14 Theory of Angular Momentum

1. Why do we want to study angular momentum?

2. We need to study the properties of chemical systems, how is angular momentum relevant?

3. Let's consider the Hamiltonian for any molecule. How does it look?

   (a) It includes a term that's called the nuclear kinetic energy: sum of kinetic energy of all nuclei. (Operator)

   (b) It includes the electronic kinetic energy: sum of kinetic energy of all electrons. (Operator)

   (c) Electron-nuclear electrostatic attraction. (Positive and negative charges attract each other.)

   (d) Electron-electron electrostatic repulsion.

   (e) Nuclear-nuclear repulsion.

4. So it is complicated and the full Hamiltonian has many terms. And the problem of time-independent quantum chemistry is to solve for the eigenstates of this Hamiltonian, since these eigenstates determine properties of molecular systems. So we have a problem.

5. What if we consider the simplest molecular system: the hydrogen atom. Well, it has no electron-electron repulsion which turns out to be a big advantage. And it does not contain nuclear-nuclear repulsion either.

6. But even the hydrogen atom turns out to be complicated.

7. So we need a general paradigm to solve these problems.

8. What if we say: We will look for a set of operators that commute with the full Hamiltonian.

9. How does this help us? We learnt earlier that if two operators commute, they have simultaneous eigenstates.

10. Hence if we look for operators that commute with the Hamiltonian, and are simpler than the Hamiltonian, we may solve for eigenstates of these simpler operators first. This way we could partition one big problem (solving for the eigenstates of the full Hamiltonian) into many small problems.

11. This is the approach we will use. OK. So what kind of “simpler” operators do we have in mind that may commute with the Hamiltonian. Well if we were to think classically, we might say...
(a) the momentum of a system is conserved in classical mechanics. So does the momentum
operator commute with the Hamiltonian? Well, it turns out that this is not the case
for molecular systems since the kinetic energy operator is basically the square of the
momentum and it does not commute with the potential due to the uncertainty principle.
(For crystals and other items of interest in the solid and condensed phase it is, however,
possible to use the momentum operator to simplify the problem.)

(b) the angular momentum is conserved in classical mechanics and it turns out that this is
important. We will see later that the total angular momentum of a molecular system
does commute with the Hamiltonian.

(c) but are there other operators that may commute with the Hamiltonian? Consider a sim-
ple water molecule. If I were to rotate the molecule about its dipole axis by 180 degrees,
the so-called C_2 axis, the molecule remains invariant. So, there are these “symmetry
operations” that also commute with the Hamiltonian. Some of you might have come
across “group theory”, which is the theory that deals with finding the symmetry opera-
tions that leave a system invariant. The reason one learns group theory is because these
symmetry operations commute with the Hamiltonian and help simplify the problem
further.

A particle moving with a momentum p and at a distance r from some point in space has an
angular momentum of \( \mathbf{L} = r \times \mathbf{p} \). Angular momentum is a vector with components:

\[
\begin{align*}
L_x &= xp_y - yp_x \\
L_y &= yp_z - zp_y \\
L_z &= zp_x - xp_z
\end{align*}
\]  

(14.36)

Now, we know that

\[
[\hat{x}, \hat{p}_x] = \left[ \hat{x}, -\hbar \frac{\partial}{\partial x} \right] = i\hbar
\]  

(14.37)

which means that the momentum along the x direction does not commute with x. But the momen-
tum along the y or z direction do commute with x since

\[
[x, \hat{p}_y] f(x, y) = \left[ \hat{x}, -\hbar \frac{\partial}{\partial y} \right] f(x, y) = -\hbar \left[ x \frac{\partial f(x, y)}{\partial y} - \frac{\partial \{xf(x, y)\}}{\partial y} \right] = -\hbar f(x, y) \frac{\partial x}{\partial y} = 0
\]  

(14.38)

Hence the following commutator relations hold for angular momentum:

\[
[\mathbf{L}_x, \mathbf{L}_y] = [yp_z - zp_y, zp_x - xp_z]
\]  

\[
= yp_z zp_x - zp_y zp_x - yp_z xp_z + xp_z yp_z
\]
\[zp_y z p_x + z p_x z p_y + z p_y x p_z - x p_z z p_y = -i\hbar y p_x + x p_y \hbar\]
\[= i\hbar L_z\]  \(14.39\)

In a similar fashion:
\[\left[ L_y, L_z \right] = i\hbar L_x\]
\[\left[ L_z, L_x \right] = i\hbar L_y\]  \(14.40\)

**Homework: Prove the last two equations.**

The total angular momentum is:
\[L = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}\]  \(14.41\)

and hence
\[L^2 = L \cdot L = L_x^2 + L_y^2 + L_z^2\]  \(14.42\)

and it is in fact \(L^2\), that commutes with the full Hamiltonian as we will see later.

**Homework: Using the commutator relations for angular momenta show that** \([L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0\). **That is the total angular momentum commutes with each of their components but the components don’t commute with each other.** (Remember here the issue of simultaneous eigenstates.

1. Eigenstates of the angular momentum operators. On account of the commutation relations that we have seen for the angular momentum operators, \(L^2\) should share simultaneous eigenstates (and is hence simultaneously measurable) with each of \(L_x, L_y\) and \(L_z\). But these individual components do not share simultaneous eigenstates with each other. In fact it turns out as we will see later that
\[L^2 \left| l, m \right> = \hbar^2 l(l+1) \left| l, m \right> \quad l = 0, 1, 2, 3, \cdots\]  \(14.43\)

and
\[L_z \left| l, m \right> = \hbar m \left| l, m \right> \quad m = \pm l, \pm(l-1), \pm(l-2), \cdots, 0\]  \(14.44\)

There is degeneracy in the eigenstates of \(L^2\) and this degeneracy is induced by the existence of operators \(L_x, L_y\) and \(L_z\).

2. The kets \(\left| l, m \right>\) are not eigenstates of \(L_x\) and \(L_y\). Why?

3. So in labeling the eigenstates with the \(l\) and \(m\) “quantum numbers” we have picked the \(L^2\) and \(L_z\) operators. **This is just a convention** and we could have equally well picked \(L^2\) and \(L_x\).

4. Angular momentum can be of various kinds. For example, when the electrons occupy an orbital there is an orbital angular momentum. Here the electrons are moving in an “orbital” about a central point (the nucleus) that is fixed relative to the electronic motion. Hence there is an angular momentum associated to the presence of an electron in a given orbital. Note: different orbitals may have different orbital momenta since they may be at different distances from the nucleus and the electrons may have different kinetic energies in different orbitals.
5. In a similar fashion there is an angular momentum associated with the spin of an electron.

6. Hence we can come up with four different useful operators: \( L^2, L_z, S^2, S_z \), the last two are for the total spin angular momentum and the z-component of the spin angular momentum. We want to use \( L \) to represent the orbital angular momentum from now on.

7. Note that in our previous considerations (last couple of pages) we have talked about commutation relations for angular momenta without bias. Hence these commutation relations can hold for both the spin and orbital angular momentum.

8. The commutation relations are particularly interesting. They state that the total angular momentum and the z-component can be specified (or measured) simultaneously with the total angular momentum. But if we do so, we cannot know what the x- and the y-components with certainty. *There exists an uncertainty relation for every pair of operators that do not commute, as we saw when we derived the uncertainty relations.*

9. Here, of course, it is important to state that there is nothing sacrosanct about the z-component and in fact we could have chosen the x-component. We have chosen the z-component to remain consistent with conventions. But the important point is once we chose the z-component we cannot measure the x- and y-components with infinite certainty.

10. Now the Stern Gerlach experiments make complete sense. Once we measure the x-component of the spin angular momentum using the second magnetic field across the x-direction, the z-component was *uncertain*. What is meant by this uncertainty? When we released silver atoms with only the \( S_x^+ \) component (which is an eigenstate of the \( S_x \) angular momentum operator, *but not an eigenstate of the \( S_z \) angular momentum operator* since they do not commute), the expectation value of the \( S_z \) operator included both eigenstates of the \( S_z \) operator. Hence a third magnetic field along the z-direction produced both states.

11. This issue of simultaneous observation of x-, y- and z-components not being possible is *purely quantum mechanical*. The reason for this is the non-commuting nature of the associated operators. In classical mechanics all three components would be measurable simultaneously. Hence something like a Stern-Gerlach experimental shock could never happen for a classical particle. *And again, all this happens only due to the linear vector space nature of the quantum mechanical states. This is of course non-existent in classical mechanics.*

12. Now lets go back to our set of operators \( L^2, L_z, S^2, S_z \) all of which commute with each other (note that the \( L \) and \( S \) operators commute with each other since they act on different variables!!). We will see in the next few lectures that the full Hamiltonian operator for a molecular system \( H \) also commutes with this set operators. Hence the set \{\( H, L^2, L_z, S^2, S_z \)\} form a commuting set of operators and hence have simultaneous eigenstates.

13. In fact we use this commuting set to simplify our approach to quantum mechanics. We obtain eigenstates of each of these operators separately and all of these must be eigenstates of the Hamiltonian and hence are what we call “orbitals”.

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14. But when we use each of these family of operators, as we will see later, we get additional information: the eigenstates of the $L^2$ operator give us orbitals with specific orbital angular momentum quantum number. (The eigenvalue in Eq. (14.43) indicates a quantum number of the eigenstate that tells us about the total orbital angular momentum. For example an $s$-orbital would have $l = 0$. A $p$-orbital would have $l = 1$ and so on.) The eigenstates of the $L_z$ operator in Eq. (14.44) give us the quantum number corresponding to the projection of the orbital angular momentum along the $z$-axis.

15. In a similar fashion the spin quantum numbers are also determined from the eigenstates of the spin angular momentum operators.

16. All these quantum numbers together are used to describe the states of the molecular systems, as we know them today.

17. Hence the family of commuting operators are very useful in getting additional information about the system.

18. The family of commuting operators also simplifies our solution to the Schrödinger Equation. As it turns out it is a lot easier to solve for eigenstates of these five separate operators, instead of the full Hamiltonian operator without information on commuting operators. (Solving 5 smaller problems is a lot easier than solving one huge problem and this is what this commuting set does for us.)

19. In more complicated problems there would be need to “search” for additional operators to obtain more information and to simplify the solution to the Schrödinger Equation. These operators are generally based on molecular symmetry.

20. We will talk about this when we get to “point groups”. As it turns out the point group symmetry of a molecule provides another set of commuting operators that simplifies our problem of solving the Schrödinger Equation even further. (And these simplifications have a way of providing us with more information. :-). Additional quantum numbers. In the case of point groups and symmetry also this is true.)

21. **There is a maximum eigenvalue for the operators $L_z$ and $S_z$.** Here we have used the $J$ to represent both spin and orbital angular momentum. So all the relations we will derive in this section are valid for all kinds of angular momenta. Consider:

$$
\langle l, m | \left( J_x^2 + J_y^2 \right) | l, m \rangle = \langle l, m | J_x^2 | l, m \rangle + \langle l, m | J_y^2 | l, m \rangle
$$

$$
= \langle l, m | J_x J_x | l, m \rangle + \langle l, m | J_y J_y | l, m \rangle
$$

$$
\geq 0 \quad (14.45)
$$

Where we obtain the last inequality by realizing that each term is the magnitude of a vector. For example $\langle l, m | J_x J_x | l, m \rangle$ is magnitude of the vector $J_x | l, m \rangle$. And the magnitude of any vector has to be greater than zero.
Now, \((J_x^2 + J_y^2) = J^2 - J_z^2\). Hence, using Eqs. (14.43) and (14.44)

\[
\langle l, m | (J_x^2 + J_y^2) | l, m \rangle = \langle l, m | (J^2 - J_z^2) | l, m \rangle = \left[ \hbar^2 (l + 1) - \hbar^2 m^2 \right] \langle l, m | l, m \rangle
\]

\[
\geq 0
\]

Therefore,

\[
m^2 \leq l(l + 1)
\] (14.46)

22. In fact we find that \(-l \leq m \leq l\).

23. Now you see why the magnetic quantum number is always bounded by the values for the azimuthal quantum number !

This means, a p-orbital that has \(l = 1\), can only have \(m\) values of +1, 0 and -1.

24. But can we convert one particular eigenstate of the \(J_z\) operator into another eigenstate of the \(J_z\) operator. That is how can we \(|l, m\rangle \rightarrow |l, m'\rangle\).

25. To achieve this in a general manner we will first need to introduce two special operators.

### 14.1 Ladder Operators or Raising and Lowering operators

26. So how do solve for the eigenstates of the angular momentum operators. It is useful to introduce two new operators here that we will represent as

\[
J_{\pm} = J_x \pm iJ_y
\] (14.48)

27. What are the properties of these operators:

\[
[J_{\pm}, J^2] = 0
\] (14.49)

since both \(J_x\) and \(J_y\) commute with \(J^2\) for both the spin and orbital angular momentum. Furthermore,

\[
[J_z, J_{\pm}] = [J_z, (J_x \pm iJ_y)] = [J_z, J_x] \pm i[J_z, J_y] = \pm \hbar J_y \pm i(\mp \hbar J_x) = \pm \hbar J_{\pm}
\] (14.50)

And this is no surprise since \(J_x\) and \(J_y\) do not commute with \(J_z\). Note further that \(J_{+}^\dagger = J_{-}\). That is these operators are not Hermitian.

**Homework:** Derive expressions for \(J_{+}J_{-}, J_{-}J_{+}\) and the commutator \([J_{+}, J_{-}]\).
28. **The ladder operators change the eigenvalue of $J_z$, but not $J^2$.** Let's consider the ket vectors $[J_\pm |l, m\rangle]$. Are these related to eigen-kets of $J_z$? And if so, what is the corresponding eigenvalue?

From Eq. (14.50) we know that $[J_z, J_\pm] = \pm \hbar J_\pm$. Hence

$J_z J_\pm |l, m\rangle - J_\pm J_z |l, m\rangle = \pm \hbar J_\pm |l, m\rangle$  \hspace{1cm} (14.51)

Or,

$J_z J_\pm |l, m\rangle = J_\pm J_z |l, m\rangle \pm \hbar J_\pm |l, m\rangle$

$= \hbar m J_\pm |l, m\rangle \pm \hbar J_\pm |l, m\rangle$

$= \hbar (m \pm 1) [J_\pm |l, m\rangle]$  \hspace{1cm} (14.52)

Hence the ket vectors $[J_\pm |l, m\rangle]$ are eigenstates of $J_z$ with eigenvalue $\hbar (m \pm 1)$. Hence, we may write:

$J_\pm |l, m\rangle \propto |l, m \pm 1\rangle$  \hspace{1cm} (14.53)

This is the reason why the operators are called “raising” or “lowering” operators. They raise or lower the magnetic quantum number by 1.

**Homework:** Using Eq. (14.49), evaluate $J^2 J_\pm |l, m\rangle$ in a similar fashion as what we have done above for $J_z$. Comment on your result with regards to the eigenvalue of the $J^2$ operator in Eq. (14.43).

29. Equation (14.53) is to be rationalized with Eq. (14.47). Since according to Eq. (14.47), $m$ has a maximum and minimum value that depends on $l$, the $J_+$ operator cannot keep “raising” $m$ as allowed by Eq. (14.53). In a similar fashion $J_-$ cannot be allowed to keep “lowering” $m$ as allowed by Eq. (14.53). It turns out that this is not an issue and is completely taken care of by the proportionality constant in Eq. (14.53), which is what we will discuss next. Let's say:

$J_\pm |l, m\rangle = C^{l,m}_\pm |l, m \pm 1\rangle$  \hspace{1cm} (14.54)

We would like to know what $C^{l,m}_\pm$ is. Using the identity:

$J_- J_+ = J^2 - J_z^2 - \hbar J_z$  \hspace{1cm} (14.55)

(Note: by now you must have proved this as homework for the problem following Eq. (14.50).) We can then write:

$\langle l, m | J_- J_+ | l, m \rangle = \langle l, m | J^2 - J_z^2 - \hbar J_z | l, m \rangle$

$= \left[ \hbar^2 l(l + 1) - \hbar^2 m^2 - \hbar^2 m \right] \langle l, m | l, m \rangle$

$= \left[ \hbar^2 l(l + 1) - \hbar^2 m (m + 1) \right]$

$= \left[ C^{l,m}_\pm \right]^2$  \hspace{1cm} (14.56)
(Note: \( \langle l, m | J_+ | l, m \rangle = \langle l, m | J_+^\dagger J_+ | l, m \rangle = \left[ C_{l,m}^d \right]^2 \) since \( |l, m\rangle \) are assumed to be normalized.

Note, from Eq. (14.56) that when \( m = l \), \( C_{l,m}^d = 0 \) Therefore,

\[
J_+ | l, m = l \rangle = 0
\] (14.57)

That is the operator \( J_+ \) is a raising operator, but does not raise the value of \( m \) any further than its maximum value \( l \).

Similarly,

\[
J_+ J_- = J^2 - J_z^2 + \hbar J_z
\] (14.58)

(which again follows as part of your homework assignment for the problem following Eq. (14.50)) and hence

\[
\langle l, m | J_+ J_- | l, m \rangle = \langle l, m | J_-^\dagger J_- | l, m \rangle = \left[ C_{l,m}^d \right]^2
\] (14.59)

where again \( \langle l, m | J_+ J_- | l, m \rangle = \langle l, m | J_-^\dagger J_- | l, m \rangle = \left[ C_{l,m}^d \right]^2 \). Hence

\[
C_{l,m}^d = \sqrt{\hbar^2 l(l + 1) - \hbar^2 m (m - 1)}
\] (14.60)

and when \( m = -l \), \( C_{l,m}^d = 0 \). And as from the operator \( J_+ \), the lowering operator \( J_- \) does not lower the value of \( m \) below its minimum value of \( m = -l \).

We summarize by stating

\[
C_{l,m}^d = \sqrt{\hbar^2 l(l + 1) - \hbar^2 m (m + 1)}
\] (14.61)

30. So we have learned the following about angular momentum:

(a) Angular momentum is a vector that has three components.

(b) But all of these components cannot be measured simultaneously. The corresponding operators do not commute (See Eqs. (14.39) and (14.40)).

(c) But all three components commute with the total angular momentum squared (\( J^2 \)).

(d) Hence we choose two operators \{\( J^2, J_z \)\} to form a commuting set of operators.

(e) A similar set of commuting operators exists for both orbital angular momentum and spin angular momentum.

(f) We noted (but did not prove) that the family of four \{\( L^2, L_z, S^2, S_z \)\} commute with the total Hamiltonian \( H \).
(g) We rationalized the Stern-Gerlach experiments using our commutation relations between the angular momentum operators. We noted based on our treatment of uncertainty that there must be a similar uncertainty relation that holds for the angular momentum operators since they do not commute. This uncertainty allowed us to understand the Stern-Gerlach experiments better.

(h) This uncertainty and the commutation relations are entirely due to the “linear vector space” nature of a state vector (or ket vector in quantum mechanics). Non-existent concept in classical mechanics.

(i) We also noted that like the angular momentum operators \( \{L_z, L^2, S_z, S^2\} \) that commute with the total Hamiltonian, in more serious problems, we could “search” for other operators that also commute with the total Hamiltonian. These “other” operators are generally given to us by molecular symmetry.

(j) The angular momentum operators provide us with additional quantum numbers to quantify the system. In particular we talked about the azimuthal quantum number and the magnetic quantum number. But due to the similarity of the \( L \) and \( S \) operators we can see that there are similar spin-angular momentum quantum numbers \( s \) and \( m_s \).

(k) We introduced two new operators: the raising and lowering operators.

(l) The raising operator \( |l, m\rangle \rightarrow |l, m + 1\rangle \), while the lowering operator \( |l, m\rangle \rightarrow |l, m - 1\rangle \).  

(m) Using the form of the raising and lowering operators we obtained that the magnetic quantum numbers are bounded by the azimuthal quantum numbers \(-l \leq m \leq l\). This relation also holds for \( s \) and \( m_s \).

(n) Hence the quantum number \( l \) and \( s \) can either be integer or half integer. Only integers and half-integers will allow \(-l \leq m \leq l\) and for the spin quantum number \(-s \leq m_s \leq s\). The spin half particles are called fermions and the particles with integral spin are called bosons.

14.2 Coupling of angular momentum operators: The Clebsch Gordon coefficients and the Wigner 3j symbols

31. In the previous section we have talked about the the orbital angular momentum and the spin angular momentum and how these commute with the total Hamiltonian.

32. There is a special case where this is not true: \( L - S \) coupling. What happens in this case is that the Hamiltonian operator “couples” the orbital angular momentum with the spin angular momentum and then it turns out to that these individual angular momentum operators do not commute with the total Hamiltonian.

33. In such case is there an angular momentum operator that does commute with the total Hamiltonian?
34. Turns out yes and this will be the subject of the current section.

35. Turns out the total angular momentum (which is sum of the the orbital angular momentum and the spin angular momentum) does commute with the total Hamiltonian in such cases.

36. We will study the general problem here by constructing a new angular momentum operator in the following fashion:

\[ J = \sum_i J(i) \]  

(14.62)

37. Another important problem where this is applicable is NMR. In NMR the nuclear spin interacts with the external magnetic field (you see it is similar to Stern-Gerlach, the only difference being that it is the electronic spin that interacts with the external magnetic field) and when there are many nuclei, the “total” angular momentum is responsible for the chemical shifts. In addition, some neighboring orbital angular momenta also contribute, thus the environmental dependence in NMR.

38. Let's consider two angular momentum operators: \{J_1, J_2\}. These may correspond to the two spin angular momentum of two separate electrons. Or it may correspond to orbital angular momentum of two separate electrons. Or one orbital angular momentum and one spin angular momentum (for L-S coupling). Here we want to see how (if they couple) they add up.

39. We have seen that the set \{J_1^2, J_{1z}\} is a commuting set of operators. Similarly, the set \{J_2^2, J_{2z}\} is also a commuting set of operators. Furthermore, since \(J_1\) and \(J_2\) act on different particles then all the operators in the set \{J_1^2, J_{1z}, J_2^2, J_{2z}\} commute with each other.

40. However, the operators \{J_1^2, J_{1z}, J_2^2, J_{2z}\} do not all commute with the total Hamiltonian, since the total Hamiltonian may contain terms that couple \(J_1\) and \(J_2\) (such as \(J_1 \cdot J_2\) in L-S coupling).

41. Now let's consider the total angular momentum operator:

\[ J = J_1 + J_2 \]  

(14.63)

and the z-component of the total angular momentum: \(J_z\).

42. The operators: \{J^2, J_z, J_1^2, J_2^2\} form a commuting set of operators as well.

43. Why? \(J^2\) and \(J_z\) certainly commute with each other as we have seen earlier for general angular momentum operators. Using Eq. (14.63), since \(J_1\) and \(J_2\) act on different particles they commute. Hence \(J^2, J_1^2\) and \(J_2^2\) commute. Since \(J_z = J_{1z} + J_{2z}\), this operator commutes with \(J^2, J_1^2\) and \(J_2^2\) as well.
44. **Homework:** Show that $[J^2, J_z] = 0$. Note that $J^2 = J_1^2 + J_2^2 + 2J_1 \cdot J_2$ from Eq. (14.63) (since $J_1$ and $J_2$ commute since they act on different particles). Note further that $J_1 \cdot J_2$ above is a dot product of two vectors (since $J_1$ and $J_2$ are vectors!!). Use $J_1 \cdot J_2 = J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z}$.

45. **Homework:** As a special case of your derivation above you will see that $[J^2, J_1 z] \neq 0$ and $[J^2, J_2 z] \neq 0$. Show this.

46. Since $\{J^2, J_z, J_1^2, J_2^2\}$ form a commuting set of operators, we can quantify the system using quantum numbers of $\{J_1^2, J_1 z, J_2^2, J_2 z\}$, i.e., $|j_1, m_{j_1}, j_2, m_{j_2}\rangle$, or quantum numbers of $\{J^2, J_z, J_1^2, J_2^2\}$, i.e., $|J, M, j_1, j_2\rangle$. Both representations are equally good. They are both a complete set of ket-vectors.

47. However, for the problem at hand, only the total angular momentum commutes with the Hamiltonian and not the individual angular momenta, $J_1$ and $J_2$. Remember, we are talking about cases like L-S coupling!. Hence it the ket $|J, M, j_1, j_2\rangle$ that is interesting to us. Is there a way we can convert the ket $|j_1, m_{j_1}, j_2, m_{j_2}\rangle$ to the ket $|J, M, j_1, j_2\rangle$?

48. If they are both complete we must be able to switch from one to the other (through a simple rotation!!)

49. Because $|J, M, j_1, j_2\rangle = |J, M, j_1, j_2\rangle = \sum_{m_{j_1}, m_{j_2}} |j_1, m_{j_1}, j_2, m_{j_2}\rangle \langle j_1, m_{j_1}, j_2, m_{j_2}| J, M, j_1, j_2\rangle$

\[ (14.64) \]

But note now, the sum is only over $m_{j_1}$ and $m_{j_2}$. Because $j_1$ and $j_2$ are fixed on the left hand side.

50. The terms $\langle j_1, m_{j_1}, j_2, m_{j_2}| J, M, j_1, j_2\rangle$ are known as the Clebsch-Gordon coefficients. These are unitary transformations (complex rotation operations) that take you from the $|j_1, m_{j_1}, j_2, m_{j_2}\rangle$ basis to the $|J, M, j_1, j_2\rangle$ basis.

51. There are various conventions to represent the Clebsch-Gordon coefficients. One other notation is to use the Wigner-3j symbols:

\[ \langle j_1, m_{j_1}, j_2, m_{j_2}| J, M, j_1, j_2\rangle \propto \left( \begin{array}{ccc} j_1 & j_2 & J \\ m_{j_1} & m_{j_2} & M \end{array} \right) \]  

\[ (14.65) \]

52. The Clebsch-Gordon coefficients are very useful in deriving “term symbols” of molecular systems.
But first we will try to understand how the value \( J \) and \( M \) are related to \( j_1, j_2, m_{j_1}, \) and \( m_{j_2} \). That is for a given, \( j_1, j_2, m_{j_1}, \) and \( m_{j_2} \) what are the values \( J \) and \( M \) can have?

We make two important observations:

(a) Since the operators \( J_1 \) and \( J_2 \) are vectors and add up to give \( J \), it must be true that the total angular momentum quantum number obeys: \( j_1 + j_2 \geq J \geq |j_1 - j_2| \).

(b) \( J \) can only change by integer values inside this range (for reasons unknown to us at this point). That is \( J \) can only have values: \( j_1 + j_2, j_1 + j_2 - 1, \ldots, 1 + |j_1 - j_2|, |j_1 - j_2| \). (The reason for \( J \) being allowed only these specific values that differ by integer amounts comes from the solution of angular momentum differential equation which will be treated during the next week.)

(c) For each value of \( J \) in this range, \( M \) being the corresponding total magnetic quantum number takes on values \(-J \leq M \leq J\). Again \( M \) changes only by integer amounts inside this range as is required by the ladder operators \( J_\pm \).

An extremely good treatment of angular momentum can be found in Chapter 3 of Sakurai. I recommend that you go through it.

Now an example of how all this can be used to derive “term symbols”. (You may also look at Section 11.5 of Levine.)

Consider the carbon atom in the following excited electronic configuration: \( 1s^2, 2s^2, 2p^1, 3d^1 \).

The s-orbital has \( l = 0 \), p- has \( l = 1 \) and d- has \( l = 2 \).

Hence the two orbitals that have non-zero orbital angular momentum have \( l \) values of 1 and 2.

The total angular momentum for Carbon commutes with the Hamiltonian for Carbon, but the individual angular momenta of the s, p and d orbitals do not necessarily commute with the full Hamiltonian of Carbon. Hence there is a need to construct kets, that are eigenstates of the total angular momentum (which commutes with the Hamiltonian).

The total orbital angular momentum can have values, \( 2 + 1, \ldots, 2 - 1 \). (That is 1, 2, 3.)

There are two unpaired electrons and four paired electrons. The four pair electrons have zero spin angular momentum.

The two unpaired electrons have spin angular momentum of \( \frac{1}{2} \). Hence the “total” spin angular momentum is \( \frac{1}{2} + \frac{1}{2}, \ldots, \frac{1}{2} - \frac{1}{2} \). (That is 0 and 1.)

Hence the total orbital angular momentum can have values 1,2,3. The total spin angular momentum can have values 0 and 1.
65. This gives the terms symbols of the states accessible to the system as: \(2S+1L : 3P, 1P, 3D, 1D, 3F, 1F\).

66. Note: In cases where L-S coupling is involved the “term” symbols include the total angular momentum value as well: \(2S+1L_J\) (where \(J\) is the “total” angular momentum=orbital+spin: \(L + S \geq J \geq |L - S|\)). So, this case the \(3P\) state would be written as: \(3P_2, 3P_1\) and \(3P_0\).

67. **Degeneracies**

   (a) There are degeneracies associated with these term symbols as well.

   (b) We already know that for a total angular momentum \(L\), \(-L \leq m_L \leq L\). That is the magnetic quantum number takes on values in this range.

   (c) Hence a state with total angular momentum \(L\) is \((2L+1)\) fold degenerate. (Because \(m_L\) can have \((2L+1)\) values in \(-L \leq m_L \leq L\).)

   (d) So let's consider the degeneracy of the \(3P\) state that we considered above. \(P\) implies at total orbital angular momentum quantum number of 1, which has degeneracy \((2L+1)=2 \times 1+1=3\). (Note these degeneracies are labeled using the total angular momentum(=orbital+spin) quantum number as seen in the last slide.)

   (e) The total spin angular momentum quantum number in the \(3P\) state is 1 which has degeneracy of 3.

   (f) Therefore the total degeneracy of the \(3P\) state is \(3 \times 3=9\).

68. The Clebsch-Gordon coefficients provide us with all this information !!

69. Let's revisit the carbon atom term symbols we did last time. But now let's look at the \(1s^2, 2s^2, 2p^1, 4f^1\) configuration just to get some practice and perhaps add a couple of new things.

70. The two unpaired electrons are in the \(p\) and \(f\) levels that have orbital angular momentum quantum numbers 1 and 3.

71. Thus the total orbital angular momentum can have values, 2, 3, 4.

72. the total spin angular momentum can have values 0, 1. (Two electrons.)

73. Our term symbols have the form \(2S+1L_J\), where \(J = L + S\).

74. Let's forget about \(J\) for now (we will use it later).

75. The available states for the system have term symbols: \(1D (L = 2, S = 0), 3D (L = 2, S = 1), 1F (L = 3, S = 0), 3F (L = 3, S = 1), 1G (L = 4, S = 0), 3G (L = 4, S = 1)\).

76. **Hund's rule:** So what else do we gain from these term symbols? Hund’s rule states that the lowest energy state is the one that has the maximum \(S\) value. And if two states have the same \(S\) value then the one that has the higher \(L\) value has lower energy. Based on this we can state that the energy of the above states are arranged in the following sequence: \(3G < 3F < 3D < 1G < 1F < 1D\).
77. What are the degeneracies of each of these states? Remember, the degeneracy of a state $2S + 1L$ is $(2L+1) 	imes (2S+1)$.

78. Hence the degeneracies are: $^1D (5)$, $^3D (15)$, $^1F (7)$, $^3F (21)$, $^1G (9)$, $^3G (27)$.

79. How do we differentiate between the degenerate states? The $^3G$ has 27 degenerate states how do these differ from each other? This is where we need the total $J$ quantum number.

80. For the $^3G$ state, the total $J$ quantum number is 5, $\cdots$, 3. ($L=4$, $S=1$.) The $J = 5$ state is 11-fold degenerate $(2J+1)$ with $J_z$ values $-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5$. The $J = 4$ state is 9-fold degenerate and the $J = 3$ state is 7-fold degenerate. This explains the total degeneracy of 27.

81. Note that each of the 27 states is labeled using the total $J$ and $J_z$ quantum numbers.

82. The state $^3G$ itself is labeled using the $L$ and $S$ quantum numbers.

83. This each state described above is essentially a $|J, J_z, L, S\rangle$ state.

84. **Homework:** Write down the term symbols for all the states accessible to the carbon atom with configuration: 1s$^2$, 2s$^2$, 2p$^1$, 3p$^1$. What are the degeneracies for each state? Distinguish the degeneracies by using total $J$ values.

### 14.3 More on Clebsch Gordon coefficients

85. We spoke about how Clebsch Gordon coefficients take us from $|j_1, m_{j_1}, j_2, m_{j_2}\rangle \rightarrow |J, M, j_1, j_2\rangle$. Here $j_1$ and $j_2$ are the angular momentum quantum numbers of two different angular momenta (for example, two different orbital angular momenta or one orbital angular momentum and one spin angular momentum or two different spin angular momenta).

86. Thus the Clebsch-Gordon coefficients allow us to go from one framework where things are defined in terms of the individual parts of a system to a framework of the full system.

87. Let us take an example to see how this is done.

88. Consider two electrons: there are four possible states of the system which we will represent as $|+, +\rangle$, $|+, -\rangle$, $|-+, \rangle$, $|-,-\rangle$. Here the first sign indicates the direction of spin on the first electron while the second sign represents the spin on the second electron.

89. (This problem has many applications: for example, spin-spin coupling in ferro-magnets, NMR, etc.)

90. Note that each of these states is an eigenstate of the set of operators $\{S_1^2, S_{1z}, S_2^2, S_{2z}\}$.

91. But now, if these spins (or angular momenta) are coupled by the Hamiltonian...
92. How do we get the states that are eigenstates of \( \{S^2, S_z, S_1^2, S_2^2\} \), that is the total spin operator \( S = S_1 + S_2 \), and the z-component of the total spin operator \( S_z \) along with \( S_1^2 \) and \( S_2^2 \).

93. We recall that the total spin angular momentum can have eigenvalues ranging from \((S_1 + S_2)\) to \(|S_1 - S_2|\). Since \( S_1 = S_2 = 1/2 \) (electrons), the total spin angular momentum quantum number can be either 1 or 0.

94. For each value of the total spin angular momentum quantum number, its z-component can go from \(-S\) to \(+S\). Hence the four eigenstates of \( \{S^2, S_z, S_1^2, S_2^2\} \) are

\[
\begin{align*}
|S = 1, S_z = 1\rangle &= |+, +\rangle \\
|S = 1, S_z = 0\rangle &= \frac{1}{\sqrt{2}} (|+, -\rangle + |-, +\rangle) \\
|S = 1, S_z = -1\rangle &= |-, -\rangle \\
|S = 0, S_z = 0\rangle &= \frac{1}{\sqrt{2}} (|+, -\rangle - |-, +\rangle)
\end{align*}
\]

(14.66)

95. This completes a simple illustration of how we can go from \(|j_1, m_{j_1}, j_2, m_{j_2}\rangle \rightarrow |J, M, j_1, j_2\rangle \). The Clebsch-Gordon coefficients are the coefficients of this transformation.

96. The term symbols are the symbols used to denote the states thus obtained.

97. These new states are interesting to us since they turn out to be eigenstates of total Hamiltonian for a molecular system. Hence there is a need to denote them in some convenient fashion. (Three-dimensional functions, do not provide as much information in an easy to understand manner.) For example by looking at the term-symbols we know the total spin, the total orbital angular momentum and even the total angular momentum (orbital+spin). This is a lot of information for a very short hand notation.
14.4 When would you need Angular momentum addition and Clebsch-Gordon coefficients?

- We have seen how one can transform eigenstates of the operators \( \{J_1^2, J_{1z}, J_2^2, J_{2z}\} \) to eigenstates of the operators \( \{J^2, J_z, J_1^2, J_2^2\} \).

- That is, we have concerned ourselves with how one might transform the \(|j_1, m_{j1}, j_2, m_{j2}\rangle\) states to \(|J, M, j_1, j_2\rangle\).

- As noted in the section dealing with angular momentum theory, the operators \(J_i\) above are generic angular momentum operators and may represent spin-, orbital- or any combination including L-S coupling.

- The reasons behind why we need to worry about angular momentum addition have been discussed in detail earlier in the notes, but we will restate it here for easier reference.

- The total Hamiltonian of a system does depend on the angular momentum. We will see this is some detail when we discuss hydrogen atom. Essentially, the angular momentum adds a term to the total Hamiltonian that reflects angular kinetic energy.

- If the physical systems that are depicted by \(J_1\) and \(J_2\) do not interact with each other then the system Hamiltonian contains angular momentum as a sum of the individual parts: \(H = A + J_1^2 + J_2^2\), where \(A\) is an operator that does not depend on angular motion.

  - In this case, \(\{H, J_1^2, J_{1z}, J_2^2, J_{2z}\}\) commute with each other and the states \(|j_1, m_{j1}, j_2, m_{j2}\rangle\) may also be considered eigenstates of the system Hamiltonian.

- If the physical systems that are depicted by \(J_1\) and \(J_2\) do interact with each other then the system Hamiltonian contains the total angular momentum, \(J = J_1 + J_2\). That is \(H = A + J^2\), which will lead to a coupling term \(J_1 \cdot J_2\).

  - In this case, \(\{H, J^2, J_z, J_1^2, J_2^2\}\) commute with each other and the states \(|J, M, j_1, j_2\rangle\) may also be considered eigenstates of the system Hamiltonian.

  - Here the Clebsch-Gordon coefficients provide us an approach to transform from the convenient \(|j_1, m_{j1}, j_2, m_{j2}\rangle\) basis to the \(|J, M, j_1, j_2\rangle\) basis.