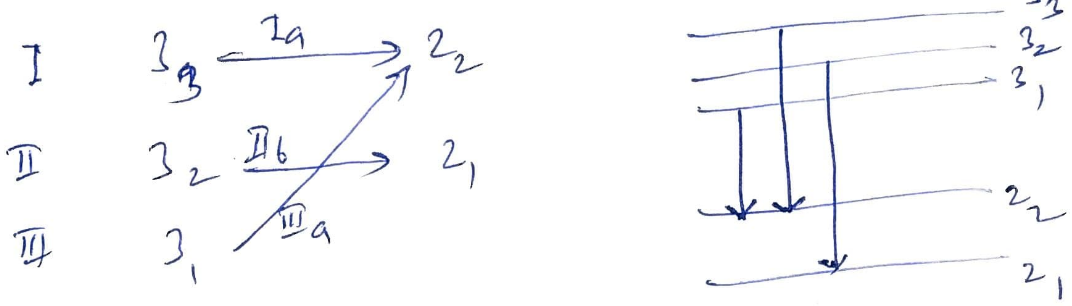
eq (1), (2), (3) and (a), (b) → displaced lines with the magnitude noted against each.

When no ~~real~~ relativity corrections applied the (1), (2) and (3) lines combine into one and (a), (b) into another



(a) (b)

<u>Allowed transitions</u> (<u>fine structure of H_α line</u>)

<u>Pauli Exclusion Principle</u> :- Wide applications in spectroscopy.

<u>Pauli (1925)</u> → certain forbidden lines in the spectrum of Hg.

<u>Need</u> ? * Distribution of extranuclear electrons in different elements.

* Experimentally found that in an ordinary series of Hg, the state 6^1S_0 is present while the state 6^3S_1 is absent

* In <u>ortho-helium</u> no transitions starting from or ending at 1^3S_1 energy state have been observed.

If no exclusion principle ? → stable state of every atom → in which every electron had the principal quantum no. 1.

No sign of periodicity

Exclusion Principle :- A completely defined quantum state can not be occupied by more than one electron → Two electrons cannot be identical in regard to all their quantum numbers

This principle excludes the entry of the electrons with same states into the configuration → exclusion principle

If two electrons have the same total quantum number n, and the same azimuthal quantum number l → they are called "equivalent electrons"

according to observations → when two electrons are equivalent → certain terms are forbidden.

Case of 1^3S_1 state of helium atom.

$n = 1$ for both electrons

l vectors → each equal to zero, s vectors are parallel.

⇒ orbits of these electrons are completely equivalent.

If strong magnetic field applied parallel to the common direction of s vectors, both electrons are characterized by the magnetic quantum numbers of the value:

$$\left.\begin{array}{l} m_l = 0 \\ m_s = \frac{1}{2} \end{array}\right\} \text{ or } \begin{array}{l} m_l = 0 \\ m_s = -\frac{1}{2} \end{array},$$

both of them must behave in the same fashion.

⟹ Two electrons have same set of quantum numbers ⟶ one is excluded to enter into the particular quantum state.

Result ⟶ $^3S_1$ state is missing.

Pauli's principle operates on equivalent electrons ⟶ equivalence principle.

" There cannot exist an atom in such a quantum state that the two electrons within it have the same set of quantum numbers."

Pauli's principle ⟶ equally applicable to all particles with spin angular momentum quantum number of $\hbar/2$! Example: electrons, protons, neutrons, muons.

If two such particles are in the same energy state except for spin ⟶ their spin must be $+\frac{1}{2}$ and $-\frac{1}{2}$

Hg atom → two equivalent electrons in the normal state of Hg atom.
for these two electrons $n = 6$, $l = 0$

Combinations	1	2	3	4
1st electron	$6\,0\,0\,\frac{1}{2}$	$6\,0\,0\,-\frac{1}{2}$	$6\,0\,0\,\frac{1}{2}$	$6\,0\,0\,-\frac{1}{2}$
2nd electron	$6\,0\,0\,\frac{1}{2}$	$6\,0\,0\,-\frac{1}{2}$	$6\,0\,0\,-\frac{1}{2}$	$6\,0\,0\,\frac{1}{2}$

Combinations 1 and 2: Completely Identical quantum states. Total angular momentum is either +1 or −1 and $S = 1$ ×

Combinations 3 and 4: exchange of quantum states between two electrons — can't be differentiated

Hence → Out of four state only a single atomic state is allowed to enter into the configuration.

⟹ the singlet $6\,^1S_0$ is allowed and $6\,^3S_1$, the triplet state is not allowed

Normal state of each alkaline-earth element → two equivalent s electrons. Only $^1S_0$ term is observed. As soon as one of the electron is excited to an s orbit of different n, the $^3S_1$ term is also observed.

Spectroscopic Notation

↓ Common way to name states in atomic physics

Standard way to write the angular momentum quantum number of a state.

The general form is

$$N\,^{2S+1}L_j$$

$N \to$ Principal quantum number (often omitted)

$S \to$ total spin number ($(2S+1) \to$ No. of spin states)

$L \to$ orbital angular momentum quantum number l.

written as S, P, D, F, ——

for $l = 0, 1, 2, 3$ ——

$j \to$ total angular momentum quantum number

Example: Single electron states, as we find in Hydrogen. These are

$1\,^2S_{1/2}$ $2\,^2S_{1/2}$ $2\,^2P_{3/2}$ $2\,^2P_{1/2}$ $3\,^2S_{1/2}$ $3\,^2P_{1/2}$ $3\,^2D_{5/2}$

$3\,^2D_{3/2}$ $4\,^2S_{1/2}$ - - -

All have pre-superscript 2 → they are all spin one-half. There are two j values for ~~each~~ each l.

For atoms with more than one electron, the total spin state has more possibilities