

## 5. Coupled Angular Momentum

Sometimes, we have to contend with the fact that both the orbital angular momentum and the spin angular momentum exist simultaneously and that they interact. This is the basis of **spin-orbit coupling**.

Can treat the problem in two ways:

### Uncoupled representation

$\mathbf{S}^2, \mathbf{L}^2, \mathbf{S}_z, \mathbf{L}_z$  can be specified

Our choice in the uncoupled representation is possible because  $[\mathbf{S}_i, \mathbf{L}_j] = 0$  (but  $\mathbf{S}+\mathbf{L}$  is not known).

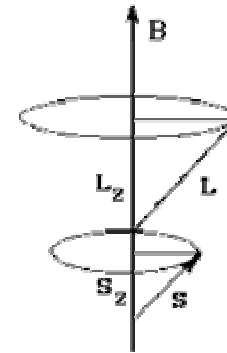
This corresponds to wave functions of the form:  $\Psi_L \Psi_s$  (our old friends).

The coupled representation implies  $[(\mathbf{S}+\mathbf{L})^2, \mathbf{L}_z] \neq 0$  which means we can not know individual components of  $\mathbf{L}$  and  $\mathbf{S}$ . This corresponds to new wave functions  $\Psi_J, \mathbf{J} = \mathbf{L}+\mathbf{S}$  (vector sum, later).

### Coupled representation

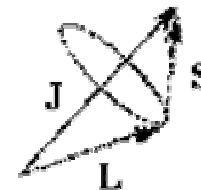
$(\mathbf{S}+\mathbf{L})^2, (\mathbf{S}_z+\mathbf{L}_z), \mathbf{S}^2, \mathbf{L}^2$  can be specified

Case 2. The Uncoupled Scheme



Precession of the Total Angular Momentum about an External Field

Case 1. The Coupled Scheme



Orbital Angular Momentum Coupled to Spin Angular Momentum

## 5.1 Properties of Total Angular Momentum, $\mathbf{J}$ (no proofs)

Consider two angular momentum  $\mathbf{J}_1$  and  $\mathbf{J}_2$

a)  $\mathbf{J}_1$  and  $\mathbf{J}_2$  has separate independent origins (spin, orbital, ...)

$$\begin{aligned} [\hat{J}_{1\eta}, \hat{J}_{2\eta}] &= 0 \quad \eta = x, y, z \\ [\hat{J}_1^2, \hat{J}_2^2] &= 0 \end{aligned}$$

Therefore, we can specify these individually.

b) The sum  $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$  is also an angular momentum with quantum numbers  $j, m_j$  such that:

$$\begin{aligned} [\hat{J}_x, \hat{J}_y] &= i\hbar \hat{J}_z \\ [\hat{J}_y, \hat{J}_z] &= i\hbar \hat{J}_x \\ [\hat{J}_z, \hat{J}_x] &= i\hbar \hat{J}_y \end{aligned} \quad [\hat{J}^2, J_\eta] = 0$$

c) Total  $\mathbf{J}^2$  commute with individual  $\mathbf{J}_i^2$ ,  $i = 1, 2$

$$\text{Thus: } \left[ \hat{\mathbf{J}}^2, \hat{\mathbf{J}}_1^2 \right] = \left[ \hat{\mathbf{J}}^2, \hat{\mathbf{J}}_2^2 \right] = 0$$

d) Total  $\mathbf{J}_z$  commutes with  $\mathbf{J}^2$  and individual  $\mathbf{J}_1^2, \mathbf{J}_2^2$ .

e) (This is the important one) Individual  $\mathbf{J}_{1z}, \mathbf{J}_{2z}$  **do not** commute with  $\mathbf{J}^2$

## Consequences:

a) Can represent system by either:

$$|j_1, m_{j_1}; j_2, m_{j_2}\rangle = |j_1, m_{j_1}\rangle |j_2, m_{j_2}\rangle = \text{uncoupled wave functions}$$

or  $|j_1, j_2, J, M_J\rangle = \text{coupled wave functions}$

but not by:  $|j_1, m_{j_1}, j_2, m_{j_2}, J, M_J\rangle$

Not all quantum numbers for commuting operators

b) Allowed values for  $j$  and  $m_j$

$$\hat{J}_z | j_1, m_{j_1}; j_2, m_{j_2} \rangle = (\hat{J}_{1z} + \hat{J}_{2z}) | j_1, m_{j_1}; j_2, m_{j_2} \rangle$$

$$\Rightarrow m_j \hbar | j_1, m_{j_1}; j_2, m_{j_2} \rangle = (m_{j_1} + m_{j_2}) \hbar | j_1, m_{j_1}; j_2, m_{j_2} \rangle$$

$$\therefore m_j = m_{j_1} + m_{j_2}$$

The maximum value of  $J = J_{\max} = j_1 + j_2 = m_{j_1\max} + m_{j_2\max}$

We have  $(2J+1)$  values of  $m_j$  but we have  $(2j_1+1)(2j_2+1)$  states to form  $J$ .

$$\begin{aligned} (2j_1+1)(2j_2+1) &= 4j_1j_2 + 2j_1 + 2j_2 + 1 \\ &= 4j_1j_2 + 2(j_1 + j_2) + 1 \\ &= 4j_1j_2 + \underbrace{2(j)}_{m_j} + 1 \end{aligned}$$

There is a redundancy in values which arises from the possibility of constructing states of same  $j$  with different  $m_j$  values

Turns out that total  $j$  can have values:

$$J = j_1 + j_2, j_1 + j_2 - 1, j_1 + j_2 - 2, \dots, |j_1 - j_2|$$

= vector sum = Clebsch-Gordon series

$$M_J = m_{j_1} + m_{j_2}$$

An example which is relevant to organic chemistry: systems with 2 electron spins

$$\uparrow\uparrow = \alpha_1\alpha_2 = |s_1, m_{s_1}; s_2, m_{s_2}\rangle = \left| \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle$$

$$\downarrow\downarrow = \beta_1\beta_2 = |s_1, m_{s_1}; s_2, m_{s_2}\rangle = \left| \frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle$$

$$\uparrow\downarrow = \alpha_1\beta_2 = |s_1, m_{s_1}; s_2, m_{s_2}\rangle = \left| \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle$$

$$\downarrow\uparrow = \beta_1\alpha_2 = |s_1, m_{s_1}; s_2, m_{s_2}\rangle = \left| \frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle$$

Uncoupled representation:

Coupled Representation

$$S = (s_1 + s_2) \rightarrow |s_1 - s_2|$$
$$= \left( \frac{1}{2} + \frac{1}{2} \right) \rightarrow \left| \frac{1}{2} - \frac{1}{2} \right| = 1, 0$$

When  $S = 0$ ,  $M_S = 0$ , and when  $S = 1$ ,  $M_S = 1, 0, -1$

Therefore, the coupled wave functions are:  $|s_1, s_2, S, M_S\rangle$

$$= \left| \frac{1}{2}, \frac{1}{2}, 0, 0 \right\rangle \quad \text{Singlet, } (2S+1) = (2 \cdot 0 + 1) = 1$$

$2S+1 = \text{spin multiplicity.}$

$$= \left| \frac{1}{2}, \frac{1}{2}, 1, 1 \right\rangle \quad \left| \frac{1}{2}, \frac{1}{2}, 1, 0 \right\rangle \quad \left| \frac{1}{2}, \frac{1}{2}, 1, -1 \right\rangle \quad \text{Triplet, } (2S+1) = (2 \cdot 1 + 1) = 3$$

Note: 4 states just like for the uncoupled representation!



Jablonski Diagram showing photophysical relaxation pathways of a typical organic compound

