
UNIT 10 ATOMIC SPECTRA

Structure

- 10.1 Introduction
 - Objectives
- 10.2 Stern–Gerlach Experiment
- 10.3 Spin Angular Momentum
- 10.4 Total Angular Momentum
- 10.5 Spectral Terms, Optical Spectra of Hydrogen-like Atoms and Selection Rules
- 10.6 Multielectron Atoms
 - Life Time of Excited States and Line Broadening
- 10.7 Summary
- 10.8 Terminal Questions
- 10.9 Solutions and Answers

10.1 INTRODUCTION

In the previous unit you have learnt about the vector model of the atom and space quantization, in connection with the concept of angular momentum. Now since angular momentum is an observable, it must be measurable. You know that it is related to the magnetic moment of an atom. Therefore, if we are able to measure magnetic moment, we can measure angular momentum. One such experiment was devised in 1922 by O. Stern and W. Gerlach to **measure** angular momentum. In this unit we start by describing the Stern–Gerlach experiment which also verified the concept of space quantization.

However, the quantitative results obtained from the Stern–Gerlach experiment could not be explained with the help of only three quantum numbers, namely, n , l and m_l . Besides, there were a good number of spectroscopic data which could not be explained by the vector model of the atom.

To break the above deadlock, two research students S. A. Goudsmit and G.E. Uhlenbeck hypothesised that every electron possesses a spin angular momentum S . The spin angular momentum combines with the orbital angular momentum L to yield total angular momentum J . Like L , the angular momenta S and J also show space quantization and yield quantum numbers (s, m_s) and (j, m_j) , respectively. You will study about these concepts in Secs. 10.3 and 10.4. The introduction of the spin angular momentum proved very valuable for the qualitative explanation of the Stern–Gerlach experimental results. It was also used to explain a large number of the existing spectroscopic data, especially for hydrogen-like atoms. In Sec. 10.5, we discuss the optical spectra of such atoms.

Finally, we discuss the spectra of **multielectron** atoms in Sec. 10.6. In **such** atoms, every electron moves in a field produced by the nucleus of the atom and the remaining electrons. Such a potential is not spherically symmetric. Hence strictly speaking, for a multielectron atom, the orbital angular momentum of the atomic electrons is not a constant of **motion**.

Nevertheless, it is a good approximation to assume that every atomic electron moves in a spherically symmetric potential and its energy state is characterized by four quantum numbers n , l , m_l and m_s or n , l , j and m_j . In **this** section, we will also discuss **Pauli** exclusion principle which has **provided** shell structure to the atoms. The above principle enables us to arrange the atomic electrons according to their energy states (**electronic configuration**). The electronic configuration is **utilised** to obtain L , S and J quantum numbers of the whole atom and thus the spectroscopic terms (defined by L , S and J) of the ground as well as excited states of the atoms.

You will learn the selection rules which are obeyed when an atom makes a transition from one state to another, **A** transition **from** an excited state to a lower one produces **a** spectral line of characteristic frequency. This gives rise to atomic spectra. Such

transitions take finite time for their completion. Thus every excited state has a finite life time τ . Hence according to the Heisenberg uncertainty principle, $(\Delta E \Delta t = A)$, every spectral line has a frequency width. The transition of inner electrons from one energy state to another give rise to spectra in a higher frequency region, namely, the X-ray spectra. In the next unit, which is also the last in this block, we shall briefly discuss X-ray spectra.

Objectives

After studying this unit you should be able to

- describe Stern–Gerlach experiment,
- explain the concept of spin angular momentum,
- calculate the total angular momentum,
- compute the spectral terms for hydrogen-like and multielectron atoms, distinguish between allowed and forbidden transitions.

10.2 STERN–GERLACH EXPERIMENT

In the previous unit you have seen that the angle between the angular momentum vector L and the z -axis takes only discrete values. The angle is given by $\cos^{-1}(m_l/\sqrt{l(l+1)})$ where for a given value of l , the magnetic quantum number m_l takes only integer values given by $-l, -l+1, \dots, l-1, l$. The phenomenon, known as space quantization, was verified by an experiment performed by Stern and Gerlach. In this experiment, a highly inhomogeneous magnetic field having magnetic induction B was applied along z -axis and an atomic beam travelling along x direction was passed through this field (see Fig. 10.1). It was found that a single atomic beam produced more than one trace on the screen S . This clearly showed that the inhomogeneous magnetic field resolved one single beam of atoms into more than one discrete component

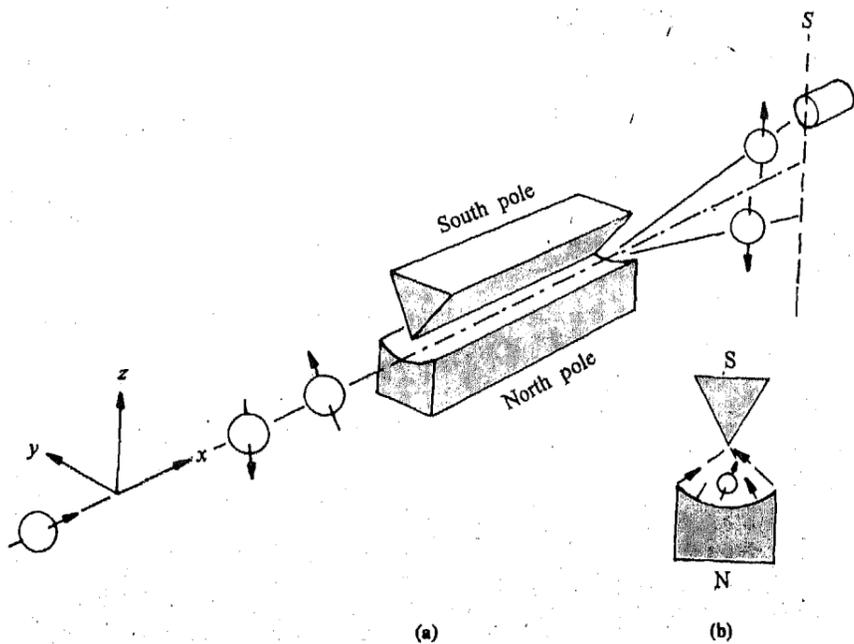


Fig. 10.1: Stern–Gerlach Experiment. Silver atoms produce two traces on the screen S . (a) The incoming beam along the x -direction is split into two as it passes through an inhomogeneous magnetic field; (b) how the inhomogeneity of the magnetic field is created. The field depends sharply on z , increasing with increasing z .

To understand this experimental result, let us assume that an electron of mass μ of the atom has an angular momentum \mathbf{L} . Since this electron has a charge e and is moving inside the atom, according to classical physics, the electron also has a magnetic moment $\boldsymbol{\mu}_L$ given by

$$\boldsymbol{\mu}_L = -\frac{e}{2\mu} \mathbf{L} \quad (10.1)$$

Classically, the deflecting force on the atom due to the inhomogeneous magnetic field is given by

$$\mathbf{F} = \nabla (\boldsymbol{\mu}_L \cdot \mathbf{B}) \quad (10.2)$$

Since \mathbf{B} is along z -axis, the force will also be along z -axis and we have

$$F_z = \mu_z \frac{\partial B}{\partial z} = -\frac{e}{2\mu} L_z \frac{\partial B}{\partial z} \quad (10.3)$$

Thus the particles in the beam should be deflected up or down in direct proportion to the z component of the magnetic dipole moment. By looking at the trace of the deflected particle on a screen, therefore, we can measure the component of its magnetic moment in the direction of the magnetic field.

In this way, the Stern-Gerlach apparatus does to a particle beam of magnetic dipoles what a prism does to white light; it refracts the magnetic dipoles and displays the spectrum of magnetic moment that the particles of the beam possess.

What would we expect classically if a beam of atomic dipoles is sent through the Stern-Gerlach prism? Classically, the spectrum of the z -component of magnetic moment — its allowed values — is continuous (ranging from $-\mu_z$ to μ_z). What did Stern and Gerlach find when they first did their experiment? A discrete line spectrum, of course! The spectrum of magnetic moment is quantized; it should be obvious; μ_z is proportional to L_z , and L_z is quantized.

To understand these results, let us convert the classical expression of F_z into the corresponding quantum mechanical expression. For this we regard F_z as an operator. Then the average value of F_z is given by

$$\langle F_z \rangle = \int \Psi_{nlm_l}^*(\mathbf{r}) F_z \Psi_{nlm_l}(\mathbf{r}) d\tau \quad (10.4)$$

Now $\Psi_{nlm_l}(\mathbf{r})$ as given by Eq. (9.50) is an eigenfunction of L_z with the eigenvalue m_l . Hence the force acting on the atom in the z direction is

$$\langle F_z \rangle = -\left(\frac{e\hbar}{2\mu}\right) m_l \frac{\partial B}{\partial z} \quad (10.5)$$

The quantity $e\hbar/2\mu$ is termed the Bohr magneton μ_B .

Stern and Gerlach also measured the distance between the traces and concluded that m_l changes by one. Thus the concept of space quantization was experimentally verified.

However, as we have said above, the number of traces obtained in the Stern-Gerlach experiment could not be explained on the basis of the quantum numbers l and m_l . It is evident from Eq. (10.5) that due to discrete values of m_l a single beam of atoms will break into $(2l + 1)$ beams and each will produce its own trace on the screens. Hence the number of traces must always be odd. But unexpectedly, when a beam of silver atoms was sent through the inhomogeneous magnetic field, it produced only two (an even number) traces. It is well known that the valency of silver is one, Hence it has only one active electron and in the ground state this electron is an s ($l = 0$) electron. Hence the only possible value of m_l is zero. Therefore, there should not have been any deflection and the screen S should have registered only one trace and not two. On the other hand if one assumes that the silver atoms were in the $(l = 1)$ state then the number of traces should have been three. Hence, It became evident that the results of Stern-Gerlach experiment could not be explained on the basis of l and m_l quantum numbers. Something was found to be missing, This discrepancy was resolved by

Goudsmit and Uhlenbeck who introduced the concept of **spin angular momentum**. You will need to study this concept carefully.

But before that, here's an exercise for you.

SAQ 1

Spend
5 min

Show that the value of the Bohr magneton in SI unit is 9.27×10^{-24} joule tesla⁻¹ (or amp meter²). Take μ as the rest mass of the electron.

10.3 SPIN ANGULAR MOMENTUM

Goudsmit and Uhlenbeck analysed a large number of spectroscopic lines and found that these also could not be explained with the help of only three quantum numbers, namely, n , l and m_l . One of the familiar example is the observation of two closely spaced lines D_1 and D_2 in the spectrum of a sodium lamp. On the basis of the above three quantum numbers there should have been only one line corresponding to $3p$ to $3s$ transition. To explain such discrepancies, Goudsmit and Uhlenbeck advanced a new hypothesis according to which **every electron has an intrinsic angular momentum S and consequently an intrinsic magnetic moment μ_s also**. However, the ratio of μ_s and S is $-e/\mu$ and not $-e/2\mu$. Their argument was based on this logic: a free electron does not have any orbital angular momentum. Thus the two-valuedness evident in the traces must be due to an intrinsic angular momentum, which is a purely quantum mechanical attribute of particles. They called it the spin angular momentum (S), or simply **spin**. Since the multiplicity ($2s + 1$) is 2, we can identify the angular momentum quantum numbers associated with spin as $1/2$. Thus electrons have spin $1/2$.

What about the vector S ? Just like the orbital angular momentum L , the spin angular momentum S also precesses about z -axis. The angle between S and z -axis is quantized, i.e., it also shows space quantization. However, since the value of the quantum number s associated with S is $1/2$, m_s has only two values equal to $\pm s$, i.e., $\pm 1/2$. Consequently, there are only two spin functions, one corresponding to $m_s = 1/2$ (spin up) and the other to $m_s = -1/2$ (spin down). These two spin functions are the eigenfunctions of the operators S^2 and S_z with eigenvalues $s(s+1)\hbar^2$ and $m_s\hbar$, respectively. Hence, the quantized angles, obtained by taking $s = 1/2$ and $m_s = \pm 1/2$, in place of l and m_l respectively, in Eq. (9.22), are $\pm \cos^{-1}(1/\sqrt{3})$.

With the help of the above hypothesis it is easy to explain the production of only two traces by the ground state of the silver atoms in the Stern–Gerlach experiment. Since $l = 0$ and $s = 1/2$ we get $m_l = 0$ and $m_s = \pm 1/2$. Each m_s produces its own trace and one silver atomic beam splits into two.

The concepts introduced above will take you some time to get used to. Here is a note of warning; you should take spin angular momentum and the corresponding magnetic moment as the intrinsic properties of an electron, just like its charge and mass. **Do not picture the electron as some sort of a spinning top spinning about its axis**. Such a description is wrong and leads to absurd results as you will discover in SAQ 2. Spin is one more strangeness of the quantum world that you will have to get accustomed to!

You may wonder; why does the electron or any other particle possess a spin angular momentum? An attempt to understand the reason for the occurrence of spin angular momentum will take us much beyond the scope of the present course. You will be able to learn about this in your higher degree studies.

SAQ 2

Spend
5 min

Show that if we assign the intrinsic angular momentum of an electron due to the spinning of the electron about its own axis, the velocity of the electron will be greater than the velocity of light.

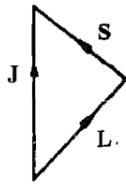


Fig. 10.2: Vector addition of L and S vectors.

The spin angular momentum vector S does not depend upon the space coordinates hence its origin is purely quantum mechanical. Further, since S^2 and S_z are constants of motion, the eigenfunction of an atomic electron is characterised by four quantum numbers n, l, m_l and m_s (the value of s is always $1/2$). Thus spin provides a fourth degree of freedom to an electron — the electron is a four-dimensional particle. We need four measurements — so we have four dimensions!

The introduction of spin angular momentum, leads us to the concept of total angular momentum.

10.4 TOTAL ANGULAR MOMENTUM

The addition of the vectors L and S gives rise to total angular momentum vector J (see Fig. 10.2).

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (10.6)$$

The values of the quantum number j are given by

$$j = l + s, l + s - 1, \dots, |l - s| + 1, |l - s| \quad (10.7)$$

Thus vector J also precesses around z -axis and the angle between J and z -axis is given by $\cos^{-1} \left(\frac{m_j}{\sqrt{j(j+1)}} \right)$, where j is the total angular momentum quantum number and m_j is its component along z -axis (see Fig. 10.3). The wave functions of an electron, including its spin part, are eigenfunctions of J^2 and J_z with eigenvalues $j(j+1)\hbar^2$ and $m_j\hbar$, respectively. Like l , the quantum number j is also always positive but it can have integral as well as half-integral values. For example, if $l = 2$ and $s = 1/2$, the values of j are $5/2$ and $3/2$. Corresponding to $j = 5/2$, the values of m_j are $5/2, 3/2, 1/2, -1/2, -3/2$ and $-5/2$ (see Fig. 10.4).

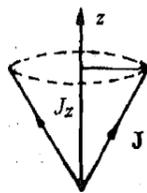


Fig. 10.3: Precession of J around z-axis.

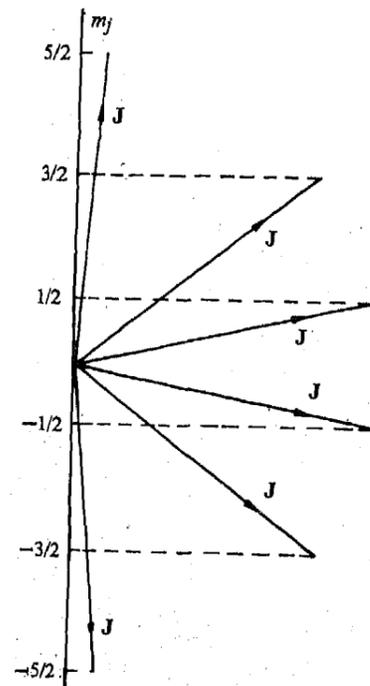


Fig. 10.4: Different discrete orientations of J vector and values of m_j for $|J| = 5/2$. The tip of J lies on a circle.

You should go slow, read carefully and absorb these ideas before studying further. The following exercise should further help you understand and concretise these ideas in the context of what you have learnt so far about the quantum world.

SAQ 3

Spend
10 min

The spin up and spin down wavefunctions of an electron are given by

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and the spin angular momentum operator is given by

$$\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}$$

where $\boldsymbol{\sigma}$ is Pauli spin matrix and its three components are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Show that α and β are eigenfunctions of S^2 and S_z and are orthogonal to each other.

Thus, through SAQ 3, you have essentially solved the eigenvalue problem of the operators S^2 and S_z for the electron. You have come to know of the spin wave functions of an electron and their eigenvalues. We have also briefly introduced you to the Pauli spin matrix $\boldsymbol{\sigma}$ and its three components. The concepts developed so far help us explain atomic spectra in the optical region of the electromagnetic spectrum.

10.5 SPECTRAL TERMS, OPTICAL SPECTRA OF HYDROGEN-LIKE ATOMS AND SELECTION RULES

All atomic systems having only one electron are classified as hydrogen-like atoms. Thus singly ionized helium (He^*), doubly ionized lithium (Li^{++}) and triply ionized beryllium (Be^{*3}) etc. are examples of hydrogen-like atoms. In general, a hydrogen-like atom has Z positive charges in its nucleus and one electron outside the nucleus. Hence the Hamiltonian of the relative motion is given by

$$H = -\frac{\hbar^2 \nabla^2}{2\mu_A} - \frac{Ze^2}{r} \quad (10.8)$$

where μ_A is the reduced mass of the system. Thus the time independent Schrödinger equation of a hydrogen-like atom will be the same as that of a hydrogen atom with the difference that e^2 and μ of Eq. (9.37a) will be replaced by Ze^2 and μ_A , respectively. Consequently, the eigenenergies and eigenfunctions of the above system will be given by Eqs. (9.44) and (9.50), respectively but e^2 and μ will have to be replaced by Ze^2 and μ_A at all the places.

The inclusion of spin gives two eigenfunctions for the same n, l and m_l : one for $m_s = +1/2$ and the other form, $= -1/2$. These are

$$\begin{aligned} \psi_{nlm_l}(\mathbf{r}, \mathbf{s}) &= \psi_{nlm_l}(\mathbf{r}) \alpha && \text{for spin up} \\ &= \psi_{nlm_l}(\mathbf{r}) \beta && \text{for spin down} \end{aligned} \quad (10.9)$$

Now for a hydrogen-like atom $s = 1/2$. Hence for a given value of l , according to Eq. (10.7), there will be two values of j given by $l \pm 1/2$. You can now learn to write the spectral terms for hydrogen-like atoms.

In spectroscopy, the spectral term of an atom is given by

$$2S+1L_J$$

where S is the total spin angular momentum, L is the total orbital angular momentum and J is the total angular momentum. The quantity $2S+1$ is known as **multiplicity**. For $L > S$, we obtain $2S+1$ values of J . However, for $L < S$ the values of J are $2L+1$. Sometimes the numerical value of n is also attached in the spectral term, which is then written as $n^{2S+1}L_J$.

Now let us consider the state of the hydrogenic atom for which $l = 0$. For this case $S = \frac{1}{2}$, $L = 0$, $J = \frac{1}{2}$. Thus we may write for a hydrogen-like atom that

$$J = \frac{1}{2} \text{ for any } l = 0 \text{ state}$$

And so we have only one term for a hydrogenic (or hydrogen-like) atom given by ${}^2S_{1/2}$. Notice that in the spectral term we have used the symbol S instead of the numerical value 0 to show that $L = 0$ for this case. Similarly, for $L = 1, 2, 3, \dots$ we use the symbols P, D, F, \dots etc, in the spectral terms instead of the numerical values of L . So we use the capital letter to denote the orbital quantum number according to the following letter code:

$$S \text{ for } L = 0, \quad P \text{ for } L = 1, \quad D \text{ for } L = 2, \quad F \text{ for } L = 3, \dots$$

Now let us consider the states for which $l \neq 0$.

$$\text{For } l = 1 \text{ and } s = \frac{1}{2}, \quad L = 1, \quad S = \frac{1}{2} \text{ and } J = \frac{3}{2}, \frac{1}{2}$$

which yields two terms: ${}^2P_{1/2}$ and ${}^2P_{3/2}$.

$$\text{Similarly, when } l = 2 \text{ and } s = \frac{1}{2}, \quad L = 2, \quad S = \frac{1}{2} \text{ and } J = \frac{5}{2}, \frac{3}{2}$$

This again yields two terms ${}^2D_{3/2}$ and ${}^2D_{5/2}$. In general, you can see that for a hydrogen-like atom only two possible values of J will result:

$$J = L + \frac{1}{2} \text{ or } L - \frac{1}{2} \text{ for any } l \neq 0 \text{ state}$$

Thus all the states with $l \geq 1$ are doublets, i.e., they have two values of J . Have you noticed from these results that for $n = 1$ we have only one ${}^2S_{1/2}$ state but $n = 2$ gives rise to three excited states? Our advice to you is, don't just read through what we have said in these lines. Work these numbers out. And to familiarise yourself further with the calculation of spectral terms work out the following SAQ.

Spend
10 min

SAQ 4

Determine all the spectral terms for $n = 2$ and $n = 3$ for a hydrogen-like atom.

According to Eq. (9.44) the eigenenergy depends only upon n hence the inclusion of spin increases the degeneracy to $2n^2$. However, if we include relativistic effects and the interactions between orbital angular momentum and spin angular momentum in our quantum mechanical treatment, it can be shown that the eigenenergy depends upon the quantum number j in addition to the quantum number n . It is given by

$$E_{nj} = -\frac{RZ^2}{n^2} \left[1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{j+1/2} - \frac{3}{4n} \right) \right] \quad (10.10)$$

where α is called the **fine** structure constant and is equal to $e^2/\hbar c$ ($\approx 1/137$). Hence the energy level diagram of a hydrogen atom as shown by Fig. 9.5b is modified to Fig. 10.5.

Notice that although ${}^2S_{1/2}$ and ${}^2P_{1/2}$ states are still degenerate, the state ${}^2P_{3/2}$ lies higher than ${}^2P_{1/2}$. Similarly, ${}^2D_{5/2}$ lies higher than ${}^2D_{3/2}$ in the energy level diagram. Thus, the spectrum of hydrogen atom and hydrogen-like atoms has a fine structure. We will come to this point again after you have done this exercise.

SAQ 5

Use Eq. (10.10) to obtain the energy difference between $3^2P_{3/2}$ and $3^2P_{1/2}$ states for the hydrogen atom in electron volts.

Spend
5 min

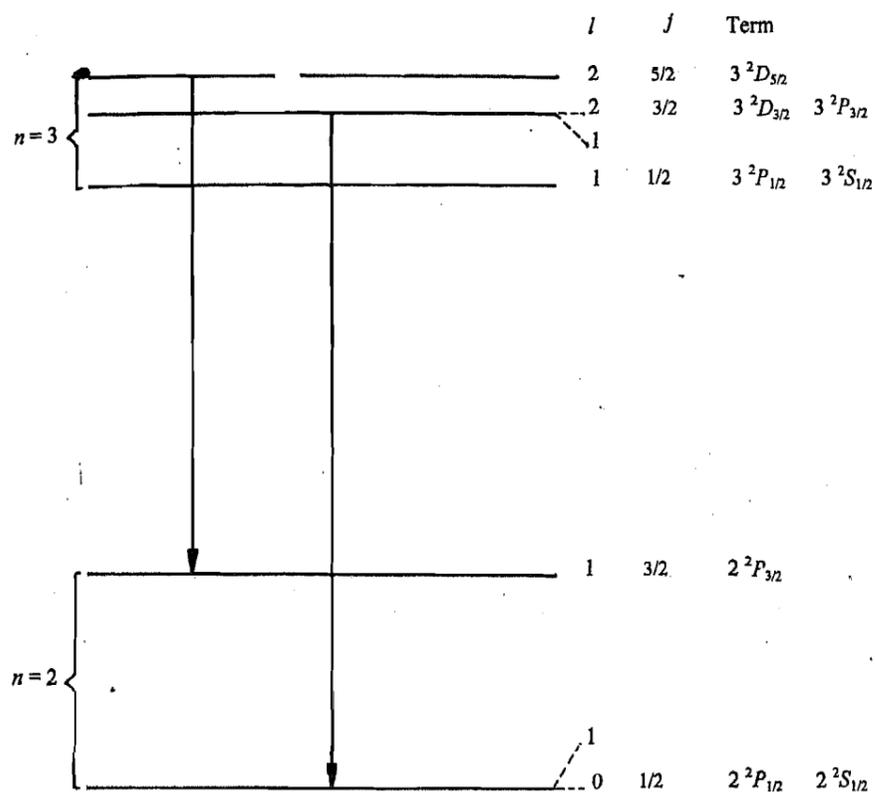


Fig. 10.5: Doublet structure of H_{α} line in hydrogen atom.

Since an atom in an **excited** state has more **energy** than its ground state, it has a natural tendency to make a transition to lower excited states or ground state and thereby reduce its energy by emitting electromagnetic radiations. An atom can also absorb electromagnetic energy and make a transition from a lower state to higher excited states. However all transitions are not allowed. Quantum mechanics gives certain selection rules for **allowed transitions** which we will now state. The remaining transitions are forbidden – they **cannot** occur.

Selection Rules

Suppose a hydrogen-like atom makes a transition from a state characterised by n, l, j to n', l', j' . Then the **selection rules** for the allowed transitions are as follows:

Selection rules for hydrogen-like atoms

- (i) $j' - j = \pm 1, 0$ or $\Delta j = \pm 1, 0$
but both j' and j cannot be zero simultaneously. (10.11)
- (ii) $l' - l = \pm 1$, or $\Delta l = \pm 1$.

Notice that there is **no** restriction on the values of $n' - n$. Since the **parity** of a state is given by $(-1)^l$ it changes in an allowed transition. According to the above rules a transition from $3^2P_{3/2}$ to $2^2S_{1/2}$ is allowed since in this case the **change** in the value of l , i.e., $\Delta l = 1 - 0 = 1$. Is the transition from $3^2D_{5/2}$ to $1^2S_{1/2}$ allowed? No, because $\Delta l = 2 - 0 = 2$ in this case.

All those transitions which do not obey the above selection rules are said to be forbidden **transitions**. Some of the forbidden transitions do take place but, with intensities which are about 10^4 times smaller than those of the allowed transitions. Using the energy level diagram shown in Fig. 10.5, we can easily explain the doublet structure, observed experimentally, of the first member of the Balmer series. They are produced by the following two transitions: $3^2D_{5/2}$ to $2^2P_{3/2}$ and $3^2P_{3/2}$ to $2^2S_{1/2}$. Similarly D_1 and D_2 lines in a sodium lamp are produced by the transitions $3^2P_{3/2}$ to $3^2S_{1/2}$ and $3^2P_{1/2}$ to $3^2S_{1/2}$. Not only the above structures but many other spectral features can be explained by associating a spin angular momentum to every electron and using the selection rules given by Eq. (10.11).

Let us now extend these ideas to multielectron atoms.

10.6 MULTIELECTRON ATOMS

Let us consider atoms having more than one electron. If \mathbf{l}_i is the orbital angular momentum vector of the i^{th} atomic electron, the total angular momentum vector \mathbf{L} of the whole system is given by

$$\mathbf{L} = \sum_i \mathbf{l}_i \quad (10.12)$$

To obtain the values of the quantum number L we first combine l_1 and l_2 to obtain their resultant l_R . Then this l_R is combined with l_3 to obtain new resultants l'_R . This process is repeated until all electrons are taken into consideration. According to the vector model of the atom the resultant l_R has following values

$$l_R = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2| + 1, |l_1 - l_2| \quad (10.13)$$

Following the above rule each l_R will combine with l_3 to yield

$$l'_R = l_R + l_3, l_R + l_3 - 1, \dots, |l_3 - l_R| + 1, |l_3 - l_R| \quad (10.14)$$

etc. For example if $l_1 = 1$, $l_2 = 1$ and $l_3 = 2$ the values of l_R will be 2, 1 and 0 and the values of l'_R will be (4, 3, 2, 1, 0), (3, 2, 1) and 2. Similarly, for the spin angular momentum we have

$$\mathbf{S} = \sum_i \mathbf{s}_i \quad (10.15)$$

and the values of the resultant S are obtained by following Eqs. (10.12) to (10.14) by replacing l_i with s_i . Since for each electron $s_i = 1/2$, therefore, for two electrons $S = 1$ and 0 and for three electrons $S = 3/2$ and $1/2$. You can easily verify that for an atom having even number of electrons the resultant S will have integer values but for atoms having odd number of electrons the values of the resultants will be half integers.

Finally L and S combine according to (10.6) to give the values of the total angular momentum quantum number J and the spectral terms given by $2S+1L_J$ are obtained. The values of J are obtained from (10.13) by replacing l_R , l_1 and l_2 with J , L and S , respectively. Thus

$$J = L + S, L + S - 1, \dots, |L - S| + 1, |L - S| \quad (10.16)$$

This kind of addition of angular momenta is called the **LS** coupling. There is another kind of addition of angular momenta called the **JJ** coupling — we are not going into its details here.

Let us now consider the assignment of four quantum number (n, l, m_l, m_s) to individual electrons in a **multielectron atom**. For the stability of the atom its energy should be **minimum**. It follows then that for all the electrons in an atom we should have $n = 1, l = 0, m_l = 0$ and $m_s = +1/2$ or $-1/2$. However, the above assignment is not correct. The distribution of atomic electrons according to their quantum numbers n and l is known as the electronic configuration of an atom. It follows the Pauli **exclusion** principle. We will discuss it in brief here.

According to this principle no two electrons in an atom can have the same four quantum numbers (n, l, m_l, m_s). For example, in the ground state of a helium atom, the four quantum numbers associated with two atomic electrons are $(1, 0, 0, +1/2)$ and $(1, 0, 0, -1/2)$. Thus, the first three quantum numbers n, l and m_l are the same, but the fourth quantum number m_s is different for the two electrons. However, in the excited states of helium one electron may be in $(1, 0, 0, +1/2)$ state while the other electron may have any other value of the quantum numbers n, l, m_l and m_s . Now if $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$, the resultant value of S can be 1 as well as 0 and we have two types of terms given by 3L_J and 1L_J . For the first term, known as a triplet, the three values of J are $L+1, L, L-1$ with $L = 1$. On the other hand for the second term, known as singlet, J has only one value equal to L .

With the help of Pauli's exclusion principle, we can now describe the shell structure of an atom.

As you have studied earlier in this unit, the central field in a multielectron atom is not spherically symmetric. Therefore, the energy of the system depends upon L as well as S . A quantum mechanical calculation shows that for a helium atom, the triplet terms have lower energies in comparison with the corresponding singlet terms. But to a good approximation, the energy of each atomic electron depends upon its principal quantum number n and orbital angular momentum quantum number l , unlike the situation for the hydrogen atom. These energies must not depend on m_l and m_s because the potential energy of each electron is spherically symmetric and spin independent. Hence, there are $2(2l+1)$ degenerate states with the same energy $E_{n,l}$, corresponding to the two possible values of m_s and $(2l+1)$ possible values of m_l . All of them will have nearly the same energy. This group of $2(2l+1)$ spin-orbitals constitutes an atomic subshell at energy $E_{n,l}$ for each pair of quantum numbers n and l . They are said to form an (n, l) energy subshell. Thus in an atom, for $n = 2$ and $l = 1$, there will be $2(2 \times 1 + 1) = 6$ electrons in the $(2p)$ subshell.

Each value of n determines an electron shell for a given atom. The number of electrons in the n th shell is $2n^2$. Thus, in the shell with $n = 1$, there will be 2 electrons; in the $n = 2$ shell there will be 8 electrons, and so on. Further, a shell consists of n subshells labelled by n and l , as l ranges from 0 to $n - 1$. And every n, l subshell contains $2(2l+1)$ spin-orbital states. For example, for $n = 2, l = 0$ and $l = 1$, there will be two subshells ($2s$) and ($2p$). In the $2s$ subshell there will be $2(2 \times 0 + 1) = 2$ electrons. In the $2p$ subshell there will be 6 electrons, and so on.

These shells are also labelled K, L, M, N, \dots according to whether $n = 1, 2, 3, 4, \dots$. In accordance with the Pauli exclusion principle, all electrons in a shell are characterised by different set of four quantum numbers and different eigenfunctions.

To sum up, the ground state of an atom with atomic number Z is the minimum energy configuration for the bound system of Z electrons organised in a shell structure. Starting with the inner-most electrons, the order of the shells and subshells with increasing energy is given as

$$1s, 2s, 2p, 3s, 3p, [4s, 3d], 4p, [5s, 4d], 5p, [6s, 4f, 5d], \dots \quad (10.17)$$

The numbers 1, 2, 3, ... represent the values of n and the letters, s, p, d, f, \dots correspond to $l = 0, 1, 2, 3, \dots$. The bracket in Eq. (10.17) enclose levels which have very nearly the same value of energy. Although we have said that electrons having same values of n and l have nearly the same energy but a detailed study shows that the rules for the filling of subshells that hold throughout the periodic table of elements are as follows:

1. Subshells are grouped under like values of $n + l$.
2. Groups are filled in the order of increasing $n + l$.
3. Within each $n + l$ group, subshells are filled in the order of decreasing l values.

Let us now apply these ideas to determine the electronic structure of elements in the periodic table, i.e., to write down the ground state configuration for any atom in the periodic table.

The ground state configuration of a neutral atom with Z electrons is obtained by distributing them according to the rules given above.

The first element ($Z=1$) is atomic hydrogen, which has the ground state configuration $1s$. For $Z=2$ (helium), both electrons occupy the $1s$ level and the configuration is $1s^2$. Thus, we may write their electron configuration as follows:

H	He
$1s$	$1s^2$

For the lithium atom, there are three electrons in its ground state and its electronic configuration is $1s^2 2s^1$, because $1s^3$ is forbidden by Pauli's exclusion principle. For $Z=4$ (beryllium), the configuration is $1s^2 2s^2$. Thus we have

Li	Be
$1s^2 2s^1$	$1s^2 2s^2$

The next element is boron ($Z=5$). Since the K shell and $2s$ subshell are full, the fifth electron occupies the $2p$ subshell. As Z increases from 5 to 10, the electrons fill the $2p$ subshell progressively, so that we have for $Z=5$ to 10:

B	C	N	O	F	Ne
$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$

Then, the electronic configuration of a sodium atom having 11 electrons is $1s^2 2s^2 2p^6 3s^1$. It has four subshells having different values of (nl) . Out of these four subshells, the first three have maximum permissible number of electrons. Such subshells are said to be closed **subshells**. The last one is called an open **subshell**.

From $Z=11$ to $Z=18$ (argon), the $3p$ levels fill progressively. For $Z=19$ (potassium), you might expect the nineteenth electron to go to $3d$ level but the $4s$ level has a lower energy than $3d$ level. Therefore, the ground state electronic configuration of a potassium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ and not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$. Similarly, the ground state electronic configuration of Scandium atom ($Z=21$) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$. These configurations agree with the experimental observations. You should concretise these ideas in your mind before studying further. The following SAQ will help you do this.

Spend
10 min

SAQ 6

Determine the electronic configurations for atoms with $Z=20$, $Z=25$, $Z=31$ and $Z=37$.

Spectral Terms of a Multielectron Atom

How do we determine the spectral terms of a multielectron atom? For such atoms, only the open subshells contribute towards total L , S and J values,

Let us consider the carbon atom ($Z=6$) as an example. Its electronic configuration is $1s^2 2s^2 2p^2$. Since only the open subshell matters, let us consider the two electrons in the $2p$ subshell. For these electrons:

$$n_1 = 2, l_1 = 1, s_1 = \frac{1}{2} \text{ and } n_2 = 2, l_2 = 1, s_2 = \frac{1}{2}$$

Thus, the total spin $S = \frac{1}{2} + \frac{1}{2}, \left| \frac{1}{2} - \frac{1}{2} \right| = 1, 0$

and the total orbital angular momentum

$$L = 1 + 1, 1 + 1 - 1, |1 - 1| \\ = 2, 1, 0.$$

Thus for $S = 0$ the possible J values are $J = 0, 1, 2$ and for $S = 1$, $J = 1, (2, 1, 0), (3, 2, 1)$.

Now the Pauli exclusion principle also tells us that $S = 0$ *should correspond to even values of L* and $S = 1$ *goes with states of odd L* . Therefore, we can only have the following L, S, J combinations:

$$S = 0, L = 0 \text{ whence } J = 0 \\ S = 0, L = 2 \text{ whence } J = 2 \\ S = 1, L = 1 \text{ whence } J = 2, 1, 0$$

Thus, the spectral terms are

$${}^1S_0, {}^3P_0, {}^3P_1, {}^3P_2 \text{ and } {}^1D_2$$

Now the question is: *which of these has the lowest energy?* We can determine this using the three **Hund's rules** given as follows:

1. The state with the largest spin has lowest energy.
2. If the incomplete subshell is less than hdf full, $J = |L - S|$ is the ground state: if it is more than hdf full $J = L + S$ is the ground state.
3. Among the levels with a given value of S , the state with the largest value of L has the smallest energy.

Let us apply these rules to Carbon atom. Rule 1 tells us that the lowest state is one of the 3P states. Rule 2 tells us that the lowest energy state is the one with $J = 0$. Thus, the ground state of carbon atom is the 3P_0 state. Using Rule 3, we can tell that 1D_2 has lower energy than 1S_0 , although neither is the ground state. Incidentally, Hund's rules are not *ad hoc* — they agree with quantum mechanical calculations.

The spectral terms are very important in spectroscopy where the L, S, J quantum numbers are part and parcel of the selection rules that govern transitions between atomic states. We will briefly state them. But before that you should fix the ideas presented here by **doing** the following exercise.

SAQ 7

Spend
10 min

Obtain the ground state terms of He, Li, Si, and Sc.

Atoms can also exist in excited states. However, to **minimise** their energies they make transitions from one excited state to lower excited states and ground state. These selection rules for allowed transitions in multielectrons atoms are as follows:

- (i) $\Delta J = 0, \pm 1$ ($J = 0 \longrightarrow J' = 0$ is not allowed)
- (ii) $\Delta L = 0, \pm 1$ (10.18)
- (iii) $\Delta S = 0$
- (iv) $\Delta l = \pm 1$

where l is the orbital angular momentum quantum number of the atomic electron which **takes** part in the transition. The same rules are followed when an atom absorbs electromagnetic radiation and **makes** a transition from a lower state to a higher **excited** state. One of the features of **atomic** line spectra **is** that the width of the emitted line is finite. This feature can be explained with the help of the concepts you have studied so **far** — it arises due to the finite life time of excited states. We will now discuss it briefly.

10.6.1 Life Time of Excited States and Line Broadening

Let us consider two stationary states of an atom having energies E_1 and $E_2 (> E_1)$. If the atom is in the upper state it will have a natural tendency to make a transition to the lower state and during the transition it will radiate electromagnetic radiations. At the start of the transition the atomic energy was E_2 and at the end the atomic energy is E_1 . Hence the excess energy decreases with time. The reduction of the excess energy with time is found to be exponential. At time t the excess energy is given by

$$E = E_0 \exp(-\gamma t) \quad (10.19a)$$

where $E_0 = E_2 - E_1$. Now the life time τ of an excited state is defined to be that time in which E reduces to a value E_0/e . You can readily verify that the above definition yields

$$\tau = 1/\gamma \quad (10.19b)$$

Due to the decrease of the excess energy E with time, the radiation emitted by the atom is not strictly monochromatic. A plot of $I(\nu)$ (energy emitted per unit frequency range) versus the frequency ν of the emitted radiation gives a curve as shown in Fig. 10.6.

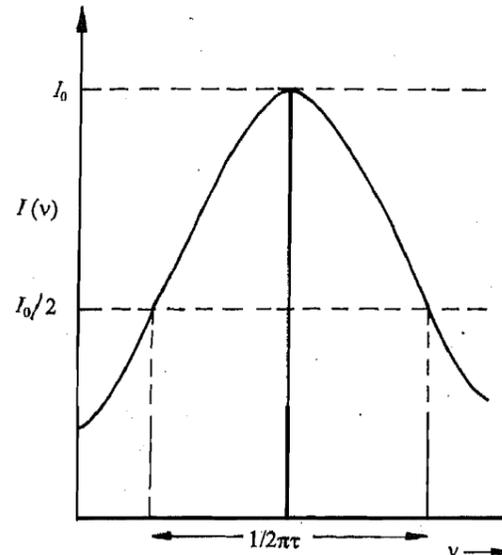


Fig. 10.6: Spectral distribution of emitted radiation.

We find that the frequency width of the curve at $I_0/2$, where I_0 is the maximum value of $I(\lambda)$, is $1/2\pi\tau$. Hence the energy width of the spectral line is given by

$$\Delta E = h \Delta \nu = h/2\pi\tau$$

or

$$\tau \Delta E = \hbar \quad (10.19c)$$

Thus the smaller is the life time, larger is the energy width of the emitted line. You may recall that the width of a line is a consequence of the uncertainty principle and τ is known as the natural life time. For excited states which are connected to the lower states by allowed transitions, the life time is of the order of 10^{-8} s. For other excited states, the life time is much longer and can be equal to several seconds. According to Eq. (10.19c), the increase of τ reduces the width of the spectral line.

Let us now summarise what you have studied in this unit.

10.7 SUMMARY

- In this unit you have studied the **Stern-Gerlach** experiment which measured the magnetic moment of an atom and also gave a direct verification of space quantization. The quantitative results of the **Stern-Gerlach experiment** could not be

explained by the help of three quantum numbers n , l and m_l . Goudsmit and Uhlenbeck introduced the concept of an intrinsic angular momentum known as spin angular momentum \mathbf{S} associated with an electron. The quantum number associated with S is always $1/2$ giving rise to $m_s = \pm 1/2$.

- The **orbital** and **spin angular momenta** couple to produce **total angular momentum \mathbf{J}** and quantum numbers j and m_j . Due to **spin-orbit coupling** (combination of \mathbf{L} and \mathbf{S}) and relativistic effects, the energy of hydrogen-like atoms depends upon n as well as j . This explains the doublet structure of the first member of **Balmer** series and the two close spectral lines produced in a sodium lamp.
- Certain **selection rules** are followed when a hydrogen-like atom or a multielectron atom makes a transition from one stationary state to another.
- Every excited state has a **finite life time τ** and when an atom makes a transition from one state to another the spectral line so produced has a **finite width**: $\Delta E = \hbar/\tau$.

10.8 TERMINAL QUESTIONS

Spend 30 min

1. Use expressions given for \mathbf{S} in SAQ 3 to show that it satisfies the following operator equation

$$\mathbf{S} \times \mathbf{S} = i\hbar\mathbf{S}$$

2. The number of allowed values of J for two different atoms in P and D states is the same and equal to three. Determine the spin angular momentum of the atoms in these states.
3. State with reasons whether following transitions for a multielectron atom are allowed:
 - (i) ${}^3P_0 \longrightarrow {}^3S_1$
 - (ii) ${}^3S_1 \longrightarrow {}^1S_0$
 - (iii) ${}^1S_{1/2} \longrightarrow {}^1P_{3/2}$
 - (iv) ${}^1S_{1/2} \longrightarrow {}^1D_{3/2}$

10.9 SOLUTIONS AND ANSWERS

Self-Assessment Questions

$$1. \mu_B = e\hbar/2m = \frac{1.60 \times 10^{-19} \text{ C} \times 1.054 \times 10^{-34} \text{ Js}}{2 \times 9.109 \times 10^{-31} \text{ kg}}$$

$$= 9.27 \times 10^{-24} \text{ Joule Tesla}^{-1} \text{ (or amp. meter}^2\text{)}$$

2. Let the radius and the linear velocity of the spinning electron be r and v , respectively. The spinning of the electron about its own axis produces a current of the order of magnitude $ev/2\pi r$. The corresponding magnetic moment is given by *

$$\mu_B = IA = \frac{ev}{2\pi r} \pi r^2$$

Equating the above quantity to the experimental value $e\hbar/2m$ we get

$$v = \hbar/mr$$

Now the classical radius of the electron is obtained by equating its self electrostatic energy e^2/r to its rest mass energy mc^2 . Thus we get

$$\frac{v}{c} = \frac{\hbar c}{e^2} = 137.$$

Hence v is greater than c and it violates the special theory of relativity.

3. You can easily show by matrix multiplication (see margin remark) that

$$\sigma_x \alpha = \beta, \quad \sigma_x \beta = \alpha, \quad \sigma_y \alpha = i\beta, \quad \sigma_y \beta = -i\alpha$$

$$\sigma_z \alpha = \alpha, \quad \sigma_z \beta = -\beta$$

Hence $S^2 \alpha = (S_x^2 + S_y^2 + S_z^2) \alpha$

$$\begin{aligned} &= \frac{\hbar^2}{4} (\sigma_x^2 + \sigma_y^2 + \sigma_z^2) \alpha \\ &= \frac{\hbar^2}{4} (\alpha \alpha + \sigma_y \sigma_y + \sigma_z \sigma_z) \alpha \\ &= \frac{\hbar^2}{4} (\sigma_x \beta + i\sigma_y \beta + \sigma_z \alpha) \\ &= \frac{\hbar^2}{4} [\alpha + \alpha + \alpha] \\ &= \frac{3\hbar^2}{4} \alpha \end{aligned}$$

and $S_z \alpha = \frac{\hbar}{2} \sigma_z \alpha = \frac{\hbar}{2} \alpha$.

Similarly, $S^2 \beta = (3/4)\hbar^2 \beta$ and $S_z \beta = -(1/2)\hbar \beta$.

Furthermore

$$\alpha \beta = (1 \ 0) \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$$

Hence α and β are orthogonal.

4. For $n = 2, l = 0, 1$ and $s = \frac{1}{2}$. Thus, for

$$L = 0, \quad J = 1/2$$

$$L = 1, \quad J = 1/2, 3/2$$

So the terms are $2^2S_{1/2}, 2^2P_{1/2}, 2^2P_{3/2}$.

For $n = 3, l = 0, 1, 2$ and $s = \frac{1}{2}$. Thus, for

$$L = 0, \quad J = 1/2$$

$$L = 1, \quad J = 1/2, 3/2$$

$$L = 2, \quad J = 3/2, 5/2$$

So the terms are $3^2S_{1/2}, 3^2P_{1/2}, 3^2P_{3/2}, 3^2D_{3/2}, 3^2D_{5/2}$.

5.
$$\Delta E = -\frac{RZ^4 \alpha^2}{n^3} [1/2 - 1/1]$$

$$= 13.6 \times \left(\frac{1}{137}\right)^2 \times \frac{1}{27} \times \frac{1}{2} \text{ eV}$$

$$= 1.34 \times 10^{-5} \text{ eV}$$

6. These are

$$Z = 20 \text{ (Calcium)} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

$$Z = 25 \text{ (Manganese)} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$$

$$Z = 31 \text{ (Gallium)} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p$$

$$Z = 37 \text{ (Rubidium)} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s$$

$$\begin{aligned} \sigma_x \alpha &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \beta \end{aligned}$$

$$\begin{aligned} \sigma_x \beta &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \alpha \end{aligned}$$

$$\begin{aligned} \sigma_y \alpha &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 \\ i \end{pmatrix} = i\beta \end{aligned}$$

$$\begin{aligned} \sigma_y \beta &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} -i \\ 0 \end{pmatrix} = -i\alpha \end{aligned}$$

$$\begin{aligned} \sigma_z \alpha &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \alpha \end{aligned}$$

$$\begin{aligned} \sigma_z \beta &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\beta \end{aligned}$$

7. For He ($Z = 2$), the configuration is $1s^2$.

$$\text{Since } n_1 = 1, l_1 = 0, s_1 = \frac{1}{2}, n_2 = 1, l_2 = 0, s_2 = \frac{1}{2}$$

Therefore

$$L = 0$$

$S = 1, 0$ whence $J = 0$ for $L = 0$ and $S = 0$ (since $S = 1$ goes only with odd values of L which are **non-existent** in this case.)

Thus, the spectral term for the ground state of He atom ($1s^2$) is 1^1S_0 .

For Li, $Z = 3$ and the configuration is $1s^2 2s^1$. Thus, for the electron in the incomplete shell,

$$n = 2, l = 0, s = \frac{1}{2} \text{ and } J = \frac{1}{2}$$

The ground state spectral term is $2^2S_{1/2}$.

For Si ($Z = 14$) the configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$. For the 2 electrons in the incomplete subshell ($3p$), we have

$$n_1 = 3, l_1 = 1, s_1 = \frac{1}{2}, n_2 = 3, l_2 = 1, s_2 = \frac{1}{2}$$

Once again $S = 1, 0$

$$L = 2, 1, 0$$

For $S = 0, L = 0, J = 0$

$$S = 1, L = 1, J = 2, 1, 0$$

$$S = 0, L = 2, J = 2$$

Hence the spectral terms are $1^1S_0, 3^1P_0, 3^1P_1, 3^1P_2$ and 1^1D_2 . The ground state is 3^1P_0 .

For Sc ($Z = 21$), the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$. For the valence electron $n = 3, l = 2, s = \frac{1}{2}$ and $J = \frac{3}{2}, \frac{5}{2}$. The spectral terms are $3^2D_{5/2}, 3^2D_{3/2}$.

According to Hund's rule 2, the ground state is $3^2D_{3/2}$ since the subshell is less than half full.

Terminal Questions

1. We have

$$\begin{aligned} (\mathbf{S} \times \mathbf{S})_x &= S_y S_z - S_z S_y \\ &= \frac{1}{4} \hbar^2 (\sigma_y \sigma_z - \sigma_z \sigma_y) \\ &= \frac{1}{4} \hbar^2 (2i \sigma_x) = i \frac{\hbar^2}{2} \sigma_x = i \hbar S_x. \quad (\because \sigma_y \sigma_z = i \sigma_x \text{ and } \sigma_z \sigma_y = -i \sigma_x) \end{aligned}$$

Similarly, we can obtain the values for y and z components of $\mathbf{S} \times \mathbf{S}$.

2. For the P state $L = 1$ and it is given that $J = 3$. Hence $S = J - L = 2$.

For the D state $L = 2$ and $J = 3$. Therefore $S = 3 - 2 = 1$.

3. (i) Allowed because it is according to the selection rules given by Eq. (10.18).

(ii) Forbidden because $\Delta S \neq 0$.

(iii) Allowed.

(iv) Forbidden because $\Delta L = 2$.