

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
UNIVERSITY GRANTS COMMISSION

CHEMICAL SCIENCES

CODE:01

2.3. Atomic structure and spectroscopy

At a Glance

Various types of states, Energy level, L—S coupling and its term symbol etc.



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Key Statements

Basic Key Statements: State (2.3.1), Energy level (2.3.2), Equivalent orbitals (2.3.3), Statistical weight (2.3.4)

Standard Key Statements: L – S coupling (2.3.5), Spectrum of molecular hydrogen (2.3.7)

Advance Key Statements: Determination of spectral terms for L – S coupling (2.3.6), Selection rules for multi electron atoms in L – S coupling (2.3.8)



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Key Facts

2.3.1. State:

The state of an atom is the condition of motion of all the electrons. It is specified by listing for Quantum numbers for each electron. If several States have same energy, they are said to be degenerate. The state with lowest energy state is ground state.

2.3.2. Energy level:

A collection of states having the same energy in the absence of external magnetic or electric field constituents an energy level. Energy level is characterized by a quantum number J that is why a particular values of total angular momentum.

2.3.3. Equivalent orbitals:

Orbitals with same n and l value are said equivalent. The electrons in equivalent orbitals are called equivalent electrons.

2.3.4. Statistical weight:

The number of distinct states in a specified collection is the statistical weight. The statistical weight of a level is $(2J+1)$; for a term it is $(2S+1)$; for single electron it is $2n^2$.

2.3.5. L – S coupling:

The L – S coupling is known as Russell-Sanders coupling after the two astronomers who first used it in in studying atomic spectra emitted by stars. In atoms which provides coupling we introduced the various perturbations in the order (a) spin-spin correlation, (b) residue electrostatic interaction, (c) spin – orbit interaction.

2.3.6. Determination of spectral terms for L – S coupling:

A. Atoms with one optical electron:

For this we have $S = \frac{1}{2}; l = 0$

So that multiplicity, $2S + 1 = 2$.

$$L = l = 0 \text{ (S - state)}$$

$$\text{And, } J = |L - S|, \dots \dots (L + S) = \frac{1}{2}$$

Thus ground state term for hydrogen like atom is $^2S_{1/2}$.

B. Atoms with two or more non equivalent optical electrons:

Assuming for 4p4d

For this we have, $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, l_1 = 1, l_2 = 2$

The possible values of S and L are

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots \dots (s_1 + s_2) = 0, 1;$$

$$\text{Multiplicity, } (2S + 1) = 1, 3$$

and

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots \dots (l_1 + l_2) = 1, 2, 3, \text{ (P, D, F States)}$$

Thus, we have in all six terms, three singlet terms and three triplet terms. All these terms are odd because the configuration 4p4d is odd ($\Sigma l = 1 + 2 = 3$). We can write these terms as

$$^1P^0, ^1D^0, ^1F^0, ^3P^0, ^3D^0, ^3F^0.$$

2.3.7. Spectrum of molecular hydrogen:

$$\Lambda = 0, 1, 2, 3 \quad (\text{same as } l = 0, 1, 2, 3)$$

Spectroscopic term, $\Sigma \pi \Delta \phi$

$$J = L + S, \text{ same as } \Omega = |\Lambda + \Sigma|$$

Selection rule:

i. $\Delta \Lambda = 0, \pm 1$

Thus transitions $\Sigma \leftrightarrow \Sigma, \Sigma \leftrightarrow \Pi, \Pi \leftrightarrow \Pi$ etc., are allowed, but $\Sigma \leftrightarrow \Delta$, for forbidden.

ii. $\Delta S = 0$

For the present we are concerned only with singlet state so this rule does not arise.

iii. $\Delta\Omega = 0, \pm 1$

This follows directly from 1 and 2 above.

- iv. There are also restrictions on symmetry changes. Σ^+ states can undergo transition only into other Σ^+ states (or, of course into Π states) while Σ^- go only into Σ^- (or Π).

2.3.8. Selection rules for multi electron atoms in L – S coupling:

- i. Most of the transition occurs in which only one electron jumps at a time, and such that its l – value change to by one unit, that is $\Delta l = \pm 1$

This is a special case of the more general Laporte rule that the parity of the configuration must change in an electric dipole transition (odd \leftrightarrow even).

In case of more than one electron jumps, Laporte rule requires that the sum of the individual must change by an odd number of units.

For example, if you have a transition involving two electrons simultaneously, then Δl must be even for one electron and odd for the other. Since we have $\Delta l = \pm 1$ for one electron transition, for two electron transition we should have $\Delta l_1 = \pm 1, \Delta l_2 = 0, \pm 2$

Thus, a double electron jump may take place from the configuration 3d4d (even) to 4s4p (odd). There are two possibilities, 4d may go to 4p ($\Delta l_1 = -1$) and 3d to 4s ($\Delta l_2 = -2$).

- ii. There is no restriction on the total quantum number n of either electron.
- iii. For the atom as whole, the quantum numbers L , S and J must change as follows
- $\Delta L = 0, \pm 1$ (In one electron atom $\Delta L = 0$)
 - $\Delta S = 0$
 - $\Delta J = 0, \pm 1$.