

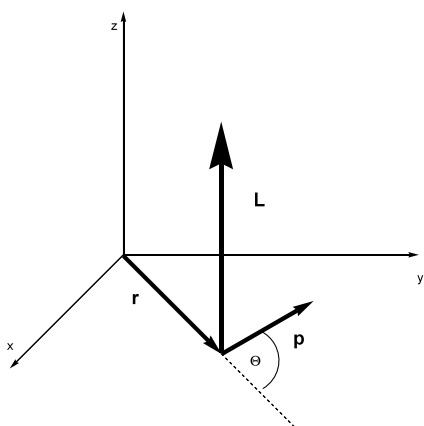
1.10 The Vector Model of the Atom

Classical Physics:

If you go back to your first year physics textbook, you will find momentum \mathbf{p} ($= m \mathbf{v}$) has an angular counterpart, angular momentum \mathbf{l} ($= \mathbf{r} \times \mathbf{p}$), as shown in the diagram below.

$$\vec{L} = \vec{r} \times \vec{p}$$

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ r_x & r_y & r_z \\ p_x & p_y & p_z \end{vmatrix} = |\mathbf{r}| |\mathbf{p}| \sin \Theta$$



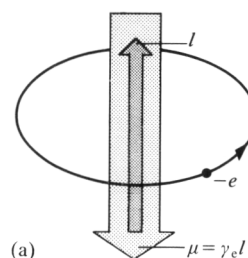
(Recall: Right-hand rule!)

- In classical physics two angular momenta can combine in any way to give a total angular momentum:

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots$$

Classical angular momentum of a circulating electron

- A simple classical “cartoon” of electronic angular momentum in the context of the Bohr model:
- An electron “orbiting” a nucleus results in an orbital angular momentum l .
- Because the electron has a charge, there also arises a magnetic moment μ_l ($= \gamma_e l$), where γ_e is a constant called the “magnetogyric ratio” of an electron. ($\gamma_e = -e/2m_e$ where e is the charge and m_e is the mass of an electron.)
- Note: This is a very simple and ultimately wrong image originating from the *Bohr Atom Model*, but serves its purpose in the context of the *vector model*.



(Source: P.W. Atkins, Physical Chemistry, 3rd edition, 1987.)

Quantum Mechanics:

- Angular momenta can only have discrete orientations relative to each other, i.e. they are *spatially quantized* ($l = 0, 1, 2, 3 \dots = s, p, d, f, \dots$), and if in any kind of force field (magnetic, electrostatic) *energy quantized*.
- The magnitude and relative orientation of the angular momentum vector **l** (for orbital angular momentum or **s** (for spin angular momentum) are described using quantum numbers and systematic combinations/sums of these numbers.

*In the following text, all **vector** quantities will be either set in **bold** or have an arrow above them, all scalar quantities (i.e. quantum numbers) in regular script.*

TABLE 2-1
Quantum numbers and their properties

<i>Symbol</i>	<i>Name</i>	<i>Values</i>	<i>Role</i>			
n	Principal	1, 2, 3, ...	Determines the major part of the energy			
l	Angular momentum	0, 1, 2, ..., $n-1$	Describes angular dependence and contributes to the energy			
m_l	Magnetic	0, ± 1 , ± 2 , ..., $\pm l$	Describes orientation in space			
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin in space			
Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:						
$l =$	0	1	2	3	4	5, ...
Label	s	p	d	f	g	continuing alphabetically

(Source: Tarr & Miessler, Inorganic Chemistry, 3rd Edition, 2004)

Single Electron Atoms: Angular Momentum in Hydrogenic Orbitals

Electronic Orbital Angular Momentum

- The orbital angular momentum vector of a single electron is given by:

$$\vec{l} = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \times \text{units}$$

- The orbital angular momentum **l** can actually be measured using the influence of magnetic fields on electrons.
(see e.g. http://www.chemistry.mcmaster.ca/esam/Chapter_3/section_3.html)

- With respect to an arbitrary reference direction (commonly one uses the principal = z axis of the laboratory or molecular reference frame) the angular momentum vector **l** can only have certain *quantized* orientations.

Example for $l = 2$ (i.e., d orbital) is shown:

Notice that **l** gives the magnitude (i.e. length of the vector arrow). The magnitude of the vector is:

$$\vec{l} = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{2(2+1)} \frac{h}{2\pi} = \sqrt{6} \frac{h}{2\pi}$$

m_l gives the possible orientations ($m_l = 0, \pm 1, \pm 2$) of the vector as the vector's projections along the z-axis have quantized magnitudes of $m_l(h/2\pi)$.

(Source: "Physical Chemistry", Atkins, 1990)

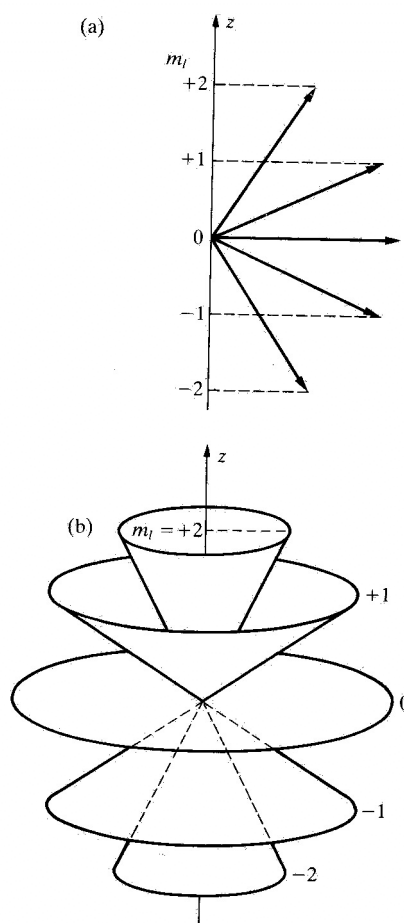


Fig. 12.17 (a) A summary of Fig. 12.15. However, since the azimuthal angle of the vector is indeterminate a better representation is as in (b), where each vector lies at an unspecified azimuth on its cone.

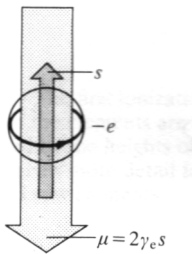
- The projections of \mathbf{l} onto the reference direction are integral multiples of $h/2\pi$ described by the quantum number m_l , with

$$m_l = l, l - 1, \dots, 0, \dots, -(l - 1), -l$$
 i.e. for any given l there $2l + 1$ possible m_l values.
- In the absence of a (magnetic or chemical) field, all $2l + 1$ values of m_l correspond to quantum states that are energetically degenerate
 e.g., p_x ($l = 1, m_l = 1$), p_y ($l = 1, m_l = 0$) and p_z ($l = 1, m_l = -1$), all have the same energies.
- The degeneracy can be lifted by an external field:

Magnetic (*Zeeman effect*)

Electrostatic (other atoms)

Electronic Spin Angular Momentum



- Electrons are *Fermions* with a half-integral spin, where the spin is an internal degree of freedom of the electron *with no classical equivalent*.
- In classical model we can describe the spin with the aid of the “cartoon” on the left.

(Source: P.W. Atkins, Physical Chemistry, 3rd edition, 1987.)

- In this classical model the rotation of the electron around its axis (“spin”) sets up a spin angular momentum \mathbf{s} and a spin magnetic moment μ_s
 - The electron spin can either be “up” or “down” and is described by:

$$\vec{s} = \sqrt{s(s + 1)} \frac{h}{2\pi} = \sqrt{\frac{1}{2}(\frac{1}{2} + 1)} \times units = \sqrt{\frac{1}{2} \times \frac{3}{2}} = \frac{1}{2} \sqrt{3} \times units$$

- The projections of \mathbf{s} onto the reference direction are integral multiples of $h/2\pi$ and described by the quantum number m_s , with

$$m_s = \frac{1}{2}, (\frac{1}{2} - 1 = -\frac{1}{2})$$

Spin Orbit Coupling and Total Angular Momentum

- As we have seen in the above “cartoons”, both the electronic and spin angular momenta result in magnetic moments:

$$\mu_l = \gamma_e \times l \quad \text{and} \quad \mu_s = 2\gamma_e \times s$$

- The two angular momenta will interact resulting in energetically different relative orientations. This is referred to as *spin-orbit coupling* and described by a total angular momentum \mathbf{j} .
- Because we are dealing with quantum phenomena, relative orientations of \mathbf{j} are quantized, i.e. only certain values are allowed (given by m_j .)
- Spin-Orbit coupling $\propto Z^4$ (Z = nuclear charge).
The spin-orbit coupling then results in a splitting of the atomic energy levels beyond that of the energies denoted by the quantum numbers n , l , and m_l .

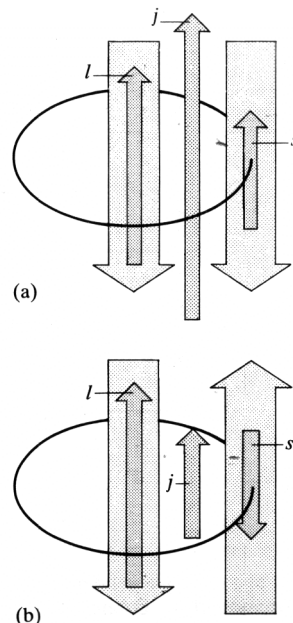


Fig. 15.18. The spin-orbit coupling is a magnetic interaction between spin and orbital magnetic moments. When the angular momenta are parallel, as in (a), the magnetic moments are aligned unfavourably; when they are opposed, as in (b), the interaction is favourable. This is the cause of the splitting of a configuration into *levels*.

(Source: P.W. Atkins, Physical Chemistry, 3rd edition, 1987.)

- In fact, many advanced textbooks list the quantum numbers as n , l , m_l and m_j .
- Only four quantum numbers are needed to totally describe an electron, but more than four exist!

- In order to describe spin-orbit coupling we need to define a new *total angular momentum* \mathbf{j} by adding the orbital and spin vectors.

$$\vec{j} = \vec{l} + \vec{s} = \sqrt{j(j+1)} \frac{h}{2\pi} = \sqrt{j(j+1)} \times \text{units}$$

where $m_j = j, (j-1), (j-2), \dots, -(j-1), -j$.

Determining the magnitude of \mathbf{j} and values of j and m_j can be done in a number of ways:

- a) By vector addition (only viable for a single electron), e.g. for $l = 1$ (i.e., p orbital)

$$l = \sqrt{2} \quad \text{and} \quad s = \frac{1}{2} \quad \text{thus} \quad s = \frac{1}{2} \sqrt{3}$$

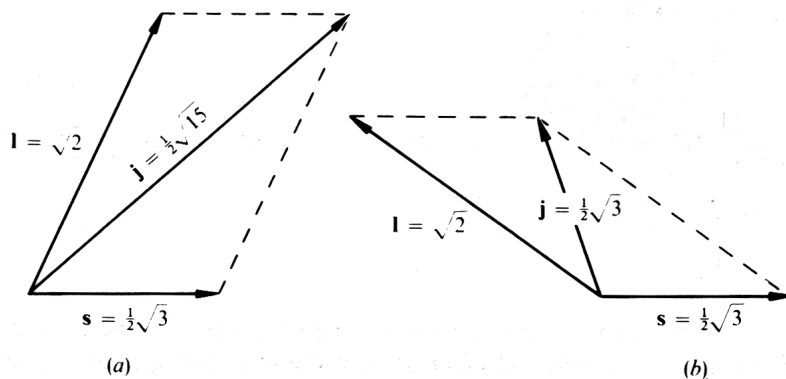


Figure 5.5 The two energy states having different total angular momentum which can arise as a result of the vector addition of $l = \sqrt{2}$ and $s = \frac{1}{2}\sqrt{3}$.

Source: "Fundamentals of Molecular Spectroscopy". C.N. Banwell and E.M. McCash, McGraw-Hill, 1994.

As stated above, j must be half-integral for a one-electron system, therefore \mathbf{j} can be:

$\mathbf{j} = (\frac{1}{2}\sqrt{3}), (\frac{1}{2}\sqrt{15}), (\frac{1}{2}\sqrt{35})$ by the formula given above for \mathbf{j} ; with $j = \frac{1}{2}, 3/2, 5/2, \dots$

b) By summation of quantum numbers m_l and m_s (i.e. the possible values of the z-component of l and s). **This method is generally applicable.**

$$j = l + s \quad \text{with} \quad m_l = \pm 1, \pm 1-1, \pm 1-2, \dots, 0$$

$$m_s = \pm \frac{1}{2}$$

Example: One electron in an atomic p orbital

- All possible vector sums of $l = 1$ and $s = \frac{1}{2}$ can be found by deriving all possible values of m_j (i.e., taking all combinations of m_l and m_s .)

For $l = 1$, $m_l = +1, 0, -1$

For $s = \frac{1}{2}$, $m_s = +\frac{1}{2}, -\frac{1}{2}$

There are six possible combinations: $m_j = 1 + \frac{1}{2}, 1 - \frac{1}{2}, 0 + \frac{1}{2}, 0 - \frac{1}{2}, -1 + \frac{1}{2}, -1 - \frac{1}{2}$
 $= 3/2, 1/2, 1/2, -1/2, -1/2, -3/2$

Thus there are TWO possible values for j (two possible vector sums of $l = 1$ and $s = \frac{1}{2}$):

$j = 3/2$ accounts for these four combinations: $m_j = 3/2, 1/2, -1/2, -3/2$

$j = 1/2$ accounts for the remaining two combinations: $m_j = 1/2, -1/2$

- **Meaning:** A single electron in an orbital can have slightly different energies depending on its particular l & s combination. The orbital angular momentum and the spin angular momentum vectors can either “reinforce” or “oppose” each other.

HOMEWORK:

What are the possible values of j arising from one electron in an f orbital?

How does this play out in terms of measurable properties?

e.g., The first excited state of a sodium atom in the gas phase

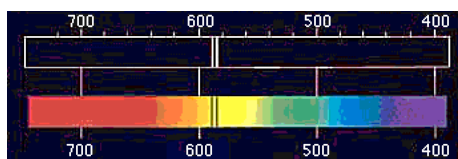
Ground state Na: $[\text{Ne}]3s^1$
 First excited state of Na: $[\text{Ne}]3s^03p^1$



A single electron in a p orbital: $l = 1$ and $s = \frac{1}{2} \rightarrow j = 3/2, 1/2$

i.e. an np^1 electron configuration will split into **two different energy levels**:

As a consequence, the emission spectrum of gaseous atomic sodium shows **two lines**:



The absorption (top) and emission (bottom) spectra of sodium.

Na 589 nm emission (orange) is actually 589.8 nm and 589.2 nm

We use **term symbols** to convey the l , s , and j value information more succinctly.

e.g., $^2S_{1/2}$ “doublet S one half”

A term symbol conveys three pieces of info:

- 1) The letter (e.g., S, P, D, etc.) indicates the orbital angular momentum L .
- 2) The left superscript indicates the **multiplicity** = $(2S + 1)$ where S is the spin angular momentum.
- 3) The right subscript indicates the total angular momentum quantum number J .

Note: Capital letters (S , L , J) are used for term symbols and multi-electron systems. Lower case letters (s , l , j) are used to describe individual electrons.

Note: You will learn how to derive term symbols for multi-electron systems in CHEM 3650.

Source: P.W. Atkins, Physical Chemistry, 4th edition, 1990.

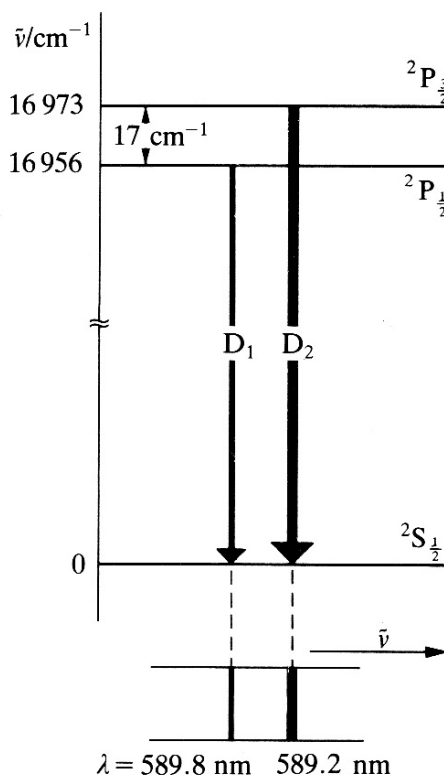


Fig. 13.21 The energy-level diagram for the formation of the D lines of sodium. The splitting of the spectral lines (by 17 cm^{-1}) reflects the splitting of the levels.