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. Lets consider the Hamiltonian for any molecule. How does it look?

   (a) It includes a term thats 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 simple 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 operations 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 $\mathbf{p}$ and at a distance $\mathbf{r}$ from some point in space has an angular momentum of $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. Angular momentum is a vector with components:

$$\begin{aligned}
\mathbf{L}_z &= xp_y - yp_x \\
\mathbf{L}_x &= yp_z - zp_y \\
\mathbf{L}_y &= zp_x - xp_z
\end{aligned}$$

(14.36)

Now, we know that

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

(14.37)

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

$$\begin{aligned}
[x, \hat{p}_y]\, f(x,y) &= \left[\hat{x}, -\imath\hbar\frac{\partial}{\partial y}\right] f(x,y) \\
&= -\imath\hbar\left[x\frac{\partial f(x,y)}{\partial y} - \frac{\partial\{xf(x,y)\}}{\partial y}\right] \\
&= -\imath\hbar f(x,y)\frac{\partial x}{\partial y} = 0
\end{aligned}$$

(14.38)

Hence the following commutator relations hold for angular momentum:

$$\begin{aligned}
[\mathbf{L}_x, \mathbf{L}_y] &= [yp_z - zp_y, zp_x - xp_z] \\
&= yp_z zp_x - zp_x yp_z - yp_z xp_z + xp_z yp_z -
\end{aligned}$$

$$zp_y zp_x + zp_x zp_y + zp_y xp_z - xp_z zp_y$$
$$= -\imath\hbar y p_x + x p_y \imath\hbar$$
$$= \imath\hbar \mathbf{L}_z \qquad (14.39)$$

In a similar fashion:

$$\begin{aligned} [\mathbf{L}_y, \mathbf{L}_z] &= \imath\hbar\mathbf{L}_x \\ [\mathbf{L}_z, \mathbf{L}_x] &= \imath\hbar\mathbf{L}_y \end{aligned} \qquad (14.40)$$

Homework: Prove the last two equations.

The total angular momentum is:

$$\mathbf{L} = \mathbf{L}_x \hat{i} + \mathbf{L}_y \hat{j} + \mathbf{L}_z \hat{k} \qquad (14.41)$$

and hence

$$\mathbf{L}^2 = \mathbf{L}\cdot\mathbf{L} = \mathbf{L}_x{}^2 + \mathbf{L}_y{}^2 + \mathbf{L}_z{}^2 \qquad (14.42)$$

and it is in fact $\mathbf{L}^2$, that commutes with the full Hamiltonian as we will see later.

Homework: Using the commutator relations for angular momenta show that $[\mathbf{L}^2, \mathbf{L}_x] = [\mathbf{L}^2, \mathbf{L}_y] = [\mathbf{L}^2, \mathbf{L}_z] = 0$. 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, $\mathbf{L}^2$ should share simultaneous eigenstates (and is hence simultaneously measurable) with each of $\mathbf{L}_x$, $\mathbf{L}_y$ and $\mathbf{L}_z$. But these individual components do not share simultaneous eigenstates with each other. In fact it turns out as we will see later that

$$\mathbf{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle \quad l = 0, 1, 2, 3, \cdots \qquad (14.43)$$

and

$$\mathbf{L}_z |l, m\rangle = \hbar m |l, m\rangle \quad m = \pm l, \pm(l-1), \pm(l-2), \cdots, 0 \qquad (14.44)$$

There is degeneracy in the eigenstates of $\mathbf{L}^2$ and this degeneracy is induced by the existence of operators $\mathbf{L}_x$, $\mathbf{L}_y$ and $\mathbf{L}_z$.

2. The kets $|l, m\rangle$ are not eigenstates of $\mathbf{L}_x$ and $\mathbf{L}_y$. Why?

3. So in labeling the eigenstates with the l and m "quantum numbers" we have picked the $\mathbf{L}^2$ and $\mathbf{L}_z$ operators. *This is just a convention* and we could have equally well picked $\mathbf{L}^2$ and $\mathbf{L}_x$.

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: $\mathbf{L}^2$, $\mathbf{L}_z$, $\mathbf{S}^2$, $\mathbf{S}_z$, the last two are for the total spin angular momentum and the z-component of the spin angular momentum. We want to use $\mathbf{L}$ 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 $\mathbf{L}^2$, $\mathbf{L}_z$, $\mathbf{S}^2$, $\mathbf{S}_z$ all of which commute with each other (note that the $\mathbf{L}$ and $\mathbf{S}$ 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 $\mathbf{H}$ also commutes with this set operators. Hence the set $\{\mathbf{H}, \mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2, \mathbf{S}_z\}$ 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".

14. But when we use each of these family of operators, as we will see later, we get additional information: the eigenstates of the $\mathbf{L}^2$ 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 $\mathbf{L}_z$ 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 $\mathbf{L}_z$ and $\mathbf{S}_z$.** Here we have used the $\mathbf{J}$ 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:

$$\begin{aligned}
\langle l, m| \left(\mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 \right) |l, m\rangle &= \langle l, m| \mathbf{J}_x{}^2 |l, m\rangle + \langle l, m| \mathbf{J}_y{}^2 |l, m\rangle \\
&= \langle l, m| \mathbf{J}_x \mathbf{J}_x |l, m\rangle + \langle l, m| \mathbf{J}_y \mathbf{J}_y |l, m\rangle \\
&\geq 0 \quad\quad\quad (14.45)
\end{aligned}$$

Where we obtain the last inequality by realizing that each term is the magnitude of a vector. For example $\langle l, m| \mathbf{J}_x \mathbf{J}_x |l, m\rangle$ is magnitude of the vector $\mathbf{J}_x |l, m\rangle$. And the magnitude of any vector has to be greater than zero.

Now, $\left(\mathbf{J}_x{}^2 + \mathbf{J}_y{}^2\right) = \mathbf{J}^2 - \mathbf{J}_z{}^2$. Hence, using Eqs. (14.43) and (14.44)

$$
\begin{aligned}
\langle l, m| \left(\mathbf{J}_x{}^2 + \mathbf{J}_y{}^2\right) |l, m\rangle &= \langle l, m| \left(\mathbf{J}^2 - \mathbf{J}_z{}^2\right) |l, m\rangle \\
&= \left[\hbar^2 l(l+1) - \hbar^2 m^2\right] \langle l, m| \, l, m\rangle \\
&= \hbar^2 l(l+1) - \hbar^2 m^2 \\
&\geq 0
\end{aligned}
\tag{14.46}
$$

Therefore,

$$
m^2 \leq l(l+1)
\tag{14.47}
$$

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 $\mathbf{J}_z$ operator into another eigenstate of the $\mathbf{J}_z$ 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

$$
\mathbf{J}_\pm = \mathbf{J}_x \pm \imath \mathbf{J}_y
\tag{14.48}
$$

27. What are the properties of these operators:

$$
\left[\mathbf{J}_\pm, \mathbf{J}^2\right] = 0
\tag{14.49}
$$

since both $\mathbf{J}_x$ and $\mathbf{J}_y$ commute with $\mathbf{J}^2$ for both the spin and orbital angular momentum. Furthermore,

$$
\begin{aligned}
[\mathbf{J}_z, \mathbf{J}_\pm] &= [\mathbf{J}_z, (\mathbf{J}_x \pm \imath \mathbf{J}_y)] \\
&= [\mathbf{J}_z, \mathbf{J}_x] \pm \imath [\mathbf{J}_z, \mathbf{J}_y] \\
&= \imath \hbar \mathbf{J}_y \pm \imath (-\imath \hbar \mathbf{J}_x) \\
&= \pm \hbar \mathbf{J}_\pm
\end{aligned}
\tag{14.50}
$$

And this is no surprise since $\mathbf{J}_x$ and $\mathbf{J}_y$ do not commute with $\mathbf{J}_z$. Note further that $\mathbf{J}_+{}^\dagger = \mathbf{J}_-$. That is these operators are not Hermitian.

Homework: Derive expressions for $\mathbf{J}_+\mathbf{J}_-$, $\mathbf{J}_-\mathbf{J}_+$ and the commutator $[\mathbf{J}_+, \mathbf{J}_-]$.

28. **The ladder operators change the eigenvalue of $\mathbf{J}_z$, but not $\mathbf{J}^2$.** Lets consider the *ket* vectors $[\mathbf{J}_\pm \, |l, m\rangle]$. Are these related to eigen-kets of $\mathbf{J}_z$? And if so what is the corresponding eigenvalue?

    From Eq. (14.50) we know that $[\mathbf{J}_z, \mathbf{J}_\pm] = \pm\hbar\mathbf{J}_\pm$. Hence

    $$\mathbf{J}_z\mathbf{J}_\pm \, |l, m\rangle - \mathbf{J}_\pm\mathbf{J}_z \, |l, m\rangle = \pm\hbar\mathbf{J}_\pm \, |l, m\rangle \tag{14.51}$$

    Or,

    $$\begin{aligned}
    \mathbf{J}_z\mathbf{J}_\pm \, |l, m\rangle &= \mathbf{J}_\pm\mathbf{J}_z \, |l, m\rangle \pm \hbar\mathbf{J}_\pm \, |l, m\rangle \\
    &= \hbar m\mathbf{J}_\pm \, |l, m\rangle \pm \hbar\mathbf{J}_\pm \, |l, m\rangle \\
    &= \hbar \, (m \pm 1) \, [\mathbf{J}_\pm \, |l, m\rangle]
    \end{aligned} \tag{14.52}$$

    Hence the *ket* vectors $[\mathbf{J}_\pm \, |l, m\rangle]$ are eigenstates of $\mathbf{J}_z$ with eigenvalue $\hbar \, (m \pm 1)$. Hence, we may write:

    $$\mathbf{J}_\pm \, |l, m\rangle \propto |l, m \pm 1\rangle \tag{14.53}$$

    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 $\mathbf{J}^2\mathbf{J}_\pm \, |l, m\rangle$ in a similar fashion as what we have done above for $\mathbf{J}_z$. Comment on your result with regards to the eigenvalue of the $\mathbf{J}^2$ 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 $\mathbf{J}_+$ operator cannot keep "raising" m as allowed by Eq. (14.53). In a similar fashion $\mathbf{J}_-$ 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. Lets say:

    $$\mathbf{J}_\pm \, |l, m\rangle = C_\pm^{l,m} \, |l, m \pm 1\rangle \tag{14.54}$$

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

    $$\mathbf{J}_-\mathbf{J}_+ = \mathbf{J}^2 - \mathbf{J}_z{}^2 - \hbar\mathbf{J}_z \tag{14.55}$$

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

    $$\begin{aligned}
    \langle l, m| \, \mathbf{J}_-\mathbf{J}_+ \, |l, m\rangle &= \langle l, m| \, \mathbf{J}^2 - \mathbf{J}_z{}^2 - \hbar\mathbf{J}_z \, |l, m\rangle \\
    &= \left[\hbar^2 l(l+1) - \hbar^2 m^2 - \hbar^2 m\right] \langle l, m| \, l, m\rangle \\
    &= \left[\hbar^2 l(l+1) - \hbar^2 m \, (m+1)\right] \\
    &= \left[C_+^{l,m}\right]^2
    \end{aligned} \tag{14.56}$$

(Note: $\langle l, m | \, \mathbf{J}_- \mathbf{J}_+ \, | l, m \rangle = \langle l, m | \, \mathbf{J}_+{}^\dagger \mathbf{J}_+ \, | l, m \rangle = \left[C_+^{l,m} \right]^2$ since $| l, m \rangle$ are assumed to be normalized.

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

$$\mathbf{J}_+ \, | l, m = l \rangle = 0 \tag{14.57}$$

That is the operator $\mathbf{J}_+$ is a raising operator, but does not raise the value of m any further than its maximum value l.

Similarly,

$$\mathbf{J}_+ \mathbf{J}_- = \mathbf{J}^2 - \mathbf{J}_z{}^2 + \hbar \mathbf{J}_z \tag{14.58}$$

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

$$
\begin{aligned}
\langle l, m | \, \mathbf{J}_+ \mathbf{J}_- \, | l, m \rangle &= \langle l, m | \, \mathbf{J}^2 - \mathbf{J}_z{}^2 + \hbar \mathbf{J}_z \, | l, m \rangle \\
&= \left[\hbar^2 l(l+1) - \hbar^2 m \, (m-1) \right] \langle l, m | \, l, m \rangle \\
&= \left[C_-^{l,m} \right]^2
\end{aligned}
\tag{14.59}
$$

where again $\langle l, m | \, \mathbf{J}_+ \mathbf{J}_- \, | l, m \rangle = \langle l, m | \, \mathbf{J}_-{}^\dagger \mathbf{J}_- \, | l, m \rangle = \left[C_-^{l,m} \right]^2$. Hence

$$C_-^{l,m} = \sqrt{\hbar^2 l(l+1) - \hbar^2 m \, (m-1)} \tag{14.60}$$

and when $m = -l$, $C_-^{l,m} = 0$. And as from the operator $\mathbf{J}_+$, the lowering operator $\mathbf{J}_-$ does not lower the value of m below its minimum value of $m = -l$.

We summarize by stating

$$C_\pm^{l,m} = \sqrt{\hbar^2 l(l+1) - \hbar^2 m \, (m \pm 1)} \tag{14.61}$$

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 ($\mathbf{J}^2$).

   (d) Hence we choose two operators $\{ \mathbf{J}^2, \mathbf{J}_z \}$ 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 $\{ \mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2, \mathbf{S}_z \}$ commute with the total Hamiltonian $\mathbf{H}$.

(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 $\{\mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2, \mathbf{S}_z\}$ 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 $\mathbf{L}$ and $\mathbf{S}$ 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 $|l, m\rangle \to |l, m+1\rangle$, while the lowering operator $|l, m\rangle \to |l, m-1\rangle$.

(m) Using the form of the raising and lowering operators we obtained that the magnetic quantum numbers are bounded by the azimuthal quantum numbers $-l \le m \le l$. 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 $-l \le m \le m$ and for the spin quantum number $-s \le m_s \le s$. The spin half particles are called fermions and the particles with integral spin are called bosons.