### 18.2 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: $\mathbf{L}$ – $\mathbf{S}$ 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 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:

$$\mathbf{J} = \sum_i \mathbf{J}(i) \tag{18.62}$$

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 externl magnetic field) and when there are many nuclei, the "total" anuglar momentum is reponsible for the chemical shifts. In addtion, some neighbouring orbital angular momenta also contribute, thus the *environmental* dependence in NMR.

38. Lets consider two angular momentum operators: $\{\mathbf{J}_1, \mathbf{J}_2\}$. 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 $\left\{{\mathbf{J}_1}^2, \mathbf{J}_{1z}\right\}$ is a commuting set of operators. Similarly, the set $\left\{{\mathbf{J}_2}^2, \mathbf{J}_{2z}\right\}$ is also a commuting set of operators. Furthermore, since $\mathbf{J}_1$ and $\mathbf{J}_2$ act on different particles then all the operators in the set $\left\{{\mathbf{J}_1}^2, \mathbf{J}_{1z}, {\mathbf{J}_2}^2, \mathbf{J}_{2z}\right\}$ commute with each other.

40. However, the operators $\left\{{\mathbf{J}_1}^2, \mathbf{J}_{1z}, {\mathbf{J}_2}^2, \mathbf{J}_{2z}\right\}$ do not all commute with the total Hamiltonian, since the total Hamiltonian may contain terms that couple $\mathbf{J}_1$ and $\mathbf{J}_2$ (such as $\mathbf{J}_1 \cdot \mathbf{J}_2$ in L-S coupling).

41. Now lets consider the total angular momentum operator:

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \tag{18.63}$$

and the z-component of the total angular momentum: $\mathbf{J}_z$.

42. The operators: $\left\{\mathbf{J}^2, \mathbf{J}_z, {\mathbf{J}_1}^2, {\mathbf{J}_2}^2\right\}$ form a commuting set of operators as well.

43. Why? $\mathbf{J}^2$ and $\mathbf{J}_z$ certainly commute with each other as we have seen earlier for general angular momentum operators. Using Eq. (18.63), since $\mathbf{J}_1$ and $\mathbf{J}_2$ act on different particles they commute. Hence $\mathbf{J}^2$, ${\mathbf{J}_1}^2$ and ${\mathbf{J}_2}^2$ commute. Since $\mathbf{J}_z = \mathbf{J}_{1z} + \mathbf{J}_{2z}$, this operator commutes with $\mathbf{J}^2$, ${\mathbf{J}_1}^2$ and ${\mathbf{J}_2}^2$ as well.

44. **Homework: Show that $[\mathbf{J}^2, \mathbf{J}_z] = 0$. Note that $\mathbf{J}^2 = {\mathbf{J}_1}^2 + {\mathbf{J}_2}^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2$ from Eq. (18.63) (since $\mathbf{J}_1$ and $\mathbf{J}_2$ commute since they act on different particles). Note further that $\mathbf{J}_1 \cdot \mathbf{J}_2$ above is a dot product of two vectors (since $\mathbf{J}_1$ and $\mathbf{J}_2$ are vectors!!). Use $\mathbf{J}_1 \cdot \mathbf{J}_2 = \mathbf{J}_{1x}\mathbf{J}_{2x} + \mathbf{J}_{1y}\mathbf{J}_{2y} + \mathbf{J}_{1z}\mathbf{J}_{2z}$.**

45. **Homework: As a special case of your derivation above you will see that $[\mathbf{J}^2, \mathbf{J}_{1z}] \neq 0$ and $[\mathbf{J}^2, \mathbf{J}_{2z}] \neq 0$. Show this.**

46. Since $\left\{\mathbf{J}^2, \mathbf{J}_z, {\mathbf{J}_1}^2, {\mathbf{J}_2}^2\right\}$ form a commuting set of operators, we can quantify the system using quantum numbers of $\left\{{\mathbf{J}_1}^2, \mathbf{J}_{1z}, {\mathbf{J}_2}^2, \mathbf{J}_{2z}\right\}$, *i.e.*, $|j_1, m_{j_1}, j_2, m_{j_2}\rangle$, or quantum numbers of $\left\{\mathbf{J}^2, \mathbf{J}_z, {\mathbf{J}_1}^2, {\mathbf{J}_2}^2\right\}$, *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, $\mathbf{J}_1$ and $\mathbf{J}_2$. 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

$$\begin{aligned} |J, M, j_1, j_2\rangle &= |J, M, j_1, j_2\rangle \\ &= \sum_{m_{j_1}, m_{j_2}} |j_1, m_{j_1}, j_2, m_{j_2}\rangle \langle j_1, m_{j_1}, j_2, m_{j_2}|\, J, M, j_1, j_2\rangle \end{aligned} \tag{18.64}$$

    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:

$$\left\langle j_1, m_{j_1}, j_2, m_{j_2} \right| J, M, j_1, j_2 \rangle \propto \begin{pmatrix} j_1 & j_2 & J \\ m_{j_1} & m_{j_2} & M \end{pmatrix} \tag{18.65}$$

52. The Clebsch-Gordon coefficients are very useful in deriving “term symbols” of molecular systems.

53. 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?

54. We make two important observations:

    (a) Since the operators $\mathbf{J}_1$ and $\mathbf{J}_2$ are vectors and add up to give $\mathbf{J}$, 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: $j_1 + j_2$, $j_1 + j_2 - 1$, $\cdots$, $1 + |j_1 - j_2|$, $|j_1 - j_2|$. (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 $\mathbf{J}_\pm$.

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

56. Now an example of how all this can be used to derive "term symbols". (You may also look at Section 11.5 of Levine.)
57. Consider the carbon atom in the following excited electronic configuration: 1s$^2$, 2s$^2$, 2p$^1$, 3d$^1$.
58. The s-orbital has $l = 0$, p- has $l = 1$ and d- has $l = 2$.
59. Hence the two orbitals that have non-zero orbital angular momentum have $l$ values of 1 and 2.
60. *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).
61. The total orbital angular momentum can have values, $2 + 1, \cdots, 2 - 1$. (That is 1, 2, 3.)
62. There are two unpaired electrons and four paired electrons. The four pair electrons have zero spin angular momentum.
63. The two unpaired electrons have spin angular momentum of $1/2$. Hence the "total" spin angular momentum is $1/2+1/2, \cdots, 1/2-1/2$. (That is 0 and 1.)
64. 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: ${}^{2S+1}L$ : ${}^3P$, ${}^1P$, ${}^3D$, ${}^1D$, ${}^3F$, ${}^1F$.

66. Note: In cases where L-S coupling is involved the "term" symbols include the total angular momentum value as well: ${}^{2S+1}L_J$ (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 (2$L$+1) fold degenerate. (Because $m_L$ can have (2$L$+1) values in $-L \leq m_L \leq L$.)

    (d) So lets 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 (2$L$+1)=2×1+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 3×3=9.

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

69. Lets revisit the carbon atom term symbols we did last time. But now lets 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 ${}^{2S+1}L_J$, where $J = L + S$.
74. Lets 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: ${}^3G <^3 F <^3 D <^1 G <^1 F <^1 D$.

77. What are the degeneracies of each of these states? Remember, the degeneracy of a state $^{2S+1}L$ is (2$L$+1)×(2$S$+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 (2$J$+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.**

### 18.3 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 $\left\{ \mathbf{S_1}^2, \mathbf{S}_{1z}, \mathbf{S_2}^2, \mathbf{S}_{2z} \right\}$.

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 $\left\{\mathbf{S}^2, \mathbf{S}_z, {\mathbf{S}_1}^2, {\mathbf{S}_2}^2\right\}$, that is the total spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, and the z-component of the total spin operator $\mathbf{S}_z$ along with ${\mathbf{S}_1}^2$ and ${\mathbf{S}_2}^2$.

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 $\left\{\mathbf{S}^2, \mathbf{S}_z, {\mathbf{S}_1}^2, {\mathbf{S}_2}^2\right\}$ are

$$\begin{aligned} |S=1, S_z=1\rangle &= |+,+\rangle \\ |S=1, S_z=0\rangle &= \frac{1}{\sqrt{2}}\left(|+,-\rangle + |-,+\rangle\right) \\ |S=1, S_z=-1\rangle &= |-,-\rangle \\ |S=0, S_z=0\rangle &= \frac{1}{\sqrt{2}}\left(|+,-\rangle - |-,+\rangle\right) \qquad (18.66) \end{aligned}$$

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.