Spectroscopic Notation

The absorption spectrum of hydrogen consists of those transitions whereby electrons in the ground state of the atom absorb energy from the incident light’s continuous spectrum and are raised to certain of the various hydrogen excited states. In emission these are the lines of the Lyman series (see Figure SN-1). In the early days of atomic spectroscopy the spectrum of hydrogen, the simplest of the atoms, was much studied and its spectrum served as a benchmark relative to which the spectra of other, more complex atoms were compared and analyzed in the search for understanding of atomic structure. When the absorption spectra of the alkali metals (lithium, sodium, potassium, etc.) were obtained, it was at once apparent that they closely resembled the hydrogen absorption spectrum. That is, like hydrogen, they consisted of series of lines with regularly decreasing separations and intensities. Thus, they were accorded the distinction of being called the principal series.

In the emission spectra of the alkali elements other series appeared in addition to the principal series of the absorption spectrum. The lines of one of the additional spectra appeared quite sharp on the photographic plates used to record them and so was given the name the sharp series. The lines of one of the other series seen in emission, less intense than those of the sharp series, appeared rather fuzzy or diffuse, so its name became the diffuse series (see Figure SN-2). Further in the infrared and less intense than the diffuse series was the fundamental series (originally called the Bergmann series after its discoverer).

The wave numbers (= 1/wavelengths) of the spectral lines of each series were determined empirically from differences between a series-specific limiting term and a running term, the latter proportional to 1 divided by the square of an integer in a way similar to the Rydberg formula. Quantum theory subsequently associated each of the spectroscopic terms with an allowed energy state of the atom. For the spectra of the alkali elements the principal series in absorption corresponded to transitions from the ground energy state (the lowest S term) to the various

SN-1 Energy-level diagram for the hydrogen atom. The hydrogen absorption spectrum, the principal series, consists of those lines originating on the 1s state. In emission these are the spectral lines of the Lyman series.
principal (P term) energy states and just the reverse for the principal emission spectrum. The sharp series corresponded to transitions from the higher sharp (S terms) energy states—the running terms—to the lowest principal (P term) state, the limiting term for the sharp series (see Figure SN-3). Similarly, the diffuse emission spectrum was the result of transitions from the higher diffuse (D terms) energy states to the lowest principal (P term) state, the same limiting term as for the sharp series. Finally, the fundamental emission spectrum was the result of transitions from the higher fundamental (F terms) energy states to the lowest D term state, the limiting term for the fundamental series.

In Figure SN-3 the principal emission series of sodium consists of those transitions originating on p states and ending on the 3s level (the lowest S term). The sharp series consists of those transitions originating on the 4s and higher s states and ending on the 3p state (the lowest P term). Similarly, the diffuse series is made up of those transitions from the d states to the 3p state and the fundamental series from the f states to the 3d state.

The concept of spectral “terms” and the use of series names such as principal, sharp, and so on has now passed from common use, replaced by the quantitative understanding of atomic structure provided by quantum mechanics. However, the notational shorthand used by the early spectroscopists was adapted and modified to describe succinctly all atomic states, not just those of the alkali elements, and ultimately the quantum states of molecules, nuclei, and particles. The notation “code” is easy to learn and, as you will discover, convenient to use. For single electrons we have

1. For single-electron states the letter code \( spdfgh \ldots \) is used in one-to-one correspondence with the values of the orbital angular momentum quantum number \( \ell \): 0 1 2 3 4 5 \ldots. For example, an electron with \( \ell = 2 \) is said to be a \( d \) electron or in a \( d \) state.

2. The single-electron (Bohr) energy levels are called shells, labeled \( KLMNO \ldots \) in one-to-one correspondence with the values of the principal quantum number \( n \): 1 2 3 4 5 \ldots. For example, an electron with \( n = 3 \) in an atom is said to be in the \( M \) shell. (This notation is less commonly used.)

For atomic states that may contain one or more electrons the notation includes the principal quantum number and the angular momenta quantum numbers. The total orbital angular momentum quantum number is denoted by a capital letter in the same sequence as in rule 1 above; that is, \( SPDF \ldots \) correspond to \( \ell \) values 0 1 2 3 \ldots.
The value of \( n \) is written as a prefix and the value of the total angular momentum quantum number \( j \) by a subscript. The magnitude of the total spin quantum number \( s \) appears as a left superscript in the form \( 2s + 1 \). Thus, a state with \( \ell = 1 \), a \( P \) state, would be written as \( n^{2s+1}P_j \).

For example, the ground state of the hydrogen atom \((n = 1, \ell = 0, s = 1/2)\) is written \( 1^2S_1/2 \), read “one doublet \( S \) one-half.” The \( n = 2 \) state can have \( \ell = 0 \) or \( \ell = 1 \), so the spectroscopic notation for these states is \( 2^2S_{1/2}, 2^2P_{3/2}, \) and \( 2^2P_{1/2} \). (The principal quantum number and spin superscript are sometimes not included if they are not needed in specific situations.) Appropriate versions of the notation are used to describe the quantum states of molecular constituents, the protons and neutrons in nuclei, and the states of fundamental particles.