7. *Screening Doublets and Screening Constants in X-ray Spectra*

In 1920 Hertz[28] announced the discovery of a new type of regularity in the x-ray energy level diagram. If the levels L_I, L_{II}, and L_{III} are plotted on a Moseley diagram ($\sqrt{\nu/R}$ against Z) the L_{II} and L_{III} levels diverge as the square of the corrected atomic number increases, as we see from eq. (8.17). Hertz noted that on the same diagram the L_I and L_{II} levels run parallel, preserving a constant $\Delta\sqrt{\nu/R}$ separation independent of atomic number. This is shown in Fig. VIII–14.

For the explanation of this behaviour we must consider the interpretation of the level L_I. The preceding two sections of this chapter have developed the hypothesis that the levels L_{II} and L_{III} arise from the configuration $2p^5$. According to Table VIII–3, there are two electrons with $n = 2$ whose l value is zero. Hence we may ascribe L_I to the configuration $2s^1$. The J value is made up entirely by the spin of the remaining electron, hence $J = \frac{1}{2}$. In the hydrogen atom the term with $n = 2$, $l = 0$, $j = \frac{1}{2}$, $2^2S_{1/2}$, coincides with $2^2P_{1/2}$, as we see from Fig. VIII–8. In an alkali, such as 11 Na, we find the $^2S_{1/2}$ and $^2P_{1/2}$ terms of the same total quantum number having a separation enormous compared to that of the corresponding $^2P_{1/2}$ and $^2P_{3/2}$, due to the effect of screening on orbits of different l values. In the x-ray region the separation of the analogous L_IL_{II} levels is also due to the effect of screening, but here it may even be smaller than the L_{II} L_{III} separation which, as we have seen, increases as the fourth power of the effective atomic number. Thus in uranium, the L_IL_{II} separation is 59.9 ν/R units, whereas the $L_{II}L_{III}$ separation in the same units is 278.5.

In addition to the L_IL_{II} separation, such screening doublets arise between the levels M_IM_{II}, $M_{III}M_{IV}$, N_IN_{II}, $N_{III}N_{IV}$, N_VN_{VI}, etc. In each case we are dealing with adjacent levels arising from configurations of equivalent electrons whose l values differ by unity. The

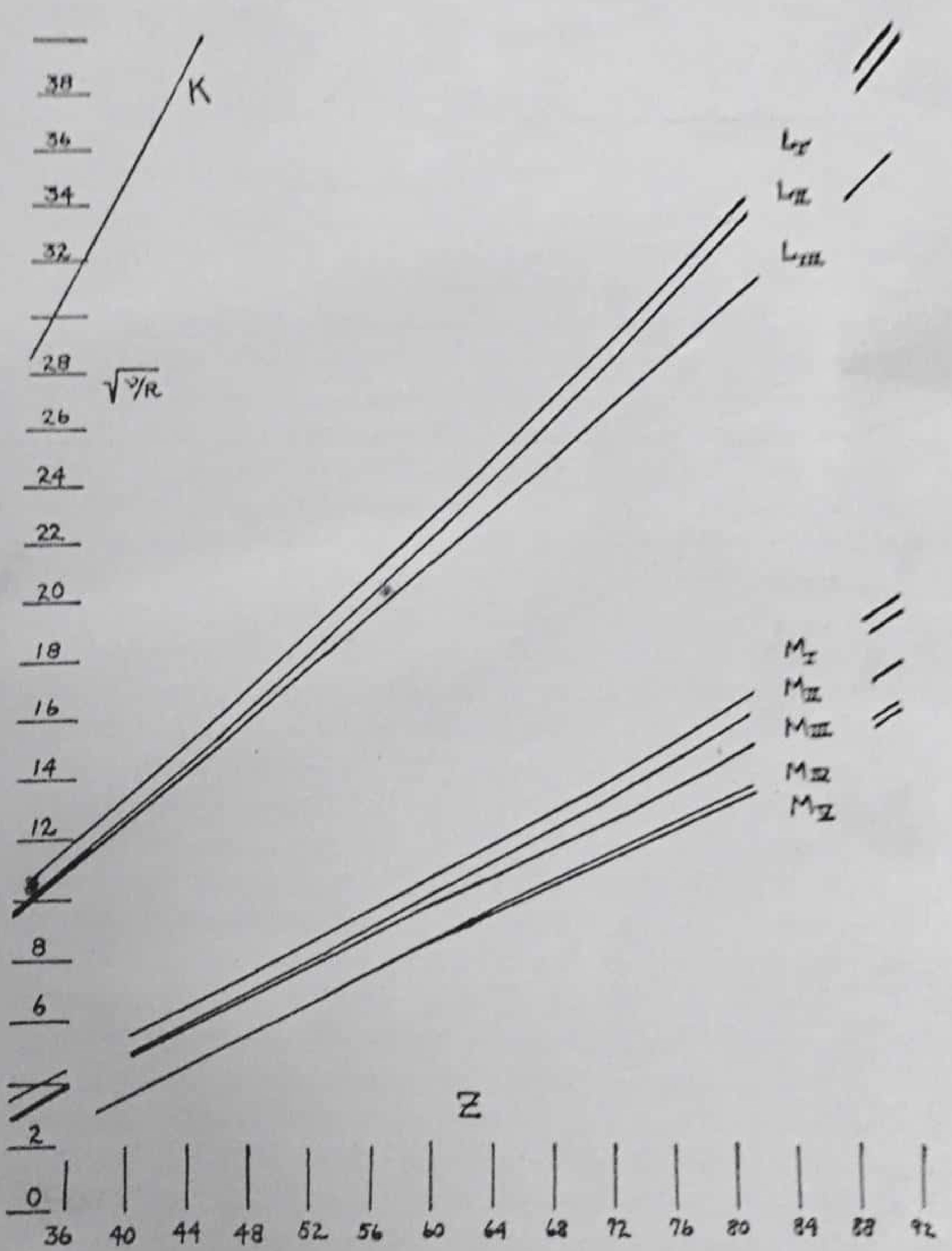

FIG. VIII-14. Moseley diagrams for the *K*, *L*, and *M* levels.

interpretation of these separations is found by writing out the appropriate expressions from eqs. (8.18) and (8.19). For the levels L_{I}, M_{I}, M_{III}, N_{I}, N_{III}, and N_{V} we have (1) (2)

$$E(n, l, j) = -Rhc\,\frac{(Z-\sigma_1)^2}{n^2} - Rhc\alpha^2\,\frac{(Z-\sigma_2)^4}{n^4}\left(\frac{n}{l+1}-\frac{3}{4}\right) - \cdots \qquad (8.33)$$

and for the levels L_{II}, M_{II}, M_{IV}, N_{II}, N_{IV}, N_{VI} we have

$$E'(n', l', j') = -Rhc\,\frac{(Z-\sigma_1')^2}{n'^2} - Rhc\alpha^2\,\frac{(Z-\sigma_2')^4}{n'^4}\left(\frac{n'}{l'}-\frac{3}{4}\right) - \cdots \qquad (8.34)$$

Using the relation

$$\frac{\nu}{R} = \left|\frac{E(n, l, j)}{Rhc}\right|$$

and taking the square root, we obtain from (8.33)

$$\sqrt{\frac{\nu}{R}} = \frac{Z-\sigma_1}{n} + \frac{\alpha^2}{2n^3}\,\frac{(Z-\sigma_2)^4}{Z-\sigma_1}\left(\frac{n}{l+1}-\frac{3}{4}\right) \qquad (8.35)$$

and an analogous expression from eq. (8.34). If now we solve for the $\Delta\sqrt{\nu/R}$ difference of a screening doublet, we have $n = n'$ and $l' = l + 1$, so that there results

$$\Delta\sqrt{\frac{\nu}{R}} = \frac{\sigma_1'-\sigma_1}{n} + \frac{\alpha^2}{2n^3}\left(\frac{n}{l+1}-\frac{3}{4}\right)\left\{\frac{(Z-\sigma_2)^4}{Z-\sigma_1} - \frac{(Z-\sigma_2')^4}{Z-\sigma_1'}\right\}. \qquad (8.36)$$

The second term in the right-hand member of eq. (8.36) may be neglected in a rough calculation, whence

$$\Delta\sqrt{\frac{\nu}{R}} = \frac{\Delta\sigma_1}{n}. \qquad (8.37)$$

Our conceptions of the unvarying character from element to element of the structure of the inner parts of the atom lead us to expect that the difference $\Delta\sigma_1$ will be independent of Z, hence the behavior of the screening doublets is explained. Sommerfeld[29] has discussed the effect of retaining the term in α^2 in eq. (8.36). We may make this correction by defining a "reduced" term value as follows, from eq. (8.33):

$$\left(\frac{\nu}{R}\right)_{\text{red.}} = \left(\frac{\nu}{R}\right) - \frac{\alpha^2}{n^4}(Z-\sigma_2)^4\left(\frac{n}{l+1} - \frac{3}{4}\right) = \frac{(Z-\sigma_1)^2}{n^2}. \quad (8.38)$$

This reducing process, if applied to the terms whose difference follows the spin doublet formula, has the effect of producing the same reduced term from both of them. In other words, they are reduced to their parent n, l level analogous to the level which would be obtained from eq. (8.07) if the third term in the bracketed part were not present. Thus for the reduced terms we may properly speak of the screening doublet as existing between L_I and $L_{II}L_{III}$, or between $N_{IV}N_V$ and $N_{VI}N_{VII}$, etc. For these reduced terms, eq. (8.36) should be strictly accurate. We may reduce all terms except L_I, M_I, N_I, etc., by using values of σ_2 from Table VIII–10. When this is done, and σ_1 values calculated by (8.38), we find that for $M_{II}M_{III}$, $M_{IV}M_V$, $N_{II}N_{III}$, $N_{IV}N_V$ and $N_{VI}N_{VII}$, $\Delta\sigma_1$ is independent of Z, as exhibited in the curves of Fig. VIII–15.

We cannot obtain values of σ_2 for the terms L_I, M_I, N_I from the spin doublet equation; they have, however, been found by the following method. The observed terms for these levels are reduced, using various assumed values of σ_2 until one is found which makes the $\Delta\sigma_1$ values independent of Z. In this way the following values of σ_2 have been found: L_I, 2.0; M_I, 6.8; N_I, 14. It is an interesting fact, as yet unexplained, that the $\Delta\sigma_1$ values obtained in this way are approximately integral multiples of 0.57.

Let us consider for a moment the difference between the screening constants σ_1 and σ_2 for a given level. By a comparison of Fig. VIII–15 and Table VIII–10 it is seen that σ_1 is larger than σ_2 and that while σ_2 is independent of atomic number, σ_1 increases as Z increases. The difference between σ_1 and σ_2 has been ascribed by Bohr and Coster[30] to the fact that while σ_1 includes the screening effects of the electrons in shells internal and external to the shell in question, σ_2 concerns the internal screening only. These statements cannot be true in a highly precise sense, since due to the interpenetration of the shells, no sharp distinction between internal and external shells is possible.

The simplest numerical calculation of the external screening effect due to a given outer shell would be based on the concept of the uniform distribution of the charge of the z electrons in that shell on a sphere of radius ρa_0, a_0 being the radius of the first Bohr orbit in

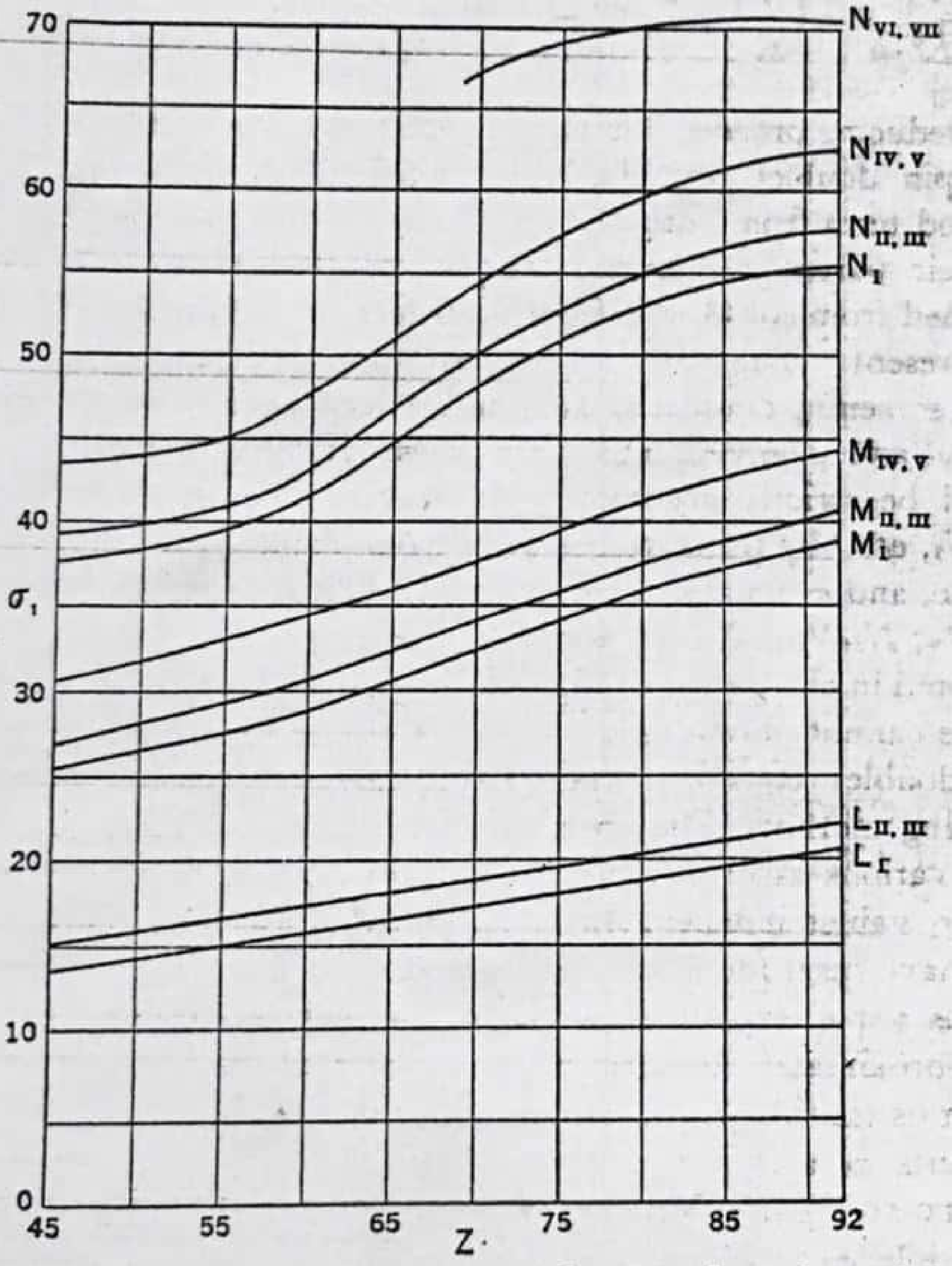

FIG. VIII–15. The screening constant σ_1 as a function of atomic number. (From Sommerfeld, Atombau und Spektrallinien, p. 309 (5th Ed.).

hydrogen. The work required to bring an electron from infinity to this shell would be

$$\frac{ze^2}{\rho a_0}$$

and the main term in the energy of the screened electrons would be

$$E(n) = -Rhc\frac{(Z-\sigma_1)^2}{n^2} = -Rhc\frac{(Z-\sigma_0)^2}{n^2} + \sum_i \frac{z_i e^2}{\rho_i a_0} \qquad (8.39)$$

in which σ_0 represents the effect of screening by levels internal to the one in question. If such a calculation is made, it is not found that σ_0 and σ_2 entirely agree, indicating the approximate nature of the considerations. From eq. (8.39), however, we see that the contribution to the external screening of a single electron is greater in a shell of smaller than in one of larger radius. This explains the sudden increase in the slope of the σ_1 against Z curve for the M and N levels near atomic number 57 (Fig. VIII–15). At $Z = 47$, where the curves begin, added electrons go into $5s$ or $5p$ shells, but at the beginning of the rare earths, at 57 La, electrons begin to enter the $4f$ shells, which are presumably of smaller effective radius.[31]

Selection Rules and Exceptions