Infra-red part of spectrum:

Paschen series ($n_a = 3$) $\rightarrow$ starts at 18751 A°

Brackett Series ($n_a = 4$) $\rightarrow$ starts at 40500 A°

Pfund series ($n_a = 5$) $\rightarrow$ at 74000 A°

The set of quantities R/n_a^2 $\rightarrow$ terms.

Rydberg $\rightarrow$ for other atoms, particularly the alkalis, the frequencies of lines could be represented approximately as difference of terms T_n, where

$$T_n = R/(n+\alpha)^2 \quad , \quad n = 1, 2, 3 \quad \text{--- (5)}$$

$\alpha \rightarrow$ constant for each particular series.

Ritz $\rightarrow$ The frequencies of all lines can be represented by the difference of terms.

$\Rightarrow$ if lines of frequencies ν_{12} and ν_{23} can be represented as $\nu_{12} = T_1 - T_2$; $\nu_{23} = T_2 - T_3$ --(6)

then a line of frequency ν_{13} will usually exist, where

$$\nu_{13} = (T_1 - T_2) + (T_2 - T_3) = T_1 - T_3 \quad \text{--(7)}$$

This is an example of, "Ritz Combination Principle"

$\Rightarrow$ If lines at frequencies ν_{ij} and ν_{jk} exist in spectrum with $j > i$ and $k > j$ then there will generally a line at ν_{ik}, where

$$\nu_{ik} = \nu_{ij} + \nu_{jk} \quad \text{—— (8)}$$

Important to note

Not all combinations of frequencies are observed
↳ certain selection rules will be applied

Atomic Units:

Bohr radius:- $a_0 \rightarrow$ radius of the orbit of the electron in the ground state of hydrogen

$$a_0 = \frac{(4\pi\epsilon_0)\hbar^2}{me^2} = 5.29177 \times 10^{-11} m \quad \text{---(9)}$$

$$\simeq 0.529 A^\circ$$

$a_0 \rightarrow$ unit of length in atomic units

Correspondingly
mass of the electron $\rightarrow$ unit of mass
$\hbar \rightarrow$ unit of angular momentum
Unit of charge is taken to be the absolute magnitude 'e' of the electronic charge and the permittivity of free space ϵ_0 is $\left(\frac{1}{4\pi}\right)$
$\Rightarrow$ In atomic units $(m = \hbar = e = 1, \ 4\pi\epsilon_0 = 1)$

$$\Rightarrow \quad E_n = -\frac{1}{2}\frac{Z^2}{n^2} \ (a.u.) \quad \text{---(10)}$$

The Ground state energy of hydrogen ($Z=1$, $n=1$) is $-\frac{1}{2}$ a.u.
$\Rightarrow$ Atomic unit of energy is equivalent to 27.2 eV.
The atomic unit of velocity is equal

to the velocity (v_0) of the electron in the first Bohr orbit of hydrogen.

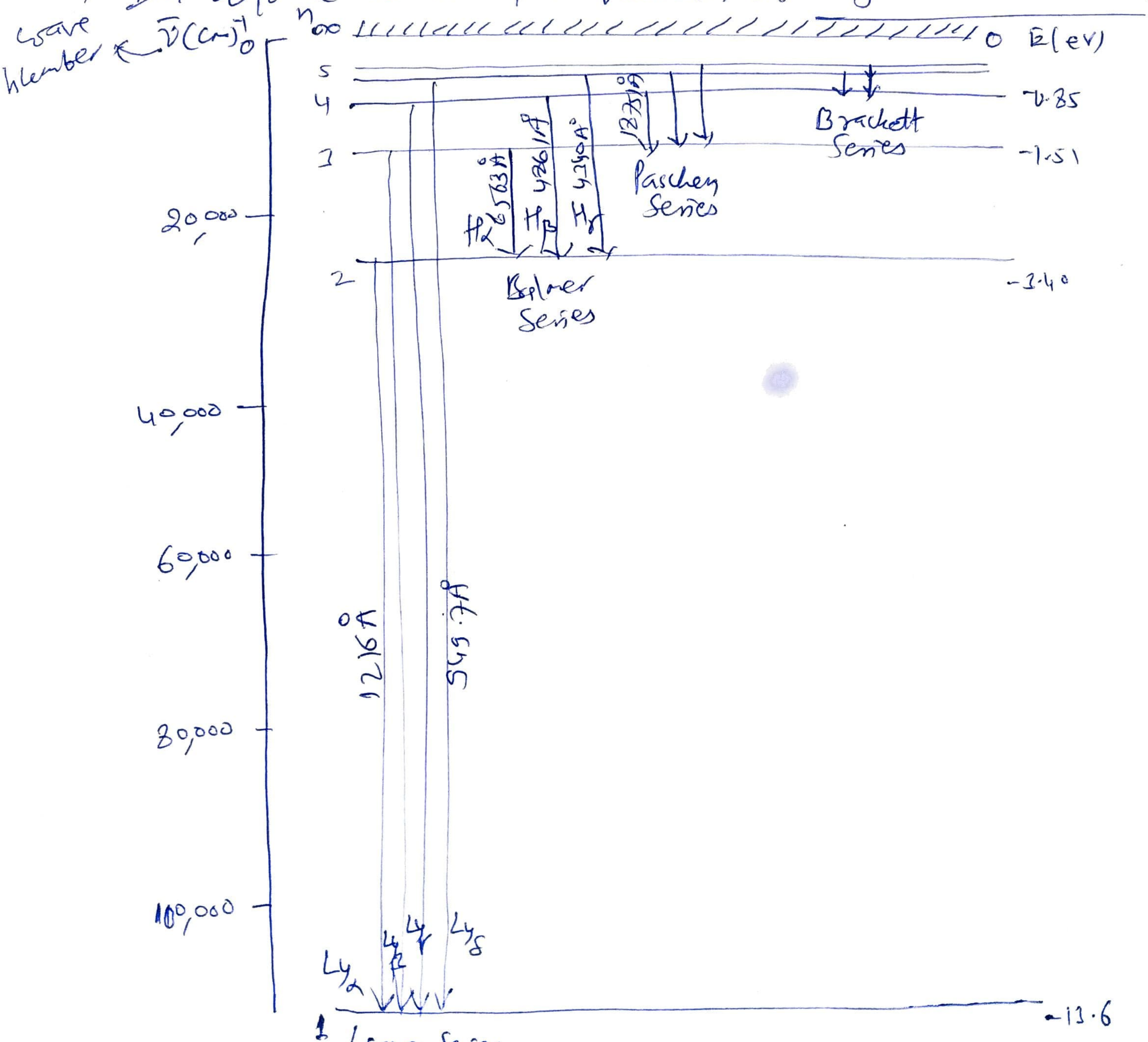
$$v_0 = \frac{e^2}{(4\pi\epsilon_0)\hbar} = \alpha c \quad \text{--- (11)}$$

$\alpha \rightarrow$ dimensionless constant

$$\alpha = \frac{e^2}{(4\pi\epsilon_0)\hbar c} \quad \text{--- (12)}$$

fine structure constant $\alpha \simeq \frac{1}{137}$

$\Rightarrow$ In atomic units the velocity of light is $c \simeq 137$ a.u.



Hydrogen I spectrum

Hydrogen II

Ionized hydrogen, hydrogen II (H-two) → hydrogen atom that has lost its electron and is positively charged.

It is detected at optical wavelengths as it releases a photon of wavelength 656.3 nm when it recaptures an electron and returns to its neutral state.

Exist throughout galaxies and interstellar gas clouds called H II regions.

The UV, visible and IR spectra of H II regions are very rich in emission lines. H II regions are also observed at radio wavelengths, emitting radio free-free emission from thermalized electrons and radio recombination lines from highly excited states of H, He and some metals.

Fine Structure of H_α Line

H_α line of hydrogen spectrum → electron jumps from $n=3$ to $n=2$.

While explaining the fine structure of spectral lines → it should be emphasized that all the theoretically possible transitions are not allowed.

Bohr theory → no restriction on the change in the value of n for the observed transitions.

Bohr-Sommerfeld → Still no restrictions on the value of n.

Only those transitions are observed for which $\Delta k = \pm 1$, azimuthal quantum number changes by ± 1.

We calculate the shift of hydrogen terms in the units of $\Delta T / R\alpha^2$.

$$\Delta T = \frac{R\alpha^2 z^4}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right)$$

$$\boxed{T_n = -\frac{E_n}{ch}}$$

for hydrogen $z = 1$

$$\frac{\Delta T}{R\alpha^2} = \frac{1}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right)$$

The values $\frac{\Delta T}{R\alpha^2}$ for different states are given below;

3_3 → total quantum number 3 and azimuthal quantum number 3

$$3_3 = \frac{1}{3^4}\left(\frac{3}{3} - \frac{3}{4}\right) = \frac{1}{3^4}\cdot\frac{1}{4} \quad \text{--- (1)}$$

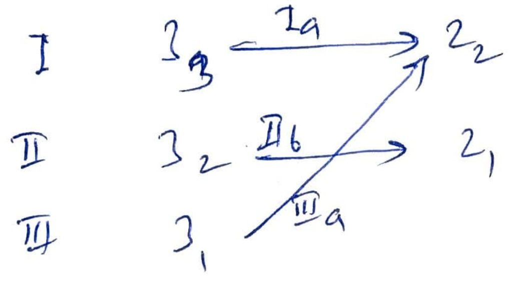
$$3_2 = \frac{1}{3^4}\left(\frac{3}{2} - \frac{3}{4}\right) = \frac{1}{3^4}\cdot\frac{3}{4} \quad \text{--- (2)}$$

$$3_1 = \frac{1}{3^4}\left(\frac{3}{1} - \frac{3}{4}\right) = \frac{1}{3^4}\cdot\frac{9}{4} \quad \text{--- (3)}$$

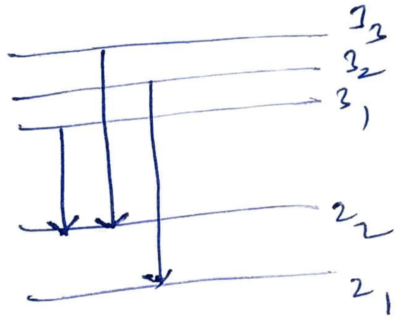
$$2_2 = \frac{1}{2^4}\left(\frac{2}{2} - \frac{3}{4}\right) = \frac{1}{2^4}\cdot\frac{1}{4} \quad \text{--- (4)}$$

$$2_1 = \frac{1}{2^4}\left(\frac{2}{1} - \frac{3}{4}\right) = \frac{1}{2^4}\cdot\frac{5}{4} \quad \text{--- (5)}$$

eq (1), (2), (3) and (a), (b) → displaced lines with the magnitude noted against each.
When no ~~real~~ relativity corrections applied the (1), (2) and (3) lines combine into one and (a), (b) into another



(a)



(b)

Allowed transitions (fine structure of H_α line)