

Main knowledge about atomic spectroscopy

1.1 The classification of levels

Standard scheme of classification of atomic state levels is the single configuration approximation (SCA) and the LS - coupling of the angular momenta.

In the single configuration approximation one assumes that every electron is moving in the effective central-symmetric field generated by the nucleus and by all other electrons. To all electrons one can ascribe definite quantum numbers, starting with the principle quantum number ($n = 1, 2, 3, \dots$) and the orbital quantum number ($l = 0, 1, \dots, n - 1$). The orbital angular momentum of an electron nl equals to $l\hbar$, where $\hbar = h/2\pi$ and h is the Planck constant. The electrons with the same n and l values differ by the values of projections of orbital angular momentum m_l and of the electron spin momentum m_s . The feasible values for m_l and m_s are $m_l = -l, -l + 1, \dots, l - 1, l$, and $m_s = -1/2, +1/2$. Electrons which have the orbital quantum number values $l = 0, 1, 2, 3, \dots$ are denoted in the atomic spectroscopy respectively by latin minuscules s, p, d, f and further in the alphabetic order. The atomic electrons with equal values of n and l are named to be equivalent ones. A set q of equivalent electrons builds up an electron shell $(nl)^q$ in which the maximal number of electrons is $2(2l + 1)$. If $q = 2(2l + 1)$ then such a shell is called to be filled.

Distribution of electrons in electron shells is termed as electron configuration. The energetically lowest state in which all electrons of the atom or of the ion have minimal possible values of n and l is called the ground configuration, all other configurations are called the excited ones. The population of electron shells undergoes definite rules. First, the electron shell $n = 1$ will be populated, thereafter electron shells with $n = 2$, etc. At a given value of n first will be filled

the shells with $l = 0$ (s - shell), thereafter $l = 1$ (p - shell), $l = 2$ (d - shell) etc. The order of population of electron shells with $n \leq 3$ is the following: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \dots$. For instance the ground configuration of carbon atom is $1s^2 2s^2 2p^2$. Here $1s^2$ and $2s^2$ are the filled shells, but the shell $2p^2$ is unfilled. The regularity in shell filling order is violated for d - shells and f - shells. So, for K and Ca atoms first will be filled the $4s$ - shell and thereafter the $3d$ - shell. The electron configurations of atomic and ion ground states are given, for example, in monographs by Moore (1949), Sobelman (1977), Allen (1973) and in a manual by Radtsig & Smirnov (1986).

For classification of atomic states of the same configuration several approximate methods, so-called coupling schemes of momenta, have been used, among which the widest use has the LS - coupling. According to this scheme the atomic states have different values of L (the total atomic orbital momentum) and S (the total atomic spin). The rule of momentum addition we shall illustrate by the example of two electrons. The values of total momentum L cover range from $|l_1 - l_2|$ to $|l_1 + l_2|$. Similar rule holds for total spin : if $s_1 = s_2 = 1/2$ then the total value of spin can be 0 or 1. The sum $J = L + S$ (called the total atomic momentum) according to general rules of addition of momenta can take values $|L - S| \leq J \leq L + S$. A definite value of J belongs to a definite energy level LSJ . The statistical weight corresponding to J is given by $g(J) = 2J + 1$ and it is the number of atomic states with the same energy, but different values of projection M_J . In the case of 3 and more electrons the addition of momenta must be carried out step by step – first for two electrons, thereafter the third electron will be added etc.

The set of levels belonging to one configuration with given values of L and S forms a spectral term (notation $^{2S+1}L_J$, where $2S+1$ specifies the term multiplicity, J describes its fine structure and LSJ – the energy level. If $S \leq L$ then the number of term energy levels equals to its multiplicity, but if $S > L$ then the term has $2L + 1$ levels. Each level consists of $2J + 1$ states. The values of L are specified by latin majuscules: $L = 0$ (S - term), 1 (P - term), 2 (D - term),

3 (F - term) etc. The terms which have $2S+1 = 1, 2, 3, 4, 5 \dots$ are named respectively singlets, doublets, triplets, quartets, quintets etc.

In addition to values of LS the terms differ by configuration parity $\pi = (-1)^{\sum l_i}$, where $\sum l_i$ is the algebraic sum of all electron orbital momenta, i.e. $\sum l_i = l_1 + l_2 + \dots + l_N$. If $\pi = -1$ (odd terms) then superscript " o " is added to the term notation on its right hand side. For three and more electrons with different values of nl in order to give unambiguous description of energy levels the additional quantum numbers are needed. Usually the genealogy of term, i.e. the intermediary values of L and S , are given. For instance, the excited configuration $1s^2 2s 2p nl$ of CII can have two groups of terms: $2s 2p(^1P^0)nlLS$ and $2s 2p(^3P^0)nlLS$. The last group of terms has energy values about 6 eV lower than the first group.

A special case are shells with equivalent electrons $(nl)^q$. The number of terms of the $(nl)^q$ shell is limited by the Pauli principle. Thus, for configuration $2p^2$ the possible three terms are $^3P^0, ^1S$ and 1D , while ignoring the Pauli principle for this configuration also terms $^1P^0, ^3S$ and 3D were the possible ones. The terms of shells $(nl)^q$ are given, for example, in monograph by Sobelman (1977). In the case of shells d^q and f^q there are various terms with equal L and S values. To discriminate them from each other the seniority quantum number $v = 1, 2, 3 \dots$ (left underscript to the term notation) is added. The real atomic states πLSJ due to approximate nature of single configuration and LS - coupling concepts are in fact some mixtures of the pure states with equal π and J values, which belong to different configurations and terms. In many cases instead of LS - coupling the other types of coupling, namely jj , LS_0 and LK (see the monograph by Nikitin & Rudzikas (1983), Rudzikas, Nikitin & Kholtygin (1990)) are used.

1.2 The radiative transitions. Line strengths and oscillator strengths.

Transition probabilities

The most important characteristic of radiative transition in atoms is its probability A_{li} defined in such a manner, that $n_l A_{li}$ is the number of transitions in spectral line $l - i$ per unit volume and per unit time. The value of A_{li} is strongly dependent on the transition type. If in transition $l - i$ there would be emitted a photon having momentum k (in \hbar units) relative to the atom, where $k = 1, 2, \dots$ and with parity $\pi = (-1)^k$, then we term it as the electric (E) radiative transition of multiplicity k (Ek - radiation), but in the case of parity $\pi = (-1)^{k+1}$ we term the transition as the magnetic (M) radiative transition of multiplicity k (Mk - radiation). The probabilities of Mk and $Ek + 1$ transitions are about $10^{-4} - 10^{-6}$ times less than these of corresponding Ek transitions. Thus, the largest transition probabilities have electric dipole ($E1$) transitions for which $A_{li} \simeq 10^8 \text{ s}^{-1}$ which are followed by electric quadruple ($E2$) transitions and magnetic dipole transitions for both of which $A_{li} \simeq 10^2 - 10^4 \text{ s}^{-1}$. The transitions of higher multiplicity in the spectra of astrophysical objects have not been observed. The transition probabilities can be expressed by the use of line strengths S_{li} . Namely holds (see Levinson & Nikitin (1962), Sobelman (1977))

$$g_l A_{li}^{E1, M1} = 2.67 \cdot 10^9 \Delta e^3 S_{li}, \quad g_l A_{li}^{E2} = 1.78 \cdot 10^3 \Delta e^5 S_{li}, \quad (1.1)$$

where the ratio $\Delta e = E_{li}/Ry$ is the transition energy expressed in Rydbergs ($Ry = 13.606 \text{ eV}$). The line strengths are connected with dimensionless quantities — the oscillator strengths f_{il} by

$$g_i f_{il}^{E1, M1} = \frac{1}{3} \Delta e S_{li}, \quad g_i f_{il}^{E2} = 2.22 \cdot 10^{-7} \Delta e^3 S_{li}, \quad (1.2)$$

Thus, the transition probabilities can be expressed by oscillator strengths in the form

$$g_l A_{li}^{E1, M1} = 8.01 \cdot 10^9 \Delta e^2 g_i f_{il}, \quad g_l A_{li}^{E2} = 8.02 \cdot 10^9 \Delta e^2 g_i f_{il}, \quad (1.3)$$

Taking into account the conservation laws of momentum, angular momentum and parity, it follows that each process of type $E1, E2$ and $M1$ can take place only if there hold definite

selection rules specifying the possible differences of quantum numbers in the initial and final states of the transition. Let us consider now the selection rules for E_k and $M1$ transitions in the LS - coupling and single configuration approximation. For E_k - transition $\beta n l L S J \rightarrow \beta' n' l' L' S' J'$ the selection rules are

$$\Delta J = 0, \pm 1, \dots, \pm k, J + J' \geq k; \Delta L = 0, \pm 1, \dots, \pm k, L + L' \geq k; \Delta S = 0, \quad (1.4)$$

where only the quantum numbers of one definite electron undergo changes, β and β' are the additional quantum numbers needed to describe the levels J and J' for which holds the selection rule $\beta = \beta'$. Further, for $E1$ -transitions holds $\Delta l = \pm 1$ and for $E2$ -transitions $\Delta l = 0, \pm 2$. For $M1$ - transition $LSJ \rightarrow L'S'J'$ the selection rules are

$$\Delta J = 0, \pm 1; \Delta L = 0, \Delta S = 0, \Delta l = 0. \quad (1.5)$$

There has been taken into account that the magnetic dipole transitions can take place only between the levels of the same term ($\Delta l = 0$). Due to approximate nature of LS - coupling and single configuration assumptions the selection rules given above are not the exact ones, i.e. these selection rules can be violated in transitions which have essentially smaller probabilities. In the atomic spectroscopy the transitions in which the selection rules hold, are termed the allowed transitions, but in the opposite case they are termed the forbidden transitions.

In the table added here we give the classification of radiative transitions used in astrophysics in the case of selection rules violation. The classification differs somewhat from the one used in atomic spectroscopy. For instance, all $E2$ transitions in astrophysics are treated as the forbidden ones independent of whether the selection rules hold or not. The typical values of the transition probabilities for the transitions under consideration are given in column 3 of the table. In the first column there are presented also the transition type notations (p - permitted, f - forbidden,

i - intercombination, 2e - dielectronic). The given typical values of A_{li} correspond to transitions in the visible and near infrared regions of spectra of light elements and low-charge ions.

Classification of the transition types

Transition type	Selection rule violation	$A_{ki}(\text{s}^{-1})$
$E1, p$	no	$10^7 - 10^9$
$E1, i$	$\Delta S \neq 0$	$10^2 - 10^4$
$E1, 2e$	quantum number change of two(three) electrons	$10^6 - 10^8$
$E2, f$	no	$1 - 10^2$
$E2, f$	$\Delta S \neq 0$	$10^{-4} - 1$
$M1, f$	no	$1 - 10$
$M1, f$	transition between levels of different terms	$10^{-4} - 1$

For illustration of several types of electron transitions we give the scheme of lower levels of OIII . In Fig. 1 the wavelengths of most important observed spectral lines together with the transition type are given. Mark \sim denotes that the transition is intercombinational. For atoms with $Z \geq 50$ and for multiple ions the selection rules do not hold exactly due to relativistic effects. For such atoms and ions the difference between the allowed and forbidden transitions weakens and can even be vanishing.