

Atomic Spectra of Alkali Elements

Rydberg primarily focused on studying the lines of alkali metals (Lithium, Potassium and Sodium).¹ Rydberg organized the various features by their appearance on the photographs: The alkali spectra were more complicated than that of hydrogen. Rydberg recognized that there were three different types of lines: lines which looked “sharp” (on photographic plates), “principal” (strong lines that showed up in emission and absorption) and those which appeared ‘diffuse’. These series were abbreviated to S, P, D. Later “Fundamental” (F) was added.

As noted earlier, Rydberg preferred to work with wavenumbers. Using data from Liveing and Deware he recast Angstrom’s formula as follows:

$$k_n = k_\infty - \frac{N}{(n + \mu)^2} \quad (1)$$

where k_n is the wavenumber of the n th line in a given series. Rydberg kept N fixed to the value measured by Balmer with $k_\infty \mu$ being free parameters.

Rydberg found the following formulae for Lithium

$$\begin{aligned}
 k_n^s &= k_\infty^s - \frac{R}{(n + S)^2}, & 2,3,4,\dots \\
 k_n^p &= k_\infty^p - \frac{R}{(n + P)^2}, & 1,2,3,\dots \\
 k_n^d &= k_\infty^d - \frac{R}{(n + D)^2}, & 1,2,3,\dots
 \end{aligned}
 \quad (2) \quad (3) \quad (4)$$

where $S = 0.5951$, $P = 0.9596$, $D = 0.9974$, $k_\infty^s = 28601.6 \text{ cm}^{-1}$, $k_\infty^p = 43487.7 \text{ cm}^{-1}$, $k_\infty^d = 28598.5 \text{ cm}^{-1}$ and we have switched to the modern notation in which N is replaced by R (the value he found was $R = 109721.6 \text{ cm}^{-1}$). Rydberg had confidence in the data that he was able to find a deeper connection between the constants between the series. For instance,

¹ At the risk of confusing the reader: alkaline applies to properties of alkalis but *alkaline earth metals* have nothing to do with alkali metals. The alkaline earth metals are Be, Mg, Ca, Sr, Ba and Ra.

within the experimental measures the limiting value of the series limit (k_∞) for the S and D series is the same.

Next, with respect to the above equations, he noticed the following:

$$\frac{R}{(1+S)^2} \approx k_\infty^p \quad (5)$$

$$\frac{R}{(1+P)^2} \approx k_\infty^s \quad (6)$$

With these coincidence noted he derived the following formulae for the S, P and D series:

$$k_n^s = \frac{R}{(1+P)^2} - \frac{R}{(n+S)^2}, \quad n = 2, 3, 4... \quad (7)$$

$$k_n^p = \frac{R}{(1+S)^2} - \frac{R}{(n+P)^2} \quad n = 1, 2, 3... \quad (8)$$

$$k_n^d = \frac{R}{(1+P)^2} - \frac{R}{(n+D)^2} \quad n = 2, 3, 4... \quad (9)$$

The above equations strongly hint that atomic lines were transitions from a base state to other states. For instance the S series are transitions from a base level which is P to S levels whereas P series are transitions from base level which is S to P levels. Furthermore the base energy level for S and D must be the same given $k_\infty^s = k_\infty^d$.

Armed with this insight review the Grotrian diagram for Lithium and Sodium (Figure 1). We now associate S levels with $l = 0$, P levels with $l = 1$ and D levels with $l = 2$; here l is the angular momentum quantum number.

We have not discussed the “fundamental” series. As you can see from Figure 1 this series is at long wavelength. The choice of terminology is terrible. There is nothing fundamental about these transitions. They were called as fundamental because of their smaller frequency (and the implicit assumption that the lowest frequency is a fundamental and higher frequencies are harmonics).

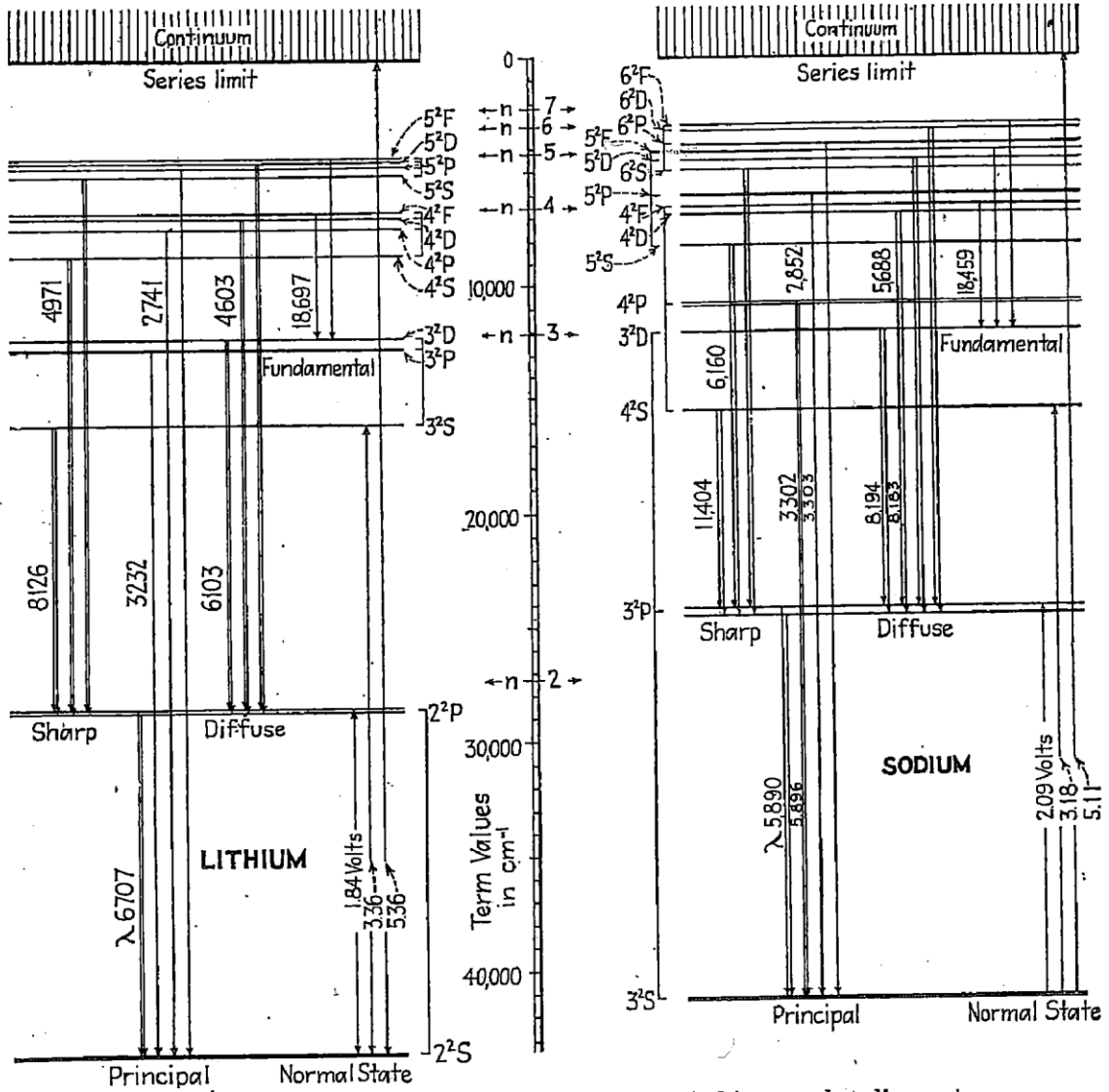


Figure 1: Grotrian diagram for Lithium ($1s^22s$) and Sodium ($1s^22s^22p^61s$). The term values (energy levels) for Hydrogen is displayed in the vertical bar.