SPECTRA OF ALKALINE EARTH ~~METALS~~ ELEMENTS

Essential Features of Alkaline Earth spectra

An alkaline - earth atom Contains two valence electrons. The examples are Be, Mg, Ca, Sr, Ba and Ra and give rise to series of singlet and triplet spectral lines. The lines of each type can be grouped into four chief series - sharp, Principal, diffuse and fundamental. Following important results have been obtained:

(I) The singlet sharp (^1S) and the singlet diffuse (^1D) Series have a common convergence limit. Similarly the triplet sharp (^3S) and triplet diffuse (^3D) Series have another common limit.

(II) The wave no. difference between the common limit of ^1S and ^1D Series and the limit of the singlet Principal (^1P) Series is equal to the wave no. of the first member of ^1P Series. Similarly the wave no. difference between the Common limit of ^3S and ^3D Series and the limit of ^3P Series is equal to the wave no. of the first member of the ^3S Series. This is Rydberg - schuster law.

(III) The wave no. difference between the Common limit of the ^1S and ^1D Series and the limit of the ^1F Series is equal to the wave no. of the first member of the ^1D Series. The same holds for the respective triplet series. This is Runge law.

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(IV) The above relations are also observed to hold when the fine structure is taken into account.

(V) All the lines of the Principal series show a three component fine structure with decreasing wave no. seperations and approach a single limit.

(VI) All the lines of the sharp series also show a three-component structure but with same wave no. seperations and approach a triple limit.

(VII) All the lines of diffuse and fundamental series are composed of six component, three strong ones and three satellites and approach triple limits.

(VIII) Some lines show a fine structure with characteristics different from normal simple and compound triplets. These are called anomalous triplet.

Certain alkaline earth spectra show lines which do not fit in any of the above chief series. These are combination and inter combination lines.

All these broad and fine structure features can be explained by the vector model of the atom.

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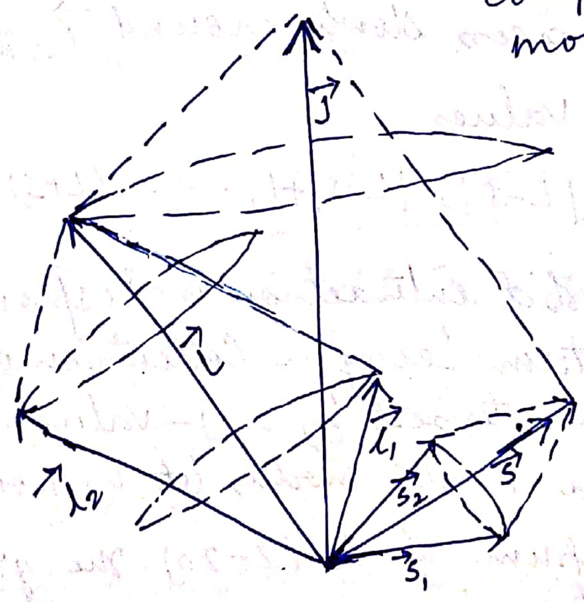
Vector atom Model for Alkaline earth element spectra

In vector atom model the orbital angular momentum of each electron is replaced by the quantum vector $\vec{l}$, and its spin angular momentum is replaced by $\vec{s}$. under varying circumstances these combine to form resultant vectors, in terms of which the spectral properties of the atom may be expressed.

For alkaline earth metals atoms, with two electrons to be considered, the vector model consists of four vectors $\vec{l_1}, \vec{l_2}, \vec{s_1}, \vec{s_2}$ and their resultant $\vec{J}$. The formation of resultant may take place by two different coupling schemes. These are known as L-S coupling and j-j coupling.

L-S Coupling

This is a common type of coupling which occurs in most of the lighter atoms.



In L-S coupling (fig) the individual orbital angular momentum vectors $\vec{l_1}$ and $\vec{l_2}$ of two electrons are strongly coupled to each other to form a resultant orbital angular momentum vector $\vec{L}$ about which both $\vec{l}_1$ and $\vec{l}_2$ precess rapidly. The corresponding quantum no. L can take the values

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots (l_1 + l_2)$$

This gives various terms of atoms. These terms are designated as S, P, D . . . . according as L = 0, 1, 2 . . .

Similarly the spin angular momentum vectors $\vec{s}_1$ & $\vec{s}_2$ of two electrons are strongly coupled to each other to form a resultant spin angular momentum vector $\vec{S}$ about which both $\vec{s}_1$ and $\vec{s}_2$ precess rapidly. The quantum no. S can take the values

$$S = |s_1 - s_2|, |s_1 - s_2| + 1 \ldots (s_1 + s_2)$$

Since $s_1 = s_2 = \frac{1}{2}$ so we have $S = 0, 1$

Thus the multiplicity $(2S+1)$ is 1 and 3 ie the two electrons lead to singlet and triplet terms.

Finally, as a result of spin-orbit interaction $\vec{L}$ and $\vec{S}$ are rather less strongly coupled with each other to form a total angular momentum $\vec{J}$ of the atom. Both $\vec{L}$ and $\vec{S}$ precess slowly around $\vec{J}$. The quantum j can take the values

$$j = |L-S|, |L-S|+1, \ldots (L+S)$$

Thus the spin orbit interaction is responsible for each multiplet term being a collection of fine-structure levels, each characterised by a j-value.

Based on this model, let us now try to explain the spectrum of Ca (Z=20). The ground state configuration is

$$\boxed{1s^2 2s^2 2p^6 3s^2 3p^6} 4s^2$$

For the optically active electrons (valence electrons) we have $l_1=0$, $l_2=0$, $s_1=\frac{1}{2}$, $s_2=\frac{1}{2}$

Thus $L=0$ (S-term)

$S=0,1$ so that $(2S+1)=1,3$

and $j=0,1$. The terms are $^1S_0$ and $^3S_1$

Since the electrons (4s2) are equivalent, the term $^3S_1$ is excluded by Pauli's Principle: Hence the normal atom gives rise to a singlet-S term $^1S_0$ only.

When the atom is excited, either or both of V. electrons to higher states. It turns out that lines of all the eight cheif series of the spectrum result from the excitation of only one of the optical electrons - The spectral lines follow the following selection rules

$$\Delta S=0, \quad \Delta L=\pm 1, \quad \Delta J=0,\pm 1 \text{ but } j=0 \not\leftrightarrow j=0$$

Applying these rules different spectral lines corresponding different allowed transitions could be obtained and can be shown by the energy level diagram which is complicated to be drawn by free hand.

II. j-j Coupling

In the vector model of a two electron atom under j-j coupling scheme, the orbital and spin vectors $\vec{l}_1$ and $\vec{s}_1$ of one electron are strongly coupled to each other to form a resultant $\vec{j}$ about which $\vec{l}_1$ and $\vec{s}_1$ precess rapidly. Similarly $\vec{l}_2$ and $\vec{s}_2$ of the other electron form $\vec{j}_2$. The vectors $\vec{j}_1$ & $\vec{j}_2$

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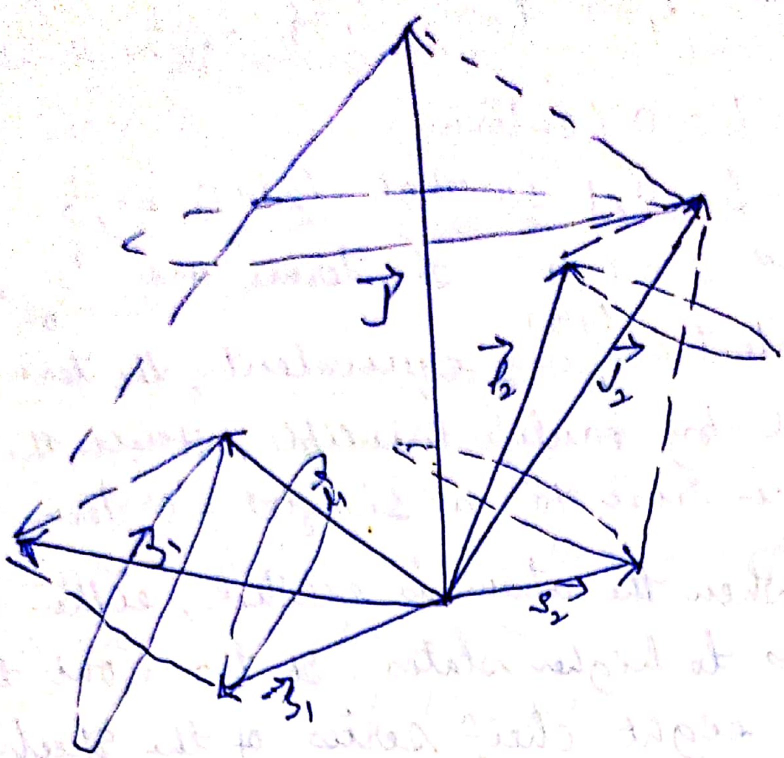

are less strongly coupled to each other and form the total angular momentum $\vec{J}$ of the atom. The vector $\vec{J_1}$ and $\vec{J_2}$ precess rather slowly about $\vec{J}$. The no. of terms and the j-values for the j-j coupling are the same as for the L-S coupling. The j-j coupling occurs relatively seldom.

Here also transitions are the same.

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