

The Origin of the s, p, d, f Orbital Labels

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Question

Why are the letters s, p, d and f used to label electronic subshells?

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Answer

Writing in 1937, the British physicist, A. C. Candler, divided the history of spectroscopy into four eras, which he called the acoustics period, the series period, the old quantum period, and the newer quantum mechanical period (1, 2). "The first period," Candler observed, "began with the earliest measurements of wave lengths and continued in the work of Boltzmann, Liveing and Dewar until 1881 ... During this period any theories put forward were based on analogies with the harmonic ratios of sound." It is in this period that the story of s, p, d, and f begins and it does so with the work of the last two scientists mentioned by Candler - the British chemists, George Liveing and Sir James Dewar, who published roughly a dozen papers between 1872 and 1880 dealing with the line spectra of the alkali metals (3). In describing these spectra, Liveing and Dewar took to qualitatively characterizing the various lines in terms of both their intensity and definition as being either principle, sharp, or diffuse, and further noted that lines of a given type appeared in groups or series.

Stimulated by Johann Balmer's discovery in 1885 of an empirical formula interrelating the four principle spectral lines of hydrogen, Candler's second or "series" period was, as suggested by its name, characterized by attempts to extend Balmer's approach to other elements. In the case of the alkali metals, this work was done largely by the German team of Heinrich Kayser and Carl Runge (4), and also independently by the Swedish spectroscopist Johannes Rydberg (5). Their work demonstrated that many of the lines in the spectra of the alkali metals could be mathematically modeled as the sum of three independent series, which



Figure 1. Friedrich Hermann Hund (1896-1997).

Rydberg, following the earlier nomenclature of Liveing and Dewar, named the principle, sharp and diffuse series. In 1907 yet a fourth series of lines was discovered in the spectra of the alkali metals by Arno Bergmann and named the fundamental series (6).

As is well known, Chandler's third period was characterized by attempts, starting with Bohr's famous paper of 1913, to provide a physical model of the atom consistent with the empirical series formulas found earlier. Extending this model from hydrogen to other elements led to the introduction of a variety of more complex quantization schemes, none of which proved wholly satisfactory until the work of Stoner, Main Smith, and Pauli and the introduction of the newer quantum mechanics in the early 1920s (Candler's fourth period). The history of this eventual resolution is far too complex to deal with in the space available. However, one of its most important consequences was the establishment of our modern electronic atomic

configurations and an understanding of their relationship to the periodic table.

This breakthrough is usually attributed to a 1922 monograph by Bohr, but close inspection of Bohr's configurations shows that his subshell assignments are incorrect (7). In actual fact, our current configurations first appeared in Max Born's 1925 monograph, *Vorlesungen über Atommechanik*, though in his introduction Born indicated that both the configuration table and the discussion of its relationship to the periodic table were actually the work of "my assistant Dr. Friedrich Hund" (8). Two years later Hund expanded this work into a monograph of his own entitled *Linienspektren und periodisches System der Elemente* (9).

In the version of the configuration table which had appeared in Born's monograph, Hund (figure 1) had followed Bohr's practice of labelling the various shells and subshells in terms of their corresponding numerical quantum numbers as 3_1 , 3_2 , 3_3 etc. In his own monograph, however, he replaced the secondary quantum number with the series notations (s, p, d, and f) used by Sommerfeld and others as abbreviations for the characteristic series constant, μ , which had appeared in Rydberg's original empirical equation for the sharp, principle, diffuse and fundamental line series found the spectra of the alkali metals, and instead wrote 3s, 3p, 3d etc. (10). Beginning in the 1930s both Hund's corrected configurations and his s, p, d, f notation began to slowly leak into the chemical literature, where they have reigned supreme ever since (11).

Literature Cited

1. A. C. Candler, *Atomic Spectra and the Vector Model*, Vol. 1, Cambridge University Press: Cambridge, 1937, pp. 1-2.
2. For a detailed history of Candler's first two periods, see W. McGucken, *Nineteenth-Century Spectroscopy: Development of the Understanding of Spectra 1802-1897*, Johns Hopkins Press: Baltimore, MD, 1969.
3. These mostly appeared in the *Proceedings of the Royal Society* and are conveniently collected together in G. Liveing, J. Dewar, *Collected Papers on Spectroscopy*, Cambridge University Press: Cambridge, 1915.
4. H. Kayser, C. Runge, "Über die Spectren der Alkalien," *Ann Physik*, **1890**, *41*, 302-320.

5. J. R. Rydberg, "Sur la constitution des spectres linéaires des éléments chimiques," *Comptes rendus*, **1890**, *110*, 394-397.

6. A. Bergmann, *Beiträge zur Kenntniss der ultrarotheren Emissionsspectren der Alkalien*, Doctoral Dissertation, Jena, 1907.

7. N. Bohr, *The Theory of Spectra and Atomic Constitution*, Cambridge University Press, Cambridge, 1922, p. 133. A more complete, but equally incorrect, table appears opposite page 129 in the second edition of 1924.

8. M. Born, *Vorlesungen über Atommechanik*, Vol. 1, Springer: Berlin, 1925, table opposite page 226.

9. F. Hund, *Linienspektren und periodisches System der Elemente*, Springer: Berlin, 1927, table opposite page 55.

10. A. Sommerfeld, *Atomic Structure and Spectral Lines*, Dutton: New York, NY, 1924, p. 376 (First German edition 1919). Interestingly Sommerfeld used *b* for Bergmann rather than *f* for fundamental as his abbreviation for the fourth series.

11. In the case of introductory textbooks this leakage was often slow. Thus both the fourth (1933) and fifth (1937) editions of James Partington's, *A Textbook of Inorganic Chemistry*, continued to use the labeling scheme found in Born and Bohr. Only in the sixth edition of 1950 did Partington finally adopt the s, p, d, f labels of Hund.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

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Since writing the column, I have discovered that one of the first advanced monographs to employ Hund's s, p, d, f orbital notation was the 1930 monograph on the periodic table by the German chemists, Eugen Rabinowitsch and Eric Thilo:

E. Rabinowitsch, E. Thilo, *Periodisches System: Geschichte und Theorie*, Enke: Stuttgart, 1930, pp. 244-245.