

ATOMIC SPECTROSCOPY

Spectroscopic notation combines observational and theoretical elements. Observationally, spectral lines are grouped in series with line spacings which decrease toward the series limit. Every line can be related theoretically to a transition between two atomic states, each identified by its quantum numbers.

Ionization levels are indicated by roman numerals. Thus C I is unionized carbon, C II is singly ionized, etc. The state of a one-electron atom (hydrogen) or ion (He II, Li III, etc.) is specified by identifying the principal quantum number $n = 1, 2, \dots$, the orbital angular momentum $l = 0, 1, \dots, n - 1$, and the spin angular momentum $s = \pm \frac{1}{2}$. The total angular momentum j is the magnitude of the vector sum of \mathbf{l} and \mathbf{s} , $j = l \pm \frac{1}{2}$ ($j \geq \frac{1}{2}$). The letters s, p, d, f, g, h, i, k, l, \dots , respectively, are associated with angular momenta $l = 0, 1, 2, 3, 4, 5, 6, 7, 8, \dots$. The atomic states of hydrogen and hydrogenic ions are degenerate: neglecting fine structure, their energies depend only on n according to

$$E_n = -\frac{R_\infty hcZ^2 n^{-2}}{1 + m/M} = -\frac{\text{Ry}Z^2}{n^2},$$

where h is Planck's constant, c is the velocity of light, m is the electron mass, M and Z are the mass and charge state of the nucleus, and

$$R_\infty = 109,737 \text{ cm}^{-1}$$

is the Rydberg constant. If E_n is divided by hc , the result is in wavenumber units. The energy associated with a transition $m \rightarrow n$ is given by

$$\Delta E_{mn} = \text{Ry}(1/m^2 - 1/n^2),$$

with $m < n$ ($m > n$) for absorption (emission) lines.

For hydrogen and hydrogenic ions the series of lines belonging to the transitions $m \rightarrow n$ have conventional names:

Transition	$1 \rightarrow n$	$2 \rightarrow n$	$3 \rightarrow n$	$4 \rightarrow n$	$5 \rightarrow n$	$6 \rightarrow n$
Name	Lyman	Balmer	Paschen	Brackett	Pfund	Humphreys

Successive lines in any series are denoted α, β, γ , etc. Thus the transition $1 \rightarrow 3$ gives rise to the Lyman- β line. Relativistic effects, quantum electrodynamic effects (e.g., the Lamb shift), and interactions between the nuclear magnetic

moment and the magnetic field due to the electron produce small shifts and splittings, $\lesssim 10^{-2} \text{ cm}^{-1}$; these last are called “hyperfine structure.”

In many-electron atoms the electrons are grouped in closed and open shells, with spectroscopic properties determined mainly by the outer shell. Shell energies depend primarily on n ; the shells corresponding to $n = 1, 2, 3, \dots$ are called K, L, M, \dots . A shell is made up of subshells of different angular momenta, each labeled according to the values of n, l , and the number of electrons it contains out of the maximum possible number, $2(2l + 1)$. For example, $2p^5$ indicates that there are 5 electrons in the subshell corresponding to $l = 1$ (denoted by p) and $n = 2$.

In the lighter elements the electrons fill up subshells within each shell in the order s, p, d, \dots , and no shell acquires electrons until the lower shells are full. In the heavier elements this rule does not always hold. But if a particular subshell is filled in a noble gas, then the same subshell is filled in the atoms of all elements that come later in the periodic table. The ground state configurations of the noble gases are as follows:

He	$1s^2$
Ne	$1s^2 2s^2 2p^6$
Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
Rn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

Alkali metals (Li, Na, K, etc.) resemble hydrogen; their transitions are described by giving n and l in the initial and final states for the single outer (valence) electron.

For general transitions in most atoms the atomic states are specified in terms of the parity $(-1)^{\sum l_i}$ and the magnitudes of the orbital angular momentum $\mathbf{L} = \sum \mathbf{l}_i$, the spin $\mathbf{S} = \sum \mathbf{s}_i$, and the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where all sums are carried out over the unfilled subshells (the filled ones sum to zero). If a magnetic field is present the projections M_L, M_S , and M of \mathbf{L}, \mathbf{S} , and \mathbf{J} along the field are also needed. The quantum numbers satisfy $|M_L| \leq L \leq \nu l, |M_S| \leq S \leq \nu/2$, and $|M| \leq J \leq L + S$, where ν is the number of electrons in the unfilled subshell. Upper-case letters S, P, D, \dots , stand for $L = 0, 1, 2, \dots$, in analogy with the notation for a single electron. For example, the ground state of Cl is described by $3p^5 \ ^2P_{3/2}^o$. The first part indicates that there are 5 electrons in the subshell corresponding to $n = 3$ and $l = 1$. (The closed inner subshells $1s^2 2s^2 2p^6 3s^2$, identical with the configuration of Mg, are usually omitted.) The symbol ‘P’ indicates that the angular momenta of the outer electrons combine to give $L = 1$. The prefix ‘2’ represents the value of the multiplicity $2S + 1$ (the number of states with nearly the same energy), which is equivalent to specifying $S = \frac{1}{2}$. The subscript $3/2$ is

the value of J . The superscript ‘o’ indicates that the state has odd parity; it would be omitted if the state were even.

The notation for excited states is similar. For example, helium has a state $1s2s\ ^3S_1$ which lies 19.72 eV ($159,856\text{ cm}^{-1}$) above the ground state $1s^2\ ^1S_0$. But the two “terms” do not “combine” (transitions between them do not occur) because this would violate, e.g., the quantum-mechanical selection rule that the parity must change from odd to even or from even to odd. For electric dipole transitions (the only ones possible in the long-wavelength limit), other selection rules are that the value of l of only one electron can change, and only by $\Delta l = \pm 1$; $\Delta S = 0$; $\Delta L = \pm 1$ or 0; and $\Delta J = \pm 1$ or 0 (but $L = 0$ does not combine with $L = 0$ and $J = 0$ does not combine with $J = 0$). Transitions are possible between the helium ground state (which has $S = 0$, $L = 0$, $J = 0$, and even parity) and, e.g., the state $1s2p\ ^1P_1^o$ (with $S = 0$, $L = 1$, $J = 1$, odd parity, excitation energy 21.22 eV). These rules hold accurately only for light atoms in the absence of strong electric or magnetic fields. Transitions that obey the selection rules are called “allowed”; those that do not are called “forbidden.”

The amount of information needed to adequately characterize a state increases with the number of electrons; this is reflected in the notation. Thus⁴³ O II has an allowed transition between the states $2p^23p'\ ^2F_{7/2}^o$ and $2p^2(^1D)3d'\ ^2F_{7/2}$ (and between the states obtained by changing J from 7/2 to 5/2 in either or both terms). Here both states have two electrons with $n = 2$ and $l = 1$; the closed subshells $1s^22s^2$ are not shown. The outer ($n = 3$) electron has $l = 1$ in the first state and $l = 2$ in the second. The prime indicates that if the outermost electron were removed by ionization, the resulting ion would not be in its lowest energy state. The expression (1D) give the multiplicity and total angular momentum of the “parent” term, i.e., the subshell immediately below the valence subshell; this is understood to be the same in both states. (Grandparents, etc., sometimes have to be specified in heavier atoms and ions.) Another example⁴³ is the allowed transition from $2p^2(^3P)3p\ ^2P_{1/2}^o$ (or $^2P_{3/2}^o$) to $2p^2(^1D)3d'\ ^2S_{1/2}$, in which there is a “spin flip” (from antiparallel to parallel) in the $n = 2, l = 1$ subshell, as well as changes from one state to the other in the value of l for the valence electron and in L .

The description of fine structure, Stark and Zeeman effects, spectra of highly ionized or heavy atoms, etc., is more complicated. The most important difference between optical and X-ray spectra is that the latter involve energy changes of the inner electrons rather than the outer ones; often several electrons participate.