

## Selection Rule for Single $e^-$ atom

Ex: Hydrogen atom

(Electrons interact with oscillating electric field of light to go to higher or lower energy states.)

For  $1 e^-$  atoms  $n, l, m, m_s$  describe states.

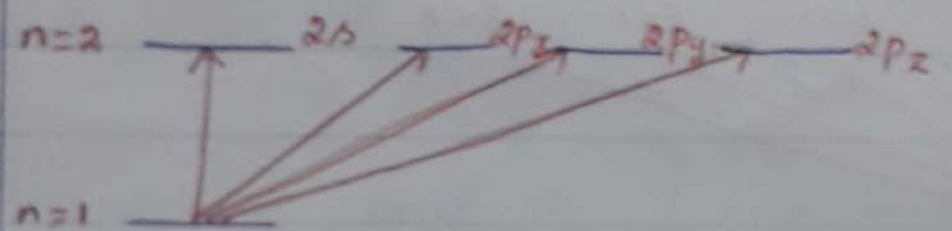
Energy depends on  $n$  ( $Z$  is charge on nucleus).

[Ex: H atom,  $He^+$ ,  $Li^{2+}$  which has only one  $e^-$ .

$$\Delta E = Z^2 R_H \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

Electronic transition can occur as follows

(from  $n=1$  to  $n=2$  where in  $n=2$  there are 4 sub levels)



For  $n=1$  there is only one  $s$  orbital

For  $n=2$  there are <sup>one</sup>  $2s$  ~~is~~ <sup>and</sup> three  $2p$  orbitals.

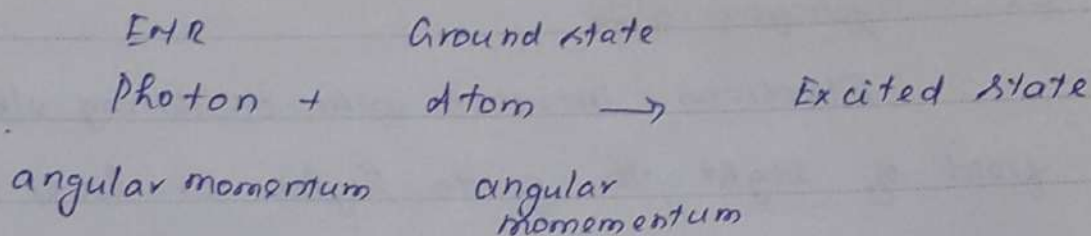
(Since the energy depends on  $n$ , the change in energy  $\Delta E$  depends <sup>only</sup> on  $n$ .)

However, Selection rule for  $1 e^-$  atoms are

$$\Delta l = \pm 1$$

$$\Delta m_l = 0, \pm 1$$

The reason for  $\Delta l = \pm 1$  is,

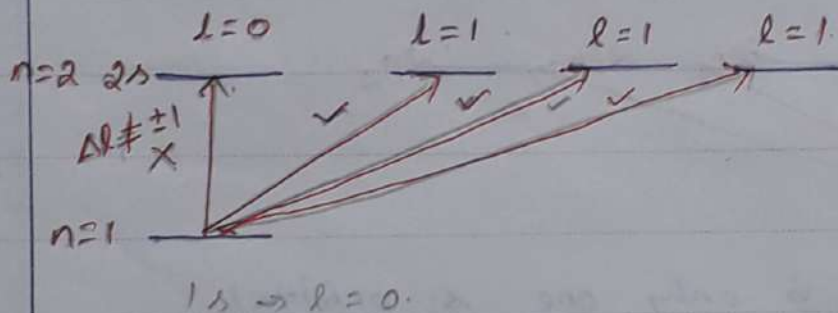


The attacking EMR have certain angular momentum and the atom will also possess some angular momentum. By the absorption of photon,

the excited state to atom will have higher angular momentum or higher energy.

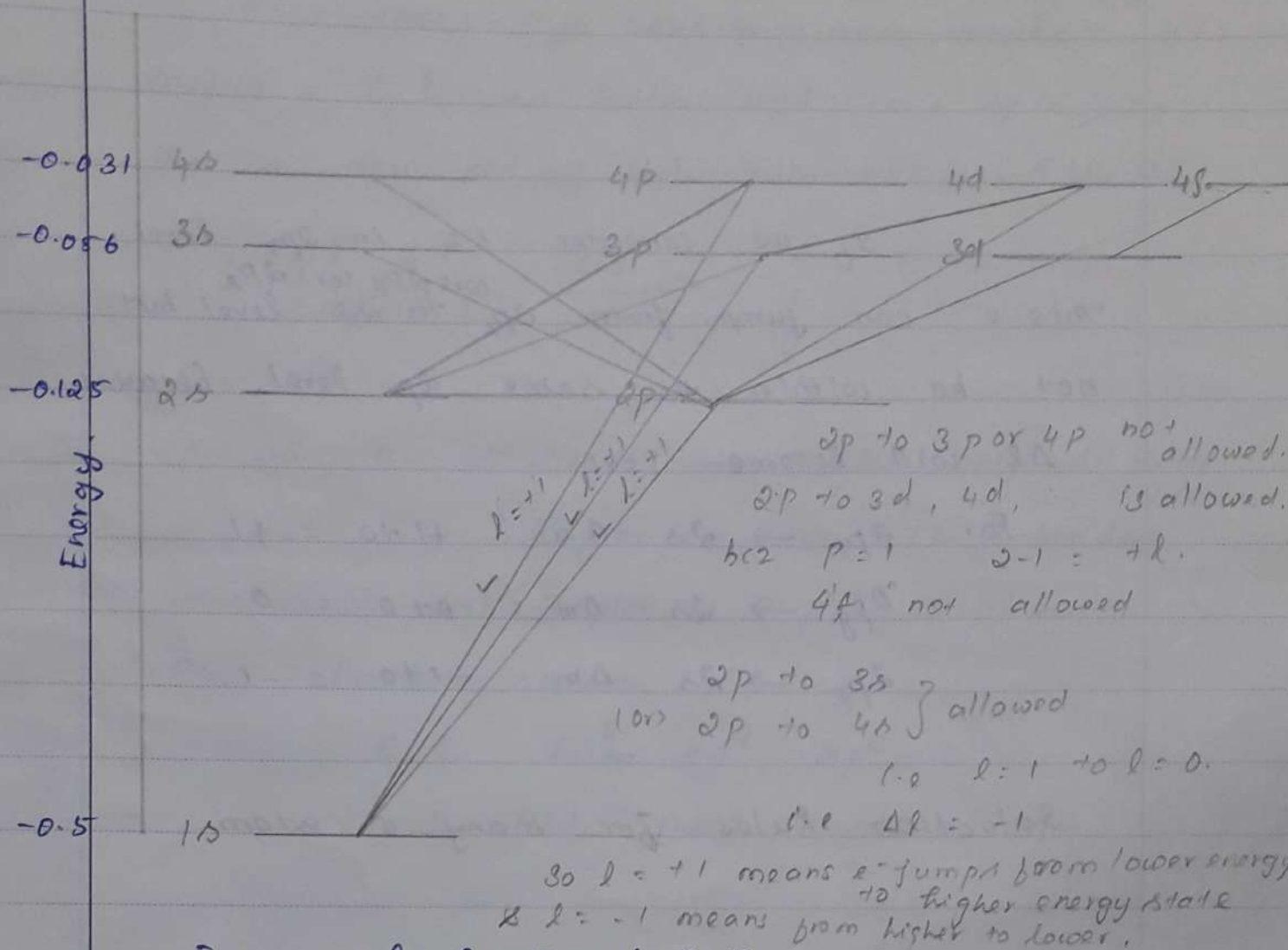
Hence  $\Delta l$  can not be zero.

$$\therefore \Delta l = \pm 1$$



(Hence, there are imaginary orbitals ( $2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f$ ) which can occur for hydrogen atom but the excitation of  $e^-$  to that levels require more energy.)

# Energy level diagram of Hydrogen atom



Energy level  $n = 1, 2, 3$

Orbital type If  $l = 0$  - s orbital

If  $l = 1$  - p orbital (irrespective of  $n$ )

If  $l = 2$  - d orbital.

If  $l = 3$  - f orbital

Specific orbital  $m_x, m_y, m_z$ .

-1 0 +1

spin  $m_s = +\frac{1}{2}$  (or)  $-\frac{1}{2}$ .



For  $\Delta m = 0, \pm 1$ , consider the following diagram.

$$2p \begin{cases} 2 & n=2, l=1, m_l=+1 \\ y & n=2, l=1, m_l=0 \\ z & n=2, l=1, m_l=-1 \end{cases}$$

$$2s \quad n=2, l=0, m_l=0.$$

If we consider 1 e<sup>-</sup> in 2p<sub>z</sub> level.

This e<sup>-</sup> can jump from 2p<sub>z</sub> to 2s level but not ~~to~~ within the same 2p level. Because  $\Delta l$  will become zero.

$$\text{For } 2p_z \rightarrow 2s \quad \Delta m = +1 + 0 = +1$$

$$2p_y \rightarrow 2s \quad \Delta m = 0 + 0 = 0.$$

$$2p_x \rightarrow 2s \quad \Delta m = -1 + 0 = -1.$$

Selection Rules for many e<sup>-</sup> atom.

$$\Delta S = 0$$

$$\Delta L = 0, \pm 1$$

$$\Delta J = 0, \pm 1 \quad (\text{except } J=0 \rightarrow 0 \text{ forbidden})$$

For single e<sup>-</sup> atom, the selection rule is

$$\Delta l = \pm 1$$

$$\Delta m_l = 0, \pm 1$$

For many e<sup>-</sup> atom, there is spin-orbit coupling

## Electronic (or) UV-Visible Spectroscopy.

### Selection Rule

There are two selection rules for UV-Visible spectroscopy.

#### 1) Spin Selection Rule.

The transition which involve a change in spin quantum number of an electron during the transition do not occur. Thus, singlet  $\rightarrow$  triplet transitions are forbidden.

~~E.g~~ ( $\Delta S = 0$ ) i.e. allowed transitions must involve the promotion of electrons without a change in their spin.

#### 2) Laporte Selection Rule.

Transitions within a given set of orbitals i.e. s (or) p (or) d are forbidden.

In centro symmetric environment, transitions between like orbitals such as s-s, p-p, d-d (or) f-f transitions are forbidden.

( $\Delta l = \pm 1$ ). i.e.  $\boxed{\uparrow\downarrow} \xrightarrow{\text{excitation}} \boxed{\downarrow\uparrow}$  forbidden

(b/c same orbital)