

Lecture 14 Title: Evaluation of Terms of an atom

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In this lecture, we will learn the method to evaluate the spectroscopic terms arising from the electronic configuration of an atom.

The terms of an atom are the energy levels evaluated by considering the electron-electron repulsion in the Hamiltonian.

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In previous lectures, we have understood that the electronic wavefunctions in the central field approximation are characterized by four basic single electron quantum numbers :

$$n, l, m_l, m_s$$

These are the good quantum numbers with respect to the Central field Hamiltonian

$$H^* \Phi = \left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i) \right\} \Phi = E \Phi$$

The reason is

$$H_1^* \phi_1 = E_1 \phi_1 \quad ; \quad H_2^* \phi_2 = E_2 \phi_2 \quad ; \quad \dots$$

$$H^* = \sum_{i=1}^N H_i^* \quad ; \quad E = \sum_i E_i$$

When non-spherical part of the electron-electron repulsion $\sum \frac{e^2}{r_{ij}}$ is included in the

Hamiltonian , these single electron quantum numbers are no more the good quantum numbers since they do not commute with the Hamiltonian

$$H = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{Z e^2}{r_1} - \frac{Z e^2}{r_2} + \frac{e^2}{r_{12}}$$

$$\text{In this case } [H, L] = 0 \quad [H, S] = 0$$

$$\text{And also } [H, L^2] = 0 \quad [H, S^2] = 0$$

Where $L = l_1 + l_2 + l_3 + \dots = \sum l_i$, similarly $S = s_1 + s_2 + s_3 + \dots = \sum s_i$

So, L and S are the good quantum numbers to characterize the total wavefunction of the system. In this regard we have discussed in the last lecture about procedure and rules of the coupling of angular momenta.

The energy levels will be in terms of L and S and are thus named as Terms. The notation for these terms are ^{2S+1}L and coupled wavefunctions are $|L, S, M_L, M_S\rangle$

Next we will use the coupling of angular momentum procedure to find out the terms arising for a multielectronic atom from its electronic configuration.

Now let us understand the degeneracy of a level arising from the electronic configuration.

The distribution of electrons with n and ℓ are known as configuration.

Example: For Helium : electronic configuration of the ground state is $1s^2$

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

Electrons in orbitals with same n and ℓ are said to be ***equivalent***.

Electrons in orbitals with different n or ℓ are said to be ***nonequivalent***

Such as Excited state of Helium: $1s^1 2s^1$ or $1s^1 2p^1$ e.t.c

The case of a sub shell (same n and ℓ) degeneracy,

$$2(2\ell + 1) \quad 2\ell + 1 \text{ for } m_\ell$$

$$2s + 1 \text{ for } m_s$$

$$\ell = 0 \quad (s) \quad \text{max. no. of electrons} = 2$$

$$\ell = 1 \quad (p) \quad \text{max. no. of electrons} = 6$$

$$\ell = 2 \quad (d) \quad \text{max. no. of electrons} = 10$$

$$\ell = 3 \quad (f) \quad \text{max. no. of electrons} = 14$$

A sub shell containing $2(2\ell + 1)$ electrons is said to be complete.

Order of degeneracy of a configuration:

- 1) A single electron in each subshell.

$$Y_i = 2(2\ell_i + 1)$$

$$\text{So degeneracy } G = \prod_i Y_i$$

Ex.

$$1s \ 2s \ 2p \quad G = 2 \times 2 \times 6 = 24$$

$$2p \ 3d \ 4f \quad G = 6 \times 10 \times 14 = 840$$

2. Several electrons in the same subshell.

$$\text{degeneracy of a shell } g = \frac{Y!}{X!(Y-X)!}$$

X = no of electrons; Y = total no of electrons occupy in that shell

Example:

What is the degeneracy G of the ground state of carbon (6)?

Configuration $1s^2 \ 2s^2 \ 2p^2$

$$\text{For } 1s \ X = 2 ; Y = 2 , g = 1$$

$$\text{For } 2s \ X = 2 ; Y = 2 , g = 1 \quad G = 15$$

$$\text{For } 2p \ X = 2 ; Y = 6 , g = 15$$

Example

$1s^2 \ 2s^2 \ 2p^2 \ 3p^1$ excited state of Nitrogen

$$1s \quad g = 1$$

$$2s \quad g = 1 \quad G = 15 \times 6 = 90$$

$$2p^2 \quad g = 15$$

$$3p \ X = 1 \ Y = 6 \ g = 6$$

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Now, we will find out the terms using the rules for the coupling of angular momenta are

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

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

$$M_L = m_{l_1} + m_{l_2} \quad M_S = m_{s_1} + m_{s_2}$$

Take the case of Helium,

The distribution of electrons with n and ℓ are known as configuration.
electronic configuration of the ground state is $1s^2$

$$1s^2 \quad ; \quad \ell_1 = 0 \quad ; \quad \ell_2 = 0 \quad ; \quad L = 0$$
$$s_1 = \frac{1}{2} \quad ; \quad s_2 = \frac{1}{2} \quad ; \quad S = 1 \text{ and } 0;$$

So the terms are 1S and 3S , but 3S will not be there because it violates the Pauli exclusion principle.

Excited states:

$$1s^1 2s^1 \quad ; \quad \ell_1 = 0 \quad ; \quad \ell_2 = 0 \quad ; \quad L = 0$$
$$s_1 = \frac{1}{2} \quad ; \quad s_2 = \frac{1}{2} \quad ; \quad S = 1 \text{ and } 0;$$

So the terms are 1S and 3S .

$$1s^1 2p^1 \quad ; \quad \ell_1 = 0 \quad ; \quad \ell_2 = 1 \quad ; \quad L = 1$$
$$s_1 = \frac{1}{2} \quad ; \quad s_2 = \frac{1}{2} \quad ; \quad S = 1 \text{ and } 0;$$

So the terms are 1P and 3P

$$1s^1 2d^1 \quad ; \quad \ell_1 = 0 \quad ; \quad \ell_2 = 2 \quad ; \quad L = 2$$
$$s_1 = \frac{1}{2} \quad ; \quad s_2 = \frac{1}{2} \quad ; \quad S = 1 \text{ and } 0;$$

So the terms are 1D and 3D and so on.

Let us take another example:

Carbon: Ground electronic configuration $1s^2 2s^2 2p^2$

$$2p^2 ; \quad \ell_1 = 1 ; \quad \ell_2 = 1 ; \quad L = 2, 1, 0$$

$$s_1 = \frac{1}{2} ; \quad s_2 = \frac{1}{2} ; \quad S = 1 \text{ and } 0;$$

So the terms are $^3D, ^1D, ^3P, ^1P, ^3S, ^1S$, however only $^1D, ^3P, ^1S$ will survive because of the Pauli exclusion principle.

Excited states :

Configuration : $2p^1 3s^1$

$$2p^1 3s^1 ; \quad \ell_1 = 1 ; \quad \ell_2 = 0 ; \quad L = 1$$

$$s_1 = \frac{1}{2} ; \quad s_2 = \frac{1}{2} ; \quad S = 1 \text{ and } 0;$$

So the terms are $^3P, ^1P$

Configuration : $2p^1 3p^1$

$$2p^1 3p^1 ; \quad \ell_1 = 1 ; \quad \ell_2 = 1 ; \quad L = 2, 1, 0$$

$$s_1 = \frac{1}{2} ; \quad s_2 = \frac{1}{2} ; \quad S = 1 \text{ and } 0;$$

So the terms are $^3D, ^1D, ^3P, ^1P, ^3S, ^1S$

This is the way terms are evaluated from the electronic configuration. We have also seen for two equivalent electrons, only terms survive with $L + S = \text{even}$. For three electrons there are no straight forward rules for that. To evaluate the terms, thus we follow the $M_L - M_S$ table. This is most general method and provides insight of the each electron quantum numbers to evaluate the terms.

$M_L - M_S$ Table:

To construct the $M_L - M_S$ table,

1. First find out the M_L from m_{l_1} and m_{l_2} and M_S from m_{s_1} and m_{s_2}
2. Use the notation to make a table. $(m_{l_1}^{m_{s_1}}, m_{l_2}^{m_{s_2}})$.
3. For filling up, we have to keep in mind the coupling rules

$$M_L = m_{l_1} + m_{l_2} \quad M_S = m_{s_1} + m_{s_2}$$
4. We have to also remember the Pauli exclusion principle i.e. not two electrons have the same quantum numbers n, l, m_l, s, m_s

Lets take an example.

Configuration : $1s^2$ (equivalent electrons) and $1s2s$ nonequivalent electrons

$$1s^2 / 1s2s \quad ; \quad \ell_1 = 0 \quad ; \quad m_{l_1} = 0 \quad \ell_2 = 0 \quad ; \quad m_{l_1} = 0$$

$$L = 0, \quad M_L = 0$$

$$s_1 = \frac{1}{2} \quad ; \quad m_{s_1} = \frac{1}{2}, -\frac{1}{2} \quad s_2 = \frac{1}{2} \quad ; \quad m_{s_2} = \frac{1}{2}, -\frac{1}{2}$$

$$S = 1 \text{ and } 0; \quad M_S = 1, 0, -1$$

m_l	m_s	Notation
0	$\frac{1}{2}$	0^+
0	$-\frac{1}{2}$	0^-

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Now make the $M_L - M_S$

For $1s^2$

$M_S \setminus M_L$	0
1	$0^+ 0^+$
0	$0^+ 0^-$ $0^- 0^+$
-1	$0^- 0^-$

Here, the crossed terms will not survive because of the Pauli Exclusion principle. Now for finding the terms, start with highest $M_L = 0$ and highest $M_S = 0$. This will arise from $L = 0$ and $S = 0$. The degeneracy is 1. So the terms is 1S

For $1s2s$

$M_S \setminus M_L$	0
1	$0^+ 0^+$
0	$0^+ 0^-$ $0^- 0^+$
-1	$0^- 0^-$

Here, the all terms will survive. Now for finding the terms, start with highest $M_L = 0$ and highest $M_S = 1$. This will arise from $L = 0$ and $S = 1$.

The degeneracy $(2L+1)(2S+1)$ is 3. There will be three combinations coming from each block corresponding to the terms is 3S .

There will be one combination in $M_L = 0$ and $M_S = 0$. The terms is 1S

So the terms arising from $1s2s$ are 3S and 1S

Now take another example.

p^2 Degeneracy of this configuration is 15

$$\ell_1 = 1 ; m_{\ell_1} = 1, 0, -1$$

$$s_1 = 1 ; m_{s_1} = \frac{1}{2}, -\frac{1}{2}$$

$$\ell_2 = 1 ; m_{\ell_2} = 1, 0, -1$$

$$s_2 = 1 ; m_{s_2} = \frac{1}{2}, -\frac{1}{2}$$

$$L(\max) = 2, M_L = 2, 1, 0, -1, -2$$

$$S(\max) = 1, M_s = 1, 0, -1$$

$M_S \setminus M_L$	2	1	0	-1	-2
1		$1^+ 0^+$	$0^+ 0^+$ $1^+ -1^+$	$-1^+ 0^+$	
0	$1^+ 1^-$	$1^+ 0^-$ $1^- 0^+$	$0^+ 0^-$ $1^+ -1^-$ $1^- -1^+$	$-1^+ 0^-$ $-1^- 0^+$	$-1^+ -1^-$
-1		$1^- 0^-$	$0^- 0^-$ $1^- -1^-$	$-1^- 0^-$	

$$\left. \begin{array}{l} L=2 \\ S=0 \end{array} \right\} \begin{array}{l} M_L = 2, 1, 0, -1, -2 \\ M_S = 0 \end{array} \Bigg\} {}^1D \Rightarrow 5 \text{ levels}$$

Remove one combination from each block of M_L and M_S .

$$\left. \begin{array}{l} L=1 \\ S=1 \end{array} \right\} \begin{array}{l} M_L = 1, 0, -1 \\ M_S = 1, 0, -1 \end{array} \Bigg\} {}^3P \Rightarrow 9 \text{ levels}$$

$$\begin{array}{l} M_L \\ M_S \end{array} \begin{array}{ccccccccc} 1 & 1 & 1 & 0 & 0 & 0 & -1 & -1 & -1 \\ 1 & 0 & -1 & 1 & 0 & -1 & 1 & 0 & -1 \end{array}$$

Remove one combination from each block of M_L and M_S

$$\left. \begin{array}{l} L=0 \\ S=0 \end{array} \right\} \begin{array}{l} M_L = 0 \\ M_S = 0 \end{array} \Bigg\} {}^1S \Rightarrow 1$$

Remove one combination from each block of M_L and M_S

Total $\Rightarrow 15$ levels

Note that p^4 will also have the same terms.

Now $p\ p$ configuration

Degeneracy of this configuration

$$(2\ell+1)(2\ell+1)(2s+1)(2s+1)$$

$$3 \times 3 \times 2 \times 2 = 36$$

$M_S \setminus M_L$	2	1	0	-1	-2
1	$1^+ 1^+$	$1^+ 0^+$ $0^+ 1^+$	$1^+ -1^+$ $-1^+ 1^+$ $0^+ 0^+$	$-1^+ 0^+$ $0^+ -1^+$	$-1^+ -1^+$
0	$1^+ 1^-$ $1^- 1^+$	$1^+ 0^-$ $1^- 0^+$ $0^+ 1^-$ $0^- 1^+$	$1^+ -1^-$ $1^- -1^+$ $-1^+ 1^-$ $-1^- 1^+$ $0^+ 0^-$ $0^- 0^+$	$-1^+ 0^-$ $-1^- 0^+$ $0^+ -1^-$ $0^- -1^+$	$-1^+ -1^-$ $-1^- -1^+$
-1	$1^- 1^-$	$1^- 0^-$ $0^- 1^-$	$1^- -1^-$ $-1^- 1^-$ $0^- 0^-$	$-1^- 0^-$ $0^- -1^-$	$-1^- -1^-$

$$\left. \begin{array}{l} L=2 \\ S=1 \end{array} \right\} \begin{array}{l} M_L = 2, 1, 0, -1, -2 \\ M_S = 1, 0, -1 \end{array} \Rightarrow 15 \text{ levels}$$

$$\left. \begin{array}{l} L=2 \\ S=0 \end{array} \right\} \begin{array}{l} M_L = 2, 1, 0, -1, -2 \\ M_S = 0 \end{array} \Rightarrow 5 \text{ levels}$$

$$\left. \begin{array}{l} L=1 \\ S=1 \end{array} \right\} \begin{array}{l} M_L = 1, 0, -1 \\ M_S = 1, 0, -1 \end{array} \Rightarrow 9 \text{ levels}$$

$$\begin{array}{ll} L=1 & M_L = 1, 0, -1 \\ S=0 & M_S = 0 \end{array} \Bigg\} \Rightarrow 3 \text{ levels}$$

$$\begin{array}{ll} L=0 & M_L = 0 \\ S=1 & M_S = 1, 0, -1 \end{array} \Bigg\} \Rightarrow 3 \text{ levels}$$

$$\begin{array}{ll} L=0 & M_L = 0 \\ S=0 & M_S = 0 \end{array} \Bigg\} \Rightarrow 1 \text{ level}$$

$$\text{Total} \quad \Rightarrow \quad 36 \text{ levels}$$

Now we calculate the energies for the splitting

For two electrons semi-empirical

$$\Delta E = \langle L M_L | \langle S M_S | a_1 \ell_1 \cdot \ell_2 + a_2 s_1 \cdot s_2 | S M_S \rangle | L M_L \rangle$$

a_1 & a_2 function of n, ℓ i.e. $a_1(n, \ell)$; $a_2(n, \ell)$

$$L = \ell_1 + \ell_2$$

$$L^2 = \ell_1^2 + \ell_2^2 + 2 \ell_1 \cdot \ell_2$$

$$\Rightarrow \ell_1 \cdot \ell_2 = \frac{L^2 - \ell_1^2 - \ell_2^2}{2}$$

$$\langle L M_L | \frac{L^2 - \ell_1^2 - \ell_2^2}{2} | L M_L \rangle = \frac{1}{2} [L(L+1) - \ell_1(\ell_1+1) - \ell_2(\ell_2+1)]$$

$$\langle S M_S | \frac{S^2 - s_1^2 - s_2^2}{2} | S M_S \rangle = \frac{1}{2} [S(S+1) - s_1(s_1+1) - s_2(s_2+1)]$$

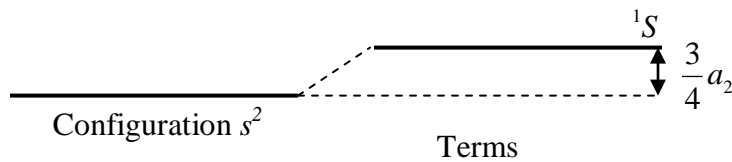
$$\Delta E = \frac{a_1}{2} [L(L+1) - \ell_1(\ell_1+1) - \ell_2(\ell_2+1)] + \frac{a_2}{2} [S(S+1) - s_1(s_1+1) - s_2(s_2+1)]$$

$$1s^2 \quad ; \quad S, L = 0 \quad ; \quad \ell_1 = 0 \quad ; \quad s_1 = 1/2$$

$$S = 0 \quad ; \quad \ell_2 = 0 \quad ; \quad s_2 = 1/2$$

$$\begin{aligned} \Delta E &= \frac{a_1}{2} [0] + \frac{a_2}{2} \left[0 - \frac{1}{2} \left(\frac{1}{2} + 1 \right) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right] \\ &= \frac{a_2}{2} \left[-\frac{3}{4} - \frac{3}{4} \right] = -\frac{3}{4} a_2 \end{aligned}$$

The energy ΔE is positive so a_2 is negative



1s 2s

$$^1S \Rightarrow L=0 ; S=0 ; \quad \ell_1=0, \ell_2=0 ; s_1=\frac{1}{2}, s_2=\frac{1}{2}$$

$$^3S \Rightarrow L=0 ; S=1 ; \quad \ell_1=0, \ell_2=0 ; s_1=\frac{1}{2}, s_2=\frac{1}{2}$$

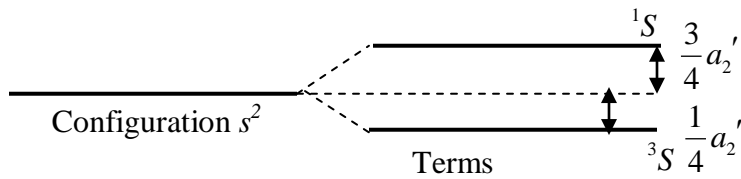
$$^1S : \Delta E = \frac{a_1'}{2}[0] + \frac{a_2'}{2}\left[0 - \frac{3}{4} - \frac{3}{4}\right]$$

$$= -\frac{3}{4}a_2'$$

$$^3S : \Delta E = \frac{a_1'}{2}[0] + \frac{a_2'}{2}\left[2 - \frac{3}{2}\right]$$

$$= \frac{a_2'}{4}$$

The constant a_2 is negative.



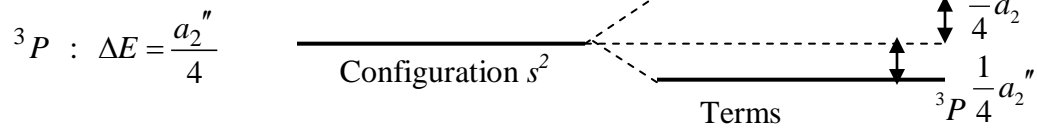
1s 2p

$$^1P \Rightarrow L=1 ; S=1 ; \quad \ell_1=1, \ell_2=0 ; s_1=\frac{1}{2}, s_2=\frac{1}{2}$$

$$^3P \Rightarrow L=1 ; S=1 ; \quad \ell_1=1, \ell_2=0 ; s_1=\frac{1}{2}, s_2=\frac{1}{2}$$

$$^1P : \Delta E = \frac{a_1''}{2}[2-2] + \frac{a_2''}{2}\left[0 - \frac{3}{2}\right]$$

$$= -\frac{3}{4}a_2''$$



Now let us look at the terms arising from three electrons configuration p^3

$$\begin{array}{ll} \ell_1 = 1 \ ; \ m_{\ell_1} = 1, 0, -1 & s_1 = 1 \ ; \ m_{s_1} = \frac{1}{2}, -\frac{1}{2} \\ \ell_2 = 1 \ ; \ m_{\ell_2} = 1, 0, -1. & s_2 = 1 \ ; \ m_{s_2} = \frac{1}{2}, -\frac{1}{2} \\ \ell_3 = 1 \ ; \ m_{\ell_3} = 1, 0, -1 & s_3 = 1 \ ; \ m_{s_3} = \frac{1}{2}, -\frac{1}{2} \end{array}$$

$$L(\max) = 3, \quad M_L = 3, 2, 1, 0, -1, -2, -3 \quad S(\max) = \frac{3}{2}, \quad M_s = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

$M_S \backslash M_L$	3	2	1	0	-1	-2	-3
$\frac{3}{2}$				$1^+ 0^+ -1^+$			
$\frac{1}{2}$		$1^+ 0^+ 1^-$	$1^+ 0^+ 0^-$ $1^+ -1^+ 1^-$	$1^+ 0^+ -1^-$ $1^+ -1^+ 0^-$ $0^+ -1^+ 1^-$	$1^+ -1^+ -1^-$ $0^+ -1^+ 0^-$	$-1^+ 0^+ -1^-$	
$-\frac{1}{2}$		$1^+ 0^- 1^-$	$1^+ 1^- -1^-$ $0^+ 1^- 0^-$	$1^+ 0^- -1^-$ $0^+ 1^- -1^-$ $-1^- 1^- 0^-$	$-1^+ 0^+ -1^-$ $0^+ -1^- 0^-$	$-1^+ 0^+ -1^-$	
$-\frac{3}{2}$				$1^- 0^- -1^-$			

Let us write down the number of combination in each block

$M_S \backslash M_L$	2	1	0	-1	-2
$\frac{3}{2}$			1		
$\frac{1}{2}$	1	2	3	2	1
$-\frac{1}{2}$	1	2	3	2	1
$-\frac{3}{2}$			1		

Terms arising from maximum $M_L = 2$ and maximum $M_S = 1/2$ is 2D . Total combination for this term is 10. Take out from each block of $M_L = 2, 1, 0, -1, -2$ and $M_S = \frac{1}{2}$ and $-\frac{1}{2}$.

That reduces to

$M_S \backslash M_L$	2	1	0	-1	-2
$\frac{3}{2}$			1		
$\frac{1}{2}$	0	1	2	1	0
$-\frac{1}{2}$	0	1	2	1	0
$-\frac{3}{2}$			1		

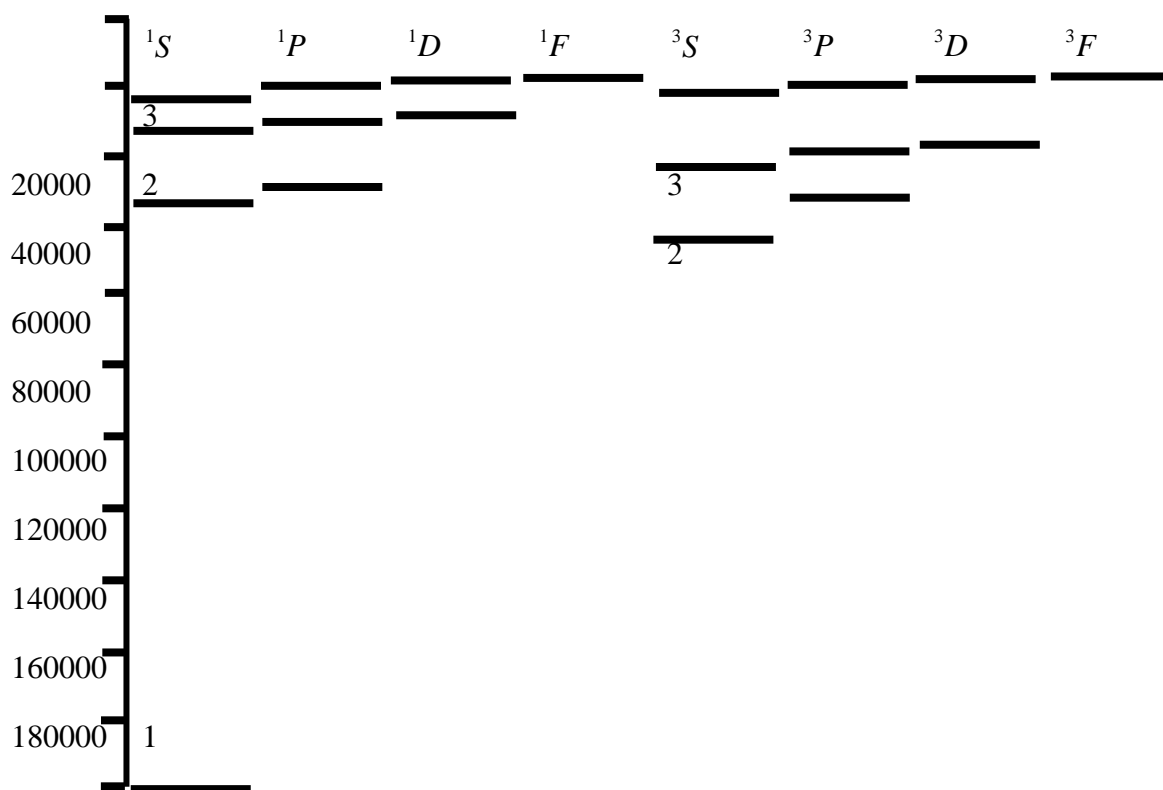
Next Terms arising from maximum $M_L = 1$ and maximum $M_S = 1/2$ is 2P . Total combination for this term is 6. Take out from each block of $M_L = 1, 0, -1$, $M_S = 1/2$ and $-1/2$.

$M_S \backslash M_L$	2	1	0	-1	-2
$3/2$			1		
$1/2$	0	0	1	0	0
$-1/2$	0	0	1	0	0
$-3/2$			1		

Next Terms arising from maximum $M_L = 0$ and maximum $M_S = 3/2$ is 4S . Total combination for this term is 4. Take out from each block of $M_L = 0$ $M_S =$

$3/2, 1/2, -1/2, -3/2$.

Helium Spectroscopic Terms



Spectroscopic terms of Equivalent electrons and their degeneracy

Electronic Configuration	Number of degeneracy	Spectroscopic Terms
ns^1	1	2S
ns^2	1	1S
np^0, np^6	1	1S
np, np^5	6	2P
np^2, np^4	15	$^1S, ^1D, ^3P$
np^3	20	$^2P, ^2D, ^4S$
nd^0, nd^{10}	1	1S
nd, nd^9	10	2D
nd^2, nd^8	45	$^1S, ^1D, ^1G, ^3P, ^3F$
nd^3, nd^7	120	$^2D(2), ^2P, ^2F, ^2G, ^2H, ^4P, ^4F$
nd^4, nd^6	210	$^1S(2), ^1D(2), ^1F, ^1G(2), ^1I, ^3P(2), ^3D, ^3F(2), ^3G, ^3H, ^5D$
nd^5	252	$^2S, ^2P, ^2D(3), ^2F(2), ^2G(2), ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$
nf, nf^{13}	14	2F

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Here we have learnt the evaluation of the spectroscopic terms arising from the electronic configuration of an atom

This way we can evaluate the terms of an atom for the ground and excited states.

We also can calculate the shift of energies of the terms using semi-empirical method.