

Alkali metals  $\rightarrow$  In ground state single valence electron moving in an s orbital outside a core consisting of a closed (sub) shell system.  
(Li, Na, K, Rb, Cs, Fr)

The spectra of these elements  $\rightarrow$  identical with the spectrum of hydrogen or singly ionized atoms of Be, Mg, Ca, or doubly ionized atoms of boron or aluminium and so on.

Li $\rightarrow$ $1s^2$	total electronic orbital angular momentum and spin angular momentum of the core are zero.
Na $\rightarrow$ $1s^2 2s^2 2p^6$	
K $\rightarrow$ $1s^2 2s^2 2p^6 3s^2 3p^6$	

$\rightarrow$  designated as  $1S_0$

The cores of rubidium, caesium and francium are also  $1S_0$ .

The core is spherically symmetric  $\rightarrow$  the valence electron of a neutral alkali atom ( $Z=Z_0$ ) moves in an effective central potential  $V(r)$ , which at large distances approaches the Coulomb potential

$$V(r) \xrightarrow{r \rightarrow \infty} -\frac{e^2}{(4\pi\epsilon_0)r} \quad (1)$$

Since the nuclear charge  $Ze$  is screened by the core which contains  $(Z-1)$  electrons.

Lowest state of the valence electron  $\rightarrow$  zero orbital angular momentum ( $l=0$ ) and the corresponding orbital is designated  $(n_0s)$ ,  $n_0=2$  for Li;  $n_0=3$  for Na and  $n_0=4$  for K and so on (To satisfy Pauli Exclusion principle). For small  $r \rightarrow$  Potential  $V(r)$  is always more attractive than  $-\frac{e^2}{4\pi\epsilon_0 r}$ .  
 B-E of the orbital  $(n_0s)$  is  $>$   $(n_0s)$  level of hydrogen.

The excited states of the valence electron  $(nl)$  with  $n \geq n_0$ . B-E of orbital  $(nl)$  is again greater than that of  $(nl)$  level of hydrogen.

For highly excited states  $\rightarrow$  The charge density of the orbital is ~~also~~ almost entirely outside the region of core  $\Rightarrow$  The orbitals approximate to true hydrogen wave functions

$\hookrightarrow$  Energy levels are very close to those of hydrogen.

$V(r) \rightarrow$  not Coulomb at short distances the energy levels are not degenerate in  $l$ , for a given  $n$ .

2s level of ~~the~~  $Li$   $\rightarrow$  well below 2p level

3s level is  $\approx$  below 3p level

$\rightarrow$  3p level below 3d level

As the excitation increases  $\rightarrow$  the levels become more hydrogenic in character

$\rightarrow$  near degeneracy in  $l$  for a given  $n$ .

Valence electron bound weakly compared with the core electrons. For each alkali  $\approx 5$  eV to detach the valence electron, compared to  $\approx 20$  eV and more for the 'least bound' of the core electrons

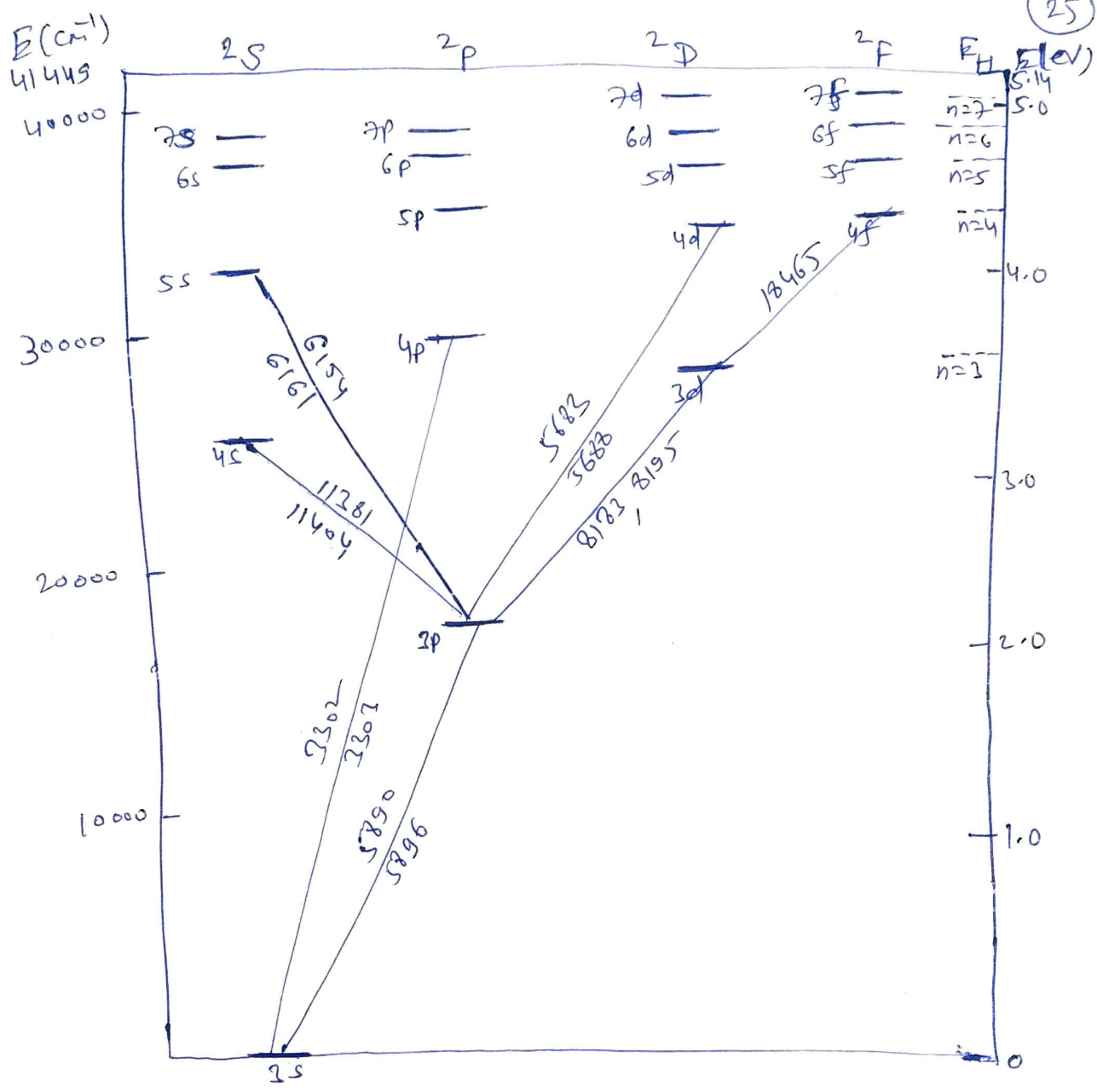
$\Downarrow$  Optical spectrum is due to transitions involving the valence electron only  $\rightarrow$  core remains inert.

Term symbol of the ground state of alkali

$\rightarrow (ns)^2 S_{1/2}$   $\rightarrow$  (omitting the core) Total angular momentum quantum number  
 $\downarrow$  multiplicity of spin states,  $s = \frac{1}{2}$

Excited states are of the form

$(ns)^2 S_{1/2}$ ,  $(np)^2 P_{1/2, 3/2}$ ,  $(nd)^2 D_{3/2, 5/2}$  and so on



Crotrian diagram of energy levels and transitions in sodium (Na)

Cross structure of the alkali spectra → combining the selection rules for one-electron atoms and knowledge of the energies of the levels (nl) of the valence electrons.

The energy levels represented by the empirical formula

$$E_{nl} = -\frac{1}{2} \frac{1}{(n - \mu_{nl})^2} \text{ a.u.} \quad (2)$$

$\mu_{ne} \rightarrow$  quantum defects.

To a good approximation  $\mu_{ne}$  is a function of  $l$  only (for a particular alkali);  $\mu_{ne} \approx \alpha(l)$ .

Effective principal quantum number (Rydberg)

$$n^* = n - \alpha(l) \quad \text{--- (3)}$$

for Li, Na, K.

Ritz made small correction

$$n^* = n - \alpha(l) - \beta(l)/n^2 \quad \text{--- (4)}$$

### Absorption Spectra

The absorption spectra  $\rightarrow$  obtained by passing light through the vapor of the alkali metal.

Most atoms will be in the ground state, and the series of absorption lines correspond to transition from  $(n_0s)$  to  $(np)$  levels  
Ground state

with frequencies

$$\nu = R \left[ \left( \frac{1}{n_{n_0s}^*} \right)^2 - \left( \frac{1}{n_{np}^*} \right)^2 \right] \quad \text{--- (5)}$$

$R \rightarrow$  Rydberg constant.

This series of lines  $\rightarrow$  Principal lines