Appendix A
Spectral Terms for Atoms and Molecules

In previous chapters, the calculation of the electronic partition function of atomic hydrogen has been carried out by using the analytical formulation of the energy levels and of the corresponding statistical weights. The situation is deeply different when dealing with the multielectron atoms. In principle, one can write the Schrödinger equation for the system and solve it through numerical methods. This approach is in general followed for the ground state and for the so-called *low-lying* excited states, i.e., for electronic states arising from the rearrangement of valence electrons. On the other hand, the solution of the Schrödinger equation for *high-lying* excited states (i.e., states characterized by values of principal quantum number different from that of the ground state) is still a prohibitive task despite the enormous progress of quantum chemistry calculations. In this case, semiempirical methods, based on known electronic levels, can be used to get a complete set of energy levels, ready for the cutoff criterion. In doing so, we must be aware of the enormous number of energy levels arising from the coupling of the angular and spin momenta in the multielectron systems. This kind of problems will be analyzed in the first part of this appendix that will give us the recipes to get complete sets of energy levels for multielectron atoms.

In the second part, we will consider similar problems for diatomic molecules.

A.1 Atomic Electronic Terms

The electrons in multielectron atoms can be identified through four quantum numbers (principal, angular, magnetic, and spin) in the order

$$(n_1, l_1, m_1, s_1)$$
$$(n_2, l_2, m_2, s_2)$$
$$(n_3, l_3, m_3, s_3)$$
$$\ldots$$

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In the frame of the *vector model* for angular momentum, let us define the following total quantities:

L Quantum number for the *orbital* angular momentum, associated to the squared modulus of the vector $\mathbf{L}$, i.e. $|\mathbf{L}|^2 = L(L+1)$, with $(2L+1)$ values of the projection on the quantization axis (the z-axis) $M_L = -L, -L+1, \ldots, 0, \ldots, L-1, L$.
S Quantum number associated to the *spin* angular momentum, corresponding to a vector $\mathbf{S}$ with modulus $|\mathbf{S}|^2 = S(S+1)$, with $(2S+1)$ values of the projection on the quantization axis $M_S = -S, -S+1, \ldots, 0, \ldots, S-1, S$.
J Total angular momentum for $\mathbf{J} = \mathbf{L} + \mathbf{S}$ with $|\mathbf{J}|^2 = J(J+1)$.

The sum rules are those of vector addition, considering their possible relative orientation. In the following, we will present the practical rules for obtaining L, S and J[1].

A.1.1 Calculation of L

One-electron atoms $L_1 = \ell_1$.
Two-electron atoms L_2 assumes all the integer values in the interval $\ell_1 + \ell_2,\ \ell_1 + \ell_2 - 1 \ldots\ |\ell_1 - \ell_2|$
Three-electron atoms L_3 assumes, for each possible value of L_2, all the values in the interval $L_2 + \ell_3,\ L_2 + \ell_3 - 1 \ldots\ |L_2 - \ell_3|$.

The procedure is extended adding one electron at a time.

A.1.2 Calculation of S

One-electron atoms $S_1 = s_1$
Two-electron atoms S_2 assumes all the integer values in the interval $s_1 + s_2,\ s_1 + s_2 - 1 \ldots\ |s_1 - s_2|$
Three-electron atoms S_3 assumes, for each possible value of S_2, all the values in the interval $S_2 + s_3,\ S_2 + s_3 - 1 \ldots\ |S_2 - s_3|$.

The procedure is extended adding one electron at a time.

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[1] It should be noted that the scheme presented in this chapter is the so-called Russell–Saunders coupling scheme, widely used for the derivation of atomic term symbols of light atoms ($Z \lesssim 40$). Alternatively, the $j-j$ coupling scheme can be considered. Within this frame, the orbital and spin angular momenta of each electron are coupled ($j_i = \ell_i + s_i$) and then the coupling of one-electron total angular momenta ($j_1, j_2, j_3 \ldots$) results in the total angular momentum of the atom J. This scheme is more appropriate for heavy atoms, when the spin-orbit coupling is the relevant interaction.

A.1.3 Calculation of J

J can assume, for each possible value of L and S, all the integer values in the range $L+S,\ L+S-1\ldots\ |L-S|$.

Before passing to practical examples, we want to remind that each electronic term, corresponding to a given electronic configuration, is characterized by a *term symbol* written in the form ${}^{2S+1}L_J$. Capital letters in the series (S, P, D, F, G, ...) correspond to different values of the orbital angular momentum L (0, 1, 2, 3, 4, ...). On the left of the capital letter, the value of spin multiplicity $2S+1$ is reported[2], while on the right the value of J is found. The total multiplicity of the state, i.e., the statistical weight is $2J+1=(2L+1)(2S+1)$. Therefore,

${}^2S_{1/2}$ identifies a state with $L=0$ (state S), total spin $S=\frac{1}{2}$, resulting in a *doublet* (multiplicity $2S+1=2$) and with $J=\frac{1}{2}$ ($J=L+S=0+\frac{1}{2}=\frac{1}{2}$). The statistical weight of the state is $2J+1=2$.

A.1.3.1 Hydrogen

For $n=1$ (ground state,) we have $H(1s)$ which corresponds to

$S=s_1=\frac{1}{2}$
$L=\ell_1=0$
$J=\frac{1}{2}$.

The electronic term is written as ${}^2S_{1/2}$. The statistical weight is given by $g_1=2J+1=2$ having energy $\varepsilon_1=0$.

For $n=2$, we have $H(2s)$ and $H(2p)$ states. The angular momentum of $H(2s)$ is analogous to the $H(1s)$ and therefore the electronic term is ${}^2S_{1/2}$ and the statistical weight is $g_{2s}=2$.

Let us now consider the excited state $H(2p)$

$S=s_1=\frac{1}{2}$
$L=\ell_1=1$
$J=\{\frac{3}{2},\frac{1}{2}\}$.

Therefore, we have two terms $\{{}^2P_{3/2},{}^2P_{1/2}\}$ with statistical weights of 4 and 2, respectively. The energy of the state is given by

$$\varepsilon_2=I_H\left(1-\frac{1}{2^2}\right)=\frac{3}{4}I_H$$

independently of the angular momentum[3]. Therefore, summing the contribution of the three terms we have $g_{n=2}=2+4+2=8$, in agreement with the general formula $g_n=2n^2$.

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[2]Depending on the spin multiplicity, electronic states of atoms are classified as *doublets* ($2S+1=2$), *triplets* ($2S+1=3$), *quartets* ($2S+1=4$), ...

[3]If the spin-orbit coupling is neglected.

A.1.3.2 Helium

The ground state configuration is $He(1s^2)$. The two electrons are not independent because, due to the *Pauli exclusion principle,* their spins must be antiparallel. Therefore, we have:

$L = 0$ being $\ell_1 = \ell_2 = 0$
$S = 0$ being $s_1 = s_2 = \frac{1}{2}$ with $m_{s_1} = -m_{s_2}$
$J = 0$

giving a configuration ${}^1S_0$, corresponding to a *closed shell atom*, characteristic of noble gas ground state, having degeneracy $g_1 = 1$.

Let us consider the $He(1s2s)$ excited configuration. The two electrons are now independent because they do not occupy the same orbital. Therefore, we have:

$L = 0$ being $\ell_1 = \ell_2 = 0$
$S = \{1, 0\}$ being $s_1 = s_2 = \frac{1}{2}$
$J = \{1, 0\}$

giving the configurations ${}^3S_1$ and ${}^1S_0$, corresponding to a triplet ($g = 3$) and a singlet ($g = 1$) states.

A.1.3.3 Two Not-Equivalent *p* Electrons (*np*, *mp*)

The two electrons are independent because are not in the same orbital. Therefore:

$L = \{2, 1, 0\}$ being $\ell_1 = \ell_2 = 1$
$S = \{1, 0\}$ being $s_1 = s_2 = \frac{1}{2}$.

To calculate J, we have to combine the different contributions giving the following terms

L	S	J	Terms
2	1	{3,2,1}	${}^3D_3$, ${}^3D_2$, ${}^3D_1$
2	0	2	${}^1D_2$
1	1	{2,1,0}	${}^3P_2$, ${}^3P_1$, ${}^3P_0$
1	0	1	${}^1P_1$
0	1	1	${}^3S_1$
0	0	0	${}^1S_0$

A.1.3.4 Two Equivalent *p* Electrons (np^2)

For two equivalent p electrons, characterized by the same principal and orbital quantum numbers (n, ℓ), not all the electronic terms derived in the previous example do exist. In this case in fact the *Pauli exclusion principle* restricts the number of allowed configurations. For the configuration np^2, i.e. ($\ell_i = 1, s_i = \frac{1}{2}$, with

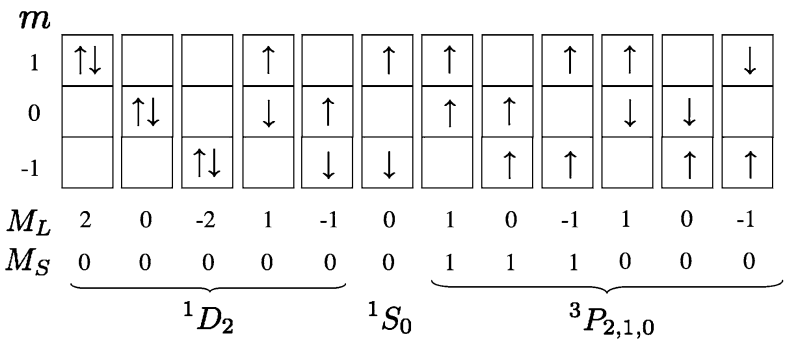

Fig. A.1 Arrangements of two electrons on three equivalent p orbitals

axial projections $m_{\ell_i} = \pm 1, 0$, $m_{s_i} = \pm\frac{1}{2}$), let us consider the possible values of the electrons angular momentum projections, algebraically summing in the resulting total angular and spin momentum projections, $M_L = m_{\ell_1} + m_{\ell_2}$ and $M_S = m_{s_1} + m_{s_2}$, as shown in Fig. A.1, where uparrows correspond to $m_s = \frac{1}{2}$ and downarrows to $-\frac{1}{2}$. The configurations originating negative total spin projection are implicitly included.

The maximum M_L value of 2, found in constructing the allowed configurations, with maximum $M_S = 0$, implies the existence of a term ^1D, thus accounting for five configurations with ($M_L = \pm 2, \pm 1, 0$ and $M_S = 0$). Repeating the procedure on the remaining configurations, $(M_L)_{\max} = 1$ and $(M_S)_{\max} = 1$, one accounts for a ^3P term with nine configurations arising from allowed values $M_L = \pm 1, 0$ and $M_S = \pm 1, 0$. Finally, the last arrangement ($M_L = 0$ and $S = 0$) leads to the ^1S term. The *group theory* offers an elegant and compact derivation of allowed terms (Bishop 1993), though beyond the scope of this book. It can be demonstrated that the spatial wavefunction for D and S terms is even, while spin wavefunction is even for triplets and odd for singles. It is straightforward that due to the antisymmetric nature of the total (spatial+spin) electronic wavefunction, only ^1S, ^1D and ^3P terms could exist.

This is the case of ground and low-lying excited states of carbon atom.

Term	Energy (cm^{-1})	g
$^3P_0$	0	1
$^3P_1$	16.40	3
$^3P_2$	43.40	5
$^1D_2$	10,192.63	5
$^1S_0$	21,648.01	1

A.1.3.5 Three Not-Equivalent p Electrons (n_1p, n_2p, n_3p)

The results of the two-electron case with configuration (L_2, S_2) must be combined with the third electron (l_3, s_3), i.e.,

L_2	ℓ_3	L	S_2	s_3	S
2	1	{3,2,1}	1	1/2	{3/2,1/2}
1	1	{2,1,0}	0	1/2	1/2
0	1	1			

Let us now compose L and S:

L	S	J	Terms	# of terms
3	3/2	{9/2,7/2,5/2,3/2}	${}^4F_{9/2,7/2,5/2,3/2}$	1
2	3/2	{7/2,5/2,3/2,1/2}	${}^4D_{7/2,5/2,3/2,1/2}$	2
1	3/2	{5/2,3/2,1/2}	${}^4P_{5/2,3/2,1/2}$	3
0	3/2	3/2	${}^4S_{3/2}$	1
3	1/2	{7/2,5/2}	${}^2F_{7/2,5/2}$	2
2	1/2	{5/2,3/2}	${}^2D_{5/2,3/2}$	4
1	1/2	{3/2,1/2}	${}^2P_{3/2,1/2}$	6
0	1/2	1/2	${}^2S_{1/2}$	2

A.1.3.6 Three Equivalent p Electrons (np^3)

It turns out (see Fig. A.2) that for np^3 electronic configuration only the terms ${}^4S$, ${}^2D$, ${}^2P$ survive. This is the case of the nitrogen atoms in ground and low-lying states with three electrons having principal quantum number $n = 2$

Term	Energy (cm^{-1})	g
${}^4S_{3/2}$	0	4
${}^2D_{5/2}$	19224.464	6
${}^2D_{3/2}$	19233.177	4
${}^2P_{1/2}$	28838.920	2
${}^2P_{3/2}$	28839.306	4

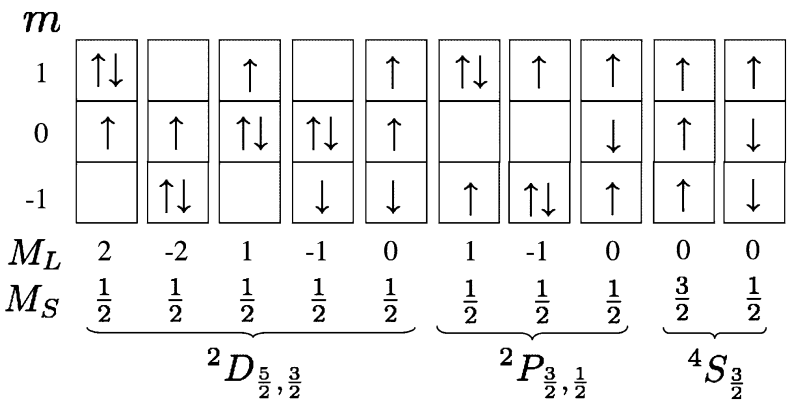

Fig. A.2 Arrangements of three electrons on three equivalent p orbitals

Table A.1 Electronic terms for atoms with equivalent-electron configurations

Configuration	Electronic terms	Atoms
$p\ p^5$	^2P	B, F
$p^2\ p^4$	$^1S\ ^3P\ ^1D$	C, O, N^+
p^3	$^4S\ ^2P\ ^2D$	N, O^+
p^6	^1S	Ne
$d\ d^9$	^2D	Sc
$d^2\ d^8$	$^1S\ ^3P\ ^1D\ ^3F\ ^1G$	Ti, Ni
$d^3\ d^7$	$^2P\ ^4P\ 2^2D\ ^2F\ ^4F\ ^2G\ ^2H$	V, Co
$d^4\ d^6$	$2^1S\ 2^3P\ 2^1D\ ^3D\ ^5D\ ^1F$ $2^3F\ 2^1G\ ^3G\ ^3H\ ^1I$	Fe
d^5	$^2S\ ^6S\ ^2P\ ^4P\ 3^2D\ ^4D\ 2^2F$ $^4F\ 2^2G\ ^4G\ ^2H\ ^2I$	Mn
d^{10}	^1S	Zn

A.1.3.7 Four Equivalent p Electrons (np^4)

This situation gives the same terms as the two equivalent p electrons. This is the case of the oxygen atoms in ground and low-lying excited states, having four electrons with principal quantum number $n = 2$, reported below

Term	Energy (cm^{-1})	g
$^3P_2$	0	5
$^3P_1$	158.265	3
$^3P_0$	226.977	1
$^1D_2$	15867.862	5
$^1S_0$	33792.583	1

In Table A.1, the electronic terms for equivalent-electron configurations are given. It should be noted that configurations having equal number of electrons or *electron-holes* have to be considered as equivalent, giving rise to the same electronic terms. Complete shell configurations, i.e. p^6, always give the ^1S term. We give here the definition of the parity of atomic terms $P = (-1)^{\sum_i \ell_i}$, being the exponent the algebraic sum of orbital angular momenta of electrons, in a given electronic configuration.

A.2 Complete Sets of Electronic Levels

The calculation of electronic partition function of atomic species needs of complete sets of energy levels and of corresponding statistical weights. Here, we want to present a very simple and rapid method based on the calculation of energy levels by an hydrogenic approximation and by calculating the statistical weight through the

L–S coupling. Some examples will explain the procedure which closely follows that one described in the previous pages. A better set of energy levels can be obtained by using semiempirical methods with the aid of existing tabulated energy levels (Capitelli and Molinari 1970) (see also Sect. A.3).

A.2.1 Helium

We want to calculate the complete set of levels with energies and statistical weights for the configurations derived from the interaction of the Helium *core* (^2S) with the (*optical*) electron jumping on the excited levels.

Let us start with the interaction

$$^2S + 2s$$

We note that the core configuration ($1s^1$) is characterized by quantum numbers $S_{\text{core}} = 1/2$ and $L_{\text{core}} = 0$, while the $2s$ excited electron has spin 1/2 and $\ell = 0$. In the frame of L-S coupling scheme, the singlet $^1S_0$ ($g = 1$) and triplet $^3S_1$ ($g = 3$) states are obtained.

Consider now the interaction

$$^2S + 2p$$

i.e., ($L_{\text{core}} = 0$, $S_{\text{core}} = 1/2$) + ($\ell = 1$, $s = 1/2$). We obtain a triplet state ($L = 1$), which corresponds to $^1P_1$ ($g = 3$), $^3P_{2,1,0}$ ($g = 9$) and the total statistical weight is $g_{n=2} = 16$.

Let us now consider the interaction of the core with one electron in the $n = 3$ shell. The interactions with the $3s$ and $3p$ states follow directly from the cases above considered for the shell $n = 2$. Additionally, the interaction with the $3d$ electron must be considered

$$^2S + 3d$$

originating, in the L–S coupling, $^1D_2$ ($g = 5$) and $^3D_{3,2,1}$ ($g = 15$), leading to the total statistical weight $g_{n=3} = g_{3s} + g_{3p} + g_{3d} = 36$.

The procedure can be continued to get all excited states coming from the interaction of the core electron with the optical electron. By comparing the total statistical weight coming from $n = 2$ and $n = 3$ we can deduce that the statistical weight of helium follows the relation

$$g = 4n^2$$

with respect to the principal quantum number.

Concerning the energy of levels, to a first approximation we can use an *hydrogenic* formula, inserting the helium ionization potential I_{He} in place of the corresponding one of the hydrogen atom

$$E_n = I_{\text{He}} - \frac{I_H}{n^2}$$

neglecting the splitting between singlet and triplet states due to spin–orbit coupling. Note also that the *He* ground state has a statistical weight $g = 1$.

A.2.2 Oxygen

We have already studied the spectroscopic terms coming from the different interactions occurring in the p^4 configuration. Now we want to study the interaction of the most stable atomic oxygen core (i.e., the ${}^4S_{3/2}$ state $L_{\text{core}} = 0$, $S_{\text{core}} = 3/2$) with the optical electron jumping on the excited states with $n \geq 3$. The stable core derives from the elimination of one electron from the p^4 to obtain the p^3 configuration.

Combining the core and an electron with $n = 4$, thus with $\ell = 0, \ldots, n-1 = 0, 1, 2, 3$, the following atomic terms can be derived

ℓ	s	L	S	J	Terms	g
0	1/2	0	{2,1}	{2,1}	${}^5S_2$, ${}^3S_1$	8
1	1/2	1	2	{3,2,1}	${}^5P_{3,2,1}$	15
1	1/2	1	1	{2,1,0}	${}^3P_{2,1,0}$	9
2	1/2	2	2	{4,3,2,1,0}	${}^5D_{4,3,2,1,0}$	25
2	1/2	2	1	{3,2,1}	${}^3D_{3,2,1}$	15
3	1/2	3	2	{5,4,3,2,1}	${}^5F_{5,4,3,2,1}$	35
3	1/2	3	1	{4,3,2}	${}^3F_{4,3,2}$	21

giving a total statistical weight $g = 128$. For $n = 3$, only the contribution of state with $\ell = 0 - 2$ must be considered, giving a total statistical weight $g = 72$.

We can deduce that the statistical weight for states obtained by the interaction of the ${}^4S$ core with the optical electron with $n > 2$ is reproduced by the general formula

$$g_n = 8n^2.$$

Again, we can approximate the energy of the excited states through an hydrogenic form

$$E_n = I_O - \frac{I_H}{n^2}.$$

We must note that other sequences can arise forming electronically excited states of oxygen atoms from different core configurations. In fact, keeping in mind that low-lying excited states of oxygen are formed from different $L - S$ of the core electrons as ${}^1S$ or ${}^1D$ states. The new series are obtained repeating the previous procedure to each core configuration, obtaining plenty of the different levels. The corresponding energy can be calculated by the hydrogenic formula

$$E_n^\star = I_O - \frac{I_H}{n^2} + E_{\text{core}},$$

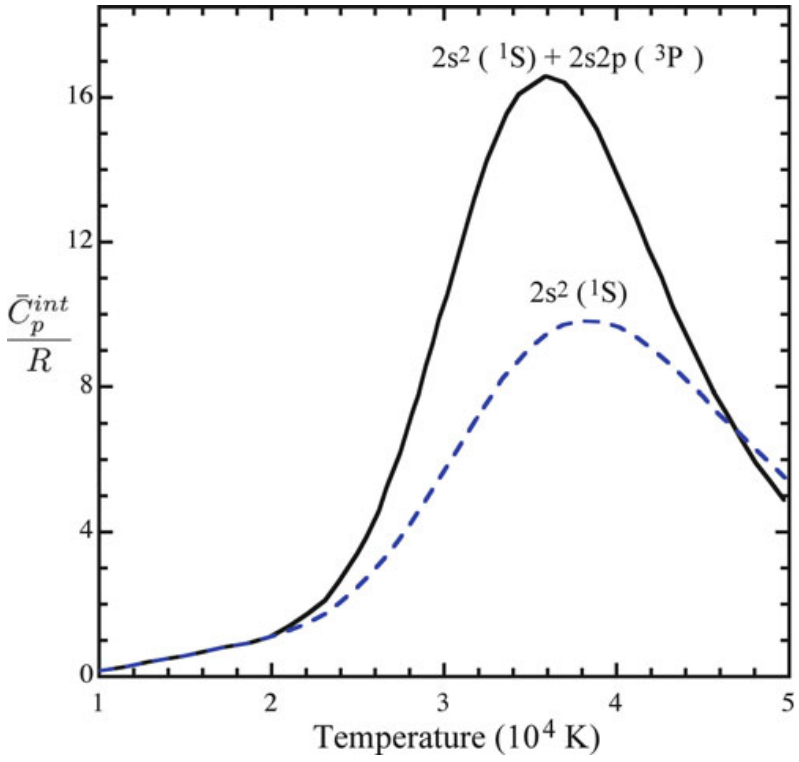

Fig. A.3 Reduced internal specific heat of C^+ as a function of temperature: comparison between calculations including levels having core $2s^2\ (^1S)$ and $2s^2\ (^1S) + 2s2p(^3P)$

where E_{core} is the energy of the excited core configuration with respect to the ground state. The energy of the states of these series rapidly overcomes the ionization potential of the ground I_O forming the autoionizing states of the atom.

These states, while having energies above the ionization potential, are in same case considered, especially in the astrophysical literature. In this context, it is interesting to analyze their effects on the partition function and on thermodynamic properties. In Fig. A.3, we can see the effects on the internal specific heat of C^+ of the autoionizing states coming from $2s2p\ (^3P)$ core.

As a general rule, we can calculate the statistical weight of excited states obtained from the interaction of a given core with the excited electron using the general formula

$$g_n = 2g_{\text{core}}n^2,$$

where g_{core} is the statistical weight of the relative core configuration. Keeping in mind that the electronic configuration of the helium core is a ^2S state we have $g_{\text{core}} = 2$, while for ^4S core of oxygen $g_{\text{core}} = 4$.

A.3 Beyond the Hydrogenoid Approximation

The available database for observed atomic electronic energy levels, as Moore (1949) and NIST tables (Chase Jr. 1998; NIST 2009), miss most of the predicted electronic levels, especially for higher quantum numbers.

In this section, we present an useful semi-empirical procedure which, applying a simplified formula to available, experimental or calculated, electronic levels, allows to complete, interpolating and/or extrapolating, the level series. We apply this method to estimate level energies of neutral carbon atom (see (Capitelli and Molinari 1970) for the nitrogen atom). The structure of the ground state is very complex, due to the presence of a few of low-lying states resulting from different L–S coupling:

Configuration	Terms
$2s^2 2p^2$	$^1S, ^3P, ^1D$
$2s^1 2p^3$	$^5S, ^3S, ^3P, ^1P, ^3D, ^1D$
$2p^4$	$^1S, ^3P, ^1D$

The first three states results from rearrangement of the spin of the p electrons, while the others are obtained from different rearrangements of the angular momenta.

The first step of the procedure is to determine the energy of the ground state configuration. If one of these terms has not been observed, it can be derived through extrapolation from energy levels of isoelectronic species. Practically, for carbon, the term $2p^4(^1S)$ is missing. We have to consider the energies of N^+, O^{+2} and F^{+3}, corresponding to the same term, and, relating these energies to the atomic number Z, we extrapolate to obtain the corresponding value for Z = 6 (carbon).

The excited states come from the excitation of one electron toward higher values of the principal quantum numbers ($n > 2$) giving for carbon atoms

$$
\begin{aligned}
&2s^2 2p(^2P)n\ell \\
&2s2p^2(^4P)n\ell \\
&2s2p^2(^2D)n\ell \\
&2s2p^2(^2S)n\ell \\
&2s2p^2(^2P)n\ell \\
&2p^3(^4S)n\ell,
\end{aligned}
$$

where each series arises from the interaction of different atomic cores, $2s^2 2p(^2P)$, $2s2p^2(^4P), \ldots$, with the excited electron, where $x = s, p, d, \ldots$. It should be noted that in the previous section we have discussed only the excited states coming from the interaction of the more stable core, $2s^2 2p(^2P)$, with the excited electron. In this case, for $\ell = s$, there are two spectroscopic terms: ^3P $(L = 1, S = 1)$, and ^1P $(L = 1, S = 0)$. NIST's tables (NIST 2009) report observed levels up to

$n = 10$ for the former and $n = 14$ (missing values $n = 11, 12$) for the latter. To extrapolate to higher principal quantum numbers, the following Ritz–Rydberg series can be used:

$$E_n = I - \frac{I_H (z+1)^2}{\left(n + A + \frac{B}{n^2}\right)^2}, \tag{A.1}$$

where z is the charge of the species and A, B are adjustable parameters. The ionization energy I is related to the specific core configuration. It is calculated as the sum of the ionization energy from the ground state and the energy of the excited state of the successive ion in the corresponding electronic state. For example, if we consider C in the $2s2p^2(^4P)n\ell$ series, I is the sum of the ionization potential of C from the ground state (11.260 eV) and the energy of the C^+ in the excited state $2s2p^2(^4P)$ (5.336 eV).

The constants A and B can be determined when at least two observed levels are available. If we have only two levels, it is straightforward to calculate A and B by solving a system of two equations in two unknowns. If more than two levels are available, the two parameters are calculated by a *best fit* procedure. When only one observed energy level is known in a series, (A.1) cannot be used and the following formula with a single adjustable parameter should be applied:

$$E_n = I - \frac{I_H (z+1)^2}{(n + A)^2} \tag{A.2}$$

obtained from (A.1) considering $B = 0$.

In some cases, as for $2s2p^2(^2P)n\ell$ for $n > 4$ and $\ell = g$, no level has been observed. As an example, to obtain the energy level of the terms corresponding to $5g$, we relate the energy levels $(5s, 5p, 5d, 5f)$ as a function of the azimuthal quantum number $\ell (= 0 - 3)$, and extrapolate to $\ell = 4$ (see also (Capitelli and Molinari 1970)).

This method has been applied up to $n = 20$ and $\ell = 19$, with the exception of those series where no observed energies are present. For $n > 20$, we assume an hydrogen-like behavior and use the following formulas:

$$E_n = I - \frac{I_H (z+1)^2}{n^2}. \tag{A.3}$$

At fixed n and for each series, the sum over the statistical weights of all the corresponding predicted spectroscopic terms for different ℓ is equal to

$$g_n = 2n^2 g_{\text{core}} \tag{A.4}$$

and for $n > 20$ we apply this last equation to determine the total statistical weight. This method is more accurate than the hydrogenic approximation (see Sect. A.2) and has been extensively used in the calculation of thermodynamic properties of thermal plasmas.