

Ay126: Quantum Defect and Clue to Orbits

S. R. Kulkarni

April 8, 2021

1 Alkali elements as one-electron system

As noted earlier in the course it was the study of spectra of alkali atoms that led to the “term framework”:

$$k_n^s = k_\infty^s - \frac{R}{(m + S)^2} \quad (1)$$

where the superscript stood for the “sharp” or s series. This is the classical Rydberg approach. With the advent of quantum mechanics this was formulation was changed to

$$k_n = k_\infty - \frac{R}{(n - \delta)^2} \quad (2)$$

where δ was called as the “quantum defect”.

The ionization potential table for Alkali elements is presented in Table 1 can be used to compute the effective quantum number, n_* and the quantum defects.

The quantum defect for Sodium, obtained from model fitting of the spectral lines, is given in the Table below. As can be seen from this Table the quantum defect (1) has almost no dependence on n but is strongly dependent on l and (2) vanishes rapidly as one proceeds to larger values of l . Below we explore the cause for this strong dependence of the term value on l .

Table 1: Ionization energies for alkalis

Element	configuration	Z	IP(ev)	n	n^*	δ
Li	$1s^2 2s$	3	5.4	2	1.59	0.41
Na	$1s^2 2s^2 2p^6 3s$	11	5.1	3	1.63	1.37
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$	19	4.3	4	1.77	2.23
Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$	37	4.2	5	1.81	3.19
Ce	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$	55	3.9	6	1.87	4.13

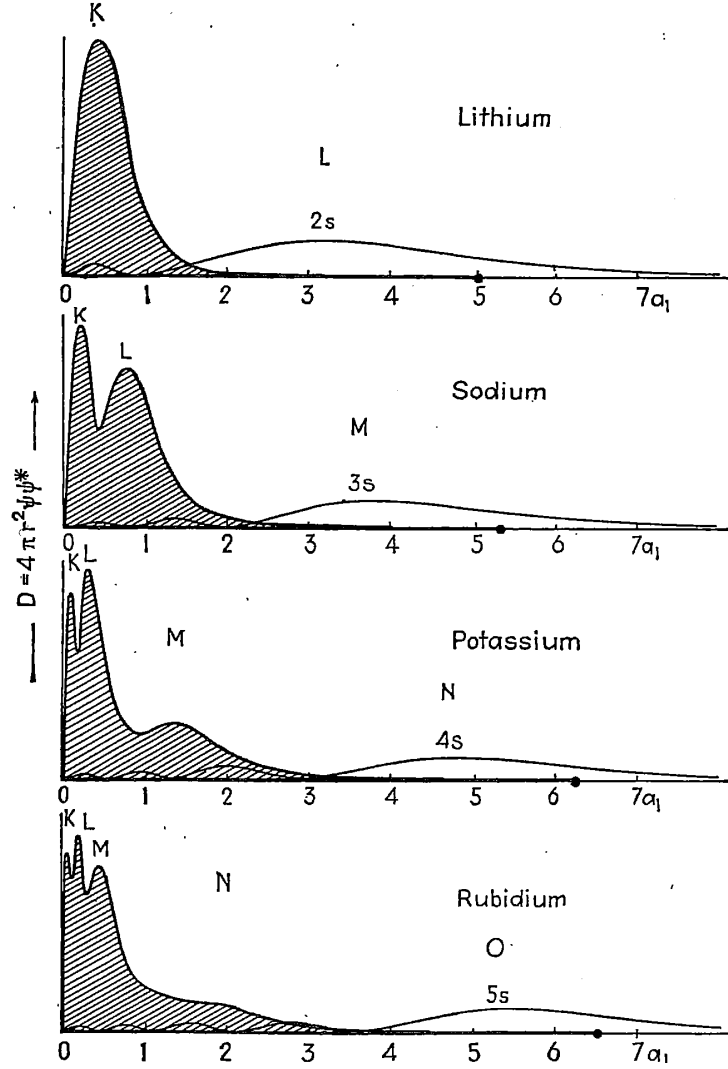


Figure 1: Probability-density distribution curves for the neutral alkali atoms. The shaded curve refers to the core and the line to the valence electron. Notice that the outermost closed shell has a long radial tail (e.g. the M shell of Potassium and the N shell of Rubidium). Here a_1 is the Bohr radius (old notation; this figure is from the classic book by White).

Table 2: Quantum Defect for Na I

l	$n = 3$	$n = 4$	$n = 5$	$n = 6$
0	1.373	1.357	1.352	1.349
1	0.883	0.867	0.862	0.856
2	0.10	0.011	0.013	0.011
3		0.0	-0.001	-0.008

2 Penetrating & Non-penetrating orbits

The data presented above gave rise to the model graphically summarized in Figure 1.

The s wave function is spherically symmetric. Next, as discussed in the class, it can be shown that the charge distribution when summed over $+l$ to $-l$ is spherically symmetric. Thus both full sub-shells and even *half-filled sub-shells* have no net angular momentum.

Consider sodium. The electron configuration is $1s^2 2s^2 2p^6 1s^1$. Thus the charge distribution of $1s^2$, $2s^2$ and $2p^6$ spherically symmetric. The same is true for the other alkali elements. The radial distribution of the electron charge distribution for alkali elements is shown in Figure 1. Going ahead, I remind everyone that the shells have historical names: K ($n = 1$), L ($n = 2$), M ($n = 3$) and so on. *This terminology is very much in current use in modern X-ray astronomy.*

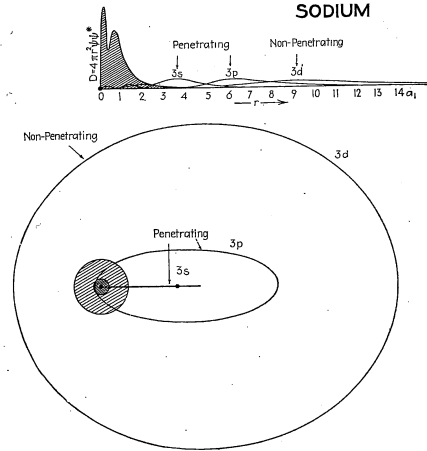


Figure 2: Comparison of the quantum-mechanical (top) with the classical model (bottom) of the neutral sodium atom. Three of the lowest possible states for the single valence electron are also shown. [From White's book].

The quantum and classical orbits for the ground and excited state of the valence electron of sodium is shown in Figure 2. The $3s$ spends more time in the core (the K and L shells) whereas the $3d$ the least amount of time. Classically the $3s$ orbit is considered to be

“penetrating” but not the $3d$. Regardless, the $3s$ electron by “penetrating” the core has a more negative energy, relative to the $3d$ electron.

Thus the origin of the splitting of energy levels of electrons with different values of l is due to the increased attraction of s and p electrons as they penetrate into the inner electron cloud (which increases the net positive charge experienced by the electron). Note that $l > 3$ electrons are almost in a hydrogenic orbit (whence $\mu \approx 0$). This brief discussion should give you a qualitative understanding of μ .

All the models considered so far (Bohr, Sommerfeld, Schrodinger) find the energy of a state is only given by n . In contrast, as can be seen from Figures 3 and 4, the alkali spectra show, for a given n , a strong dependence on the angular momentum (or l).

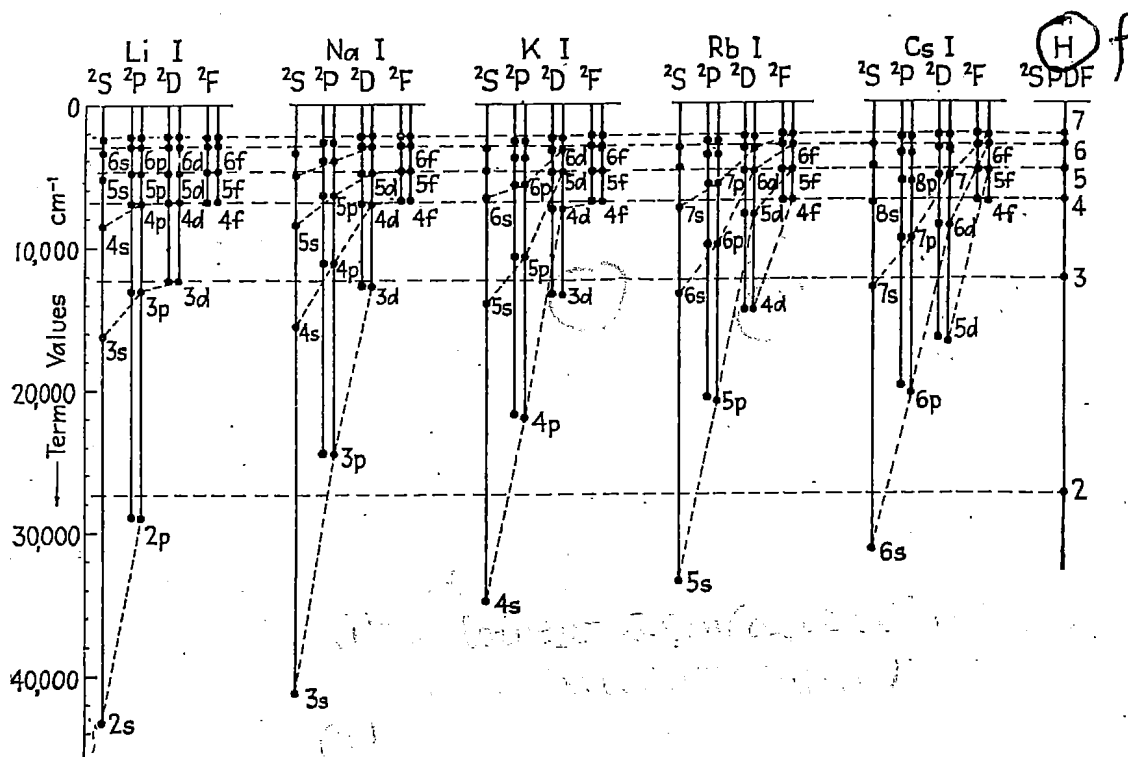


Figure 3: Grotrian diagram for alkali elements. The energy levels of hydrogen are shown on the extreme right. For the same value of n the s states of the alkali elements are considerably more negative relative that of hydrogen.

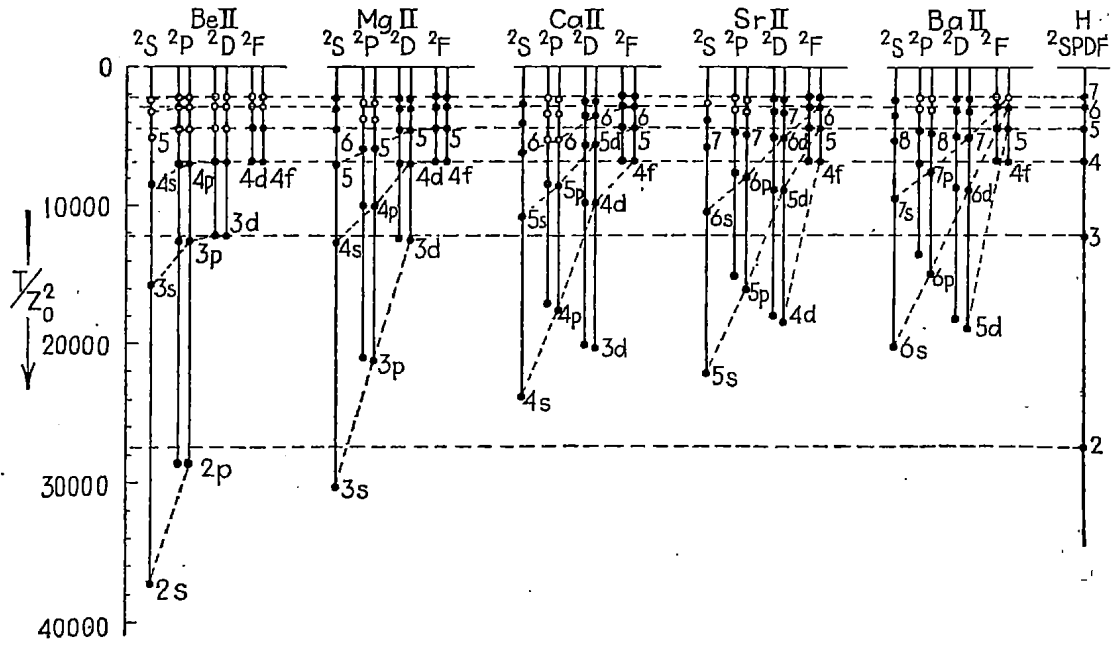


Figure 4: Grotrian diagram for once ionized alkaline earth metals. Note that the term value scale is scaled down by $1/4$ for the alkaline elements whereas that for Hydrogen (right) is not.

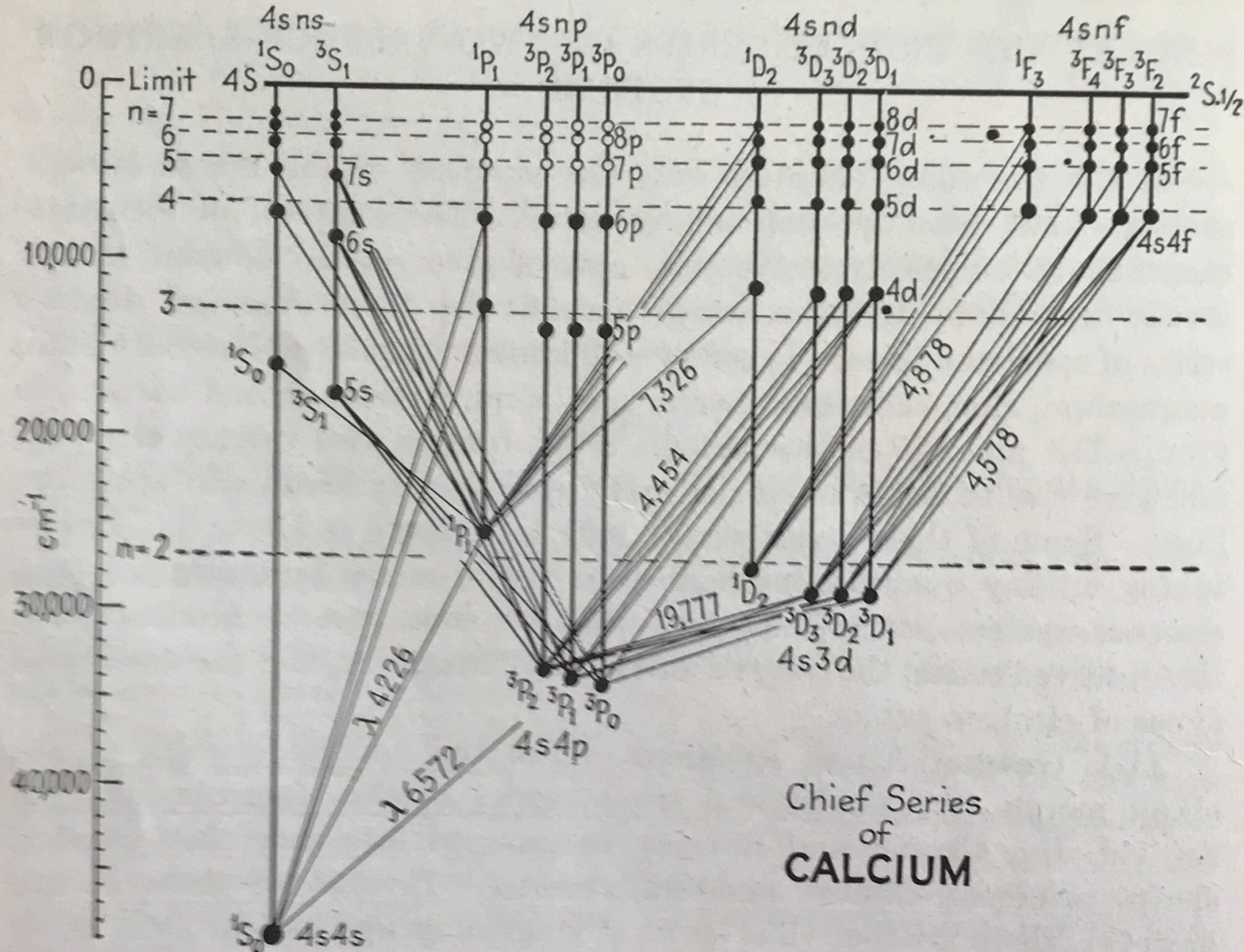


FIG. 11.1.—Energy level diagram for the four chief singlet and triplet series of the neutral calcium atom. For complete diagram, see Fig. 11.9.

As in the doublet series of the alkali metals nearly all of the observed singlet or triplet series are closely represented by the general series formula

