SCREENING CONSTANTS IN X-RAY SPECTRA: A REVIEW

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Abstract:
Sommerfeld, in his pioneering work of analyzing the effect of electrons present in different orbits on the nuclear charge, introduced two screening parameters $\sigma_1$ and $\sigma_2$ in the Sommerfeld-Dirac relativistic energy expression. But the relativistic expression was used in the expanded form in the initial works and approximation was made to truncate the infinite series after a certain term. A number of researches and efforts were made since the introduction of screening parameters to get complete information about their behavior. Some authors questioned the need of two separate screening parameters but Sommerfeld gave a perfect justification for the need of two parameters $\sigma_1$ for the screening effect of the electrons situated in orbits both internal and external to the one under consideration and $\sigma_2$ for the screening of nuclear charge by the electrons present in the orbits inner to the one under consideration. As the work on screening parameters progressed, precise and accurate energy data became available thereby enabling the research work to provide a comprehensive and reliable list of $\sigma_1$ and $\sigma_2$ values. The present review paper gives an account of studies made on screening parameters right from the time of their inception to the work done during early seventies. As a lot of work is done after this period also, it would be justified for convenience of the reader to divide the entire work into segments. The later studies in this field would be analyzed in forthcoming review papers.

Keywords: Screening parameter, fine structure, Sommerfeld-Dirac relativistic energy expression, spins doublets, elliptic orbits.

1. INTRODUCTION

The attempts to reflect, refract, diffract and polarize X-rays were unsuccessful in the initial stages of investigation. Max Von Laue, in 1912 recognized the problem and suggested that failure in reflecting, refracting and other phenomena of X-rays was merely due to the requirement of proper medium that was suitable for X-rays. The medium that was good for visible and UV rays was not suited for X-rays on account of their short wave length. Von Laue’s best-known contribution: the discovery of diffraction of X-rays by crystals established the fact that crystals are the most suited medium for X-rays. Before the discovery of diffraction of X-rays by crystals, characteristic X-rays were detected and examined by Barkla and Sadler [1]. They designated the hardest and most penetrating characteristic X-rays as K-series and comparatively less penetrating group as L-series. In addition to these groups, series named M and N and a few lines of O group were discovered [2, 3, 4].

A systematic and comprehensive study of the characteristic X-ray spectra was made by Moseley [5]. ‘Rotating Crystal Photographic Method’ with a crystal of potassium ferrocyanide for diffracting X-rays was used for this purpose. The appearance of K series lines of the elements 20 Ca to 30 Zn was studied and their characteristic behavior was analyzed. It was found that the square root of the frequency of a typical line in the K group is a linear function of atomic number. This behavior was found to be strikingly the same with L series spectral lines. Moseley, in the process of analyzing the experimental results suggested the following expression for the frequency of spectral line:

$$\nu = A(z - b)^2$$  \hspace{1cm} (1)

Where A and b are constants characteristic of each line.

For Ka line

$$A = \left(\frac{1}{27} - \frac{1}{23}\right) \nu_0 \quad \text{and} \quad b=1$$

For La line

$$A = \left(\frac{1}{27} - \frac{1}{23}\right) \nu_0 \quad \text{and} \quad b=7.4$$

Where $\nu_0 = \frac{2h^2e^4m}{h^2}$

As is evident from these expressions, the presence of constant b reduces the effect of nuclear charge on the electron under consideration. This reduction in nuclear charge is actually the screening effect produced by the presence of other electrons. Greater value of b for L series as compared to its value for K series was interpreted by Moseley as resulting from the fact that L electron system is situated farther from the nucleus, leading to greater number of electrons shielding the nuclear charge. Moseley
also found experimentally the value of constant A appearing in eq 1 to be equal to 82,303 cm\(^{-1}\) for K\(\alpha\) line. According to Bohr’s theory for corresponding line A= 82,275 cm\(^{-1}\)showing a close agreement between Bohr’s theory and Moseley’s findings.

2. FINE STRUCTURE AND SOMMERFELD’S RELATIVISTIC ATOM MODEL

Bohr’s theory [6] of circular orbits could not give satisfactory explanation to certain peculiar phenomena observed in Hydrogen spectrum. High resolution instruments had shown that the individual spectral lines were not single but made up of several closely packed lines named as ‘fine structure’. Bohr’s theory of circular orbits assigned only one orbit to each quantum number \(n\), whereas the experimental observation of fine structure indicates the presence of many orbits of slightly different energy associated with a given quantum number. Sommerfeld [7] introduced the idea of motion of electrons in elliptical orbits. Thus, two quantum numbers \(n\) and \(n_\phi\) appeared in the expression of total energy of electron in an elliptic orbit.

\[
W = -\frac{2\pi^2 mE^2\alpha^2}{h^2}\left(\frac{1}{n_r + n_\phi}\right)^2
\]

\[
= -\frac{2\pi^2 mE^2e^2}{h^2n^2}
\]

Where \(n_r\) and \(n_\phi\) are the radial and azimuthal quantum numbers respectively.

It is evident from eq (2) that the energy is the same for all the elliptical orbits having the same quantum number \(n\). Hence the energy of any of these elliptical orbits is the same as that of circular Bohr orbit. Therefore, the theory of elliptic orbits could not explain occurrence of fine structure lines but this extension of Bohr’s theory to elliptic orbits enabled Sommerfeld [8,9] to find the solution to this problem of fine structure of spectral lines on the basis of relativistic variation of mass of electron. The velocity of electron moving in an elliptic orbit varies depending on its position in the orbit. Theory of relativity suggests the variation of mass associated with the variation in velocity. The total energy \(W\) of an electron corrected for the relativistic variation of the mass of electron was shown as:

\[
1 + \frac{W}{m_0 c^2} = 1 + \left\{ 1 + \frac{\alpha^2 Z^2}{(n_r + n_\phi - \alpha^2 Z^2)^2} \right\}^{-\frac{1}{2}}
\]

(3)

Where \(\alpha\) is the fine structure constant, \(m_0\) is the rest mass of the electron.

\[
\alpha = \frac{2\pi e^2}{\hbar c} = 7.283 \times 10^{-3}
\]

Sommerfeld [10] at this stage made a very important statement: ‘that to make the final formula, as given as eq. (3) above, more convenient for purpose of calculation, can be expanded in powers of the small quantity \(\alpha^2\). If \(Z\) is not a large number (H, He\(^+\)) it is sufficient to retain first two powers of \(\alpha^2\). This is not so in the case of the visible and ultra violet spectra. If \(Z\) is a great number the third and the fourth powers of \(\alpha^2\) must also be taken into consideration. This is so in the case of X-ray spectra.’

The general relativistic formula for all hydrogen-like series can be written by citing Bohr’s fundamental equation:

\[
h\nu = W_1 - W_2
\]

Where \(W_1\) is the energy of the initial or orbit of the electron and \(W_2\) is the energy in the final orbit. If the expressions for \(W_1\) and \(W_2\) are substituted, the complete expression for the term is obtained as:

\[
W = -RhcZ^2\left\{ \frac{1}{n_r^2} + \frac{\alpha^2}{n_\phi^4} Z^2 \left( \frac{n}{n_\phi} - \frac{3}{4} \right) \right. \\
+ \frac{\alpha^4}{n_\phi^6} Z^4 \left[ \frac{1}{4 n_\phi^4} - \frac{15}{8} \left( \frac{n}{n_\phi} - \frac{3}{4} \right)^2 \right] \left. + \frac{\alpha^6}{n_\phi^8} Z^6 \left[ \frac{1}{8 n_\phi^5} - \frac{15}{8} \left( \frac{n}{n_\phi} - \frac{3}{4} \right)^3 \right] \right\}
\]

(4)

The first term of this expression which gives the major part of the energy, is the same as that derived by Bohr for circular orbits without taking into account the effect of relativity.
2.1 RELATIVISTIC DOUBLETS IN THE X-RAY REGION

In order to employ the one electron expression for calculating term values for the doublets of the X-ray spectra, Sommerfeld pointed out that the K shell is situated within L orbit and that the electrons of the K shell screen the nuclear charge. The L shell is also occupied by several electrons and they also exert a screening effect on the nuclear charge. In place of the true nuclear charge Sommerfeld introduced “effective nuclear charge” which is smaller than Z. At this stage of studying the relativistic doublets, Sommerfeld introduced a special feature in the general term-expression for X-rays by choosing the screening number in the first term (principal term or Moseley term) different from the screening number in the higher terms (relativistic correction terms of the first, second……..order). Sommerfeld [10] denoted the former number \( \sigma \) and the latter s. In this manner the general term-expression for X-rays:

\[
\frac{\nu}{R} = \frac{1}{n^2} (Z - \sigma)^2 + \frac{\alpha^2}{n^4} (Z - s)^4 \left( \frac{n - 3}{n^2} \right) + \frac{\alpha^4}{n^6} (Z - s)^6 \left[ \left( \frac{1}{4} n^4 \right) + \frac{3}{4} \left( \frac{n - 3}{n^2} \right)^2 - \frac{3}{2} n \right] + \frac{5}{8} \left[ \ldots \ldots \ldots \ldots \right]
\]

(5)

It is remarkable that this formula was developed by Sommerfeld on the basis of the older relativistic quantum theory without inclusion of wave mechanics and the concept of spinning electron. The latest basis for the formula is Dirac’s relativistic theory of electron [11]. The formula under consideration can be written for the members of a spin doublet as:

For \( j = l + \frac{1}{2} \):

\[
E(n, l, j) = -\frac{4\pi}{\hbar c} \left[ (2\sigma - 1)^2 \frac{n^2}{n^4} + \frac{a^2 (2\sigma - 1)^2}{n^4} \left( \frac{n - 3}{n^2} \right) + \frac{a^4 (2\sigma - 1)^2}{n^6} \left( \frac{1}{4} n^4 \right) + \frac{3}{4} \left( \frac{n - 3}{n^2} \right)^2 - \frac{3}{2} n \right] + \frac{5}{8} \left[ \ldots \ldots \ldots \ldots \right]
\]

(6)

For \( j = l - \frac{1}{2} \):

\[
E(n, l, j) = -\frac{4\pi}{\hbar c} \left[ (2\sigma - 1)^2 \frac{n^2}{n^4} + \frac{a^2 (2\sigma - 1)^2}{n^4} \left( \frac{n - 3}{n^2} \right) + \frac{a^4 (2\sigma - 1)^2}{n^6} \left( \frac{1}{4} n^4 \right) + \frac{3}{4} \left( \frac{n - 3}{n^2} \right)^2 - \frac{3}{2} n \right] + \frac{5}{8} \left[ \ldots \ldots \ldots \ldots \right]
\]

(7)

The difference between the above two equations gives the expression for \( \frac{\Delta \nu}{R} \) in terms of only \( (Z - \sigma_2) \), \( n \) and \( l \). The first term has the same value for both the members of the spin doublet. Thus the energy level difference \( \frac{\Delta \nu}{R} \) comes out in the form of an infinite series in ascending powers of \( (Z - \sigma_2) \). Sommerfeld and Wentzel [12] retained the terms only up to \( (Z - \sigma_2)^6 \) and obtained the following expression for \( \frac{\Delta \nu}{R} \):

\[
\frac{\Delta \nu}{R} = \gamma (Z - \sigma_2)^2 \left[ 1 + a(Z - \sigma_2)^2 + (Z - \sigma_2)^4 \right]
\]

(8)

Where \( \gamma, a \) and \( b \) are constants and have the following expressions:

\[
\gamma = \frac{\alpha^2}{n^6} \left( \frac{n}{l^2} - \frac{n}{l^2+1} \right)
\]

(9)

\[
a = \frac{\alpha^2}{n^6} \left[ \left( \frac{n}{l^2} \right)^2 + \frac{n^2}{l^2+1} + \left( \frac{n}{l^2+1} \right)^2 \right] + \frac{2}{n^2} \left[ \frac{n}{l^2+1} + \frac{n}{l^2+1} \right] - \frac{3}{2}
\]

(10)

\[
b = \frac{\alpha^2}{n^6} \left[ \left( \frac{n}{l^2} \right)^4 + \left( \frac{n}{l^2} \right)^2 \left( \frac{n}{l^2+1} \right)^2 + \left( \frac{n}{l^2+1} \right)^4 \right] + \frac{3}{n^2} \left[ \left( \frac{n}{l^2+1} \right)^2 + \left( \frac{n}{l^2+1} \right)^2 + \left( \frac{n}{l^2+1} \right)^2 \right]
\]

(10)

To express \( (Z - \sigma_2) \) in terms of \( \frac{\Delta \nu}{R} \), Sommerfeld and Wentzel obtained:
\[ (Z - \sigma_2)^2 = \left[ \frac{1}{\gamma} \sqrt{\frac{\Delta v}{R}} - \frac{a}{2} \frac{\Delta v}{R} \right] \left[ 1 + \left( 1 + \frac{5a^2 - b}{8} \right) \frac{1}{2} \frac{\Delta v}{R} \right] \]  \hspace{1cm} (11)

The explicit expression for various doublets by using the equations (8) to (11) are as given below:

For \( L_2L_3 \) doublet:

\[ (Z - \sigma_2)^2 = \left[ \frac{4}{\alpha} \sqrt{\frac{\Delta v}{R}} - \frac{5}{16} \frac{\Delta v}{R} \right] \left[ 1 + \frac{19}{32} \alpha^2 \frac{\Delta v}{R} \right] \]  \hspace{1cm} (12)

For \( M_2M_3 \) doublet:

\[ (Z - \sigma_2)^2 = \left[ \frac{3}{\alpha} \sqrt{\frac{6\Delta v}{R}} - \frac{279}{16} \frac{\Delta v}{R} \right] \left[ 1 + \frac{191}{32} \alpha^2 \frac{\Delta v}{R} \right] \]  \hspace{1cm} (13)

For \( M_4M_5 \) doublet:

\[ (Z - \sigma_2)^2 = \left[ \frac{9}{\alpha} \sqrt{\frac{2\Delta v}{R}} - \frac{225}{16} \frac{\Delta v}{R} \right] \left[ 1 + \frac{589}{1024} \alpha^2 \frac{\Delta v}{R} \right] \]  \hspace{1cm} (14)

For \( N_2N_3 \) doublet:

\[ (Z - \sigma_2)^2 = \left[ \frac{8}{\alpha} \sqrt{\frac{2\Delta v}{R}} - \frac{40}{3} \frac{\Delta v}{R} \right] \left[ 1 + \frac{191}{32} \alpha^2 \frac{\Delta v}{R} \right] \]  \hspace{1cm} (15)

For \( N_4N_5 \) doublet:

\[ (Z - \sigma_2)^2 = \left[ \frac{8}{\alpha} \sqrt{\frac{6\Delta v}{R}} - \frac{112}{3} \frac{\Delta v}{R} \right] \left[ 1 + \frac{1935}{864} \alpha^2 \frac{\Delta v}{R} \right] \]  \hspace{1cm} (16)

For \( N_6N_7 \) doublet:

\[ (Z - \sigma_2)^2 = \left[ \frac{16}{\alpha} \sqrt{\frac{3\Delta v}{R}} - \frac{92}{3} \frac{\Delta v}{R} \right] \left[ 1 + \frac{169}{288} \alpha^2 \frac{\Delta v}{R} \right] \]  \hspace{1cm} (17)

Sommerfeld and Wentzel [12] and Sommerfeld [13, 14, 15, 16] calculated the values of screening parameter \( \sigma_2 \) for various spin doublets by using the corresponding values of \( \frac{\Delta v}{R} \). For \( L_2L_3 \) doublet these calculations covered the atomic number range \( Z=41 \) to 92 and a mean value of \( \sigma_2 = 3.487 \) was reported [17]. It was mentioned that individual values of \( \sigma_2 \) fluctuate about the mean value in quite an unsystematic way. Similar calculations were repeated for the other spin doublets and it was observed that \( \sigma_2 \) comes out to be nearly constant for a given spin doublet. Sommerfeld summarized the observations and drew the following conclusion:

1. The screening parameter \( \sigma_2 \) is a constant for a given spin doublet.
2. \( \sigma_2 \) increases as the principal quantum n increases.
3. \( \sigma_2 \) also increases as the azimuthal quantum number increases for a given shell.
Karnatak and Varshni [17] quoted the average of $\sigma_2$ values reported by Sommerfeld and Wentzel and Sommerfeld as:

<table>
<thead>
<tr>
<th>Doublet</th>
<th>$\sigma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L\text{II}L\text{III}</td>
<td>3.5</td>
</tr>
<tr>
<td>M\text{II}M\text{III}</td>
<td>8.5</td>
</tr>
<tr>
<td>M\text{IV}M\text{V}</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Pauling [18] also reported the values of screening constant $\sigma_2$ and they are found to be close to the values reported by Sommerfeld and Wentzel and Sommerfeld.

Karnatak and Varshni, citing the availability of more accurate data for energy values of spin doublets, recalculated $\sigma_2$ using the method suggested by Sommerfeld. They made use of energy values published by CAUCHOIS [19, 20] and reported values of screening constant $\sigma_2$ for $\text{LII}_1\text{LL}_{\text{III}}$ in the atomic number range $23 \leq Z \leq 92$, $\text{MII}_1\text{MM}_{\text{III}}$ in the atomic number range $33 \leq Z \leq 92$ and $\text{MIV}_1\text{MV}$ in the atomic number range $49 \leq Z \leq 92$. These authors found some discrepancies and deviation in the calculated values of $\sigma_2$ from the normal behavior. It was suggested by the authors that the deviation may be due to the influence of shell formation. But mainly the reason of discrepancies was attributed to the experimental error present in the energy values reported by CAUCHOIS. But the deviation and fluctuations found in $\sigma_2$ values were found to be exceeding the limit of experimental error in some cases. One reason for this discrepancy was attributed to the fact that the mathematical expression was developed on the theory for free atoms whereas experimental data were collected with the samples in solid state. One more important point was suggested by these authors for the observed deviation in $\sigma_2$ values and that is the role of approximation made by Sommerfeld in the expression for $(Z - \sigma_2)$.

Clementi and Raimondi [21] calculated the screening parameter $\sigma$ as obtained by the Self Consistent Field method for atoms with 2 to 36 electrons. The best values of $\sigma$ for the atoms were obtained by employing self consistent method when each individual electron is considered to be described by a single exponential function with variable exponents. The orbital exponent $\xi$ of such function is $\xi = (Z - \sigma) / \eta$; $(Z - \sigma)$ being the effective Z, $\sigma$ the screening constant and $\eta$ the principal quantum number. The self consistent field functions were computed with a minimal basis set of Slater type orbital [22]. The cycle of individual optimization of orbital exponents was repeated four times until $\xi$ reached the optimal value. The rules obtained for the 1s, 2s, 3s, 4s, 2p, 3p, 4p and 3d electronic configurations were compared with those prepared by Slater. According to Slater rules, screening constant $\sigma$ is a function of $n$ and $N_1$ where $n$ is the principal quantum number and $N_1$ is the total number of electrons present in the orbits inner to the one under consideration. But Clementi and Raimondi found from their analysis that there is a need of accounting for screening due to the outside electrons. Reinhardt et al [23] extended the calculation of minimal basis set atomic function for the ground state atoms for Rb ($Z=37$) to Rn ($Z=86$) and consequently the screening constants were obtained for this range of atomic numbers.

Mande and Damle [24] refuted the idea of using two screening constants $\sigma_1$ and $\sigma_2$ to account for screening in the calculation of orbital energies. Two constants were replaced by a single screening parameter $\sigma$ and the calculation of this parameter was done for levels K, L\text{I}, L\text{II} and L\text{III} in the atomic number range between 25 and 90. The experimental energy value data reported by Sandstrom [25] were used for the calculation of $\sigma$. Mande and Damle have reported that the value of screening constant $\sigma$ was different for different levels and $\sigma_{\text{LIII}} - \sigma_{\text{LII}}$ is found to be nearly constant for elements of high atomic numbers.

Damle and Mande [26] in a communication reported their work in which they used the screening constant obtained in their previous work to obtain shifts in the K, L\text{I}, L\text{II} and L\text{III} levels due to nuclear finite size effect taking into account the screening effect. Meligy [27] and Babushkin [28] had studied the shifting of energy levels caused by taking into account the nuclear finite size but this shifting was calculated without taking into account the screening due to orbital electrons. Damle and Mande reported the data for energy shift for energy levels K, L\text{I}, L\text{II} and L\text{III} for certain elements in the atomic number range $Z=37$ to $Z=92$. In another communication Mande and Damle [29] reported values of screening parameter $\sigma$ for K, L\text{I}, L\text{II} L\text{III}, M\text{I}, M\text{II}, M\text{III}, M\text{IV}, N\text{I}, N\text{II}, N\text{III} and N\text{IV} levels and categorized the doublets as real screening doublets and apparent screening doublets.

Using the energy level data reported by Bearden and Burr [30], Padalia [31] recalculated the parameter $\sigma_2$ for the spin doublet $L\text{I}L\text{II}$ in the range of atomic number $17 \leq Z \leq 103$, for doublet $M_2M_3$ in the range of atomic number $31 \leq Z \leq 103$, for doublet $M_4M_5$ in the range of atomic number $35 \leq Z \leq 103$. Padalia employed the approximate method of Sommerfeld and Wentzel for his calculation of $\sigma_2$. This study was extended by Paehdes and Phadnis [32] to cover the spin doublets N\text{II}N\text{I}, N_3N_2, N_4N_3, N_5N_4 and N_6N_5. In some cases some anomalies were found by these authors in $\sigma_2$ values as they were not fitting in the regular variation of $\sigma_2$ with Z. The deviations were attributed by these authors as the reflection of some anomalies present in the energy value data.
As discussed in the preceding paragraphs, all the approaches employed to calculate \( \sigma_2 \) discussed so far were based on the Sommerfeld-Dirac relativistic energy expression in its approximate form which was truncated after the term \((Z - \sigma_2)^2\). All the attempts to get accurate values of \( \sigma_2 \) were aimed at employing more precise energy values. Bergvall and Hagstrom [33] were the first to consider the effect of truncating the infinite series of Sommerfeld-Dirac energy equation.

They used the following expression for calculating the energy level separation of spin doublet \( L_2L_3 \):

\[
\Delta E = \frac{\hbar c}{a^2}\left(\sqrt{4 - \alpha^2 (Z - \sigma_2)^2} - \sqrt{2 + 2\sqrt{1 - \alpha^2 (Z - \sigma_2)^2}}\right)
\]  

(18)

The screening parameter \( \sigma_2 \) was adjusted to give that value of \( \Delta E \) which is in closest agreement with the experimental results. The average value of \( \sigma_2 = 3.58 \) was reported by these authors for \( L_2L_3 \) in the rare earth region.

Burr and Carson [34] calculated screening parameter for the doublet \( L_2L_3 \) \((Z=13 \text{ to } 103)\), \( M_2M_1 \) \((Z=31 \text{ to } 103)\), \( M_1M_1 \) \((Z=35,37,53,55,103)\), \( N_2N_1 \) \((Z=55, 56, 70-88, 88, 90-95)\), \( N_2N_7 \) (74, 77-83, 90-92), \( O_2O_2 \) \((55,56, 72-83,88,90,92,94)\), \( O_2O_4 \) \((81-83,90,92-95)\). The significance of this work lies in the fact that they employed the two body relativistic energy expression in its closed form thus ruling out the series truncation errors. The energy values were those reported by Bearden and Burr [35].

3. CONCLUSION

In this review paper the main focus is on Sommerfeld screening parameters, though at some places screening parameters other than Sommerfeld’s were mentioned. The entire field covering all the studies based on screening parameters is too vast to cover in one review article. The future communications by the author would be a comprehensive compilation of all studies made in this field.

4. REFERENCES