The right-hand-side is the *torque* exerted by the magnetic field on the magnetic moment.

In operator language, this equation implies that the rate of change of the spin angular momentum vector equals the applied torque.

This implies that the spin vector with $q < 0$ precesses in a positive sense about the magnetic field direction as shown in the figure below.

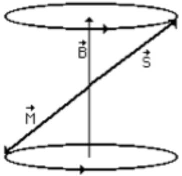

Figure: Motion of Spin

Suppose that $\vec{B}(t) = B_0\hat{z}$ (independent of t). We then have

$$\frac{d\hat{S}_z(t)}{dt} = 0 \tag{7.252}$$

$$\frac{d\hat{S}_x(t)}{dt} = \frac{gqB_0}{2mc}\hat{S}_y(t) \tag{7.253}$$

$$\frac{d\hat{S}_y(t)}{dt} = -\frac{gqB_0}{2mc}\hat{S}_x(t) \tag{7.254}$$

These coupled differential equations have the solutions

$$\hat{S}_x(t) = \hat{S}_x(0)\cos\omega_0 t + \hat{S}_y(0)\sin\omega_0 t \tag{7.255}$$

$$\hat{S}_y(t) = -\hat{S}_x(0)\sin\omega_0 t + \hat{S}_y(0)\cos\omega_0 t \tag{7.256}$$

$$\hat{S}_z(t) = \hat{S}_z(0) \tag{7.257}$$

where

$$\omega_0 = \frac{gqB_0}{2mc} \tag{7.258}$$

Now suppose that at $t = 0$, the spin is in the $+x$-direction, which says that

$$\left\langle \hat{S}_x(0) \right\rangle = \langle \hat{x}+ | \, \hat{S}_x(0) \, | \hat{x}+ \rangle = \frac{\hbar}{2} \tag{7.259}$$

$$\left\langle \hat{S}_y(0) \right\rangle = \left\langle \hat{S}_z(0) \right\rangle = 0 \tag{7.260}$$

Therefore, the expectation values of the solutions become

$$\left\langle \hat{S}_x(t) \right\rangle = \frac{\hbar}{2}\cos\omega_0 t \tag{7.261}$$

$$\left\langle \hat{S}_y(t) \right\rangle = -\frac{\hbar}{2}\sin\omega_0 t \tag{7.262}$$

$$\left\langle \hat{S}_z(0) \right\rangle = 0 \tag{7.263}$$

which says that the expectation value of the spin vector rotates in a negative sense in the $x-y$ plane (precession about the z-axis).

Now let us return to the Schrodinger picture to see what precession looks like there. We will do the calculation a couple of different ways.

First we use the time-development operator. For $\hat{B} = B\hat{n}$ we have

$$\hat{H} = -\frac{gq\hbar B}{4mc}\vec{\sigma}_{op} \cdot \hat{n} \tag{7.264}$$

If we define

$$\omega_L = \frac{qB}{mc} = \text{ Larmor frequency} \tag{7.265}$$

and let $g = 2$ we have

$$\hat{H} = -\frac{1}{2}\hbar\omega_L\vec{\sigma}_{op} \cdot \hat{n} \tag{7.266}$$

In the Schrodinger picture,

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = \hat{H}_{spin}(t)\left|\psi(t)\right\rangle \tag{7.267}$$

When $\hat{H}_{spin}(t)$ is time-independent, we have the solution

$$\left|\psi(t)\right\rangle = \hat{U}(t)\left|\psi(0)\right\rangle \tag{7.268}$$

where

$$\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t} \tag{7.269}$$

or

$$|\psi(t)\rangle = e^{i\frac{\omega_L t}{2}\vec{\sigma}_{op}\cdot\hat{n}}\,|\psi(0)\rangle \tag{7.270}$$

Since $\hat{n}$ = a unit vector, we have $(\vec{\sigma}_{op}\cdot\hat{n})^2 = \hat{I}$, which gives, as before,

$$|\psi(t)\rangle = \left(\cos\frac{\omega_L t}{2} + i(\vec{\sigma}_{op}\cdot\hat{n})\sin\frac{\omega_L t}{2}\right)|\psi(0)\rangle \tag{7.271}$$

This is the solution to the Schrodinger equation in this case.

Now let

$$|\psi(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \left|\widehat{z}\uparrow\right\rangle = \left|\widehat{z}+\right\rangle = |+\rangle \tag{7.272}$$

From earlier we have

$$\vec{\sigma}_{op}\cdot\hat{n} = \begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix} \tag{7.273}$$

We then have

$$
\begin{aligned}
|\psi(t)\rangle &= \cos\frac{\omega_L t}{2}|+\rangle + i\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix}|+\rangle \sin\frac{\omega_L t}{2} \\
&= \cos\frac{\omega_L t}{2}|+\rangle + i\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\sin\frac{\omega_L t}{2} \\
&= \cos\frac{\omega_L t}{2}|+\rangle + i\sin\frac{\omega_L t}{2}\begin{pmatrix} n_z \\ n_x + in_y \end{pmatrix} \\
&= \cos\frac{\omega_L t}{2}|+\rangle + i\sin\frac{\omega_L t}{2}\left(n_z|+\rangle + (n_x + in_y)|-\rangle\right) \\
&= \left(\cos\frac{\omega_L t}{2} + in_z\sin\frac{\omega_L t}{2}\right)|+\rangle + i(n_x + in_y)\sin\frac{\omega_L t}{2}|-\rangle
\end{aligned}
\tag{7.274}
$$

This says that as the initial state $|+\rangle$ develops in time it picks up some amplitude to be in the $|-\rangle$ state.

Special Case

Let

$$\hat{n} = \hat{y} \rightarrow \vec{B} \text{ is in the } y\text{- direction}$$
$$n_y = 1\ ,\ n_x = n_z = 0$$

This gives

$$|\psi(t)\rangle = \cos\frac{\omega_L t}{2}\,|+\rangle - \sin\frac{\omega_L t}{2}\,|-\rangle \tag{7.275}$$

which implies that $\langle \hat{s}_z \rangle$ flips with frequency $\nu = \omega_L/4\pi$ or that the spin vector is precessing around the direction of the magnetic field.

Finally, let us just solve the Schrodinger equation directly. We have

$$i\hbar\frac{d}{dt}\left(\begin{array}{c}\langle\hat{n}+\mid\psi(t)\rangle\\ \langle\hat{n}-\mid\psi(t)\rangle\end{array}\right)$$
$$=-\frac{1}{2}\frac{q\hbar}{mc}\left(\begin{array}{cc}B_z & B_x-iB_y\\ B_x+iB_y & -B_z\end{array}\right)\left(\begin{array}{c}\langle\hat{n}+\mid\psi(t)\rangle\\ \langle\hat{n}-\mid\psi(t)\rangle\end{array}\right) \tag{7.276}$$

If we choose $\hat{n}=\hat{x}$,then we have

$$i\hbar\frac{d}{dt}\left(\begin{array}{c}a(t)\\ b(t)\end{array}\right)=-\frac{1}{2}\hbar\omega_L\left(\begin{array}{cc}0 & 1\\ 1 & 0\end{array}\right)\left(\begin{array}{c}a(t)\\ b(t)\end{array}\right) \tag{7.277}$$

where $a(t)=\langle\hat{n}+\mid\psi(t)\rangle$ and $b(t)=\langle\hat{n}-\mid\psi(t)\rangle$

and $|a|^2+|b|^2=1$

This gives two coupled differential equations

$$\dot{a}=i\frac{\omega_L}{2}b \text{ and } \dot{b}=i\frac{\omega_L}{2}a \tag{7.278}$$

which are solved as follows:

$$(\dot{a}+\dot{b}) = i\frac{\omega_L}{2}(\dot{a}+\dot{b}) \to a+b = (a(0)+b(0))e^{i\frac{\omega_L}{2}t} \tag{7.279}$$

$$(\dot{a}-\dot{b}) = -i\frac{\omega_L}{2}(\dot{a}-\dot{b}) \to a-b = (a(0)-b(0))e^{-i\frac{\omega_L}{2}t} \tag{7.280}$$

or

$$a(t) = a(0)\cos\frac{\omega_L}{2}t + ib(0)\sin\frac{\omega_L}{2}t \tag{7.281}$$

$$b(t) = ia(0)\sin\frac{\omega_L}{2}t + b(0)\cos\frac{\omega_L}{2}t \tag{7.282}$$

For the initial state

$$|\psi(0)\rangle = \begin{pmatrix} a(0) \\ b(0) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{7.283}$$

we get

$$a(t) = \cos\frac{\omega_L}{2}t \quad , \quad b(t) = i\sin\frac{\omega_L}{2}t \tag{7.284}$$

and

$$a(t) = \cos\frac{\omega_L}{2}t \quad , \quad b(t) = i\sin\frac{\omega_L}{2}t \tag{7.285}$$

as before.

7.4.1 Spin Resonance

Let us now consider the addition of an oscillating magnetic field perpendicular to the applied field $\vec{B} = B_0\hat{z}$. In particular, we add the field

$$\vec{B}_1 = B_1 \cos\omega t\hat{x} \tag{7.286}$$

In the Schrodinger picture, we then have the equation of motion

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = -\frac{e\hbar}{2mc}\frac{g}{2}\left(B_0\hat{\sigma}_z + B_1\cos\omega t\hat{\sigma}_x\right)\left|\psi(t)\right\rangle \tag{7.287}$$

Now we first make the transformation (shift to rotating coordinate system since we know that if the extra field were not present the spin would just be precessing about the direction of the applied field)

$$\left|\psi(t)\right\rangle = e^{i\frac{\omega t}{2}\hat{\sigma}_z}\left|\psi'(t)\right\rangle \tag{7.288}$$

which gives

$$i\hbar\frac{d}{dt}\left(e^{i\frac{\omega t}{2}\hat{\sigma}_z}\left|\psi'(t)\right\rangle\right) = -\frac{e\hbar}{2mc}\frac{g}{2}\left(B_0\hat{\sigma}_z + B_1\cos\omega t\hat{\sigma}_x\right)e^{i\frac{\omega t}{2}\hat{\sigma}_z}\left|\psi'(t)\right\rangle \tag{7.289}$$

$$i\hbar e^{-i\frac{\omega t}{2}\hat{\sigma}_z}\frac{d}{dt}\left(e^{i\frac{\omega t}{2}\hat{\sigma}_z}\left|\psi'(t)\right\rangle\right) \tag{7.290}$$

$$= -\frac{e\hbar}{2mc}\frac{g}{2}\left(B_0 e^{-i\frac{\omega t}{2}\hat{\sigma}_z}\hat{\sigma}_z e^{i\frac{\omega t}{2}\hat{\sigma}_z} + B_1\cos\omega t e^{-i\frac{\omega t}{2}\hat{\sigma}_z}\hat{\sigma}_x e^{i\frac{\omega t}{2}\hat{\sigma}_z}\right)\left|\psi'(t)\right\rangle$$

or

$$i\hbar e^{-i\frac{\omega t}{2}\hat{\sigma}_z}\left(e^{i\frac{\omega t}{2}\hat{\sigma}_z}\frac{d}{dt}\left|\psi'(t)\right\rangle + i\frac{\omega}{2}\hat{\sigma}_z e^{i\frac{\omega t}{2}\hat{\sigma}_z}\left|\psi'(t)\right\rangle\right)$$

$$= -\frac{e\hbar}{2mc}\frac{g}{2}\left(B_0\hat{\sigma}_z + B_1\cos\omega t e^{-i\frac{\omega t}{2}\hat{\sigma}_z}\hat{\sigma}_x e^{i\frac{\omega t}{2}\hat{\sigma}_z}\right)\left|\psi'(t)\right\rangle \tag{7.291}$$

Now

$$
\begin{aligned}
\cos\omega t e^{-i\frac{\omega t}{2}\hat{\sigma}_z}\hat{\sigma}_x e^{i\frac{\omega t}{2}t\hat{\sigma}_z} &= \cos\omega t\hat{\sigma}_x e^{i\omega t\hat{\sigma}_z} \\
&= \hat{\sigma}_x(\cos^2\omega t + i\hat{\sigma}_z\cos\omega t\sin\omega t) \\
&= \hat{\sigma}_x(\frac{1}{2} + \frac{1}{2}\cos 2\omega t + i\hat{\sigma}_z\frac{1}{2}\sin 2\omega t) \\
&= \frac{\hat{\sigma}_x}{2} + \frac{1}{2}\left(\hat{\sigma}_x\cos 2\omega t + i\hat{\sigma}_x\hat{\sigma}_z\sin 2\omega t\right) \\
&= \frac{\hat{\sigma}_x}{2} + \frac{1}{2}\left(\hat{\sigma}_x\cos 2\omega t + \hat{\sigma}_y\sin 2\omega t\right)
\end{aligned} \tag{7.292}
$$

Defining

$$
\omega_0 = \frac{geB_0}{4mc} \text{ and } \omega_1 = \frac{geB_1}{4mc} \tag{7.293}
$$

we get

$$
\begin{aligned}
i\hbar\frac{d}{dt}\left|\psi'(t)\right\rangle = &\left(\left(\frac{\omega-\omega_0}{2}\right)\hat{\sigma}_z - \frac{\omega_1}{2}\hat{\sigma}_x\right)\left|\psi'(t)\right\rangle \\
&+ \frac{\omega_1}{2}\left(\hat{\sigma}_x\cos 2\omega t + \hat{\sigma}_y\sin 2\omega t\right)\left|\psi'(t)\right\rangle
\end{aligned} \tag{7.294}
$$

The two higher frequency terms produce high frequency wiggles in $|\psi'(t)\rangle$. Since we will be looking at the average motion of the spin vector (expectation values changing in time), these terms will average to zero and we can neglect them in this discussion.

We thus have

$$i\hbar\frac{d}{dt}\left|\psi'(t)\right\rangle = \left(\left(\frac{\omega-\omega_0}{2}\right)\hat{\sigma}_z - \frac{\omega_1}{2}\hat{\sigma}_x\right)\left|\psi'(t)\right\rangle \tag{7.295}$$

which has a solution

$$\left|\psi'(t)\right\rangle = e^{-i\frac{\Omega t}{2}\hat{\sigma}}\left|\psi'(0)\right\rangle \tag{7.296}$$

$$\Omega = \left[(\omega-\omega_0)^2+\omega_1^2\right]^{1/2} \text{ and } \hat{\sigma} = \frac{\omega-\omega_0}{\Omega}\hat{\sigma}_z - \frac{\omega_1}{\Omega}\hat{\sigma}_x \tag{7.297}$$

We note that

$$\hat{\sigma}^2 = \frac{(\omega-\omega_0)^2+\omega_1^2}{\Omega^2}\hat{I} = \hat{I} \tag{7.298}$$

The final solution to the original problem (again neglecting the higher frequency terms) is then(after leaving the rotating system)

$$\left|\psi(t)\right\rangle = e^{-i\frac{\omega t}{2}\hat{\sigma}_z}e^{-i\frac{\Omega t}{2}\hat{\sigma}}\left|\psi(0)\right\rangle \tag{7.299}$$

Example

Let us choose

$$|\psi(0)\rangle = |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{7.300}$$

We get

$$|\psi(t)\rangle = e^{-i\frac{\omega t}{2}\hat{\sigma}_z} e^{-i\frac{\Omega t}{2}\hat{\sigma}} |+\rangle = e^{-i\frac{\omega t}{2}\hat{\sigma}_z} \left(\cos\frac{\Omega t}{2} - i\hat{\sigma}\sin\frac{\Omega t}{2} \right) |+\rangle \tag{7.301}$$

$$= e^{-i\frac{\omega t}{2}\hat{\sigma}_z} \left(\cos\frac{\Omega t}{2}|+\rangle - i\frac{\omega - \omega_0}{\Omega}\sin\frac{\Omega t}{2}\hat{\sigma}_z|+\rangle + i\frac{\omega_1}{\Omega}\sin\frac{\Omega t}{2}\hat{\sigma}_x|+\rangle \right)$$

Now using

$$\hat{\sigma}_z|+\rangle = |+\rangle \text{ and } \hat{\sigma}_x|+\rangle = |-\rangle \tag{7.302}$$

$$e^{-i\frac{\omega t}{2}\hat{\sigma}_z} = \cos\frac{\omega t}{2} - i\sin\frac{\omega t}{2}\hat{\sigma}_z \tag{7.303}$$

we have

$$|\psi(t)\rangle = A^{(+)}|+\rangle + A^{(-)}|-\rangle \tag{7.304}$$

$$\begin{aligned} A^{(+)} &= \cos\frac{\omega t}{2}\cos\frac{\Omega t}{2} - i\sin\frac{\omega t}{2}\cos\frac{\Omega t}{2} \\ &\quad - i\frac{\omega-\omega_0}{\Omega}\cos\frac{\omega t}{2}\sin\frac{\Omega t}{2} - \frac{\omega-\omega_0}{\Omega}\sin\frac{\omega t}{2}\sin\frac{\Omega t}{2} \end{aligned} \tag{7.305}$$

$$A^{(-)} = -i\frac{\omega_1}{\Omega}\cos\frac{\omega t}{2}\sin\frac{\Omega t}{2} + \frac{\omega_1}{\Omega}\sin\frac{\omega t}{2}\sin\frac{\Omega t}{2} \tag{7.306}$$

Therefore, the amplitude for spin flip to the state $|\hat{z}\downarrow\rangle = |-\rangle$ at time t is

$$\begin{aligned} \langle - \mid \psi(t)\rangle = A^{(-)} &= -i\frac{\omega_1}{\Omega}\cos\frac{\omega t}{2}\sin\frac{\Omega t}{2} + \frac{\omega_1}{\Omega}\sin\frac{\omega t}{2}\sin\frac{\Omega t}{2} \\ &= -i\frac{\omega_1}{\Omega}\sin\frac{\Omega t}{2}e^{i\frac{\omega t}{2}} \end{aligned} \tag{7.307}$$

and the probability of spin flip is

$$P_{flip}(t) = |\langle - \mid \psi(t)\rangle|^2 = \frac{\omega_1^2}{\Omega^2}\sin^2\frac{\Omega t}{2} = \frac{\omega_1^2}{2\Omega^2}(1-\cos\Omega t) \tag{7.308}$$

What is happening to the spin vector? If we plot $P_{flip}(t)$ versus t as in the figure below we get

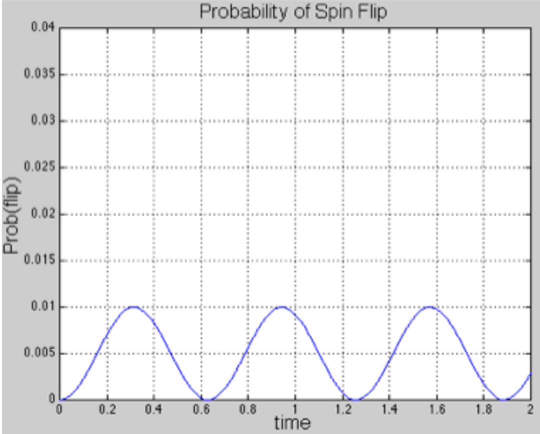

Figure: Spin=Flip Probability verus Time

where the peak values are given by ω_1^2/Ω^2.

What is the value of ω_1^2/Ω^2 and can it be large? If we plot ω_1^2/Ω^2 versus ω (the frequency of the added field) we get as in the figure the result

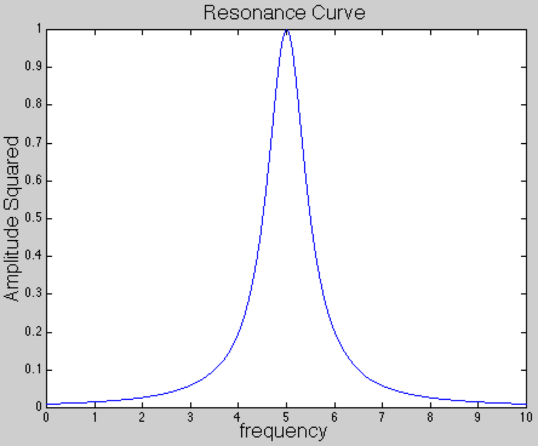

Figure: Resonance Curve

The peak occurs at $\omega - \omega_0 \approx 0$ (called a *resonance*).

Therefore, if $\omega - \omega_0 \gg \omega_1$ (called *off-resonance*), the maximum probability for spin flip is small(that corresponds to the Figure 9.2). However, if $\omega - \omega_0 \approx 0$, which corresponds to resonance, the maximum probability ≈ 1 and the spin has flipped with certainty. The spin system preferentially absorbs energy (flipping spin) near resonance.

This spin resonance process is used to determine a wide variety of spin properties of systems.

7.3 **Addition of Angular Momentum**

A derivation of the addition process for arbitrary angular momentum values is very complex. We can, however, learn and understand all of the required steps within the context of a special case, namely, combining two spin $= 1/2$ systems into a new system. We will do the general derivation after the special case.

7.3.1 **Addition of Two Spin = 1/2 Angular Momenta**

We define

$$\vec{S}_{1,op} = \text{ spin operator for system 1} \tag{7.309}$$

$$\vec{S}_{2,op} = \text{ spin operator for system 2} \tag{7.310}$$

The operators for system 1 are assumed to be independent of the operators for system 2, which implies that

$$\left[\hat{S}_{1i}, \hat{S}_{2j}\right] = 0 \text{ for all } i \text{ and } j \tag{7.311}$$

We characterize each system by eigenvalue/eigenvector equations

$$\vec{S}^2_{1,op} \left|s_1, m_1\right\rangle = \hbar^2 s_1(s_1+1) \left|s_1, m_1\right\rangle \tag{7.312}$$

$$\hat{S}_{1,z} \left|s_1, m_1\right\rangle = \hbar m_1 \left|s_1, m_1\right\rangle \tag{7.313}$$

$$\vec{S}^2_{2,op} \left|s_2, m_2\right\rangle = \hbar^2 s_2(s_2+1) \left|s_2, m_2\right\rangle \tag{7.314}$$

$$\hat{S}_{2,z} \left|s_2, m_2\right\rangle = \hbar m_2 \left|s_2, m_2\right\rangle \tag{7.315}$$

where

$$s_1 = s_2 = \frac{1}{2} \text{ and } m_1 = \pm\frac{1}{2}\ ,\ m_2 = \pm\frac{1}{2} \tag{7.316}$$

Since both s_1 and s_2 are fixed and unchanging during this addition process we will drop them from the arguments and subscripts to lessen the complexity of the equations.

Each space (1 and 2) is 2-dimensional and thus each has two $(2s+1=2)$ basis states corresponding to the number of m-values in each case

$$\left|s_1 = \frac{1}{2}, m_1 = \frac{1}{2}\right\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle_1 = \left|\uparrow\right\rangle_1 = \left|+\right\rangle_1 \tag{7.317}$$

$$\left|s_1 = \frac{1}{2}, m_1 = -\frac{1}{2}\right\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle_1 = \left|\downarrow\right\rangle_1 = \left|-\right\rangle_1 \tag{7.318}$$

$$\left|s_2 = \frac{1}{2}, m_2 = \frac{1}{2}\right\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle_2 = \left|\uparrow\right\rangle_2 = \left|+\right\rangle_2 \tag{7.319}$$

$$\left|s_2 = \frac{1}{2}, m_2 = -\frac{1}{2}\right\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle_2 = \left|\downarrow\right\rangle_2 = \left|-\right\rangle_2 \tag{7.320}$$

This means that there are 4 possible basis states for the combined system that we can construct using the direct product procedure. We label them as

$$|\uparrow\uparrow\rangle = |{+}{+}\rangle = |+\rangle_1 \otimes |+\rangle_2 \quad , \quad |\uparrow\downarrow\rangle = |{+}{-}\rangle = |+\rangle_1 \otimes |-\rangle_2 \tag{7.321}$$

$$|\downarrow\uparrow\rangle = |{-}{+}\rangle = |-\rangle_1 \otimes |+\rangle_2 \quad , \quad |\downarrow\downarrow\rangle = |{-}{-}\rangle = |-\rangle_1 \otimes |-\rangle_2 \tag{7.322}$$

so that the first symbol in the combined states corresponds to system 1 and the second symbol to system 2. These are not the only possible basis states as we shall see. The "1" operators operate only on the "1" part of the direct product, for example,

$$\vec{S}_{1,op}^2 |{+}{-}\rangle = \hbar^2 s_1(s_1+1) |{+}{-}\rangle = \frac{3}{4}\hbar^2 |{+}{-}\rangle \tag{7.323}$$

$$\hat{S}_{1,z} |{+}{-}\rangle = \hbar m_1 |{+}{-}\rangle = \frac{\hbar}{2} |{+}{-}\rangle \tag{7.324}$$

$$\vec{S}_{2,op}^2 |{+}{-}\rangle = \hbar^2 s_2(s_2+1) |{+}{-}\rangle = \frac{3}{4}\hbar^2 |{+}{-}\rangle \tag{7.325}$$

$$\hat{S}_{2,z} |{+}{-}\rangle = \hbar m_2 |{+}{-}\rangle = -\frac{\hbar}{2} |{+}{-}\rangle \tag{7.326}$$

The total spin angular momentum operator for the combined system is

$$\vec{S}_{op} = \vec{S}_{1,op} + \vec{S}_{2,op} \tag{7.327}$$

It obeys the same commutation rules as the individual system operators, i.e.,

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\varepsilon_{ijk}\hat{S}_k \tag{7.328}$$

This tells us to look for the same kind of angular momentum eigenstates and eigenvalues

$$\vec{S}_{op}^2 \left|s, m\right\rangle = \hbar^2 s(s+1) \left|s, m\right\rangle \tag{7.329}$$

$$\hat{S}_z \left|s, m\right\rangle = \hbar m \left|s, m\right\rangle \tag{7.330}$$

To proceed, we need to derive some relations. Squaring the total spin operator we have

$$\begin{aligned} \vec{S}_{op}^2 &= \left(\vec{S}_{1,op} + \vec{S}_{2,op}\right)^2 = \vec{S}_{1,op}^2 + \vec{S}_{2,op}^2 + 2\vec{S}_{1,op} \cdot \vec{S}_{2,op} \\ &= \frac{3}{4}\hbar^2 \hat{I} + \frac{3}{4}\hbar^2 \hat{I} + 2\hat{S}_{1z}\hat{S}_{2z} + 2\hat{S}_{1x}\hat{S}_{2x} + 2\hat{S}_{1y}\hat{S}_{2y} \end{aligned} \tag{7.331}$$

Now using

$$\hat{S}_{1\pm} = \hat{S}_{1x} \pm i\hat{S}_{1y} \text{ and } \hat{S}_{2\pm} = \hat{S}_{2x} \pm i\hat{S}_{2y} \tag{7.332}$$

we have

$$2\hat{S}_{1x}\hat{S}_{2x} + 2\hat{S}_{1y}\hat{S}_{2y} = \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} \tag{7.333}$$

and therefore

$$\vec{S}_{op}^2 = \frac{3}{2}\hbar^2\hat{I} + 2\hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} \tag{7.334}$$

Now suppose we choose the four states $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$ as the orthonormal basis for the 4-dimensional vector space of the combined system. We then ask the following question.

Are these basis states also eigenstates of the spin operators for the combined system?

We have

$$\begin{aligned}
\hat{S}_z |{+}{+}\rangle &= (\hat{S}_{1z} + \hat{S}_{2z}) |+\rangle_1 \otimes |+\rangle_2 \\
&= (\hat{S}_{1z} |+\rangle_1) \otimes |+\rangle_2 + |+\rangle_1 \otimes (\hat{S}_{2z} |+\rangle_2) \\
&= (\frac{\hbar}{2} |+\rangle_1) \otimes |+\rangle_2 + |+\rangle_1 \otimes (\frac{\hbar}{2} |+\rangle_2) = (\frac{\hbar}{2} + \frac{\hbar}{2}) |+\rangle_1 \otimes |+\rangle_2 \\
&= \hbar |{+}{+}\rangle
\end{aligned} \tag{7.335}$$

and similarly

$$\hat{S}_z |{+}{-}\rangle = 0 \tag{7.336}$$

$$\hat{S}_z |{-}{+}\rangle = 0 \tag{7.337}$$

$$\hat{S}_z |{-}{-}\rangle = -\hbar |{-}{-}\rangle \tag{7.338}$$

This says that the direct-product basis states are eigenvectors of (total) $\hat{S}_z$ and that the eigenvalues are $m = 1, 0, -1$ and 0 (a second time).

Since each value s of the total angular momentum of the combined system must have $2s+1$ associated m-values, these results tell us that the combined system will have

$$s = 1 \rightarrow m = 1, 0, -1 \text{ and } s = 0 \rightarrow m = 0 \tag{7.339}$$

which accounts for all of the four states. What about the $\hat{S}_{op}^2$ operator?

We have

$$\begin{aligned} \vec{S}_{op}^2 \left|{+}{+}\right\rangle &= \left(\frac{3}{2}\hbar^2 \hat{I} + 2\hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} \right) \left|{+}{+}\right\rangle \\ &= \left(\frac{3}{2}\hbar^2 + 2\frac{\hbar}{2}\frac{\hbar}{2} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} \right) \left|{+}{+}\right\rangle \end{aligned} \tag{7.340}$$

Now using

$$\hat{S}_{1+} \left|{+}{+}\right\rangle = 0 = \hat{S}_{+} \left|{+}{+}\right\rangle \tag{7.341}$$

we get

$$\vec{S}_{op}^2 \left|++\right\rangle = 2\hbar^2 \left|++\right\rangle = \hbar^2 1(1+1) \left|++\right\rangle \tag{7.342}$$

or the state $\left|++\right\rangle$ is also an eigenstate of $\hat{S}_{op}^2$ with $s = 1$

$$\left|++\right\rangle = \left|s = 1, m = 1\right\rangle = \left|1, 1\right\rangle \tag{7.343}$$

Similarly, we have

$$\vec{S}_{op}^2 \left|--\right\rangle = 2\hbar^2 \left|--\right\rangle = \hbar^2 1(1+1) \left|--\right\rangle \tag{7.344}$$

or the state $\left|--\right\rangle$ is also an eigenstate of $\hat{S}_{op}^2$ with $s = 1$

$$\left|--\right\rangle = \left|s = 1, m = -1\right\rangle = \left|1, -1\right\rangle \tag{7.345}$$

In the same manner we can show that $\left|+-\right\rangle$ and $\left|-+\right\rangle$ are *not* eigenstates of $\hat{S}_{op}^2$. So the simple direct-product states are not appropriate to describe the combined system if we want to characterize it using

$$\vec{S}_{op}^2 \text{ and } \hat{S}_z \tag{7.346}$$

However, since the direct-product states are a complete basis set, we should be able to construct the remaining two eigenstates of $\hat{S}_{op}^2$ and $\hat{S}_z$ as linear combinations of the direct-product states

$$|s,m\rangle = \sum_{m_1,m_2} a_{smm_1m_2} |m_1,m_2\rangle \tag{7.347}$$

where we have left out the s_1 and s_2 dependence in the states and coefficients.

In a formal manner, we can identify the so-called *Clebsch-Gordon coefficients* $a_{smm_1m_2}$ by using the orthonormality of the direct-product basis states. We have

$$\begin{aligned} \langle m_1', m_2' \mid s, m \rangle &= \sum_{m_1,m_2} a_{smm_1m_2} \langle m_1', m_2' \mid m_1, m_2 \rangle \\ &= \sum_{m_1,m_2} a_{smm_1m_2} \delta_{m_1' m_1} \delta_{m_2' m_2} = a_{smm_1'm_2'} \end{aligned} \tag{7.348}$$

where we have used

$$\langle m_1', m_2' \mid m_1, m_2 \rangle = \delta_{m_1' m_1} \delta_{m_2' m_2} \tag{7.349}$$

This does not help us actually compute the coefficients because we do not know the states $|s, m\rangle$. A procedure that works in this case and that can be generalized, is the following.

We already found that $|{+}{+}\rangle = |1, 1\rangle$ and $|{-}{-}\rangle = |1, -1\rangle$. Now we define the operators

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y = (\hat{S}_{1x} + \hat{S}_{2x}) \pm i(\hat{S}_{1y} + \hat{S}_{2y}) = \hat{S}_{1\pm} + \hat{S}_{2\pm} \tag{7.350}$$

These are the raising and lowering operators for the combined system and thus they satisfy the relations

$$\hat{S}_\pm |s, m\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}\, |s, m \pm 1\rangle \tag{7.351}$$

This gives

$$\hat{S}_+ |1, 1\rangle = 0 = \hat{S}_- |1, -1\rangle \tag{7.352}$$

as we expect.

If, however, we apply $\hat{S}_-$ to the topmost state (*maximum s and m values*) we get

$$\begin{aligned}
\hat{S}_- |1,1\rangle &= \hbar\sqrt{1(1+1)-1(1-1)}\,|1,0\rangle = \hbar\sqrt{2}\,|1,0\rangle \\
&= (\hat{S}_{1-} + \hat{S}_{2-})\,|+\rangle_1 \otimes |+\rangle_2 \\
&= (\hat{S}_{1-}\,|+\rangle_1) \otimes |+\rangle_2 + |+\rangle_1 \otimes (\hat{S}_{2-}\,|+\rangle_2) \\
&= \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}-1)}\,|-\rangle_1 \otimes |+\rangle_2 \\
&\qquad + \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}-1)}\,|+\rangle_1 \otimes |-\rangle_2 \\
&= \hbar\,|-+\rangle + \hbar\,|+-\rangle
\end{aligned} \tag{7.353}$$

or

$$|1,0\rangle = |s=1, m=0\rangle = \frac{1}{\sqrt{2}}\,|-+\rangle + \frac{1}{\sqrt{2}}\,|+-\rangle \tag{7.354}$$

Note that the only terms that appear on the right hand side are those that have $m = m_1 + m_2$. We can easily see that this is a general property since

$$\hat{S}_z |s,m\rangle = m\hbar |s,m\rangle = \sum_{m_1,m_2} a_{smm_1m_2}(\hat{S}_{1z} + \hat{S}_{2z}) |m_1,m_2\rangle$$
$$= \hbar \sum_{m_1,m_2} a_{smm_1m_2}(m_1 + m_2) |m_1,m_2\rangle \tag{7.355}$$

The only way to satisfy this equation is for $m = m_1 + m_2$ in *every term* in the sum. Thus, our linear combination should really be written as a single sum of the form

$$|s,m\rangle = \sum_{\substack{m_1,m_2 \\ m_1+m_2=m}} a_{smm_1m_2} |m_1,m_2\rangle = \sum_{m_1} a_{smm_1,m-m_1} |m_1, m-m_1\rangle \tag{7.356}$$

These three states

$$|1,1\rangle = |{+}{+}\rangle \rightarrow a_{1,1,\frac{1}{2},\frac{1}{2}} = 1 \tag{7.357}$$

$$|1,0\rangle = \frac{1}{\sqrt{2}}(|{-}{+}\rangle + |{+}{-}\rangle) \rightarrow a_{1,1,-\frac{1}{2},\frac{1}{2}} = a_{1,1,\frac{1}{2},-\frac{1}{2}} = \frac{1}{\sqrt{2}} \tag{7.358}$$

$$|1,-1\rangle = |{-}{-}\rangle \rightarrow a_{1,1,-\frac{1}{2},-\frac{1}{2}} = 1 \tag{7.359}$$

are called a *triplet*.

The state $|s=0,m=0\rangle = |0,0\rangle$ can then be found as follows: the state has $m=0$, $\hat{S}_z|0,0\rangle = 0$ and thus each state(term) in the linear combination must have $m = m_1 + m_2 = 0$, which means we must be able to write

$$|0,0\rangle = a\,|+-\rangle + b\,|-+\rangle \tag{7.360}$$

where

$$|a|^2 + |b|^2 = 1 \text{ (state is normalized to 1)} \tag{7.361}$$

Now we must also have

$$\langle 1,0 \mid 0,0\rangle = 0 \text{ (since the } |s,m\rangle \text{ states are orthogonal)} \tag{7.362}$$

which implies that

$$\frac{1}{\sqrt{2}}a + \frac{1}{\sqrt{2}}b = 0 \rightarrow b = -a \tag{7.363}$$

We then have

$$2\,|a|^2 = 1 \rightarrow a = \frac{1}{\sqrt{2}} = -b \tag{7.364}$$

and

$$|0,0\rangle = |s = 0, m = 0\rangle = \frac{1}{\sqrt{2}}\,|+-\rangle - \frac{1}{\sqrt{2}}\,|-+\rangle \tag{7.365}$$

This is called a *singlet state*. That completes the construction of the angular momentum states for the combined system of two spin-1/2 systems.

We now *generalize* this procedure for the addition of any two angular momenta.

7.5.2 **General Addition of Two Angular Momenta**

Given two angular momenta $\vec{J}_{1,op}$ and $\vec{J}_{2,op}$, we have the operators and states for each separate system

$$\vec{J}_{1,op} \to \vec{J}^2_{1,op}, \hat{J}_{1z}, \hat{J}_{1\pm} \to |j_1, m_1\rangle$$
$$\vec{J}_{2,op} \to \vec{J}^2_{2,op}, \hat{J}_{2z}, \hat{J}_{2\pm} \to |j_2, m_2\rangle$$

with

$$\vec{J}^2_{1,op} |j_1, m_1\rangle = \hbar^2 j_1(j_1+1) |j_1, m_1\rangle \,, \hat{J}_{1z} |j_1, m_1\rangle = \hbar m_1 |j_1, m_1\rangle \tag{7.366}$$

$$\hat{J}_{1\pm} |j_1, m_1\rangle = \hbar\sqrt{j_1(j_1+1) - m_1(m_1 \pm 1)} |j_1 \pm 1, m_1\rangle \tag{7.367}$$

$$\vec{J}^2_{2,op} |j_2, m_2\rangle = \hbar^2 j_2(j_2+1) |j_2, m_2\rangle \,, \hat{J}_{2z} |j_2, m_2\rangle = \hbar m_2 |j_2, m_2\rangle \tag{7.368}$$

$$\hat{J}_{2\pm} |j_2, m_2\rangle = \hbar\sqrt{j_2(j_2+1) - m_2(m_2 \pm 1)} |j_2 \pm 1, m_2\rangle \tag{7.369}$$

Remember that there are $2j_1 + 1$ possible m_1 values and $2j_2 + 1$ possible m_2 values.

Since all of the "1" operators commute with all of the "2" operators, we can find a common eigenbasis for the four operators $\vec{J}^2_{1,op}, \hat{J}_{1z}, \vec{J}^2_{2,op}, \hat{J}_{2z}$ in terms of the direct-product states

$$|j_1, j_2, m_1, m_2\rangle = |j_1, m_1\rangle \otimes |j_2, m_2\rangle \tag{7.370}$$

For the combined system we define total operators as before

$$\vec{J}_{op} = \vec{J}_{1,op} + \vec{J}_{2,op} = \text{ total angular momentum} \tag{7.371}$$

$$\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}, \left[\vec{J}^2_{op}, \hat{J}_z\right] = 0 \tag{7.372}$$

$$\left[\vec{J}^2_{op}, \hat{J}^2_{1,op}\right] = 0 \quad , \quad \left[\vec{J}^2_{op}, \hat{J}^2_{2,op}\right] = 0 \tag{7.373}$$

$$\left[\hat{J}^2_{1,op}, \hat{J}_z\right] = 0 \quad , \quad \left[\hat{J}^2_{2,op}, \hat{J}_z\right] = 0 \tag{7.374}$$

These commutators imply that we can construct a common eigenbasis of $\vec{J}^2_{1,op}$, $\hat{J}_{1z}$,$\vec{J}^2_{2,op}$,$\hat{J}_{2z}$ using the states $|j_1, j_2, m_1, m_2\rangle$ where

$$\vec{J}_{op}^2 \left| j, m \right\rangle = \hbar^2 j(j+1) \left| j, m \right\rangle \text{ and } \hat{J}_z \left| j, m \right\rangle = \hbar m \left| j, m \right\rangle \quad (7.375)$$

There are $2j + 1$ possible m values for each allowed j value. We cannot use the operators $\hat{J}_{1z}, \hat{J}_{2z}$ to construct the eigenbasis for the combined system because they do not commute with $\vec{J}_{op}^2$.

Remember that in order for a label to appear in a ket vector it must be one of the eigenvalues of a set of commuting observables since only such a set shares a common eigenbasis.

We now determine how to write the $\left| j_1, j_2, m_1, m_2 \right\rangle$ in terms of the $\left| j_1, m_1 \right\rangle \otimes \left| j_2, m_2 \right\rangle$ basis. We have

$$\begin{aligned} &\left| j_1, j_2, j, m \right\rangle \\ &\qquad = \sum_{j_1'} \sum_{j_2'} \sum_{m_1} \sum_{m_2} \left| j_1', j_2', m_1, m_2 \right\rangle \left\langle j_1', j_2', m_1, m_2 \mid j_1, j_2, j, m \right\rangle \end{aligned} \quad (7.376)$$

where

$$\left\langle j_1', j_2', m_1, m_2 \mid j_1, j_2, j, m \right\rangle = \text{ Clebsch - Gordon coefficients} \tag{7.377}$$

This corresponds to inserting an identity operator of the form

$$\hat{I} = \sum_{j_1'} \sum_{j_2'} \sum_{m_1} \sum_{m_2} \left| j_1', j_2', m_1, m_2 \right\rangle \left\langle j_1', j_2', m_1, m_2 \right| \tag{7.378}$$

Since

$$\begin{aligned} &\left\langle j_1', j_2', m_1, m_2 \right| \vec{J}^{\,2}_{1,op} \left| j_1, j_2, j, m \right\rangle \\ &\qquad = \hbar^2 j_1'(j_1'+1) \left\langle j_1', j_2', m_1, m_2 \mid j_1, j_2, j, m \right\rangle \\ &\qquad = \hbar^2 j_1(j_1+1) \left\langle j_1', j_2', m_1, m_2 \mid j_1, j_2, j, m \right\rangle \end{aligned}$$

the Clebsch-Gordon(CG) coefficients must vanish unless $j_1' = j_1$ and similarly unless $j_2' = j_2$.

Thus we have

$$|j_1, j_2, j, m\rangle = \sum_{m_1} \sum_{m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 \mid j_1, j_2, j, m\rangle \tag{7.379}$$

Also, as we saw earlier, since $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$ we must have

$$\begin{aligned}
&\langle j_1, j_2, m_1, m_2| \hat{J}_z |j_1, j_2, j, m\rangle \\
&\qquad = \hbar(m_1 + m_2) \langle j_1, j_2, m_1, m_2 \mid j_1, j_2, j, m\rangle \\
&\qquad = \hbar m \langle j_1, j_2, m_1, m_2 \mid j_1, j_2, j, m\rangle
\end{aligned}$$

which implies that the CG coefficients must vanish unless $m_1 + m_2 = m$. Thus the only non-vanishing coefficients are

$$\langle j_1, j_2, m_1, m_2 \mid j_1, j_2, j, m = m_1 + m_2\rangle \tag{7.380}$$

and we can write

$$\begin{aligned}
|j_1, j_2, j, m\rangle &= \sum_{m_1} \sum_{m_2 = m - m_1} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 \mid j_1, j_2, j, m\rangle \\
&= \sum_{m_1} |j_1, j_2, m_1, m_2 = m - m_1\rangle \langle j_1, j_2, m_1, m_2 = m - m_1 \mid j_1, j_2, j, m\rangle
\end{aligned}$$

For fixed j_1 and j_2 there are $2j_1 + 1$ possible m_1 values and $2j_2 + 1$ possible m_2 values. Thus, there are $(2j_1 + 1)(2j_2 + 1)$ linearly independent states of the form

$$|j_1, j_2, m_1, m_2\rangle = |j_1, m_1\rangle \otimes |j_2, m_2\rangle$$

and hence the vector space describing the combined system is $(2j_1 + 1)(2j_2 + 1)$-dimensional.

This says that there must be $(2j_1 + 1)(2j_2 + 1)$ states of the form $|j_1, j_2, j, m\rangle$ also.

We notice that there is only *one* state with $m = m_1 + m_2 = j_1 + j_2$, namely,

$$m_1 = j_1 \text{ and } m_2 = j_2 \tag{7.381}$$

This state has the *maximum possible m value.*

There are two states with $m = m_1 + m_2 = j_1 + j_2 - 1$, namely,

$$m_1 = j_1 - 1, m_2 = j_2 \text{ and } m_1 = j_1, m_2 = j_2 - 1 \tag{7.382}$$

and so on.

For *example*

$$j_1 = 2 \ , \ j_2 = 1 \rightarrow (2(2)+1))(2(1)+1)) = 15 \text{ states} \qquad (7.383)$$

If we label these states by the m-values only (since j_1 and j_2 do not change) or $|m_1, m_2\rangle$, then we have(in this example)

$$\begin{aligned}
m &= 3 \rightarrow 1 \text{ state} \rightarrow |2,1\rangle \\
m &= 2 \rightarrow 2 \text{ states} \rightarrow |2,0\rangle \ , \ |1,1\rangle \\
m &= 1 \rightarrow 3 \text{ states} \rightarrow |1,0\rangle \ , \ |0,1\rangle \ , \ |2,-1\rangle \\
m &= 0 \rightarrow 3 \text{ states} \rightarrow |0,0\rangle \ , \ |1,-1\rangle \ , \ |-1,1\rangle \\
m &= -1 \rightarrow 3 \text{ states} \rightarrow |-1,0\rangle \ , \ |0,-1\rangle \ , \ |-2,1\rangle \\
m &= -2 \rightarrow 2 \text{ states} \rightarrow |-2,0\rangle \ , \ |-1,-1\rangle \\
m &= -3 \rightarrow 1 \text{ state} \rightarrow |-2,-1\rangle
\end{aligned}$$

for a total of 15 states.

The combined system, as we shall see by construction, has these states

$$j = 3 \to m = 3, 2, 1, 0, -1, -2, -3 \to 7 \text{ states}$$
$$j = 2 \to m = 2, 1, 0, -1, -2 \to 5 \text{ states}$$
$$j = 1 \to m = 1, 0, -1 \to 3 \text{ states}$$

for a total of 15 states.

The general rules, which follows from group theory, are

1. The combined system has allowed j values given by
$$j_1 + j_2 \geq j \geq |j_1 - j_2| \text{ in integer steps} \tag{7.384}$$
2. The total number of states is given by the total number of m-values for all the allowed j-values or
$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \tag{7.385}$$

We write the addition of two angular momenta symbolically as

$$j_1 \otimes j_2 = |j_1 - j_2| \oplus |j_1 - j_2| + 1 \oplus |j_1 - j_2| + 2 \oplus ...... \oplus j_1 + j_2 - 1 \oplus j_1 + j_2 \tag{7.386}$$

Examples

Our original special case of adding two spin = 1/2 systems gives

$$j_1 = j_2 = \frac{1}{2} \rightarrow j = 0, 1 \rightarrow \frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1 \rightarrow 4 \text{ states} \quad (7.387)$$

which is the result we found earlier.

Other cases are:

$$j_1 = j_2 = 1 \rightarrow j = 0, 1, 2 \rightarrow 1 \otimes 1 = 0 \oplus 1 \oplus 2 \rightarrow 9 \text{ states}$$
$$j_1 = 2, j_2 = 1 \rightarrow j = 1, 2, 3 \rightarrow 2 \otimes 1 = 1 \oplus 2 \oplus 3 \rightarrow 15 \text{ states}$$
$$j_1 = 2, j_2 = 3 \rightarrow j = 1, 2, 3, 4, 5 \rightarrow 2 \otimes 3 = 1 \oplus 2 \oplus 3 \oplus 4 \oplus 5 \rightarrow 35 \text{ state}$$

7.5.3 **Actual Construction of States**

Notation

1. states labeled $|7, 6\rangle$ are $|j, m\rangle$ states
2. states labeled $|3, 2\rangle_\otimes$ are $|m_1, m_2\rangle$ states
3. we suppress the j_1, j_2 labels everywhere

Procedure

1. choose j_1 and j_2
2. write down the direct-product $|m_1, m_2\rangle$ basis
3. determine the allowed j values
4. write down the maximum m state ($m = j_1 + j_2$); it is unique
5. the maximum m-value corresponds to the maximum j-value
6. use the lowering operator to generate all other m-states for this J-value; there are $2j + 1$, i.e.,

$$\hat{J}_- |j, m\rangle = \hbar\sqrt{j(j+1) - m(m-1)}\, |j, m-1\rangle$$

7. find the maximum m-state for the next lowest j-value; it is constructed from the same basis states as in the corresponding m-states for higher j-values; use orthonormality properties to figure out coefficients
8. repeat (6) and (7) until all j-values have been dealt with.

More Detailed Examples (we must learn this process by doing it)

#1 - Individual system values

$$j_1 = j_2 = \frac{1}{2} \rightarrow m_1, m_2 = \frac{1}{2}, -\frac{1}{2} \text{ (we already did this example)} \tag{7.388}$$

The basis states are (we use the notation $|+-\rangle$ here instead of $|1/2, -1/2\rangle_\otimes$)

$$\begin{array}{rcccc} & |++\rangle \quad , & |+-\rangle \quad , & |-+\rangle \quad , & |--\rangle \\ m = m_1 + m_2 = & 1 & 0 & -1 & 0 \end{array}$$

Construction Algebra

Allowed j-values are $j = 1, 0$

$j = 1$ has $2j + 1 = 3$ m-values $= 1, 0, -1$

$j = 0$ has $2j + 1 = 1$ m value $= 0$

$|1,1\rangle = |{+}{+}\rangle$ maximum or topmost (j,m) state is always unique

$\hat{J}_- |1,1\rangle = \sqrt{2}\hbar\, |1,0\rangle = (\hat{J}_{1-} + \hat{J}_{2-}) |{+}{+}\rangle = \hbar\, |{+}{-}\rangle + \hbar\, |{-}{+}\rangle$

$|1,0\rangle = \frac{1}{\sqrt{2}} |{+}{-}\rangle + \frac{1}{\sqrt{2}} |{-}{+}\rangle$

$$\hat{J}_- |1,0\rangle = \sqrt{2}\hbar\, |1,-1\rangle = (\hat{J}_{1-} + \hat{J}_{2-}) \left(\frac{1}{\sqrt{2}} |{+}{-}\rangle + \frac{1}{\sqrt{2}} |{-}{+}\rangle \right)$$
$$= \sqrt{2}\hbar\, |{-}{-}\rangle$$

$|1,-1\rangle = |{-}{-}\rangle$

We must now have $|0,0\rangle = a\, |{+}{-}\rangle + b\, |{-}{+}\rangle$ (Rule 7) with

$$|a|^2 + |b|^2 = 1 \text{ and } \langle 1,0\, | \,, 0,0\rangle = \frac{1}{\sqrt{2}} a + \frac{1}{\sqrt{2}} b = 0$$

which gives

$$a = -b = \frac{1}{\sqrt{2}}$$

or

$|0,0\rangle = \frac{1}{\sqrt{2}} |{+}{-}\rangle - \frac{1}{\sqrt{2}} |{-}{+}\rangle$

All the $j-$values are now done. We end up with the Clebsch-Gordon coefficients.

#2 - Individual system values

$$j_1 = j_2 = 1 \rightarrow m_1, m_2 = 1, 0, -1 \tag{7.389}$$

The basis states are

$$\begin{array}{cccccc} & |1,1\rangle_\otimes & |1,0\rangle_\otimes & |1,-1\rangle_\otimes & |0,1\rangle_\otimes & |0,0\rangle_\otimes \\ m = m_1 + m_2 = & 2 & 1 & 0 & 1 & 0 \end{array}$$

$$\begin{array}{ccccc} & |0,-1\rangle_\otimes & |-1,1\rangle_\otimes & |-1,0\rangle_\otimes & |-1,-1\rangle_\otimes \\ m = m_1 + m_2 = & -1 & 0 & -1 & -2 \end{array}$$

Construction Algebra

Allowed j-values are $j = 2, 1, 0$

$j = 2$ has $2j + 1 = 3$ m-values $= 2, 1, 0, -1, -2$

$j = 1$ has $2j + 1 = 3$ m-values $= 1, 0, -1$

$j = 0$ has $2j + 1 = 1$ m value $= 0$

$|2,2\rangle = |1,1\rangle_\otimes$ maximum or topmost (j,m) state is always unique

$\hat{J}_- |2,2\rangle = 2\hbar |2,1\rangle = (\hat{J}_{1-} + \hat{J}_{2-}) |1,1\rangle_\otimes =$

$\sqrt{2}\hbar |1,0\rangle_\otimes + \sqrt{2}\hbar |0,1\rangle_\otimes$

$|2,1\rangle = \frac{1}{\sqrt{2}} |1,0\rangle_\otimes + \frac{1}{\sqrt{2}} |0,1\rangle_\otimes$

$\hat{J}_- |2,1\rangle = \sqrt{6}\hbar |2,0\rangle = (\hat{J}_{1-} + \hat{J}_{2-}) \left(\frac{1}{\sqrt{2}} |1,0\rangle_\otimes + \frac{1}{\sqrt{2}} |0,1\rangle_\otimes \right)$

$= \hbar |1,-1\rangle_\otimes + 2\hbar |0,0\rangle_\otimes + \hbar |-1,1\rangle_\otimes$

$|2,0\rangle = \frac{1}{\sqrt{6}} |1,-1\rangle_\otimes + \frac{2}{\sqrt{6}} |0,0\rangle_\otimes + \frac{1}{\sqrt{6}} |-1,1\rangle_\otimes$

Continuing we have

$$|2,-1\rangle = \frac{1}{\sqrt{2}} |-1,0\rangle_\otimes + \frac{1}{\sqrt{2}} |0,-1\rangle_\otimes$$
$$|2,-2\rangle = |-1,-1\rangle_\otimes$$

which completes the five $j = 2$ states.

We must now have $|1,1\rangle = a\,|1,0\rangle_\otimes + b\,|0,1\rangle_\otimes$ with

$$|a|^2 + |b|^2 = 1 \text{ and } \langle 2,1\,|\,,1,1\rangle = \tfrac{1}{\sqrt{2}}a + \tfrac{1}{\sqrt{2}}b = 0$$

which gives

$$a = -b = \frac{1}{\sqrt{2}}$$

or

$|1,1\rangle = \frac{1}{\sqrt{2}} |1,0\rangle_{\otimes} - \frac{1}{\sqrt{2}} |0,1\rangle_{\otimes}$

We now find all of the $j = 1$ states

$$\hat{J}_{-} |1,1\rangle = \sqrt{2}\hbar |1,0\rangle = (\hat{J}_{1-} + \hat{J}_{2-})(\frac{1}{\sqrt{2}} |1,0\rangle_{\otimes} - \frac{1}{\sqrt{2}} |0,1\rangle_{\otimes})$$
$$= \hbar |1,-1\rangle_{\otimes} - \hbar |-1,1\rangle_{\otimes}$$
$$|1,0\rangle = \frac{1}{\sqrt{2}} |1,-1\rangle_{\otimes} - \frac{1}{\sqrt{2}} |-1,1\rangle_{\otimes}$$

and continuing

$$|1,-1\rangle = \frac{1}{\sqrt{2}} |0,-1\rangle_{\otimes} - \frac{1}{\sqrt{2}} |-1,0\rangle_{\otimes}$$

which completes the three $j = 1$ states.

We must now have $|0,0\rangle = a |1,-1\rangle_{\otimes} + b |0,0\rangle_{\otimes} + c |-1,1\rangle_{\otimes}$ with

$$|a|^2 + |b|^2 = 1 \text{ and } \langle 2,0 \,|\, ,0,0\rangle = \frac{1}{\sqrt{6}}a + \frac{2}{\sqrt{6}}b + \frac{1}{\sqrt{6}}c = 0$$
$$\text{and } \langle 1,0 \,|\, ,0,0\rangle = \frac{1}{\sqrt{6}}a - \frac{1}{\sqrt{6}}c = 0$$

which gives

$$a = -b = c = \frac{1}{\sqrt{3}}$$

or

$$|0,0\rangle = \frac{1}{\sqrt{3}}|1,-1\rangle_{\otimes} - \frac{1}{\sqrt{3}}|0,0\rangle_{\otimes} + \frac{1}{\sqrt{3}}|-1,1\rangle_{\otimes}$$

All the j-values are now done.

7.6 Two- and Three-Dimensional Systems

We now turn our attention to 2− and 3−dimensional systems that can be solved analytically.

In the position representation, the wave function

$$\psi(\vec{r}) = \langle \vec{r} \mid \psi \rangle \tag{7.390}$$

contains all the information that is knowable about the state of a physical system. The equation that determines the wave function is the Schrodinger equation, which we derived from the energy eigenvalue equation

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{7.391}$$

The general form of the Schrodinger equation in three

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \tag{7.392}$$

We will use a succession of concrete examples to elucidate the solution techniques and the physical principles that are involved. 7.6.1 **2- and 3-Dimensional Infinite Wells**

2-Dimensional Infinite Square Well - Cartesian Coordinates

The potential energy function is

$$V(x,y) = \begin{cases} 0 & |x| < \frac{a}{2} \text{ and } |y| < \frac{a}{2} \rightarrow \text{ region I} \\ \infty & \text{otherwise} \rightarrow \text{ region II} \end{cases} \tag{7.393}$$

This is a simple extension of the 1−dimensional infinite well problem, but it is useful because it illustrates all the ideas we will need for more complicated problems.

In region I

$$\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2} = -\frac{2mE}{\hbar^2}\psi(x,y) \tag{7.394}$$

In region II

$$\psi(x,y) = 0 \tag{7.395}$$

since the potential is infinite over an extended region.

We solve this equation by the separation of variables (SOV) technique. We assume

$$\psi(x,y) = X(x)Y(y) \tag{7.396}$$

Upon substitution we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2} \tag{7.397}$$

Each term on the left-hand side of the equation is a function only of a single variable and hence the only way to satisfy the equation for all x and y is to set each function of a single variable equal to a constant. We have

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2mE_x}{\hbar^2} = \text{constant} \tag{7.398}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE_y}{\hbar^2} = \text{constant} \tag{7.399}$$

$$E = E_x + E_y \tag{7.400}$$

If we choose

$$\frac{2mE_x}{\hbar^2} = k_x^2 \quad , \quad \frac{2mE_y}{\hbar^2} = k_y^2 \quad , \quad \frac{2mE}{\hbar^2} = k^2 \tag{7.401}$$

we get the solutions

$$X(x) = A\sin k_x x + B\cos k_x x \tag{7.402}$$

$$Y(y) = C\sin k_y y + D\cos k_y y \tag{7.403}$$

with the boundary conditions

$$X\left(\pm\frac{a}{2}\right) = 0 = Y\left(\pm\frac{a}{2}\right) \tag{7.404}$$

For the function $X(x)$ each boundary condition implies two solution types

$$A = 0 \text{ or } \sin\frac{k_x a}{2} = 0 \text{ and } B = 0 \text{ or } \cos\frac{k_x a}{2} = 0 \tag{7.405}$$

These are both summarized in the solution

$$X(x) = \begin{cases} \sin\frac{n_x \pi x}{a} & n_x = \text{ even} \\ & \qquad\qquad k_x = \frac{n_x \pi}{a} \quad n_x = \text{ integer} \\ \cos\frac{n_x \pi x}{a} & n_x = \text{ odd} \end{cases} \tag{7.406}$$

and similarly for $Y(y)$

$$Y(y) = \begin{cases} \sin \frac{n_y \pi y}{a} & n_y = \text{ even} \\ & \qquad\qquad k_y = \frac{n_y \pi}{a} \quad n_y = \text{ integer} \\ \cos \frac{n_y \pi y}{a} & n_y = \text{ odd} \end{cases} \tag{7.407}$$

The corresponding energy eigenvalues are

$$E = (n_x^2 + n_y^2) \frac{\pi^2 \hbar^2}{2ma^2} \quad , \quad n_{\mathrm{x}}, \mathrm{n_y} = 1, 2, 3, 4 \ldots \tag{7.408}$$

The 1−dimensional result we found earlier was

$$E_{1\,\mathrm{dim}} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad , n = 1, 2, 3, 4 \ldots \tag{7.409}$$

A plot of these levels for comparison is shown in the figure below; we choose $\frac{\pi^2 \hbar^2}{2ma^2} = 1$

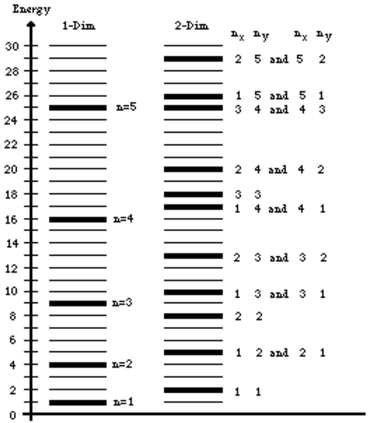

Figure: Comparison of 1D and 2D Infinite Wells

The major change is not only that the level structure gets more complex, but also that a major new feature appears, namely, *degeneracy*.

Several of the 2−dimensional well levels are degenerate, which means that *different* sets of quantum numbers give the *same energy eigenvalue.*

In the energy level diagram above the $E = 5, 10, 13, 17, 20, 25, 26$ and 29 levels are all two-fold degenerate. This degeneracy arises from the fact that $V(x, y) = V(-x, -y)$ and hence parity is conserved. This means that the correct physical eigenstates should be simultaneous eigenstates of both the parity and the energy.

The first three wave functions are

$$\psi_{11}(x, y) = \cos\frac{\pi x}{a}\cos\frac{\pi y}{a} \quad , \quad E = E_{11} \tag{7.410}$$

$$\psi_{12}(x, y) = \cos\frac{\pi x}{a}\sin\frac{2\pi y}{a} \quad , \quad E = E_{12} \tag{7.411}$$

$$\psi_{21}(x, y) = \sin\frac{2\pi x}{a}\cos\frac{\pi y}{a} \quad , \quad E = E_{21} = E_{12} \tag{7.412}$$

A simple calculation shows that we have

$$\langle 11 \mid 12 \rangle = \langle 11 \mid 21 \rangle = 0 \rightarrow \text{ orthogonal and } \langle 21 \mid 12 \rangle \neq 0 \rightarrow \text{ not ortho} \tag{7.413}$$

We can construct two new eigenfunctions from the degenerate pair that are orthogonal using the Gram-Schmidt process. We get

$$\psi_{12}^{+} = \psi_{12} + \psi_{21} \text{ and } \psi_{12}^{-} = \psi_{12} - \psi_{21} \tag{7.414}$$

We then have

$$\langle 12+ \mid 12- \rangle = 0 \rightarrow \text{ orthogonal} \tag{7.415}$$

We also note that for the parity operator $\wp$ we have

$$\hat{\wp}\,|11\rangle = |11\rangle \quad , \quad \hat{\wp}\,|12+\rangle = |12+\rangle \quad , \quad \hat{\wp}\,|12-\rangle = -\,|12-\rangle \tag{7.416}$$

so that the new eigenfunctions are *simultaneous eigenstates of parity and energy.*

Two of the wave functions are plotted in the figures below as $|\psi|^2$.

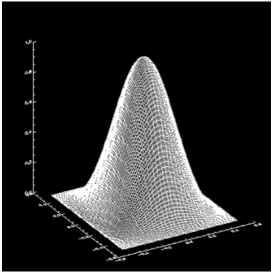

Figure: $|\psi_{11}|^2$

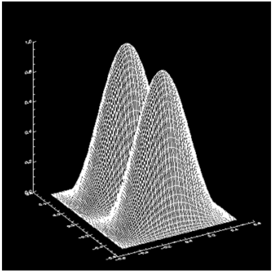

Figure: $|\psi_{12}^{+}|^2$

Now let us turn to the infinite circular well in two dimensions.

7.6.2 **Two-Dimensional Infinite Circular Well**

We consider the potential in two dimensions

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases} \tag{7.417}$$

The Schrodinger equation in plane-polar coordinates is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right]\psi(r,\varphi) = E\psi(r,\varphi) \qquad r < a \tag{7.418}$$

$$\psi(r,\varphi) = 0 \qquad r < a \tag{7.419}$$

We assume(SOV)

$$\psi(r,\varphi) = R(r)\Phi(\varphi) \tag{7.420}$$

which gives

$$-\frac{\hbar^2}{2m}\left[\frac{1}{rR}\frac{\partial}{\partial r}\left(r\frac{\partial R}{\partial r}\right)+\frac{1}{r^2}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}\right]=E \qquad r<a \tag{7.421}$$

We choose a separation constant

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=-\alpha^2\rightarrow\Phi(\varphi)=B\sin(\alpha\varphi+\delta) \tag{7.422}$$

The requirement of single-valuedness under a φ-rotation of 2π says that

$$\begin{aligned}&\sin(\alpha\varphi+\delta)=\sin(\alpha\varphi+\delta+\alpha\pi)\\ &\rightarrow\alpha=\text{ integer }=0,1,2,3\ldots\end{aligned}$$

Alternatively, we could write

$$\begin{aligned}&\Phi(\varphi)=Be^{i\alpha\varphi}\\ &\alpha=\text{ integer }=\ldots-3,-2,-1,0,1,2,3,\ldots\end{aligned}$$

Substitution of this solution leaves the radial differential equation

$$r^2 \frac{d^2 R}{dr^2} + r\frac{dR}{dr} + \left[\lambda^2 r^2 - \alpha^2\right] R = 0 \text{ where } \lambda^2 = \frac{2mE}{\hbar^2} \tag{7.423}$$

This is Bessel's equation. The general solution is

$$R(r) = NJ_\alpha(\lambda r) + MY_\alpha(\lambda r) \tag{7.424}$$

Now $Y_\alpha(\lambda r) \to \infty$ as $r \to 0$. Therefore, in order to have a normalizable solution in the region $r < a$ (which includes $r = 0$), we must choose $M = 0$ and thus we have

$$R(r) = NJ_\alpha(\lambda r) \tag{7.425}$$

and the complete solution is then

$$\psi_{k\alpha}(r, \varphi) = R(r)\Phi(\varphi) = NJ_\alpha(\lambda r)e^{i\alpha\varphi} \tag{7.426}$$

The continuity (or boundary) condition at $r = a$ is

$$\psi_{k\alpha}(a,\varphi) = 0 \rightarrow R(a) = 0 \rightarrow J_\alpha(\lambda a) = 0 \tag{7.427}$$

Thus, the allowed values of λ and hence the allowed values of E are given by

$$\lambda_{n\alpha} a = z_{n\alpha} = \text{ the } n^{th} \text{ zero of } J_\alpha \rightarrow E_{n\alpha} = \frac{\hbar^2}{2ma^2} z_{n\alpha}^2 \tag{7.428}$$

We compare the infinite square and circular wells in 2−dimensions using the energy level diagram in the figiure below.

Note the rather dramatic differences in both the location and degeneracies for the two sets of energy levels.

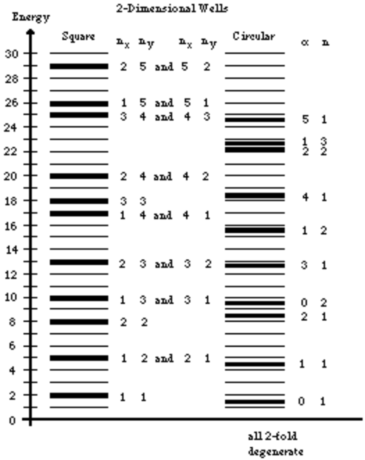

Figure: Two Dimensional Wells

Some of the wave functions for the 2−dimensional circular well are shown in the figures below.

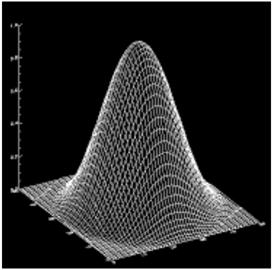

Figure: $|\psi_{01}|^2$

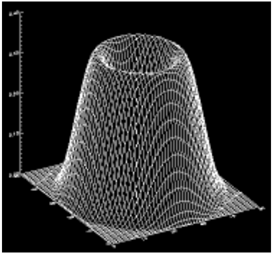

Figure: $|\psi_{11}|^2$

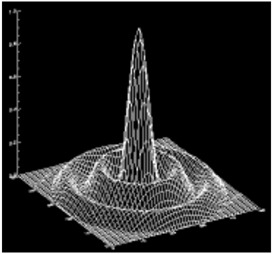

Figure: $|\psi_{03}|^2$

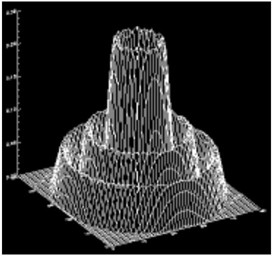

Figure: $|\psi_{23}|^2$

The 3−*dimensional infinite square well* is a simple extension of the 2−dimensional infinite square well. The result for the energies is

$$E = (n_x^2 + n_y^2 + n_z^2)\frac{\pi^2\hbar^2}{2ma^2} \quad , \quad n_x, n_y, n_z = 1, 2, 3, 4 \ldots \tag{7.429}$$

The 3−*dimensional infinite spherical well* involves the potential

$$V(r,\theta,\varphi) = \begin{cases} 0 & r < a \quad \text{region I} \\ \infty & r > a \quad \text{region II} \end{cases} \tag{7.430}$$

The Schrodinger equation is:

Region I

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} = -\frac{2m}{\hbar^2}E \tag{7.431}$$

Region II

$$\psi(r,\theta,\varphi) = 0 \tag{7.432}$$

The equation in region I can be rewritten in terms of the $\vec{L}_{op}^2$ operator as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{\vec{L}_{op}^2\psi}{\hbar^2 r^2} = -\frac{2m}{\hbar^2}E\psi \tag{7.433}$$

Since the potential energy is spherically symmetric, we have

$$\left[\vec{L}_{op}^2, \hat{H}\right] = 0 \tag{7.434}$$

and thus the operators $\vec{L}_{op}^2$ and $\hat{H}$ have a common eigenbasis.

Earlier, we found the eigenfunctions of $\vec{L}_{op}^2$ to be the spherical harmonics $Y_{\ell m}(\theta,\varphi)$, where

$$\vec{L}_{op}^2 Y_{\ell m}(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\varphi) \tag{7.435}$$

Therefore, we can write(SOV)

$$\psi(r,\theta,\varphi) = R_\ell(r)Y_{\ell m}(\theta,\varphi) \tag{7.436}$$

Substitution of this form of the solution gives the radial equation in region I

$$\frac{d^2 R_\ell}{dr^2} + \frac{2}{r}\frac{dR_\ell}{dr} - \frac{\ell(\ell+1)}{r^2} R_\ell + k^2 R_\ell = 0 \tag{7.437}$$

where

$$E = \frac{h^2 k^2}{2m} \tag{7.438}$$

In region II we have $R_\ell(r) = 0$.

The most general solution of the radial equation(which is a different form of Bessel's equation) is

$$R_\ell(r) = A j_\ell(kr) + B\eta_\ell(kr) \tag{7.439}$$

where

$$j_\ell(kr) = \left(\frac{\pi}{2kr}\right)^{1/2} J_{\ell+1/2}(kr) \tag{7.440}$$

$$\eta_\ell(kr) = (-1)^{\ell+1}\left(\frac{\pi}{2kr}\right)^{1/2} J_{-\ell-1/2}(kr) \tag{7.441}$$

are the spherical Bessel functions.

Now $\eta_\ell(kr) \to \infty$ as $r \to 0$. Therefore, the normalizable solution in region I (which contains $r = 0$) is

$$R_\ell(r) = A j_\ell(kr) \tag{7.442}$$

The first few of these functions are

$$j_0(x) = \frac{\sin x}{x} \tag{7.443}$$

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \tag{7.444}$$

$$j_2(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3}{x^2}\cos x \tag{7.445}$$

The boundary conditions give

$$j_\ell(k_{n\ell}a) = 0 \text{ where } k_{n\ell} = \text{ the } n^{th} \text{ zero of } j_\ell \tag{7.446}$$

The full solution is

$$\psi_{n\ell m}(\theta, \varphi) = R_{n\ell}(r) Y_{\ell m}(\theta, \varphi) = j_\ell(k_n r) P_\ell^m(\cos\theta) e^{im\varphi} \tag{7.447}$$

Some of the wavefunctions (absolute squares) are shown in the figures below.

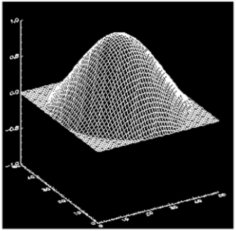

Figure: $n\ell m = 100$

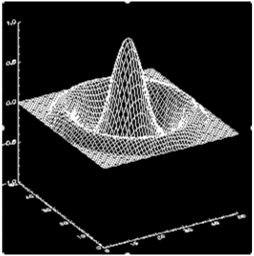

Figure: $n\ell m = 200$

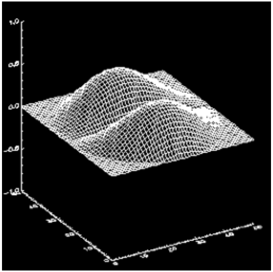

Figure: $n\ell m = 111$

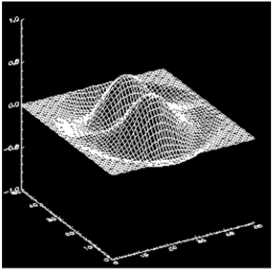

Figure: $n\ell m = 211$

7.6.3 **3-Dimensional Finite Well**

We now consider the potential function in three dimensions

$$V(r) = \begin{cases} -V_0 & r \leq a \quad \text{region I} \\ 0 & r > a \quad \text{region II} \end{cases} \tag{7.448}$$

The Schrodinger equation is

Region I (same as infinite well)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2m}{\hbar^2}V_0\psi = -\frac{2m}{\hbar^2}E\psi \tag{7.449}$$

Region II

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} = -\frac{2m}{\hbar^2}E\psi \tag{7.450}$$

If we choose $E = -|E| < 0$ for bound states, we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) - \frac{\vec{L}_{op}^2\psi}{\hbar^2 r^2} + \frac{2m}{\hbar^2}V_0\psi = \frac{2m}{\hbar^2}\left|E\right|\psi \text{ in region I} \tag{7.451}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) - \frac{\vec{L}_{op}^2\psi}{\hbar^2 r^2} = \frac{2m}{\hbar^2}\left|E\right|\psi \text{ in region II} \tag{7.452}$$

We then write, as before,

$$\psi(\theta,\varphi) = R_\ell(r)Y_{\ell m}(\theta,\varphi) \tag{7.453}$$

and get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{\ell(\ell+1)R}{r^2} + \frac{2m}{\hbar^2}V_0 R = \frac{2m}{\hbar^2}\left|E\right|R \quad \text{in region I} \tag{7.454}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{\ell(\ell+1)R}{r^2} = \frac{2m}{\hbar^2}\left|E\right|R \quad \text{in region II} \tag{7.455}$$

which finally becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[1 - \frac{\ell(\ell+1)}{\rho^2}\right] R = 0 \tag{7.456}$$

$$\rho = \alpha r \quad , \quad \alpha^2 = \frac{2m}{\hbar^2}\left(V_0 - |E|\right) \qquad \text{in region I} \tag{7.457}$$

and

$$\frac{d^2R}{d\gamma^2} + \frac{2}{\gamma}\frac{dR}{d\gamma} + \left[1 - \frac{\ell(\ell+1)}{\gamma^2}\right] R = 0 \tag{7.458}$$

$$\gamma = i\beta r \quad , \quad \beta^2 = \frac{2m}{\hbar^2}|E| \qquad \text{in region II} \tag{7.459}$$

The solutions are

$$R(r) = A j_\ell(\alpha r) \qquad\qquad r \leq a \tag{7.460}$$

$$R(r) = B h_\ell^{(1)}(i\beta r) = B\left[j_\ell(i\beta r) + i\eta_\ell(i\beta r)\right] \qquad r > a \tag{7.461}$$

where

$$j_0(x) = \frac{\sin x}{x} \tag{7.462}$$

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \tag{7.463}$$

$$j_2(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right) \sin x - \frac{3}{x^2} \cos x \tag{7.464}$$

$$j_\ell(x) = x^\ell \left(-\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x} \tag{7.465}$$

which are *spherical Bessel functions of the* 1^{st} *kind*, and

$$\eta_0(x) = -\frac{\cos x}{x} \tag{7.466}$$

$$\eta_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x} \tag{7.467}$$

$$\eta_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x}\right) \cos x - \frac{3}{x^2} \sin x \tag{7.468}$$

$$\eta_\ell(x) = -x^\ell \left(-\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x} \tag{7.469}$$

which are *spherical Bessel functions of the 2^{nd} kind*, and

$$h_0^{(1)}(ix) = -\frac{1}{x}e^{-x} \tag{7.470}$$

$$h_1^{(1)}(ix) = i\left(\frac{1}{x} + \frac{1}{x^2}\right)e^{-x} \tag{7.471}$$

$$h_2^{(1)}(ix) = \left(\frac{1}{x} + \frac{3}{x^2} + \frac{3}{x^3}\right)e^{-x} \tag{7.472}$$

$$h_\ell^{(1)}(ix) = j_\ell(ix) + i\eta_\ell(ix) \tag{7.473}$$

which are *spherical Hankel functions of the 1^{st} kind.*

There is another independent solution for $r > a$, namely,

$$h_\ell^{(2)}(ix) = j_\ell(ix) - i\eta_\ell(ix) \tag{7.474}$$

which is a *spherical Hankel functions of the 2^{nd} kind*, but we must exclude it because it behaves like $e^{\beta r}$ as $r \to \infty$ and, hence, is not normalizable.

We have also excluded $\eta_\ell(\alpha r)$ from the solution for $r \leq a$ because it diverges at $r = 0$.

Note for future reference that the asymptotic behaviors are

$$j_\ell(x) \underset{x\to 0}{\rightarrow} \frac{x^\ell}{1\cdot 3\cdot 5\cdot\cdots\cdot(2\ell+1)} \text{ and } \eta_\ell(x) \underset{x\to 0}{\rightarrow} \frac{1\cdot 3\cdot 5\cdot\cdots\cdot(2\ell-1)}{x^\ell} \tag{7.475}$$

$$j_\ell(x) \underset{x\to\infty}{\rightarrow} \frac{1}{x}\cos\left[x - \frac{(\ell+1)\pi}{2}\right] \text{ and } \eta_\ell(x) \underset{x\to\infty}{\rightarrow} \frac{1}{x}\sin\left[x - \frac{(\ell+1)\pi}{2}\right] \tag{7.476}$$

$$h_\ell^{(1)}(x) \underset{x\to\infty}{\rightarrow} \frac{1}{x}e^{i\left[x-\frac{1}{2}(\ell+1)\pi\right]} \text{ and } h_\ell^{(2)}(x) \underset{x\to\infty}{\rightarrow} \frac{1}{x}e^{-i\left[x-\frac{1}{2}(\ell+1)\pi\right]} \tag{7.477}$$

Since both R and dR/dr are continuous at $r = a$, we can combine the two continuity equations into one using the continuity of the so-called logarithmic derivative

$$\frac{1}{R}\frac{dR}{dr} \text{ at } r = a \tag{7.478}$$

For *each* value of ℓ this gives a transcendental equation for the energy E.

Examples:

$$\ell = 0 \qquad \xi \cot \xi = -\zeta \quad \text{and} \quad \xi^2 + \zeta^2 = \frac{2mV_0 a^2}{\hbar^2} \tag{7.479}$$

$$\xi = \alpha a \quad \text{and} \quad \zeta = \beta a$$

$$\ell = 1 \qquad \frac{\cot \xi}{\xi} - \frac{1}{\xi^2} = \frac{1}{\zeta} + \frac{1}{\zeta^2} v \xi^2 + \zeta^2 = \frac{2mV_0 a^2}{\hbar^2} \tag{7.480}$$

$$\xi = \alpha a \quad \text{and} \quad \zeta = \beta a$$

A graphical solution for the $\ell = 0$ case is shown in the figure below.

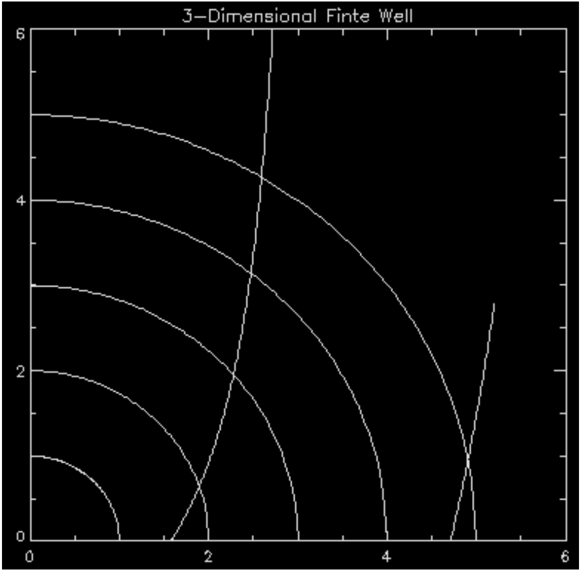

Figure: Graphical Solution

For a given well, only one circle exists on the plot. The solutions (energy eigenvalues) are given by the intersection of that circle with the cotangent curves.

The big change from the finite well in one dimension is that the quantity

$$\frac{2mV_0a^2}{\hbar^2} \tag{7.481}$$

must be larger than some minimum value before any bound state exists (this corresponds to the radius of the smallest circle that intersects the cotangent curves). In particular,

$$\frac{2mV_0a^2}{\hbar^2} < \left(\frac{\pi}{2}\right)^2 \rightarrow \text{ no solution} \tag{7.482}$$

$$\frac{2mV_0a^2}{\hbar^2} < \left(\frac{3\pi}{2}\right)^2 \rightarrow \text{ 1 solution} \tag{7.483}$$

$$\frac{2mV_0a^2}{\hbar^2} < \left(\frac{5\pi}{2}\right)^2 \rightarrow \text{ 2 solutions} \tag{7.484}$$

7.6.4 **Two-Dimensional Harmonic Oscillator**

The 2-dimensional harmonic oscillator system has the Hamiltonian

$$\begin{aligned}\hat{H} &= \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2\right) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2) \\ &= \left(\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\right) + \left(\frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2\right) \\ &= \hat{H}_x + \hat{H}_y \end{aligned} \tag{7.485}$$

where we have the commutation relations

$$\left[\hat{H}_x, \hat{H}_y\right] = 0 = \left[\hat{H}, \hat{H}_x\right] = \left[\hat{H}, \hat{H}_y\right] \tag{7.486}$$

These commutators imply that $\hat{H}$, $\hat{H}_x$ and $\hat{H}_y$ have a common eigenbasis. We label their common state vectors by

$$|E\rangle = |E_x, E_y\rangle = |E_x\rangle\,|E_y\rangle \tag{7.487}$$

with

$$\hat{H}_x |E_x\rangle = E_x |E_x\rangle \tag{7.488}$$

$$\hat{H}_y |E_y\rangle = E_y |E_y\rangle \tag{7.489}$$

$$\begin{aligned} \hat{H} |E\rangle = E |E\rangle &= (\hat{H}_x + \hat{H}_y) |E_x\rangle |E_y\rangle \\ &= (E_x + E_y) |E\rangle \end{aligned} \tag{7.490}$$

or

$$E = E_x + E_y \tag{7.491}$$

Now $\hat{H}_x$ (and $\hat{H}_y$) each represent a 1−dimensional oscillator. This suggests that we define new operators for the x coordinate

$$a_x = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}_x = \left(a_x^+\right)^+ \tag{7.492}$$

where

$$[\hat{x}, \hat{p}_x] = i\hbar \to \left[\hat{a}_x, a_x^+\right] = 1 \tag{7.493}$$

and

$$\hat{H}_x = \hbar\omega\left(\hat{a}_x^+\hat{a}_x + \frac{1}{2}\right) = \hbar\omega\left(\hat{N}_x + \frac{1}{2}\right) \tag{7.494}$$

As we found earlier, $\hat{N}_x$ has an eigenvalue equation

$$\hat{N}_x \left|n_x\right\rangle = n_x \left|n_x\right\rangle \quad , \quad n_x = 0, 1, 2, 3, ... \tag{7.495}$$

We then have

$$\hat{H}_x \left|n_x\right\rangle = \hbar\omega \left(\hat{N}_x + \frac{1}{2}\right) \left|n_x\right\rangle = \hbar\omega \left(n_x + \frac{1}{2}\right) \left|n_x\right\rangle \tag{7.496}$$

or

$$E_x = \hbar\omega \left(n_x + \frac{1}{2}\right) \tag{7.497}$$

In a similar manner, we repeat this process for the y coordinate

$$a_y = \sqrt{\frac{m\omega}{2\hbar}}\hat{y} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}_y = \left(a_y^+\right)^+ \tag{7.498}$$

where

$$\left[\hat{y}, \hat{p}_y\right] = i\hbar \to \left[\hat{a}_y, a_y^+\right] = 1 \tag{7.499}$$

and

$$\hat{H}_y = \hbar\omega\left(\hat{a}_y^+\hat{a}_y + \frac{1}{2}\right) = \hbar\omega\left(\hat{N}_y + \frac{1}{2}\right) \tag{7.500}$$

As we found earlier, $\hat{N}_y$ has an eigenvalue equation

$$\hat{N}_y\left|n_y\right\rangle = n_y\left|n_y\right\rangle \quad , \quad n_y = 0, 1, 2, 3, ... \tag{7.501}$$

We then have

$$\hat{H}_y\left|n_y\right\rangle = \hbar\omega\left(\hat{N}_y + \frac{1}{2}\right)\left|n_y\right\rangle = \hbar\omega\left(n_y + \frac{1}{2}\right)\left|n_y\right\rangle \tag{7.502}$$

or

$$E_y = \hbar\omega\left(n_y + \frac{1}{2}\right) \tag{7.503}$$

Putting this all together we get

$$E = E_x + E_y = \hbar\omega(n_x + n_y + 1) = \hbar\omega(n + 1) \tag{7.504}$$

The table below gives the resulting energy level structure.

n_x	n_y	$E/\hbar\omega$	n
0	0	1	0
1	0	2	1
0	1	2	1
0	2	3	2
2	0	3	2
1	1	3	2

Table: Energy Levels - 2D Oscillator

Each energy value, which is characterized by the quantum number n, has a *degeneracy* equal to $(n+1)$.

The existence of degeneracy indicates (*this is a general rule*) that there is another operator that commutes with $\hat{H}$.

Since this is a central force in the $x-y$ plane, it is not difficult to guess that the other operator that commutes with $\hat{H}$ is the angular momentum about the axis perpendicular to the plane (the $z-$axis), $\hat{L}_z$.

Since all of the x-type operators commute with all of the y-type operators we can write

$$\hat{L}_z = (\vec{r}_{op} \times \vec{p}_{op})_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \tag{7.505}$$

Inverting the standard operator definitions we have

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_x + \hat{a}_x^+) \quad , \quad \hat{p}_x = \frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}_x - \hat{a}_x^+) \tag{7.506}$$

$$\hat{y} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_y + \hat{a}_y^+) \quad , \quad \hat{p}_y = \frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}_y - \hat{a}_y^+) \tag{7.507}$$

which gives

$$\hat{L}_z = \frac{\hbar}{i}(\hat{a}_x^+\hat{a}_y - \hat{a}_y^+ a_x) \tag{7.508}$$

Now using

$$\left[\hat{a}_x, \hat{N}_x\right] = \hat{a}_x \quad , \quad \left[\hat{a}_x^+, \hat{N}_x\right] = -\hat{a}_x^+ \tag{7.509}$$

$$\left[\hat{a}_y, \hat{N}_y\right] = \hat{a}_y \quad , \quad \left[\hat{a}_y^+, \hat{N}_y\right] = -\hat{a}_y^+ \tag{7.510}$$

we get

$$\left[\hat{H}_x, \hat{L}_z\right] = \frac{\hbar}{i}(\hat{a}_y\hat{a}_x^+ + \hat{a}_x\hat{a}_y^+) = -\left[\hat{H}_y, \hat{L}_z\right] \tag{7.511}$$

or

$$\left[\hat{H}, \hat{L}_z\right] = 0 \tag{7.512}$$

Therefore, $\hat{H}$ and $\hat{L}_z$ share a common eigenbasis. This new eigenbasis will not be an eigenbasis for $\hat{H}_x$ or $\hat{H}_y$ separately since they do not commute with $\hat{L}_z$.

This suggests that we use linear combinations of the degenerate eigenstates to find the eigenstates of $\hat{L}_z$. This works because linear combinations for fixed n remain eigenstates of $\hat{H}$ (they are no longer eigenstates of $\hat{H}_x$ or $\hat{H}_y$ however).

We define the eigenstates and eigenvalues of $\hat{L}_z$ by the equation

$$\hat{L}_z \left|m\right\rangle = m\hbar \left|m\right\rangle \tag{7.513}$$

and the common eigenstates of $\hat{H}$ and $\hat{L}_z$ by $\left|n, m\right\rangle$ where

$$\hat{H}\,|n,m\rangle = \hbar\omega(n+1)\,|n,m\rangle \tag{7.514}$$

$$\hat{L}_z\,|n,m\rangle = m\hbar\,|n,m\rangle \tag{7.515}$$

For notational clarity we will write the old states as $|n_x\rangle\,|n_y\rangle$.

For the $n = 0$ states (there is only one) we have

$$\hat{L}_z\,|0,0\rangle = \hat{L}_z\,|0\rangle\,|0\rangle = 0 \rightarrow m = 0\ ,\ n = 0 \tag{7.516}$$

Now we look at the $n = 1$ states. We let

$$|\psi\rangle = a\,|0\rangle\,|1\rangle + b\,|1\rangle\,|0\rangle \text{ where } |a|^2 + |b|^2 = 1 \text{ (normalization)} \tag{7.517}$$

Since the two states that make up the linear combination are both eigenstates of $\hat{H}$ with $n = 1$, the linear combination is an eigenstate of $\hat{H}$ with $n = 1$ for any choice of a and b. We therefore choose a and b to make this state an eigenstate of $\hat{L}_z$.

We must have

$$\begin{aligned}
\hat{L}_z |\psi\rangle = \hat{L}_z |1, m\rangle &= \hat{L}_z(a|0\rangle|1\rangle + b|1\rangle|0\rangle) \\
&= \frac{\hbar}{i}(\hat{a}_x^+ \hat{a}_y - \hat{a}_y^+ a_x)(a|0\rangle|1\rangle + b|1\rangle|0\rangle) \\
&= m\hbar(a|0\rangle|1\rangle + b|1\rangle|0\rangle)
\end{aligned} \tag{7.518}$$

Using

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \quad , \quad \hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle \tag{7.519}$$

we get

$$a\frac{\hbar}{i}|1\rangle|0\rangle - b\frac{\hbar}{i}|0\rangle|1\rangle = m\hbar(a|0\rangle|1\rangle + b|1\rangle|0\rangle) \tag{7.520}$$

or

$$ma = ib \quad and \quad mb = -ia \tag{7.521}$$

Dividing these two equations we get

$$\frac{a}{b} = -\frac{b}{a} \tag{7.522}$$

which implies that

$$a^2 = -b^2 \to a = \pm ib \tag{7.523}$$

and

$$m = -\frac{b}{ia} = \begin{cases} +1 & a = +ib \\ -1 & a = -ib \end{cases} \tag{7.524}$$

Normalization then says that

$$m = \begin{cases} +1 & a = \frac{1}{\sqrt{2}}, b = -\frac{i}{\sqrt{2}} \\ -1 & a = \frac{1}{\sqrt{2}}, b = +\frac{i}{\sqrt{2}} \end{cases} \tag{7.525}$$

or

$$|1, \pm 1\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle |1\rangle \mp |1\rangle |0\rangle \right) \tag{7.526}$$

This gives a new characterization of the first two excited energy levels as shown in the table below.

n	m	$E/\hbar\omega$
0	0	1
1	+1	2
1	-1	2

Table: Energy Levels - (n,m) Characterization

Let us now do the $n = 2$ states. In the same way we assume

$$|\psi\rangle = a\,|2\rangle\,|0\rangle + b\,|1\rangle\,|1\rangle + c\,|0\rangle\,|2\rangle \tag{7.527}$$

where normalization gives

$$|\mathrm{a}|^2 + |\mathrm{b}|^2 + |\mathrm{c}|^2 = 1 \tag{7.528}$$

We then have

$$\begin{aligned}
\hat{L}_z |\psi\rangle &= \hat{L}_z |2,m\rangle = m\hbar |\psi\rangle \\
&= m\hbar a |2\rangle |0\rangle + m\hbar b |1\rangle |1\rangle + m\hbar c |0\rangle |2\rangle \\
&= \frac{\hbar}{i}(\hat{a}_x^+ \hat{a}_y - \hat{a}_y^+ \hat{a}_x)(a |2\rangle |0\rangle + b |1\rangle |1\rangle + c |0\rangle |2\rangle) \\
&= \frac{\hbar}{i}\left[\sqrt{2}b |2\rangle |0\rangle + \sqrt{2}(c-a) |1\rangle |1\rangle - \sqrt{2}b |0\rangle |2\rangle\right]
\end{aligned} \tag{7.529}$$

which gives

$$ma = -i\sqrt{2}b \tag{7.530}$$

$$mc = +i\sqrt{2}b \tag{7.531}$$

$$mb = -i\sqrt{2}(c-a) \tag{7.532}$$

$$\begin{aligned}
&\frac{a}{c} = -1 \rightarrow c = -a \\
&\frac{c}{b} = -\frac{b}{c-a} \rightarrow \frac{a}{b} = -\frac{b}{2a} \rightarrow b^2 \\
&\quad = -2a^2 \rightarrow b = \pm i\sqrt{2a}
\end{aligned}$$

Putting these pieces all together we have

$$a = \frac{1}{2} = -c \quad , \quad b_{\pm} = \pm i\frac{\sqrt{2}}{2} \tag{7.533}$$

This implies the m-values

$$m = \begin{cases} \frac{\sqrt{2}b_+}{ia} & +2 \\ \frac{\sqrt{2}b_-}{ia} & -2 \end{cases} \tag{7.534}$$

or

$$|2,0\rangle = \frac{1}{\sqrt{2}}\,|2\rangle\,|0\rangle + \frac{1}{\sqrt{2}}\,|0\rangle\,|2\rangle \tag{7.535}$$

Thus, the final energy levels are as shown in the table below.

n	m	$E/\hbar\omega$
0	0	1
1	+1	2
1	-1	2
2	+2	3
2	0	3
2	-2	3

Table: Energy Levels - (n,m) Characterization

What a strange result? The allowed m-values are separated by $\Delta m = \pm 2$.

Let us look at this system using the Schrodinger equation to help us understand what is happening.

We have (using plane-polar coordinates)

$$-\frac{h^2}{2M}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2\psi}{\partial\varphi^2}\right)+\frac{1}{2}M\omega^2r^2\psi=E\psi \quad (7.536)$$

Choosing

$$\psi(r,\varphi)=R(r)\Phi(\varphi) \quad (7.537)$$

we get

$$-\frac{h^2}{2M}\frac{1}{R}\left(\frac{d^2R}{dr^2}+\frac{1}{r}\frac{dR}{dr}\right)-\frac{h^2}{2Mr^2}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}+\frac{1}{2}M\omega^2r^2=E \quad (7.538)$$

Now we must have

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=-m^2=\text{constant} \quad (7.539)$$

which produces a radial equation of the form

$$-\frac{h^2}{2M}\left(\frac{d^2R}{dr^2}+\frac{1}{r}\frac{dR}{dr}\right)+\left(\frac{h^2m^2}{2Mr^2}+\frac{1}{2}M\omega^2r^2\right)R=ER \quad (7.540)$$

Now we change the variables using

$$r=\rho y \quad , \quad \rho=\frac{\hbar}{M\omega} \quad (7.541)$$

and get

$$\frac{d^2R}{dy^2}+\frac{1}{y}\frac{dR}{dy}+\left(\varepsilon-y^2-\frac{m^2}{y^2}\right)R=0 \quad (7.542)$$

where

$$\varepsilon=\frac{E}{\hbar\omega} \quad (7.543)$$

As with the solution of other differential equations, the procedure to follow is to extract out the asymptotic behavior as $y\to 0,\infty$ and solve the equation for the remaining function by recognizing the *well-known* equation that results.

As $y \to \infty$ the dominant term will be y^2 and the equation for this behavior is

$$\frac{d^2R}{dy^2} - y^2 R = 0 \tag{7.544}$$

which has a solution $R \to e^{-y^2/2}$.

As $y \to 0$ the dominant term will be $1/y^2$ and the equation for this behavior is

$$\frac{d^2R}{dy^2} - \frac{m^2}{y^2} R = 0 \tag{7.545}$$

which has a solution $R \to y^{|m|}$, where we have excluded any negative powers since that solution would diverge at $y = 0$.

Therefore we assume $R = y^{|m|} e^{-y^2/2} G(y)$. Substitution gives the equation for G as

$$\frac{d^2G}{dy^2} + \left(\frac{2|m| + 1}{y} - 2y \right) \frac{dG}{dy} + (\varepsilon - 2 - 2|m|) G = 0 \tag{7.546}$$

Changing the variable again to $z = y^2$ we have

$$\frac{d^2G}{dz^2} + \left(\frac{|m|+1}{z} - 1\right)\frac{dG}{dz} + \left(\frac{\varepsilon - 2(|m|+1)}{4z}\right)G = 0 \quad (7.547)$$

If we are clever, we recognize this as Laguerre's equation. If not, we make a series solution substitution

$$G(z) = \sum_{s=0}^{\infty} b_s z^s \quad (7.548)$$

which gives the recursion relation

$$\frac{b_{s+1}}{b_s} = \frac{s + \frac{|m|+1}{2} - \frac{\varepsilon}{4}}{(s+1)(s+|m|+1)} \to \frac{1}{s} \text{ for large } s \quad (7.549)$$

This says that unless the series terminates (becomes a polynomial in z) it will behave like $e^z = e^{y^2}$ which implies that the solution for $R(y)$ will diverge for large y and thus, not be normalizable.

If we choose the maximum s-value to be $s_{max} = n_r$, then we can terminate the series by choosing

$$\varepsilon = 2|m| + 2 + 4n_r \tag{7.550}$$

which then gives us the allowed energy eigenvalues

$$E_{n_r,m} = \hbar\omega(|m| + 2n_r + 1) \tag{7.551}$$

The polynomial solutions are the generalized Laguerre polynomials $L_{n_r}^{|m|}(z)$.

The first few Laguerre polynomials are

$$L_0^k(z) = 1 \quad , \quad L_1^k(z) = 1 + k - z \tag{7.552}$$

$$L_2^k(z) = \frac{1}{2}(2 + 3k + k^2 - 2z(k+2) + z^2) \tag{7.553}$$

The full wave function is

$$\psi_{n_r,m}(r,\varphi) = r^{|m|} e^{-\frac{r^2}{2\rho^2}} L_{n_r}^{|m|}\left(\frac{r^2}{\rho^2}\right) e^{im\varphi} \tag{7.554}$$

and the energy level structure is shown in the table below.

$E/\hbar\omega$	n_r	m	degeneracy
1	0	0	1
2	0	+1	2
2	0	-1	
3	0	+2	3
3	1	0	
3	0	-2	
4	0	+3	4
4	1	+1	
4	1	-1	
4	0	-3	

Table: Energy Levels - 2D Oscillator

which is the same structure (with different labels) as in the operator solution. The fact that $\Delta m = 2$ in the 2-dimensional case is one of many peculiarities associated with two dimensions that does not appear three dimensions.

7.6.5 **What happens in 3 dimensions?**

In Cartesian coordinates we have a simple extension of the 2-dimensional case.

$$E = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right) = \hbar\omega\left(n + \frac{3}{2}\right) \tag{7.555}$$

The degeneracy is

$$\frac{(n+1)(n+2)}{2} \tag{7.556}$$

The energy level structure is shown in the table below.

$E/\hbar\omega$	n_x	n_y	n_z	n	degeneracy
3/2	0	0	0	0	1
5/2	1	0	0	1	3
5/2	0	1	0	1	
5/2	0	0	1	1	
7/2	2	0	0	2	6
7/2	0	2	0	2	
7/2	0	0	2	2	
7/2	1	1	0	2	
7/2	1	0	1	2	
7/2	0	1	1	2	

Table: Energy Levels - 3D Oscillator

In spherical-polar coordinates, we can follow a procedure similar to the plane-polar 2-dimensional case to get

$$\psi_{n_r,\ell,m}(y,\theta,\varphi) = y^\ell e^{-\frac{y^2}{2}} L_{n_r}^{\ell+\frac{1}{2}}(y^2) Y_{\ell m}(\theta,\varphi) \tag{7.557}$$

where

$$r = \rho y \quad , \quad \rho^2 = \frac{\hbar^2}{M\omega} \tag{7.558}$$

The corresponding energy values are

$$E_{n_r,\ell} = \hbar\omega(2n_r + \ell + \frac{3}{2}) \tag{7.559}$$

which gives Table 7.6 below.

$E/\hbar\omega$	n_r	ℓ	$n = 2n_r + \ell$	degeneracy
3/2	0	0	0	1
5/2	0	1	1	3 $\rightarrow$ m=$\pm$ 1,0
7/2	1 or 0	0 or 2	2	6 $\rightarrow$ m=$\pm$ 2, $\pm$ 1

Table: Energy Levels - 3D Oscillator

Finally, we look at a case we skipped over(because it is the most difficult example of this type).

7.6.6 **Two-Dimensional Finite Circular Well**

We consider the potential in two dimensions

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r > a \end{cases} \tag{7.560}$$

The Schrodinger equation in plane-polar coordinates is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right]\psi(r,\varphi) - V_0\psi(r,\varphi) = E\psi(r,\varphi) \;\; r < a \tag{7.561}$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right]\psi(r,\varphi) = E\psi(r,\varphi) \;\; r > a \tag{7.562}$$

We assume(SOV)

$$\psi(r,\varphi) = R(r)\Phi(\varphi) \tag{7.563}$$

which gives

$$-\frac{\hbar^2}{2m}\left[\frac{1}{rR}\frac{\partial}{\partial r}\left(r\frac{\partial R}{\partial r}\right)+\frac{1}{r^2}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}\right]=E+V_0 \qquad r<a \tag{7.564}$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{rR}\frac{\partial}{\partial r}\left(r\frac{\partial R}{\partial r}\right)+\frac{1}{r^2}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}\right]=E \qquad r>a \tag{7.565}$$

We choose a separation constant

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=-\alpha^2\rightarrow\Phi(\varphi)=B\sin(\alpha\varphi+\delta) \tag{7.566}$$

The requirement of single-valuedness under a φ-rotation of 2π says that

$$\sin(\alpha\varphi+\delta)=\sin(\alpha\varphi+\delta+\alpha\pi)$$
$$\rightarrow\alpha=\text{ integer }=0,1,2,3\ldots$$

Alternatively, we could write

$$\Phi(\varphi)=Be^{i\alpha\varphi}$$
$$\alpha=\text{ integer }=\cdots-3,-2,-1,0,1,2,3,\ldots$$

Substitution of this solution leaves the radial differential equations

$$r^2\frac{d^2R}{dr^2}+r\frac{dR}{dr}+\left[\beta^2r^2-\alpha^2\right]R=0 \;\; r<a \quad where \;\; \beta^2=\frac{2m(E+V_0)}{\hbar^2} \tag{7.567}$$

$$r^2\frac{d^2R}{dr^2}+r\frac{dR}{dr}+\left[\lambda^2r^2-\alpha^2\right]R=0 \quad r>a \quad where \quad \lambda^2=\frac{2mE}{\hbar^2} \tag{7.568}$$

These are Bessel's equations. The general solutions are

$$R(r)=NJ_\alpha(\beta r)+MY_\alpha(\beta r) \quad r<a \tag{7.569}$$

$$R(r)=PJ_\alpha(\lambda r) \quad r>a \tag{7.570}$$

and the complete solutions are then

$$\psi_{k\alpha}(r,\varphi)=\left\{\begin{array}{c} R(r)\Phi(\varphi)=(NJ_\alpha(\beta r)+MY_\alpha(\beta r))e^{i\alpha\varphi} \quad r<a \\ R(r)\Phi(\varphi)=PJ_\alpha(\lambda r)e^{i\alpha\varphi} \quad r>a \end{array}\right\} \tag{7.571}$$

The continuity (or boundary) conditions at $r = a$ are

$$NJ_\alpha(\beta a) + MY_\alpha(\beta a) = PJ_\alpha(\lambda a) \tag{7.572}$$

$$N\beta \left.\frac{dJ_\alpha(\beta r)}{d(\beta r)}\right|_{r=a} + M\beta \left.\frac{dY_\alpha(\beta r)}{d(\beta r)}\right|_{r=a} = P\lambda \left.\frac{dJ_\alpha(\lambda r)}{d(\lambda r)}\right|_{r=a} \tag{7.573}$$

Let us consider the case $\alpha = 0$. We have

$$NJ_0(\beta a) + MY_0(\beta a) = PJ_0(\lambda a) \tag{7.574}$$

$$N\beta \left.\frac{dJ_0(\beta r)}{d(\beta r)}\right|_{r=a} + M\beta \left.\frac{dY_0(\beta r)}{d(\beta r)}\right|_{r=a} = P\lambda \left.\frac{dJ_0(\lambda r)}{d(\lambda r)}\right|_{r=a} \tag{7.575}$$

where

$$J_0(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 4} - \frac{x^6}{2^2 4^2 6} + ... \tag{7.576}$$

$$\frac{dJ_0(x)}{dx} = -J_1(x) = -\left(\frac{x}{2} - \frac{x^3}{2^2 4} + \frac{x^5}{2^2 4^2 6} - \frac{x^7}{2^2 4^2 6^2 8} + ...\right) \tag{7.577}$$

$$Y_0(x) = \frac{2}{\pi}\left[\ell n\left(\frac{x}{2}\right) + \gamma\right] J_0(x)\gamma = 0.5772156 \tag{7.578}$$

$$\frac{dY_0(x)}{dx} = \frac{2}{\pi}\left[\ell n\left(\frac{x}{2}\right) + \gamma\right] \frac{dJ_0(x)}{dx} + \frac{2}{\pi x} J_0(x) \tag{7.579}$$

Clearly, the 2-dimensional finite well is very difficult.

7.6.7 **The 3-Dimensional Delta Function**

We now consider a particle is moving in 3-dimensions under the action of the attractive delta function potential given by

$$V(r) = -\frac{\hbar^2}{2M\alpha}\delta(r-a) \tag{7.580}$$

Since this is a central force we know that we can write the solutions in the form

$$\psi(r,\theta,\varphi) = R(r)Y_{\ell m}(\theta,\varphi) \tag{7.581}$$

The Schrodinger equation is

$$-\frac{\hbar^2}{2M}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{\ell(\ell+1)}{r^2}R\right)-\frac{\hbar^2}{2M\alpha}\delta(r-a)R-\frac{\hbar^2k^2}{2M}R=0 \tag{7.582}$$

where, since we are looking for bound states, we have set

$$E=-\frac{\hbar^2k^2}{2M}<0 \tag{7.583}$$

Now the function $R(r)$ must be continuous everywhere. But as we saw earlier in the 1-dimensional case, the derivative of R is not continuous for delta functions. The discontinuity at $r=a$ is found by integrating the radial equation around the point $r=a$.

$$-\frac{\hbar^2}{2M}\int_{a^-}^{a^+} r^2dr\left(\frac{d^2R(r)}{dr^2}+\frac{2}{r}\frac{dR(r)}{dr}-\frac{\ell(\ell+1)}{r^2}R(r)\right)$$

$$-\frac{\hbar^2}{2M\alpha}\int_{a^-}^{a^+} r^2dr\delta(r-a)R(r)-\frac{\hbar^2k^2}{2M}\int_{a^-}^{a^+} r^2drR(r)=0$$

which gives the second boundary (continuity) condition

$$\alpha\left[\frac{dR(a^+)}{dr}-\frac{dR(a^-)}{dr}\right]=-R(a) \tag{7.584}$$

For $r > a$ and $r < a$ we then have the equation

$$-\frac{\hbar^2}{2M}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{\ell(\ell+1)}{r^2}R\right)-\frac{\hbar^2k^2}{2M}R=0 \tag{7.585}$$

which has as a solution for the case $\ell = 0$

$$R(r)=\frac{1}{r}(Ae^{-kr}+Be^{kr}) \tag{7.586}$$

For $R(r)$ to be well behaved at $r = 0$ we must choose $B = -A$. Therefore, the solution for $r < a$ is

$$R(r)=\frac{c}{r}\sinh kr \tag{7.587}$$

For $R(r)$ to be well behaved as $r \to \infty$ we must choose $B = 0$. Therefore the solution for $r > a$ is

$$R(r)=\frac{b}{r}e^{-kr} \tag{7.588}$$

The boundary conditions at $r = a$ then give the equations

$$\frac{c}{a}\sinh ka = \frac{b}{a}e^{-ka} \rightarrow c\sinh ka = be^{-ka} \tag{7.589}$$

and

$$0 = -k\alpha(be^{-ka} + c\cosh ka) + c\sinh ka \tag{7.590}$$

Eliminating b and c we get a transcendental for k (or E)

$$\frac{\alpha}{a} = \frac{1 - e^{-2ka}}{2ka} \tag{7.591}$$

The right-hand side of this equation has a range

$$0 < \frac{1 - e^{-2ka}}{2ka} < 1 \tag{7.592}$$

Therefore, the allowed range of the parameter α, in order that an $\ell = 0$ bound state exist, is $0 < \alpha < a$.

Just this once let us ask .... what can we say about $\ell \neq 0$? This will illustrate some properties of the spherical Bessel functions. We have the radial equation

$$r^2\frac{d^2R}{dr^2}+2r\frac{dR}{dr}+\left(k^2r^2-\ell(\ell+1)\right)R=0 \tag{7.593}$$

which as we have seen before is the spherical Bessel function equation with the general solution

$$R(r)=Aj_\ell(kr)+B\eta_\ell(kr) \tag{7.594}$$

For $r<a$ we must choose $B=0$ ($\eta_\ell(kr)$ diverges at $r=0$) and for $r>a$ we must choose $B=iA$, which leads to a solution that drops off exponentially as $r\to\infty$. So we finally have

$$r<a \qquad R(r)=Gj_\ell(kr) \tag{7.595}$$

$$r>a \qquad R(r)=Hh_\ell^{(1)}(kr)=H(j_\ell(kr)+i\eta_\ell(kr)) \tag{7.596}$$

The boundary conditions then give

$$Gj_\ell(ka)=Hh_\ell^{(1)}(ka)=H(j_\ell(ka)+i\eta_\ell(ka)) \tag{7.597}$$

$$\begin{aligned}-\frac{G}{\alpha}j_\ell(ka)&=H\frac{dh_\ell^{(1)}(ka)}{dr}-G\frac{dj_\ell(ka)}{dr}\\&=\frac{dj_\ell(ka)}{dr}(H-G)+iG\frac{d\eta_\ell(ka)}{dr}\end{aligned} \tag{7.598}$$

Now

$$\frac{dj_\ell(kr)}{dr} = \frac{k}{2\ell+1}\left[\ell j_{\ell-1}(kr) - (\ell+1)j_{\ell+1}(kr)\right] \tag{7.599}$$

and similarly for η_ℓ and $h_\ell^{(1)}$. Therefore, we get

$$Gj_\ell(ka) = (j_\ell(ka) + i\eta_\ell(ka))H \tag{7.600}$$

$$\begin{aligned}\frac{Gk}{2\ell+1}&\left[\ell j_{\ell-1}(ka) - (\ell+1)j_{\ell+1}(ka)\right]\\ &\qquad - i\frac{Gk}{2\ell+1}\left[\ell\eta_{\ell-1}(ka) - (\ell+1)\eta_{\ell+1}(ka)\right] - \frac{G}{\alpha}j_\ell(ka)\\ &= \frac{k}{2\ell+1}\left[\ell j_{\ell-1}(ka) - (\ell+1)j_{\ell+1}(ka)\right]H\end{aligned} \tag{7.601}$$

or

$$\frac{\eta_\ell(ka)}{j_\ell(ka)+i\eta_\ell(ka)} = \frac{\left[\ell\eta_{\ell-1}(ka) - (\ell+1)\eta_{\ell+1}(ka)\right] - \frac{i(2\ell+1)}{k\alpha}j_\ell(ka)}{\left[\ell j_{\ell-1}(ka) - (\ell+1)j_{\ell+1}(ka)\right]}$$

This is the *transcendental equation* for the energy!!! That is enough for nonzero angular momentum!

7.6.8 **The Hydrogen Atom**

Schrodinger Equation Solution

The potential energy function

$$V(r) = -\frac{Ze^2}{r} \tag{7.602}$$

represents the attractive Coulomb interaction between an atomic nucleus of charge $+Ze$ and an electron of charge $-e$.

The Schrodinger equation we have been using describes the motion of a single particle in an external field. In the hydrogen atom, however, we are interested in the motion of two particles (nucleus and electron) that are attracted to each other via the potential above (where r is the *separation distance* between the two particles).

We start by writing the Schrodinger equation for the two particle system. It involves six coordinates (three for each particle). We use Cartesian coordinates to start the discussion. We have

$$\hat{H} = \frac{\vec{p}_{1,op}^{\,2}}{2m_1} + \frac{\vec{p}_{2,op}^{\,2}}{2m_2} + V(\vec{r}) \quad where \quad \vec{r} = \vec{r}_1 - \vec{r}_2 \tag{7.603}$$

which gives

$$\begin{aligned}
-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right)\phi(x_1, y_1, z_1, x_2, y_2, z_2) \\
-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right)\phi(x_1, y_1, z_1, x_2, y_2, z_2) \\
+V(x_1 - x_2, y_1 - y_2, z_1 - z_2)\phi(x_1, y_1, z_1, x_2, y_2, z_2) \\
= E\phi(x_1, y_1, z_1, x_2, y_2, z_2)
\end{aligned} \tag{7.604}$$

We now introduce relative and center-of-mass(CM) coordinates by

$$x = x_1 - x_2 \quad , \quad y = y_1 - y_2 \quad , \quad z = z_1 - z_2$$
$$\vec{r} = (x, y, z)$$
$$MX = m_1 x_1 + m_2 x_2 \quad , \quad M\mathrm{Y} = m_1 y_1 + m_2 y_2 \quad , \quad M\mathrm{Z} = m_1 z_1 + m_2$$
$$\vec{R} = (X, Y, Z)$$
$$M = m_1 + m_2 = \text{ total mass of the system}$$

Substitution gives

$$\begin{aligned} &-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right)\phi(x, y, z, X, Y, Z) \\ &\qquad -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\phi(x, y, z, X, Y, Z) \\ &\qquad + V(x, y, z)\phi(x, y, z, X, Y, Z) = E\phi(x, y, z, X, Y, Z) \end{aligned} \tag{7.605}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{ the reduced mass} \tag{7.606}$$

We can now separate the variables by assuming a solution of the form

$$\phi(x, y, z, X, Y, Z) = \psi(x, y, z)\Psi(X, Y, Z) \tag{7.607}$$

which gives the two equations

$$-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{r}}\psi(\vec{r}) + V(r)\psi(\vec{r}) = E\psi(\vec{r}) \tag{7.608}$$

$$-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}}\Psi(\vec{R}) = E'\Psi(\vec{R}) \tag{7.609}$$

The second equation says that the CM of the two particles is like a free particle of mass M.

The first equation describes the relative motion of the two particles and is the same as the equation of motion of a particle of mass μ in an external potential energy $V(r)$.

In the hydrogen atom problem we are only interested in the energy levels E associated with the relative motion. In addition, since the nuclear mass is so much larger than the electron mass, we have

$$\mu \approx m_e = m_{electron} \tag{7.610}$$

This is a central force so we assume a solution of the form

$$\psi(\vec{r}) = R(r)Y_{\ell m}(\theta, \varphi) \tag{7.611}$$

and obtain the radial equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{Ze^2}{r}R + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}R = ER \tag{7.612}$$

where $E < 0$ for a bound state. We follow the same approach as before. We change the variables so that the equation is in dimensionless form by introducing $\rho = \alpha r$ where

$$\alpha^2 = \frac{8\mu\,|E|}{\hbar^2} \quad and \quad \lambda = \frac{2\mu Z e^2}{\alpha\hbar^2} = \frac{Ze^2}{\hbar}\left(\frac{\mu}{2\,|E|}\right)^{1/2} \tag{7.613}$$

We get

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{dr}\rho\right) + \left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\right)R = 0 \tag{7.614}$$

For $\rho \to \infty$ the equation becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{dr}\rho\right) - \frac{1}{4}R = 0 \tag{7.615}$$

which has the solution

$$R \to \rho^n e^{\pm\frac{1}{2}\rho} \tag{7.616}$$

where n can have any finite value. Since we want a normalizable solution, we will look for a solution of the form

$$R \to F(\rho)e^{-\frac{1}{2}\rho} \tag{7.617}$$

Substitution gives an equation for F

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]F = 0 \qquad (7.618)$$

We solve this equation (it is Laguerre's equation) by series substitution.

$$F(\rho) = \rho^s(a_0 + a_1\rho + a_2\rho^2 + ...) = \rho^s L(\rho) \qquad (7.619)$$

where $a_0 \neq 0$ and $s|ge0$. We must also have that $F(0)$ is finite. Substitution gives an equation for L.

$$\rho^2\frac{d^2L}{d\rho^2} + \rho\left[2(s+1) - \rho\right]\frac{dL}{d\rho} + \left[\rho(\lambda - s - 1) + s(s+1) - \ell(\ell+1)\right]L = 0 \qquad (7.620)$$

If we set $\rho = 0$ in this equation and use the fact that L is a power series we get the condition

$$s(s+1) - \ell(\ell+1) = 0 \qquad (7.621)$$

or

$$s = \ell \text{ or } s = -(\ell+1) \qquad (7.622)$$

Since R must be finite at the origin we exclude the second possibility and choose $s = \ell$. This gives

$$\rho^2 \frac{d^2 L}{d\rho^2} + \rho \left[2(\ell + 1) - \rho\right] \frac{dL}{d\rho} + \left[\rho(\lambda - \ell - 1)\right] L = 0 \qquad (7.623)$$

Substituting the power series gives a recursion relation for the coefficients

$$a_{\nu+1} = \frac{\nu + \ell + 1 - \lambda}{(\nu + 1)(\nu + 2\ell + 2)} a_\nu \qquad (7.624)$$

If the series does not terminate, then this recursion relation behaves like

$$\frac{a_{\nu+1}}{a_\nu} \to \frac{1}{\nu} \qquad (7.625)$$

for large ν. This corresponds to the series for $\rho^n e^\rho$. Since this will give a non-normalizable result, we must terminate the series by choosing

$$\lambda = n = \text{ positive integer } = n' + \ell + 1 = \text{ total quantum number} \tag{7.626}$$

where n'(= radial quantum number) is the largest power of ρ in the solution L. Since n' and n are non-negative integers, $n = 1, 2, 3, 4, \ldots$

We thus obtain the solution for the energies

$$E_n = -|E_n| = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} = -\frac{Z^2 e^2}{2a_0 n^2} \tag{7.627}$$

where

$$a_0 = \text{ Bohr radius } = \frac{\hbar^2}{\mu e^2} \tag{7.628}$$

Unlike the finite square well, where we had a finite number of bound state levels, in this case, we obtain an infinite set of discrete energies. This results from the very slow decrease of the Coulomb potential energy with distance.

The Laguerre polynomial solutions are given by the generating function

$$G(\rho, s) = \frac{e^{-\frac{\rho s}{1-s}}}{1-s} = \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q \quad , \quad s < 1 \tag{7.629}$$

By differentiating the generating function with respect to ρ and s we can show that

$$\frac{dL_q}{d\rho} - q\frac{dL_{q-1}}{d\rho} = -qL_{q-1} \tag{7.630}$$

$$L_{q+1} = (2q+1-\rho)L_q - q^2 L_{q-1} \tag{7.631}$$

The lowest order differential equation involving only L_q that can be constructed from these two equations is

$$\rho\frac{d^2 L_q}{d\rho^2} + (1-\rho)\frac{dL_q}{d\rho} + qL_q = 0 \tag{7.632}$$

This is not quite our original equation. However, if we define the associated Laguerre polynomials by

$$L_q^p(\rho) = \frac{d^p}{d\rho^p} L_q(\rho) \tag{7.633}$$

then differentiating the differential equation p times we get

$$\rho \frac{d^2 L_q^p}{d\rho^2} + (p+1-\rho)\frac{dL_q^p}{d\rho} + (q-p)L_q^p = 0 \tag{7.634}$$

Setting $\lambda = n$ we then see that the solutions to the Schrodinger equation are

$$L_{n+\ell}^{2\ell+1}(\rho) \tag{7.635}$$

which are polynomials of order $(n+\ell)-(2\ell+1) = n-\ell-1$ in agreement with the earlier results.

We can differentiate the generating function p times to get

$$G_p(\rho,s) = \frac{(-s)^p e^{-\frac{\rho s}{1-s}}}{(1-s)^{p+1}} = \sum_{q=0}^{\infty} \frac{L_q^p(\rho)}{q!} s^q \quad , \quad s < 1 \tag{7.636}$$

Explicitly, we then have

$$L_{n+\ell}^{2\ell+1}(\rho) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{\left[(n+\ell)!\right]^2 \rho^k}{(n-\ell-1-k)!(2\ell+1+k)!k!} \tag{7.637}$$

The normalized radial wave functions are of the form

$$R_{n\ell}(\rho) = -\left\{ \left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3} \right\}^{1/2} e^{-\frac{1}{2}\rho} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) \tag{7.638}$$

with

$$a_0 = \frac{\hbar^2}{\mu e^2} \text{ and } \rho = \frac{2Z}{na_0} r \tag{7.639}$$

and

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r) Y_{\ell m}(\theta,\varphi) \tag{7.640}$$

The first few radial wave functions are

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2e^{-\frac{Zr}{a_0}} \tag{7.641}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \tag{7.642}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0\sqrt{3}} e^{-\frac{Zr}{2a_0}} \tag{7.643}$$

What about degeneracy since the energy values do not depend on ℓ and m?

For each value of n, ℓ can vary between 0 and $n-1$, and for each value of these ℓ values m can vary between $-\ell$ and ℓ ($2\ell+1$ values). Therefore the total degeneracy of an energy level E_n is given by

$$\sum_{\ell=0}^{n-1}(2\ell+1) = 2\frac{n(n-1)}{2} + n = n^2 \tag{7.644}$$

The degeneracy with respect to m is true for any central force (as we have seen in other examples). The ℓ degeneracy, however, is characteristic of the Coulomb potential alone. It is called an *accidental* degeneracy.

Some useful expectation values are:

$$\langle r \rangle_{n\ell m} = \frac{a_0}{2Z}\left[3n^2 - \ell(\ell+1)\right] \qquad \left\langle \frac{1}{r} \right\rangle_{n\ell m} = \frac{Z}{a_0 n^2} \tag{7.645}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{n\ell m} = \frac{Z^2}{a_0^2 n^3 (\ell + \frac{1}{2})} \qquad \left\langle \frac{1}{r^3} \right\rangle_{n\ell m} = \frac{Z^3}{a_0^3 n^3 \ell(\ell + \frac{1}{2})(\ell+1)} \tag{7.646}$$

7.6.9 **Algebraic Solution of the Hydrogen Atom**

Review of the Classical Kepler Problem

In the classical Kepler problem of an electron of charge -e moving in the electric force field of a positive charge Ze located at the origin, the angular momentum

$$\vec{L} = \vec{r} \times \vec{p} \tag{7.647}$$

is constant. The motion takes place in a plane perpendicular to the constant angular momentum direction. Newton's second law tells us that the rate of change of the momentum is equal to the force

$$\frac{d\vec{p}}{dt} = -\frac{Ze^2}{r^2}\hat{r} \text{ where } r = |\vec{r}| \text{ and } \hat{r} = \frac{\vec{r}}{r} = \text{ unit vector} \tag{7.648}$$

The so-called *Runge-Lenz* vector is defined by

$$\vec{A} = \frac{1}{Ze^2 m}(\vec{L} \times \vec{p}) + \hat{r} \tag{7.649}$$

If we take its time derivative we find

$$\frac{d\vec{L}}{dt} = 0 \text{ and } \vec{L} = m\vec{r} \times \frac{d\vec{r}}{dt} = mr^2\hat{r} \times \frac{d\hat{r}}{dt} + mr(\hat{r} \times \hat{r})\frac{dr}{dt} = mr^2\hat{r} \times \frac{d\hat{r}}{dt} \tag{7.650}$$

$$\begin{aligned}\frac{d\vec{A}}{dt} &= \frac{1}{Ze^2 m}(\vec{L} \times \frac{d\vec{p}}{dt} + \frac{d\vec{L}}{dt} \times \vec{p}) + \frac{d\hat{r}}{dt} = \frac{1}{Ze^2 m}(\vec{L} \times \frac{d\vec{p}}{dt}) + \frac{d\hat{r}}{dt} \\ &= -\frac{1}{m}(\vec{L} \times \frac{\hat{r}}{r^2}) + \frac{d\hat{r}}{dt} = -(\hat{r} \times \frac{d\hat{r}}{dt}) \times \hat{r} + \frac{d\hat{r}}{dt} \\ &= -(\frac{d\hat{r}}{dt}(\hat{r} \cdot \hat{r}) - (\hat{r} \cdot \frac{d\hat{r}}{dt})) + \frac{d\hat{r}}{dt} = -\frac{d\hat{r}}{dt} + \frac{d(\hat{r} \cdot \hat{r})}{dt} + \frac{d\hat{r}}{dt} = 0\end{aligned} \tag{7.651}$$

Thus, the vector $\vec{A}$ is a constant of the motion. It corresponds physically to the length and direction of the *semi-major axis* of the classical elliptical orbit. The equation of the elliptical orbit is easily found using the $\vec{A}$ vector.

$$\vec{A}\cdot\vec{r} = ar\cos\theta = \frac{1}{Ze^2m}(\vec{L}\times\vec{p})\cdot\vec{r} + \hat{r}\cdot\vec{r}$$
$$= -\frac{1}{Ze^2m}\vec{L}\cdot(\vec{r}\times\vec{p}) + r \quad (7.652)$$
$$ar\cos\theta = -\frac{L^2}{Ze^2m} + r \quad (7.653)$$
$$\rightarrow \frac{1}{\mathrm{r}} = \frac{Ze^2m}{L^2}(1 - a\cos\theta) \rightarrow \text{ orbit equation (conic sections)} \quad (7.654)$$

where

$$a = \left|\vec{A}\right| \quad (7.655)$$
$$= \text{ eccentricity and the direction of } \vec{A} \text{ is from origin to the aphelion}$$

The Quantum Mechanical Problem

In order to make this useful in quantum mechanics, the classical Runge-Lenz vector must be generalized. In classical physics

$$\vec{L} \times \vec{p} = -\vec{p} \times \vec{L} \tag{7.656}$$

In quantum mechanics, this identity is not valid since the components of $\vec{L}_{op}$ *do not commute*. The correct quantum mechanical generalization (remember it must be a Hermitian operator if it is a physical observable) of the vector $\vec{A}$ is

$$\vec{A}_{op} = \frac{1}{2Ze^2m}(\vec{L}_{op} \times \vec{p}_{op} - \vec{p}_{op} \times \vec{L}_{op}) + \left(\frac{\vec{r}}{r}\right)_{op} \tag{7.657}$$

This satisfies $[\hat{H}, \vec{A}_{op}] = 0$, which says $\vec{A}$ is a constant. It also satisfies $\vec{A}_{op} \cdot \vec{L}_{op} = 0$.

We can derive the following commutators:

$$[\hat{L}_i, \hat{A}_j] = i\hbar\varepsilon_{ijk}\hat{A}_k \quad , \quad [\hat{L}_i, \hat{p}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k \quad , \quad [\hat{L}_i, \hat{r}_j] = i\hbar\varepsilon_{ijk}\hat{r}_k \tag{7.658}$$

which gives

$$\vec{A}_{op} = \frac{1}{2Ze^2m}(2\vec{L}_{op} \times \vec{p}_{op} + i\hbar\vec{p}_{op}) + \left(\frac{\vec{r}}{r}\right)_{op} \tag{7.659}$$

We now derive two important properties of $\vec{A}$. The first property follows from the commutators

$$\left[\left(\vec{L}_{op} \times \vec{p}_{op}\right)_i, \hat{p}_j\right] + \left[\hat{p}_i, \left(\vec{L}_{op} \times \vec{p}_{op}\right)_j\right] = 0 \tag{7.660}$$

$$\left[\left(\vec{L}_{op} \times \vec{p}_{op}\right)_i, \left(\vec{L}_{op} \times \vec{p}_{op}\right)_j\right] = -i\hbar\varepsilon_{ijk}\hat{L}_k p^2 = -i\hbar\varepsilon_{ijk}p^2\hat{L}_k \tag{7.661}$$

$$\left[\left(\vec{L}_{op} \times \vec{p}_{op}\right)_i, \frac{\hat{r}_j}{r}\right] + \left[\frac{\hat{r}_i}{r}, \left(\vec{L}_{op} \times \vec{p}_{op}\right)_j\right] = 2i\hbar\varepsilon_{ijk}\frac{\hat{L}_k}{r} \tag{7.662}$$

which leads to

$$\left[\hat{A}_i, \hat{A}_j\right] = i\hbar\left(\frac{-2\hat{H}}{Z^2e^4m}\right)\varepsilon_{ijk}\hat{L}_k \tag{7.663}$$

where

$$\hat{H} = \text{ Hamiltonian } = \frac{\vec{p}_{op}^2}{2m} - Ze^2 \left(\frac{1}{r}\right)_{op} \tag{7.664}$$

The second property follows from the relations

$$(\vec{L}_{op} \times \vec{p}_{op}) \cdot (\vec{L}_{op} \times \vec{p}_{op}) = \vec{L}_{op}^2 \vec{p}_{op}^2 \tag{7.665}$$

$$\left(\frac{\vec{r}}{r}\right)_{op} \cdot (\vec{L}_{op} \times \vec{p}_{op}) + (\vec{L}_{op} \times \vec{p}_{op}) \cdot \left(\frac{\vec{r}}{r}\right)_{op}$$

$$= -\frac{2\vec{L}_{op}^2}{r} + 2i\hbar \left(\frac{\vec{r}}{r}\right)_{op} \cdot \vec{p}_{op} \tag{7.666}$$

$$\vec{p}_{op} \cdot \left(\frac{\vec{r}}{r}\right)_{op} = \left(\frac{\vec{r}}{r}\right)_{op} \cdot \vec{p}_{op} - 2i\hbar \left(\frac{1}{r}\right)_{op} \tag{7.667}$$

$$\vec{p}_{op} \cdot \vec{L}_{op} = \vec{L}_{op} \cdot \vec{p}_{op} = 0 \tag{7.668}$$

$$\vec{p}_{op} \cdot (\vec{L}_{op} \times \vec{p}_{op}) + (\vec{L}_{op} \times \vec{p}_{op}) \cdot \vec{L}_{op} = 2i\hbar \vec{p}_{op}^2 \tag{7.669}$$

which lead to

$$\vec{A}_{op}^2 = \vec{A}_{op} \cdot \vec{A}_{op} = 1 + \frac{2\hat{H}}{Z^2 e^4 m}(\vec{L}_{op}^2 + \hbar^2) \tag{7.670}$$

We now define the two new operators (they are *ladder operators*) by

$$\vec{I}_{op}^{\pm} = \frac{1}{2}\left[\vec{L}_{op} \pm \left(-\frac{2\hat{H}}{Z^2 e^4 m}\right)^{1/2} \vec{A}_{op}\right] \tag{7.671}$$

Using the relations we have derived for $\left[\hat{A}_i, \hat{A}_j\right]$ and $\left[\hat{L}_i, \hat{A}_j\right]$ we have

$$\left[\vec{I}_{op}^{+}, \vec{I}_{op}^{-}\right] = 0 \tag{7.672}$$

which means they have a common eigenbasis. We also have

$$\left[\hat{I}_{op,i}^{\pm}, \hat{I}_{op,j}^{\pm}\right] = i\hbar\varepsilon_{ijk}\hat{I}_{op,k}^{\pm} \tag{7.673}$$

which are the standard angular momentum component commutation relations. Since they each commute with $\hat{H}$, they also have a common eigenbasis with $\hat{H}$.

Therefore, we can find a set of states such that

$$(\vec{I}_{op}^{\pm})^2 |\psi\rangle = i_\pm(i_\pm + 1)\hbar^2 |\psi\rangle \text{ and } \hat{H} |\psi\rangle = E |\psi\rangle \tag{7.674}$$

We can show that $(\vec{I}_{op}^{+})^2 = (\vec{I}_{op}^{-})^2$, which implies that $i_+ = i_-$. We also have(as before)

$$i_+ = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \ldots \tag{7.675}$$

Since $\vec{A}_{op} \cdot \vec{L}_{op} = 0$ we get

$$2\left[(\vec{I}_{op}^{+})^2 + (\vec{I}_{op}^{-})^2\right] + \hbar^2 = -\frac{Z^2 e^4 m}{2\hat{H}} \tag{7.676}$$

$$\left[4i_+(i_+ + 1) + 1\right]\hbar^2 = -\frac{Z^2 e^4 m}{2E} \tag{7.677}$$

$$E = -\frac{Z^2 e^4 m}{2(2i_+ + 1)^2} = -\frac{Z^2 e^4 m}{2n^2} \tag{7.678}$$

where we have set $n = 2i_+ + 1 = 1, 2, 3, 4, 5, \ldots$, which are the correct energy values for hydrogen.

While the energy depends only on the quantum number i_+ (or n) each state has a degeneracy depending on the number of z-component values for each i_+ value. This is

$$(2i_+ + 1)(2i_- + 1) = (2i_+ + 1)^2 = n^2 \tag{7.679}$$

which is the correct degeneracy.

7.6.10 The Deuteron

A deuteron is a bound state of a neutron and a proton. We can consider this system as a single particle with reduced mass

$$\mu = \frac{m_{proton} m_{neutron}}{m_{proton} + m_{neutron}} \approx \frac{m_{proton}}{2} = \frac{m_p}{2} \tag{7.680}$$

moving in a fixed potential $V(r)$, where r is the proton-neutron separation.

As a first approximation, we assume that the nuclear interaction binding the proton and the neutron into a deuteron is a finite square well in 3−dimensions.

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r \geq a \end{cases} \tag{7.681}$$

The physical properties of the deuteron system are: 1. Almost an $\ell = 0$ state (a small admixture of $\ell = 2$ is present). We will assume $\ell = 0$.

2. Only one bound state exists.

3. The depth and range of the potential is such that the deuteron is weakly bound. The energy level in the potential corresponds to the binding energy of the system, where

$$E = \text{ binding energy } = m_{deuteron}c^2 - (m_{proton} + m_{neutron})c^2 < 0 \tag{7.682}$$

Experimentally, it has been found that $E = -2.228\, MeV$.

4. By weakly bound we mean

$$\frac{|E|}{(m_{proton} + m_{neutron})c^2} << 1 \tag{7.683}$$

In fact, for the deuteron we have

$$\frac{|E|}{(m_{proton} + m_{neutron})c^2} \approx 0.001 \tag{7.684}$$

5. This system is so weakly bound that any small decrease in the radius of the well a or small reduction in the depth of the well V_0 would cause the system to break up (no bound state exists).

We derived the solutions for this potential earlier.

$$R(r) = Aj_0(\alpha r) \qquad r < a$$
$$R(r) = Bh_0^{(1)}(i\beta r) \qquad r \geq a$$

where

$$\alpha^2 = \frac{2m}{\hbar^2}(V_0 - |E|) \text{ and } \beta^2 = \frac{2m}{\hbar^2}|E| \tag{7.685}$$

The transcendental equation arising from matching boundary conditions at $r = a$ gave us the equations

$$\eta = -\xi \cot \xi \text{ and } \xi^2 + \eta^2 = \frac{2mV_0a^2}{\hbar^2} \tag{7.686}$$

where

$$\xi = \alpha a \text{ and } \eta = \beta a \tag{7.687}$$

The graphical solution as shown below in the figure below plots

$$\eta = -\xi \cot \xi \text{ and } \eta^2 = \frac{2mV_0a^2}{\hbar^2} - \xi^2 \text{ versus } \xi \tag{7.688}$$

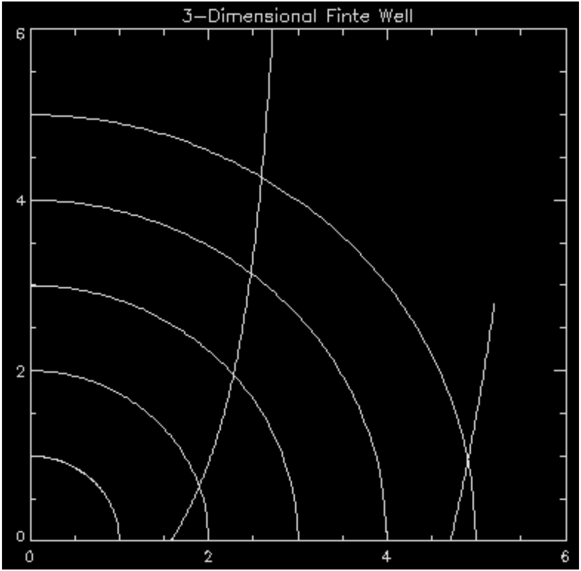

Figure: Deuteron Solution

We found a finite number of bound states for given values of the well parameters. In particular

$$\frac{2mV_0a^2}{\hbar^2} < \left(\frac{\pi}{2}\right)^2 \rightarrow \text{ no solution}$$

$$\frac{2mV_0a^2}{\hbar^2} < \left(\frac{3\pi}{2}\right)^2 \rightarrow \text{ 1 solution}$$

$$\frac{2mV_0a^2}{\hbar^2} < \left(\frac{5\pi}{2}\right)^2 \rightarrow \text{ 2 solutions}$$

For the weakly bound deuteron system we expect that

$$\xi = \frac{\pi}{2} + \varepsilon \quad , \quad \varepsilon \ll \frac{\pi}{2} \tag{7.689}$$

i.e., the radius of the circle is barely large enough to get a single (weakly) bound state.

Substituting into the transcendental equation we get

$$
\begin{aligned}
\eta &= -\left(\frac{\pi}{2}+\varepsilon\right)\cot\left(\frac{\pi}{2}+\varepsilon\right) = -\left(\frac{\pi}{2}+\varepsilon\right)\frac{\cos\left(\frac{\pi}{2}+\varepsilon\right)}{\sin\left(\frac{\pi}{2}+\varepsilon\right)} \\
&= -\left(\frac{\pi}{2}+\varepsilon\right)\frac{\cos\left(\frac{\pi}{2}\right)\cos\left(\varepsilon\right)-\sin\left(\frac{\pi}{2}\right)\sin\left(\varepsilon\right)}{\sin\left(\frac{\pi}{2}\right)\cos\left(\varepsilon\right)+\cos\left(\frac{\pi}{2}\right)\sin\left(\varepsilon\right)} \\
&\approx \left(\frac{\pi}{2}+\varepsilon\right)\frac{\sin\left(\varepsilon\right)}{\cos\left(\varepsilon\right)} \approx \left(\frac{\pi}{2}+\varepsilon\right)\frac{\varepsilon-\frac{\varepsilon^3}{6}}{1-\frac{\varepsilon^2}{2}} \approx \left(\frac{\pi}{2}+\varepsilon\right)\left(\varepsilon-\frac{\varepsilon^3}{6}\right)\left(1+\frac{\varepsilon^2}{2}\right) \\
&\approx \frac{\pi}{2}\varepsilon+(1+\frac{\pi}{4})\varepsilon^2
\end{aligned}
$$

Now substituting into the circle equation we get

$$
\begin{aligned}
\left(\frac{\pi}{2}+\varepsilon\right)^2+\left(\frac{\pi}{2}\varepsilon+(1+\frac{\pi}{4})\varepsilon^2\right)^2 &= \frac{2mV_0a^2}{\hbar^2} \\
\frac{\pi^2}{4}+\pi\varepsilon+\left(1+\frac{\pi^2}{4}\right)\varepsilon^2 &\approx \frac{2mV_0a^2}{\hbar^2} \qquad (7.690)
\end{aligned}
$$

Dropping the small quadratic terms in ε we get

$$\varepsilon \approx \frac{2mV_0a^2}{\pi\hbar^2} - \frac{\pi}{4} \tag{7.691}$$

Therefore,

$$|E| = \frac{\hbar^2}{2ma^2}\eta^2 \approx \frac{\hbar^2\pi^2}{8ma^2}\left(\frac{2mV_0a^2}{\pi\hbar^2} - \frac{\pi}{4}\right)^2 \tag{7.692}$$

A typical value for the range of the interaction is the order of 2 Fermi or $a \approx 2 \times 10^{-13}\ cm$. In order to get $|E| \approx 2.3\, MeV$, we would need a well depth of $V_0 \approx 42\, MeV$ which is reasonable (according to experimentalists).

7.6.11 The Deuteron - Another Way

Experiment (scattering) indicates that instead of a square well (very unrealistic) the actual potential is of the form

$$V(r) = -Ae^{-\frac{r}{a}} \tag{7.693}$$

where

$$A \approx 32MeV \text{ and } a \approx 2.25x10^{-13}cm \tag{7.694}$$

We can solve for this potential ($\ell = 0$ case) exactly using this clever trick I first learned from Hans Bethe at Cornell University.

The radial equation in this case is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left(Ae^{-\frac{r}{a}} - |E|\right)R = 0 \tag{7.695}$$

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left(Ae^{-\frac{r}{a}} - |E|\right)R = 0 \tag{7.696}$$

Now let

$$R(r) = \frac{\chi(r)}{r} \tag{7.697}$$

which implies that

$$\frac{dR}{dr} = \frac{d\left(\frac{\chi}{r}\right)}{dr} = \frac{1}{r}\frac{d\chi}{dr} - \frac{1}{r^2}\chi \tag{7.698}$$

$$\frac{d^2R}{dr^2} = -\frac{2}{r^2}\frac{d\chi}{dr} + \frac{1}{r}\frac{d^2\chi}{dr^2} + \frac{2}{r^3}\chi \tag{7.699}$$

Substitution gives

$$\frac{d^2\chi}{dr^2} + \frac{2m}{\hbar^2}\left(Ae^{-\frac{r}{a}} - |E|\right)\chi = 0 \tag{7.700}$$

We now change the variables using

$$\xi = e^{-\frac{r}{2a}} \rightarrow \frac{d}{dr} = \frac{d\xi}{dr}\frac{d}{d\xi} = -\frac{\xi}{2a}\frac{d}{d\xi}$$

$$\frac{d^2}{dr^2} = \frac{d}{dr}\left(-\frac{\xi}{2a}\frac{d}{d\xi}\right) = \frac{d\xi}{dr}\frac{d}{d\xi}\left(-\frac{\xi}{2a}\frac{d}{d\xi}\right) = \left(\frac{\xi}{2a}\right)^2\frac{d^2}{d\xi^2} + \frac{\xi}{4a^2}\frac{d}{d\xi}$$

We then get the equation

$$\xi^2\frac{d^2\chi}{d\xi^2} + \xi\frac{d\chi}{d\xi} + ((\alpha a)^2\xi^2 - (ka)^2)\chi = 0 \tag{7.701}$$

where

$$(\alpha a)^2 = \frac{2mA}{\hbar^2}a^2 \text{ and } (ka)^2 = \frac{2m\,|E|}{\hbar^2}a^2 \tag{7.702}$$

Now Bessel's equation has the form

$$x^2 \frac{d^2y}{dx^2} + x\frac{dy}{dx} + (x^2 - \nu^2)y = 0 \tag{7.703}$$

Therefore, we have Bessel's equation with a general solution

$$\chi(r) = CJ_{ka}(\alpha a\xi) + BY_{ka}(\alpha a\xi) \tag{7.704}$$

$$R(r) = \frac{1}{r}(CJ_{ka}(\alpha a\xi) + BY_{ka}(\alpha a\xi)) \tag{7.705}$$

As $r \to \infty$, $\xi = e^{-\frac{r}{2a}} \to 0$, which implies we must choose $B = 0$ or the solution diverges.

As $r \to 0$, $\xi = e^{-\frac{r}{2a}} \to 1$, which implies we must have

$$J_{ka}(\alpha a) = 0 \tag{7.706}$$

or the solution diverges. This is then the energy eigenvalue condition. For the values of A and a given earlier we have

$$J_{ka}(6.28) = 0 \tag{7.707}$$

and if we let $|E| = qA$, this becomes

$$J_{1/2}(6.28) = 0 \tag{7.708}$$

Now

$$J_{6.4q}(6.28) = 0 \tag{7.709}$$

Therefore we have

$$6.4q = \frac{1}{2} \to q = \frac{1}{12.8} \to |E| = qA = 2.34\, MeV \tag{7.710}$$

which is an excellent result for the bound state energy of the deuteron. 7.6.12 **Linear Potential**

We now consider a *linear* potential energy function given by

$$V(r) = \alpha r - V_0 \tag{7.711}$$

The Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) - \frac{\vec{L}_{op}^2}{\hbar^2 r^2}\psi\right) + (\alpha r - V_0 - E)\psi = 0 \tag{7.712}$$

Since it is a central potential, we can write

$$\psi = R(r)Y_{\ell m}(\theta, \varphi) \tag{7.713}$$

which implies

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\ell(\ell+1)}{r^2}R\right) + (\alpha r - V_0 - E)R = 0 \tag{7.714}$$

If we let

$$\chi(r) = rR(r) \tag{7.715}$$

we get

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + (\alpha r - V_0 - E + \frac{\hbar^2\ell(\ell+1)}{2mr^2})\chi = 0 \tag{7.716}$$

For $\ell > 0$ there is no closed form solution for this equation and numerical methods must be applied.

For $\ell = 0$, we have

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + (\alpha r - V_0 - E)\chi = 0 \tag{7.717}$$

Now we let

$$\xi = \left(r - \frac{E + V_0}{\alpha}\right)\left(\frac{2m\alpha}{\hbar^2}\right)^{1/3} \tag{7.718}$$

which implies that

$$\begin{aligned}
\frac{d}{dr} &= \frac{d\xi}{dr}\frac{d}{d\xi} = \left(\frac{2m\alpha}{\hbar^2}\right)^{1/3}\frac{d}{d\xi} \\
\frac{d^2}{dr^2} &= \frac{d}{dr}\left(\frac{d\xi}{dr}\frac{d}{d\xi}\right) = \frac{d\xi}{dr}\frac{d}{d\xi}\left(\left(\frac{2m\alpha}{\hbar^2}\right)^{1/3}\frac{d}{d\xi}\right) \\
&= \left(\frac{2m\alpha}{\hbar^2}\right)^{2/3}\frac{d^2}{d\xi^2}
\end{aligned}$$

We then get the equation

$$\frac{d^2\chi}{d\xi^2} - \xi\chi = 0 \tag{7.719}$$

This equation is *not as simple* as it looks. Let us try a series solution of the form

$$\chi(\xi) = \sum_{n=0}^{\infty} a_n \xi^n \tag{7.720}$$

Substitution gives the relations

$$a_2 = 0 \text{ and } a_{m+2} = \frac{a_{m-1}}{(m+2)(m+1)} \tag{7.721}$$

The solution that goes to zero as $\xi \rightarrow \pm\infty$ is then of the form

$$\chi(\xi) = c_1 f(\xi) - c_2 g(\xi) = CAi(\xi) = \text{ Airy function} \tag{7.722}$$

where

$$f(x) = 1 + \frac{1}{3!}x^3 + \frac{1 \cdot 4}{6!}x^6 + \frac{1 \cdot 4 \cdot 7}{9!}x^9 + \ldots \tag{7.7233}$$

$$g(x) = x + \frac{2}{4!}x^4 + \frac{2 \cdot 5}{7!}x^7 + \frac{2 \cdot 5 \cdot 8}{10!}x^{10} + \ldots \tag{7.724}$$

Now to insure that the wave function is normalizable we must also have

$$\chi(\xi(r=0)) = 0 \tag{7.725}$$

$$Ai\left(-\frac{E+V_0}{\alpha}\left(\frac{2m\alpha}{\hbar^2}\right)^{1/3}\right) = 0 \tag{7.726}$$

This says that

$$-\frac{E_n+V_0}{\alpha}\left(\frac{2m\alpha}{\hbar^2}\right)^{1/3} = z_n = n^{th}\text{zeroofAi}(\xi) \tag{7.727}$$

Thus, the allowed energies are given by

$$E_n = -z_n\left(\frac{\hbar^2\alpha^2}{2m}\right)^{1/3} - V_0 \tag{7.728}$$

The first three zeroes are

$$z_1 = -2.3381 \quad , \quad z_2 = -4.0879 \quad , \quad z_3 = -5.5209 \tag{7.729}$$

Programming the numerical method we described earlier for solving the Schrodinger equation allows us to determine E values For simplicity, we have chosen $\hbar = m = \alpha = V_0 = 1$ which gives the $\ell = 0$ energies as

$$E_n = -z_n \left(\frac{1}{2}\right)^{1/3} - 1 = -0.794 z_n - 1 \tag{7.730}$$

The general ℓ equation is (in this case)

$$\frac{d^2\chi}{dr^2} - 2(r - 1 - E + \frac{\ell(\ell+1)}{2r^2})\chi = 0 \tag{7.731}$$

For $\ell = 0$ we theoretically expect the first three energy values 0.856, 2.246 and 3.384 and the program produces the values 0.855750, 2.24460, 3.38160 which is good agreement.

We now use the linear potential to look at quark-quark bound states at low energies.

7.6.13 Modified Linear Potential and Quark Bound States

Over the past three decades the quark model of elementary particles has had many successes. Some experimental results are the following:

1. Free (isolated) quarks have never been observed.
2. At small quark separations *color charge* exhibits behavior similar to that of ordinary charge.
3. Quark-Antiquark pairs form bound states.

We can explain some of the features of these experimental results by describing the quark-quark force by an effective potential of the form

$$V(r) = -\frac{A}{r} + Br \tag{7.732}$$

and using non-relativistic quantum mechanics.

The linear term corresponds to a long-range confining potential that is responsible for the fact that free, isolated quarks have not been observed.

In simple terms, a linear potential of this type means that it costs more and more energy as one of the quarks in a bound system attempts to separate from the other quark. When this extra energy is twice the rest energy of a quark, a new quark-antiquark pair can be produced. So instead of the quark getting free, one of the newly created quarks joins with one of the original quarks to recreate the bound pair (so it looks like nothing has happened) and the other new quark binds with the quark attempting to get free into a new meson. We never see a free quark! A lot of energy has been expended, but the outcome is the creation of a meson rather than the appearance of free quarks.

The other term, which resembles a Coulomb potential, reflects the fact that at small separations the so-called "color charge" forces behave like ordinary charge forces.

The original observations of quark-quark bound states was in 1974, The experiments involved bound states of charmed quarks called charmonium (named after the similar bound states of electrons and positrons called positronium). The observed bound-state energy levels were as shown in the table below:

n	ℓ	$E(GeV)$
1	0	3.097
2	1	3.492
2	0	3.686
3	0	4.105
4	0	4.414

Table: Observed Bound-State Energy Levels

The Schrodinger equation for this potential becomes

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)-\frac{\vec{L}_{op}^2}{\hbar^2 r^2}\psi\right)+(V(r)-E)\psi=0 \quad (7.733)$$

Since it is a central potential, we can write

$$\psi = R(r)Y_{\ell m}(\theta, \varphi) \tag{7.734}$$

which implies

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\ell(\ell+1)}{r^2}R\right) + (V(r) - E)R = 0 \tag{7.735}$$

If we let

$$\chi(r) = rR(r) \tag{7.736}$$

we get

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + (V(r) - E + \frac{\hbar^2\ell(\ell+1)}{2mr^2})\chi = 0 \tag{7.737}$$

or

$$\frac{d^2\chi}{dr^2} - (aE - \frac{\ell(\ell+1)}{r^2} + \frac{b}{r} - cr)\chi = 0 \tag{7.738}$$

We must solve this system numerically. The same program as earlier works again with a modified potential function.

The results for a set of parameters ($a = 0.0385$, $b = 2.026$, $c = 34.65$) chosen to get the right relationship between the levels are shown in the table below:

n	ℓ	$E(calculated)$	$E(rescaled)$
1	0	656	3.1
2	1	838	3.4
2	0	1160	3.6
3	0	1568	4.1
4	0	1916	4.4

Table: Quark Model-Numerical Results

which is a reasonably good result and indicates that validity of the model. The rescaled values are adjusted to correspond to the the earlier table. A more exact parameter search produces almost exact agreement.