Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 27
Nov 11th, 2013

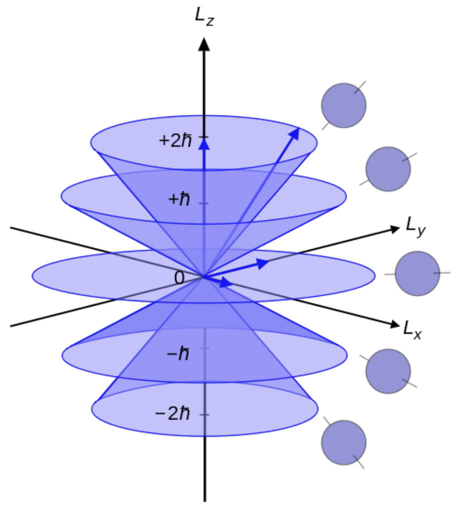
Objectives

- To remind the students the main properties of the quantum orbital angular momentum.
- To show how two angular momenta are added.
- To introduce the rules of addition of angular momenta.
- To introduce the concept of the total angular momentum for an atom.
- To pictorially show the Rusell-Saunders coupling and work out an example of the *LS* coupling.

The angular momentum is quantized: A graphic reminder

- We have learned that the angular momentum in quantum mechanics is quantized, an so is its z-component

$$\boxed{\begin{aligned}&\hat{L}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m \\ &\hat{L}_z Y_l^m = \hbar m_l Y_l^m \\ &m_l = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l\end{aligned}}$$



3

Angular momentum in many-electron atoms

Each electron in a many-electron atom contributes to the total orbital angular momentum **L** and the total spin angular momentum **S**. These properties of an atom are important because they are conserved, i.e., the total **L** and **S** do not change unless the atom is perturbed.

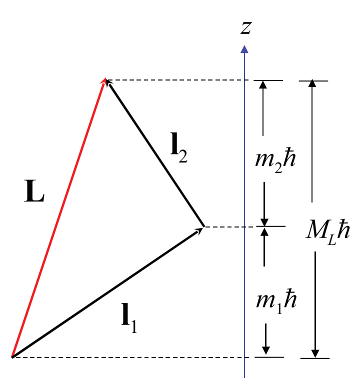
A conserved quantity is called a *constant of motion*, and its quantum-mechanical operator commutes with the Hamiltonian operator. For example, $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$ commute with $\hat{H}$.

Since angular momentum is a vector quantity, the contributions of individual electrons are added as vectors:

$$\mathbf{L} = \sum_i \mathbf{l}_i$$

The z-component of the orbital angular momentum, M_L, is the sum (in units of $\hbar$):

$$M_L = \sum_i m_i$$



4

Addition of quantized vectors: An example

Suppose we have two electrons with $l_1 = 2$ and $l_2 = 1$. What are the possible values of the total angular momentum quantum number L?

The total angular momentum **vector** is $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$, where the possible orientations of $\mathbf{l}_1$ and $\mathbf{l}_2$ are represented by $2l + 1$ cones of uncertainty which are characterized by the magnetic quantum numbers

$$m_1 = 2, 1, 0, -1, -2 \quad \text{and} \quad m_2 = 1, 0, -1$$

The possible values of the total magnetic quantum number M_L are obtained as all possible combinations (sums) of values of m_1 and m_2:

$$\begin{aligned} M_L = 3, 2, 1, 0, -1,& \\ 2, 1, 0, -1, -2,& \\ 1, 0, -1, -2, -3& \end{aligned}$$

This set can be rearranged as three sets of M_L values:

$$\left.\begin{array}{ll} M_L = 3, 2, 1, 0, -1, -2, -3 & \Rightarrow L=3 \\ M_L = \quad 2, 1, 0, -1, -2 & \Rightarrow L=2 \\ M_L = \quad\quad 1, 0, -1 & \Rightarrow L=1 \end{array}\right\}$$

Answer: these are the three possible values of L. The largest is l_1+l_2, the smallest is $|l_1-l_2|$

5

Rules for vector addition of angular momenta

In general, when the quantum numbers for the angular momenta of two electrons are l_1 and l_2, the possible quantum numbers for the **orbital angular momentum** of the two-electron system are

$$L = l_1+l_2,\ l_1+l_2-1,\ ...,\ |l_1-l_2|$$

Example: If $l_1 = 2,\ l_2 = 3$, then $L = 5, 4, 3, 2, 1$.

Similarly, for the **spin angular momentum**:

$$S = s_1+s_2,\ s_1+s_2-1,\ ...,\ |s_1-s_2|$$

Example: If $s_1 = s_2 = ½$, then $S = 1, 0$.

If the system (atom) contains more than two electrons, these relations should be applied consecutively for:

electron 1 + electron 2
(the system of electrons 1,2) + electron 3
(the system of electrons 1,2,3) + electron 4
and so on...

Total angular momentum for an atom

The **total angular momentum** $\mathbf{J}$ of an atom is the vector sum of all the orbital and spin angular momenta of electrons in it.

Like all other angular momenta $\mathbf{J}$ is quantized, and its quantum number J can take on only certain values.

For light atoms ($Z < 40$), electron-electron interactions are such that the atom can have definite observable values of the total orbital and spin angular momenta. Thus, for light atoms, the operators $\hat{L}^2$ and $\hat{S}^2$ commute with $\hat{H}$. Since the vectors $\mathbf{L}$ and $\mathbf{S}$ in this case have definite values, one can obtain the total angular momentum $\mathbf{J}$ by combining $\mathbf{L}$ and $\mathbf{S}$. This procedure is referred to as LS or **Russell–Saunders coupling**:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

As discussed above, the quantum number J for the total angular momentum of the atom in the JS coupling scheme has values given by

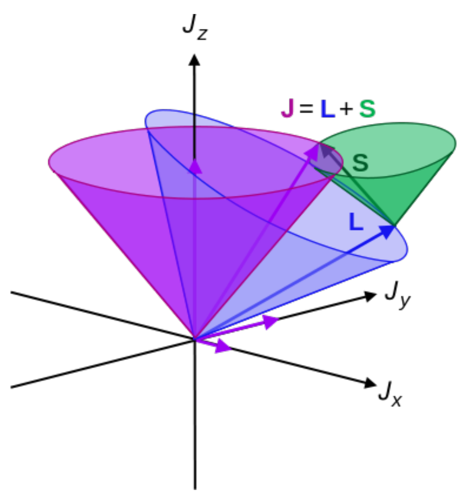
$$J = L+S,\ \ L+S-1,\ ...,\ |L-S|$$

Example: If $L = 2,\ \ S = 2$, then $J = 4, 3, 2, 1, 0.$

Graphic representation of the LS or Russell-Saunders coupling

- Based on the "conical" picture of angular momentum, it is possible to "visualize" the *LS* coupling.

- Just like is usually performed, when adding to vectors graphically, the base of one of them (S in this case) should be placed at the end of the other one (L in this case).



Finding the total L, S and J values for an atomic configuration

Specification of the electronic configuration of an atom such as

Carbon: $1s^2\ 2s^2\ 2p^2$

does **not** uniquely determine the energy of the atom because depending on how the spin and orbital angular momenta of the electrons combine, the atom may have different energies. For a given electron configuration, the energy of an atom also depends on L, S, and J. For this reason, we need to know how to determine the possible values of L, S, J.

Closed subshells contribute zero to the total orbital and spin angular momenta of an atom because the individual angular momenta of electrons in a closed subshell add up to zero. Thus, *only the open subshells need to be considered*.

Example: What are the possible L, S, J values for lithium and boron in their lowest states?

Li: $1s^2\ 2s$ $\quad L = 0;\ S = ½;\ J = ½$

B: $1s^2\ 2s^2\ 2p$ $\quad L = 1;\ S = 1/2;\ J = 3/2,\ 1/2$

9