Radiative Processes in Astrophysics

Lecture 12

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Books

- Astronomical Spectroscopy, Jonathan Tennyson
- Physics of the Interstellar and Intergalactic Medium, Bruce T. Draine
- Physics and Chemistry of the Interstellar Medium, Sun Kwok
- Astrophysics of the Diffuse Universe, Michael A. Dopita & Ralph S. Sutherland

Schrödinger Equation

- Time-independent Schrödinger equation for an atom with N electrons and nuclear charge (atomic number) Z.

$$\left[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Ze^2}{r_i}\right)+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$$

where $\mathbf{r}_i$ is the coordinate of the ith electron, with its origin at the nucleus.

The first term contains a kinetic energy operator for the motion of each electron and the Coulomb attraction between that electron and the nucleus.

The second term contains the electron-electron Coulomb repulsion term.

The Coulomb repulsion between pairs of electrons means the above equation is not analytically soluble, even for the simplest case, the helium atom for which $N = 2$.

[Central Field Approximation]

- Even in complete atoms with *N* electrons it is useful to consider single-electron states.

  Self-consistent field approximation: We assume that each electron moves in the potential of the nucleus plus the averaged potential due to the other *N* - 1 electrons.

  Central field approximation (or orbital approximation): In addition, when this averaged potential is assumed to be spherically symmetric, the force acting on each electron only depends on its distance from the nucleus at the center. It provides a useful classification of atomic states and also a starting point.

  Let us assume that each electron moves in its own (angle-independent) central potential given by $V_i(r_i)$. This gives a simplified Schrödinger equation for the motion of each electron:

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_i(r_i)\right]\phi_i(\mathbf{r}_i) = E_i\phi_i(\mathbf{r}_i) \quad \text{where} \quad V_i(r_i) = -\frac{Ze^2}{r_i} + \sum_{j\neq i}\left\langle \frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}\right\rangle$$

  orbits: The solutions of the above equation are known as orbitals.

  Using this approximation, the total energy and the total wave function of the system are given by the sum of single electron energies and the product of single electron wave functions, respectively.

$$E = \sum_i E_i \qquad \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

  However, the wave function ignores the fact that one cannot distinguish between electron *i* and electron *j*.

[Indistinguishable Particles]

- Consider a system with **two identical particles**. We note that it is not the wave function but the probability distribution, which is physically observable. This distribution cannot be altered by interchanging the particles. This means that

  $$|\Psi(1,2)|^2 = |\Psi(2,1)|^2$$

  The equation has two possible solutions:

  - symmetric solution $\Psi(1,2) = \Psi(2,1)$
  - antisymmetric solution $\Psi(1,2) = -\Psi(2,1)$

  Pauli Principle: Wave functions are **antisymmetric** with respect to interchange of identical Fermions.

  Within the central field approximation, a two-electron wave function which obeys the Pauli Principle can be written

  $$\Psi(1,2) = \frac{1}{\sqrt{2}}\left[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right] = -\Psi(2,1)$$

  Pauli exclusion principle: If the two spin-orbitals are the same $(\phi_a = \phi_b)$, then the total wave function is zero, i.e., $\Psi(1,2) = 0$, and no physical (normalizable) state exists. The Pauli exclusion principle is summarized as "**No two electrons can occupy the same spin-orbital.**"

  This exclusion provides the degeneracy pressure which holds up the gravitational collapse of white dwarfs and neutron stars.

[Electron Configuration]

- The electron configuration is the distribution of electrons of an atom (or molecule) in atomic (or molecular) orbitals. Electronic configurations describe electrons as each moving independently in an orbital, in an average field created by all other orbitals.

  The configuration of an atomic system is defined by specifying the *nl* values of all the electron orbitals: nl^x means *x* electrons in the orbital defined by *n* and *l*. Following the Pauli exclusion principle, each orbital labelled *nl* actually consists of orbitals with 2*l*+1 different *m* values, each with two possible values of s_z. Thus the *nl* orbital can hold a maximum 2(2*l*+1) electrons.

- **Energy ordering**:

  For a hydrogen-like atom, the energy of the individual orbitals is determined by principal quantum number *n*.

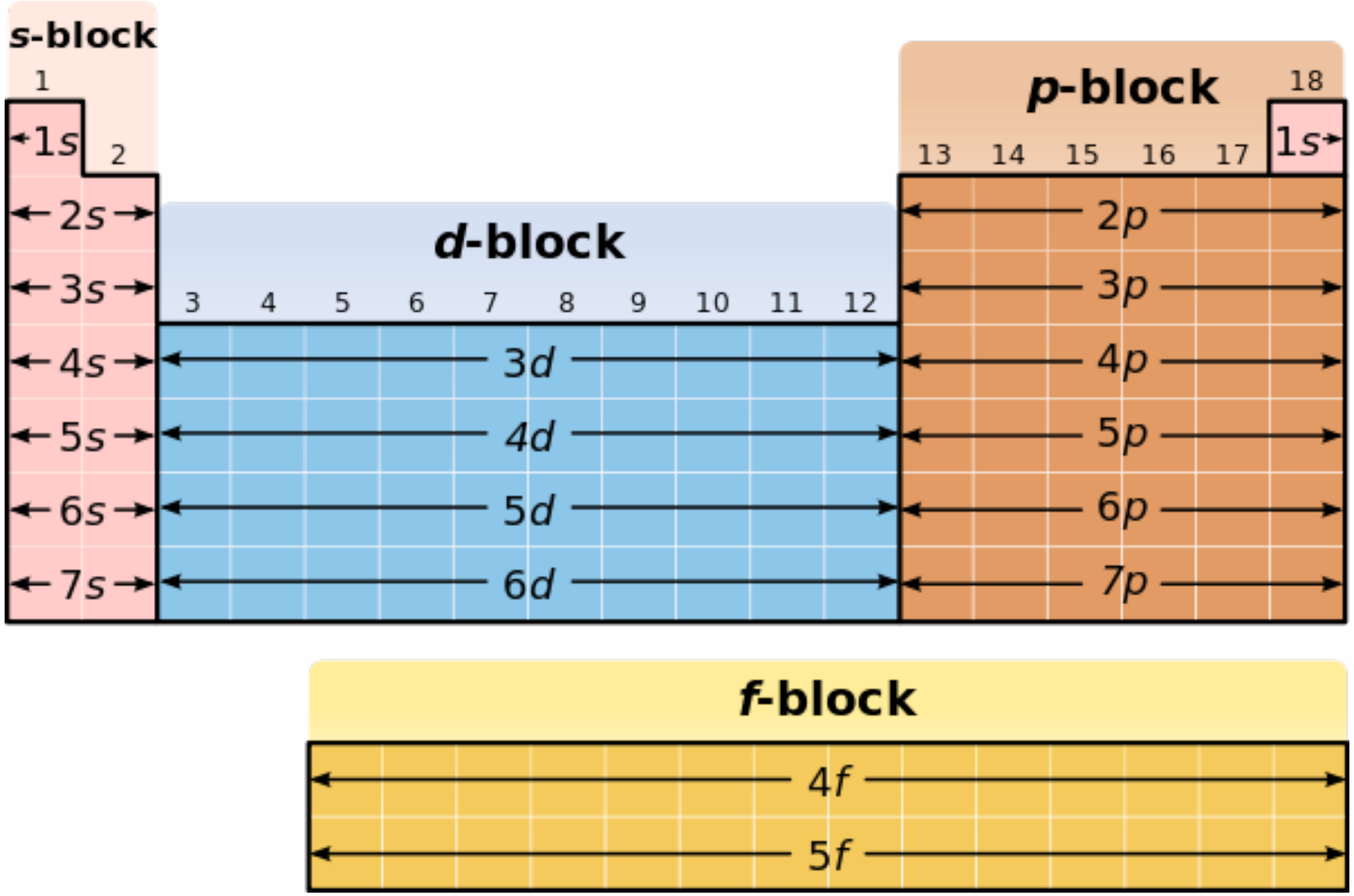
$$E(1s) < E(2s) = E(2p) < E(3s) = E(3p) = E(3d) < E(4s)\cdots$$

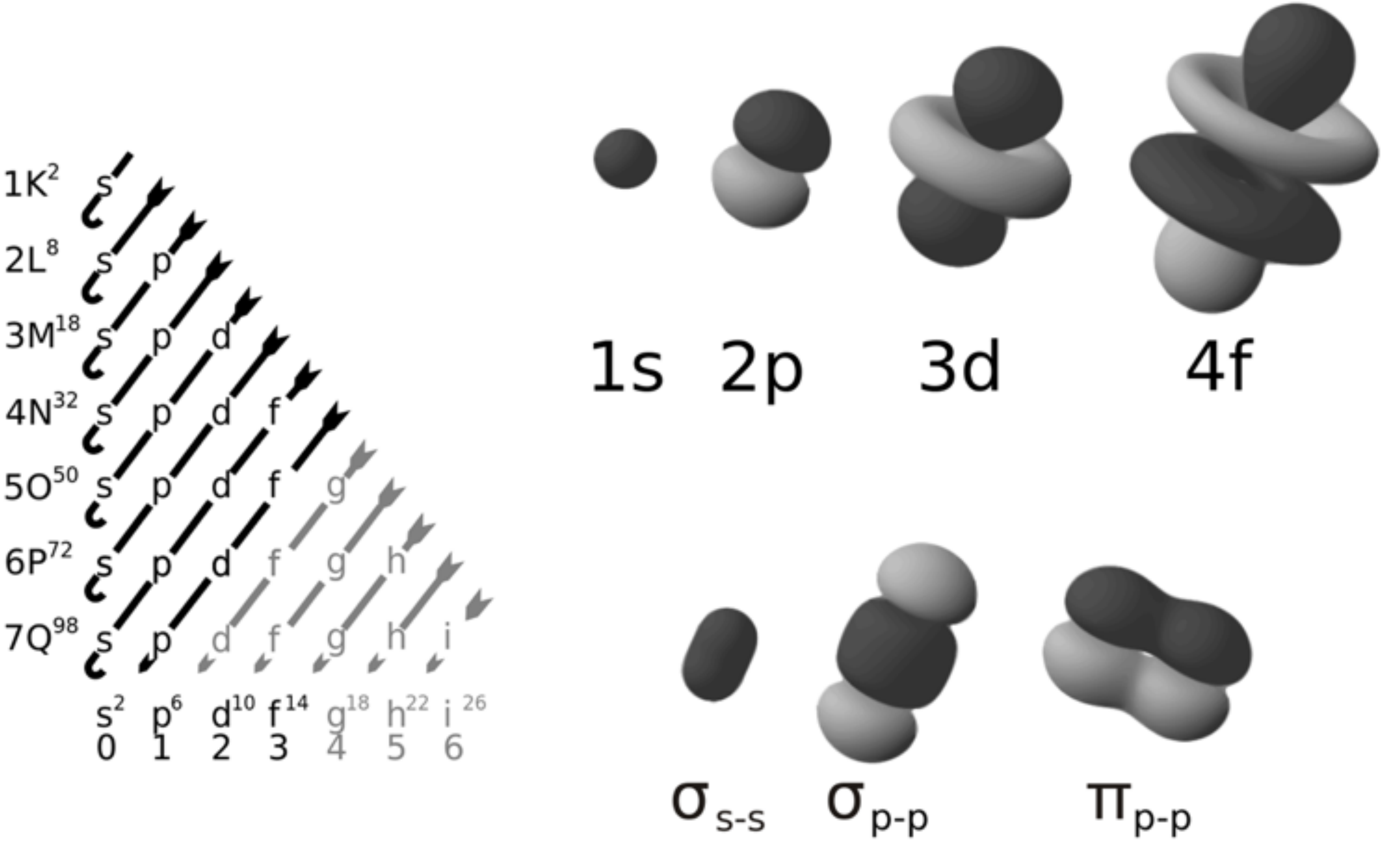
  For complex atoms, the degeneracy on the orbital angular momentum quantum number *l* is lifted. This is because electrons in low *l* orbits 'penetrate', i.e., get inside orbitals with lower *n*-values. Penetration by the low *l* electrons means that they spend some of their time nearer the nucleus experiencing an enhanced Coulomb attraction. This lowers their energy relative to higher *l* orbitals which penetrate less or not at all.

$$E(1s) < E(2s) < E(2p) < E(3s) < E(3p) < E(3d) \simeq E(4s)\cdots$$

  The lowest energy or ground state configuration involves filling the atomic orbitals in energy order from the lowest energy orbitals upwards.

Atom		K	L		M			N			O	Ground
		1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	level
H	1	1										${}^2S_{\frac{1}{2}}$
He	2	2										${}^1S_0$
Li	3	2	1									${}^2S_{\frac{1}{2}}$
Be	4	2	2									${}^1S_0$
B	5	2	2	1								${}^2P^0_{\frac{1}{2}}$
C	6	2	2	2								${}^3P_0$
N	7	2	2	3								${}^4S^0_{1\frac{1}{2}}$
O	8	2	2	4								${}^3P_1$
F	9	2	2	5								${}^2P^0_{1\frac{1}{2}}$
Ne	10	2	2	6								${}^1S_0$
Na	11	2	2	6	1							${}^2S_{\frac{1}{2}}$
Mg	12				2							${}^1S_0$
Al	13				2	1						${}^2P^0_{\frac{1}{2}}$
Si	14		10		2	2						${}^3P_0$
P	15				2	3						${}^4S^0_{1\frac{1}{2}}$
S	16		Ne core		2	4						${}^3P_2$
Cl	17				2	5						${}^2P^0_{1\frac{1}{2}}$
Ar	18				2	6						${}^1S_0$
K	19	2	2	6	2	6		1				${}^2S_{\frac{1}{2}}$
Ca	20							2				${}^1S_0$
Sc	21						1	2				${}^2D_{1\frac{1}{2}}$
Ti	22						2	2				${}^3F_2$
V	23			18			3	2				${}^4F_{1\frac{1}{2}}$
Cr	24						5	1				${}^7S_3$
Mn	25			A core			5	2				${}^6S_{2\frac{1}{2}}$
Fe	26						6	2				${}^5D_4$
Co	27						7	2				${}^4F_{4\frac{1}{2}}$
Ni	28						8	2				${}^3F_4$
Cu	29	2	2	6	2	6	10	1				${}^2S_{\frac{1}{2}}$
Zn	30							2				${}^1S_0$





$1s^2_2\,2s^2_4\,2p^6_{10}\,3s^2_{12}\,3p^6_{18}\,4s^2_{20}\,3d^{10}_{30}\,4p^6_{36}\,5s^2_{38}\,4d^{10}_{48}\,5p^6_{54}\,6s^2_{56}\,4f^{14}_{70}\,5d^{10}_{80}\,6p^6_{86}\,7s^2_{88}\,5f^{14}_{102}\,6d^{10}_{112}\,7p^6_{118}$

- shells, subshells:

  Shells correspond with the principal quantum numbers (1, 2, 3, ...). They are labeled alphabetically with letters used in the X-ray notation (K, L, M, ...).

  Each shell is composed of one or more subshells. The first (K) shell has one subshell, called "1s"; The second (L) shell has two subshells, called "2s" and "2p".

  The valence shell is the outermost shell of an atom. A valence electron is an electron that can participate in the formation of a chemical bond.

- open shell configuration, closed shell configuration:

  the ground state configuration of carbon, which has six electrons: $1s^2 2s^2 2p^2$

  the ground state configuration of neon atom, which has ten electrons: $1s^2 2s^2 2p^6$

  A closed shell or sub-shell makes no contribution to the total orbital or spin angular momentum (L or S).

- Atomic ions which have the same number of electrons form what are called **isoelectronic series**.

- Electronically-excited states of atoms usually arise when one of the outermost electrons jumps to a higher orbital.

  States with two electrons simultaneously excited are possible but are less important. For many systems, all of these states are unstable. They have sufficient energy to autoionize by spontaneously ejecting an electron.

- Negative ions:

  Not all atoms can bind an extra electron to form a stable negative ion. H, C and O can bind an electron while H and N cannot.

  Most negative ions have only one stable level, and so possess no line ('bound-bound') spectrum. The only possible transitions are continuous bound-free absorption (photoionization).

- **The Electrostatic Interaction**

  The specification of the electron configuration (the n, l vales of all electrons) leaves a great deal of unspecified information, since we are not given the values of m_l and m_s. In the central field approximation all of these states are degenerate.

  The exact Hamiltonian is

$$\begin{aligned}
H &= \sum_{i=1}^{N}\left(\frac{P_i^2}{2m}-\frac{Ze^2}{r_i}\right)+\sum_{i=1}^{N}\sum_{j\neq i}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}+H_{so} \\
&= \sum_{i=1}^{N}\left(\frac{P_i^2}{2m}+V_i(r_i)\right)+\sum_{i=1}^{N}\sum_{j\neq i}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}-\sum_{i=1}^{N}\sum_{j\neq i}\left\langle\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right\rangle+H_{so} \\
&= H_0+H_{es}+H_{so}
\end{aligned}$$

$H_0 \equiv$ central field approximation

$$H_{es} \equiv \sum_{i=1}^{N}\sum_{j\neq i}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}-\sum_{i=1}^{N}\sum_{j\neq i}\left\langle\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right\rangle$$

$=$ electronstatic interaction

$H_{so} \equiv$ spin-orbit interaction

[LS coupling]

- **LS coupling (Russell-Saunders coupling): Terms and Levels**

: splitting of the configurations by the electrostatic interaction.

The individual orbital angular momenta will not remain constant under this interaction, although their total $\mathbf{L} = \sum_i \mathbf{l}_i$ will be constant. Also the sum of the spin angular momenta, $\mathbf{S} = \sum_i \mathbf{s}_i$, will be constant.

(1) The orbital and spin angular momenta of the electrons are added separately to give the total orbital angular momentum and the total electron spin angular momentum.

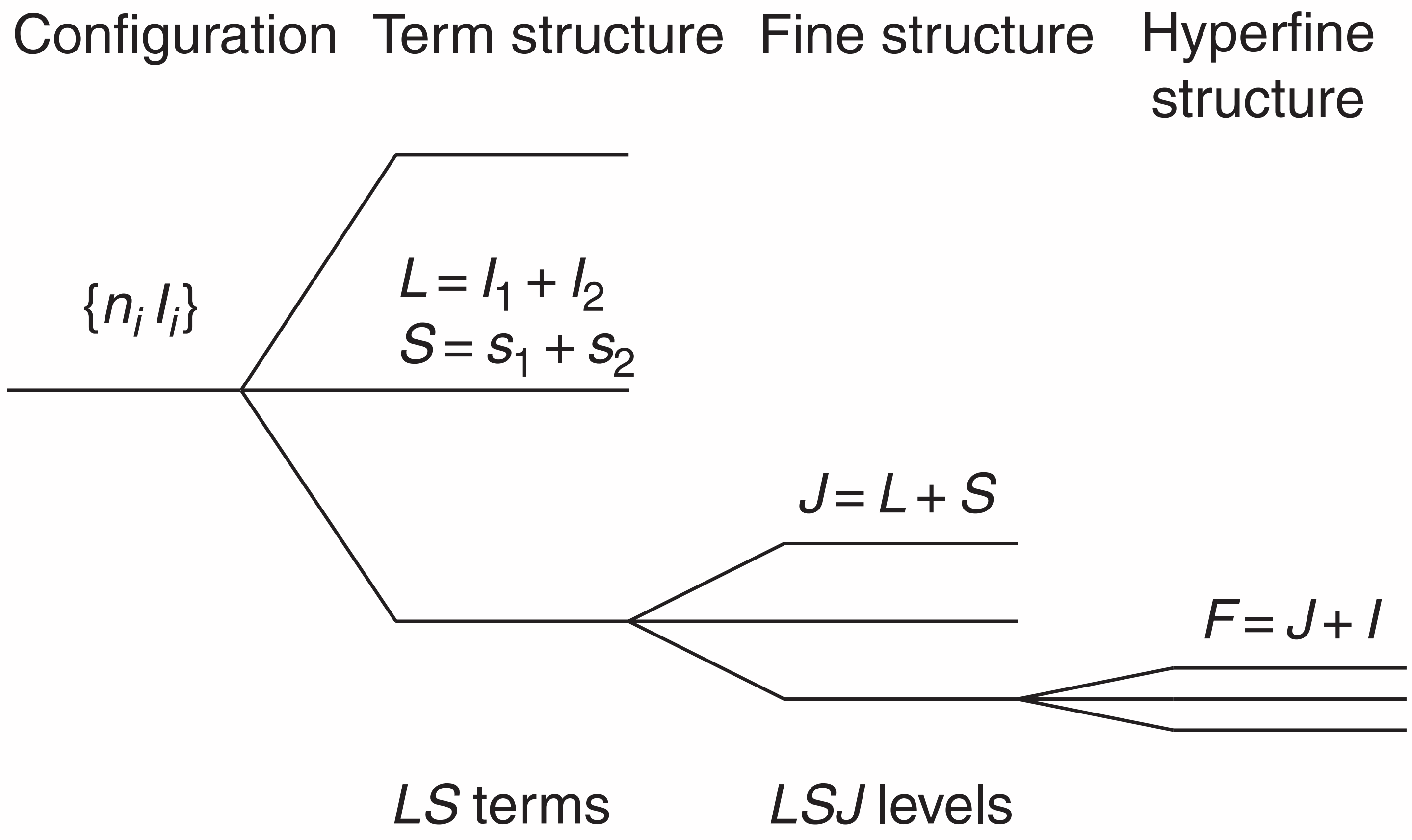
The configurations are splitted into **terms** with particular values of L and S.

As a result of the Pauli Principle, closed shells and sub-shells have both L = 0 and S = 0. This means that it is only necessary to consider 'active' electrons, those in open or partially-filled shells.

(2) These are then added to give $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

Fine-structure splitting: Relativistic effects couple electron orbital angular momentum and electron spin to give the so-called fine structure in the energy levels. Inclusion of relativistic effects splits the terms into **levels** according to their J value.

- Electronic configuration and energy level splitting



Configuration

Term structure

Fine structure

Hyperfine structure

$\{n_i\, l_i\}$

$L = l_1 + l_2$
$S = s_1 + s_2$

$J = L + S$

$F = J + I$

LS terms

LSJ levels

- **Equivalent and Nonequivalent Electrons**

  Nonequivalent electrons are those differing in either *n* or *l* values, whereas equivalent electrons have the same *n* and *l* values.

- **Parity of the wave function**

  The parity of the wave function is determined by how the wave function behaves upon inversion. The square of the wave function, i.e., the probability distribution of the electrons, must be unchanged by the inversion operation.

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)=\pm\Psi(-\mathbf{r}_1,-\mathbf{r}_2,\cdots,-\mathbf{r}_N)$$

  Even parity states are given by + sign and odd parity states are given by - sign.

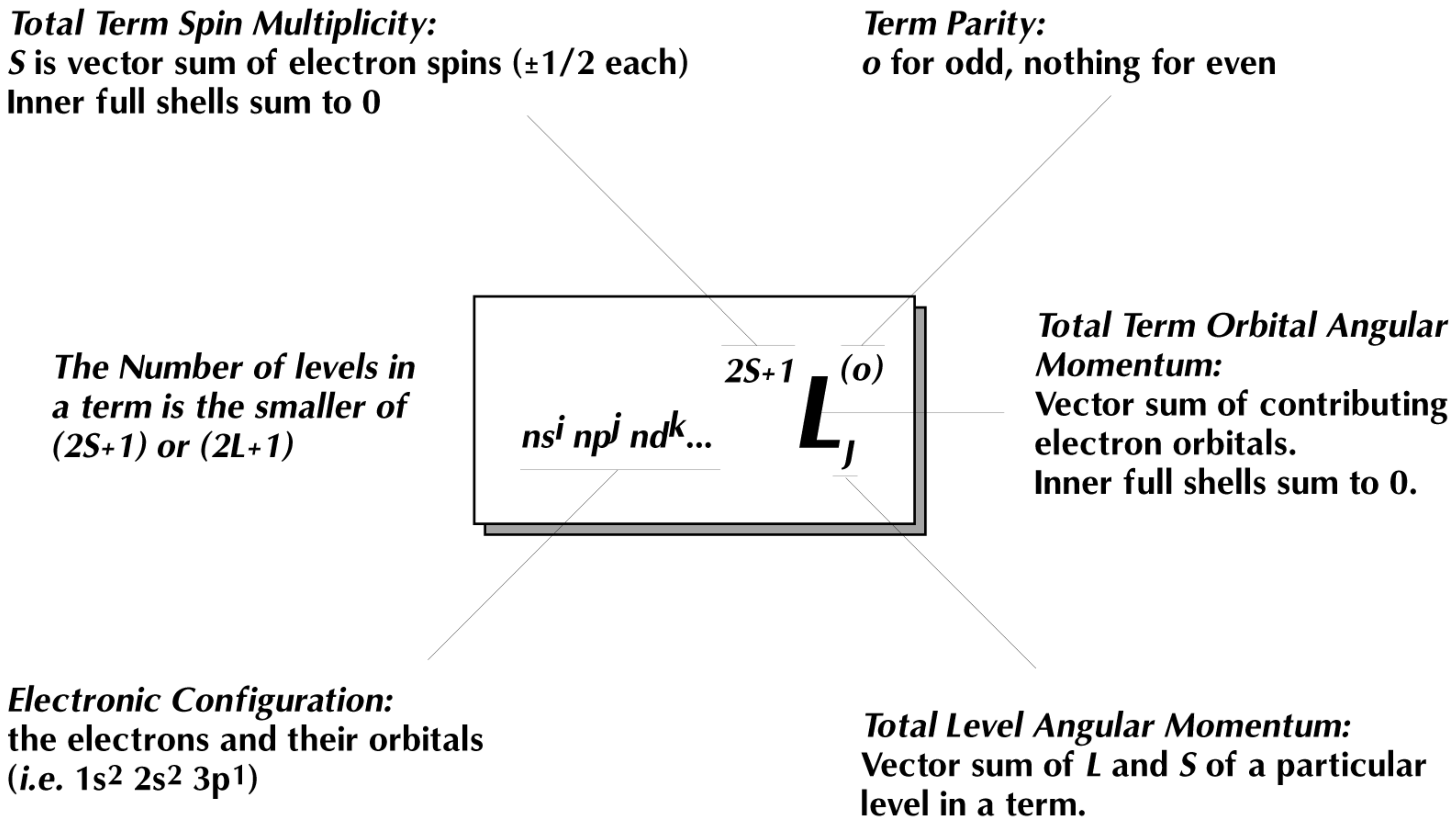
  The parity arising from a particular configuration can be determined simply by summing the orbital angular momentum quantum numbers for each of the electrons.

$$(-1)^{l_1+l_2+\cdots l_N}$$

  As closed shells and sub-shells have an even number of electrons, it is only necessary to explicitly consider the active electrons.

[Spectroscopic Notation]

- **Spectroscopic Notation**



Total Term Spin Multiplicity:
S is vector sum of electron spins (±1/2 each)
Inner full shells sum to 0

Term Parity:
o for odd, nothing for even

The Number of levels in a term is the smaller of $(2S+1)$ or $(2L+1)$

$$ns^i\, np^j\, nd^k \ldots \quad {}^{2S+1}L_J^{(o)}$$

Total Term Orbital Angular Momentum:
Vector sum of contributing electron orbitals.
Inner full shells sum to 0.

Electronic Configuration:
the electrons and their orbitals
(*i.e.* $1s^2\ 2s^2\ 3p^1$)

Total Level Angular Momentum:
Vector sum of L and S of a particular level in a term.

A state with S = 0 is a ‘singlet’ as 2S+1 = 1.

A state with S = 1/2 is a ‘doublet’

One with S = 1 is a ‘triplet’

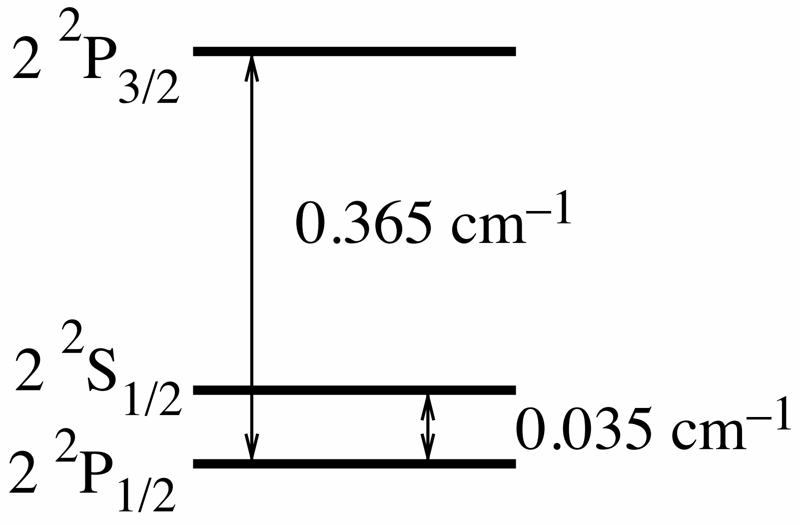
- Fine Structure of Hydrogen

Table 3.5. Fine structure effects in the hydrogen atom: splitting of the nl orbitals due to fine structure effect for $l = 0,1,2,3$. The resulting levels are labelled using H atom, and the more general spectroscopic notation of terms and levels (see Sec. 4.8).

Configuration	l	s	j	H atom	Term	Level
ns	0	$\frac{1}{2}$	$\frac{1}{2}$	$n\mathrm{s}_{\frac{1}{2}}$	$n\ ^2\mathrm{S}$	$n\ ^2\mathrm{S}_{\frac{1}{2}}$
np	1	$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$n\mathrm{p}_{\frac{1}{2}}, n\mathrm{p}_{\frac{3}{2}}$	$n\ ^2\mathrm{P}^{\mathrm{o}}$	$n\ ^2\mathrm{P}^{\mathrm{o}}_{\frac{1}{2}}, n\ ^2\mathrm{P}^{\mathrm{o}}_{\frac{3}{2}}$
nd	2	$\frac{1}{2}$	$\frac{3}{2}, \frac{5}{2}$	$n\mathrm{d}_{\frac{3}{2}}, n\mathrm{d}_{\frac{5}{2}}$	$n\ ^2\mathrm{D}$	$n\ ^2\mathrm{D}_{\frac{3}{2}}, n\ ^2\mathrm{D}_{\frac{5}{2}}$
nf	3	$\frac{1}{2}$	$\frac{5}{2}, \frac{7}{2}$	$n\mathrm{f}_{\frac{5}{2}}, n\mathrm{f}_{\frac{7}{2}}$	$n\ ^2\mathrm{F}^{\mathrm{o}}$	$n\ ^2\mathrm{F}^{\mathrm{o}}_{\frac{5}{2}}, n\ ^2\mathrm{F}^{\mathrm{o}}_{\frac{7}{2}}$

- Splitting in the n = 2 levels of atomic hydrogen. The larger splitting is the fine structure and the smaller one the Lamb shift.

  According to the Dirac equation, the $^2S_{1/2}$ and $^2P_{1/2}$ orbitals should have the same energies. However, the interaction between the electron and the vacuum (which is not accounted for by the Dirac equation) causes a tiny energy shift on $^2S_{1/2}$.



- Hyperfine Structure in the H atom

Coupling the nuclear spin I to the total electron angular momentum J gives the final angular momentum F. For hydrogen this means

$$\begin{aligned} F &= J + I \\ &= J \pm \frac{1}{2} \end{aligned}$$

The ground state of H is $1s_{\frac{1}{2}}$ or $^2S_{\frac{1}{2}}$ and has $j = \frac{1}{2}$. This means that nuclear spin coupling can split this state into two levels with $f = 0$ or 1. There is a very small, 6×10^{-5} eV, splitting between the lower $f = 0$ and higher $f = 1$ levels of H caused by magnetic effects. The $f = 0-1$ transition between these levels has a frequency of 1420.406 MHz which corresponds to a wavelength of 21 cm. The 21 cm line is probably the single most important line in astronomy. It is used to map H-atom densities throughout the ISM

- O III

Worked Example: Consider O III with the configuration: $1s^2 2s^2 2p3d$.
$1s^2$ and $2s^2$ are closed, so contribute no angular momentum.
For the 2p electron $l_1 = 1$ and $s_1 = \frac{1}{2}$;
for the 3d electron $l_2 = 2$ and $s_2 = \frac{1}{2}$.
$\underline{L} = \underline{l}_1 + \underline{l}_2 \Rightarrow L = 1, 2, 3$;
$\underline{S} = \underline{s}_1 + \underline{s}_2 \Rightarrow S = 0, 1$.

Combining these using all possible combinations of L and S, and the rules of vector addition, gives:

$\underline{J} = \underline{L} + \underline{S} \Rightarrow$

L	S	J	Level
1	0	1	$^1P^o_1$
1	1	0, 1, 2	$^3P^o_0, {}^3P^o_1, {}^3P^o_2$
2	0	2	$^1D^o_2$
2	1	1, 2, 3	$^3D^o_1, {}^3D^o_2, {}^3D^o_3$
3	0	3	$^1F^o_3$
3	1	2, 3, 4	$^3F^o_2, {}^3F^o_3, {}^3F^o_4$.

Thus twelve levels arise from the configuration $1s^2 2s^2 2p3d$.

=> 6 terms and 12 levels

- Helium

Example 1: The helium atom.

(1) The ground state is $1s^2$.
This is a closed shell, with $L = 0$ and $S = 0$, hence it gives rise to a single, even parity term ^{1}S, and level $^1S_0$.

(2) The first excited configuration is 1s2s.
This has $l_1 = l_2 = 0$ and hence $L = 0$,
but $s_1 = s_2 = \frac{1}{2}$ giving both $S = 0$ (singlet) or $S = 1$ (triplet) states. The energy ordering of atomics states is given by Hund's rules. Hund's first rule governs ordering of terms with different spin multiplicities:

For a given configuration, the state with the maximum spin multiplicity is lowest in energy.

So the ^{3}S term ($^3S_1$ level) is lower in energy than the ^{1}S term ($^1S_0$ level).
In practice the splitting between these terms is 0.80 eV.

(3) The next excited configuration is 1s2p, which has odd parity.
This has $l_1 = 0$ and $l_2 = 1$, giving $L = 1$;
again $s_1 = s_2 = \frac{1}{2}$, giving both $S = 0$ and $S = 1$ terms.
Following the rule above, the $^3P^o$ term is lower than the $^1P^o$ term, in this case by 0.25 eV. The $^3P^o$ is also split into three levels: $^3P^o_0$, $^3P^o_1$ and $^3P^o_2$.

- Carbon

Example 2: The carbon atom.

(1) Start by considering the excited state configuration $ls^2 2s^2 2p3p$.
It is only necessary to consider the outer two electrons for which:

$$l_1 = 1, \quad s_1 = \tfrac{1}{2}\,,$$
$$l_2 = 1, \quad s_2 = \tfrac{1}{2}\,.$$

These give $L = 0, 1, 2$ and $S = 0, 1$, which give rise to the following terms, all with even parity: ^{1}S, ^{3}S,^{1}P, ^{3}P, ^{1}D and ^{3}D.

(2) Now consider the ground state configuration of carbon $ls^2 2s^2 2p^2$.
This configuration also has $l_1 = 1, s_1 = \frac{1}{2}$ and $l_2 = 1, s_2 = \frac{1}{2}$.
However the Pauli Principle restricts which terms are allowed. For example the term ^{3}D includes the state:

$$\left(l_1 = 1, m_1 = +1,\ s_1 = \tfrac{1}{2},\ s_{1z} = +\tfrac{1}{2}\right)$$
$$\left(l_2 = 1, m_2 = +1,\ s_2 = \tfrac{1}{2},\ s_{2z} = +\tfrac{1}{2}\right)$$

which is allowed when $n_1 = 2, n_2 = 3$, but is forbidden when $n_1 = 2, n_2 = 2$ by the Pauli exclusion principle since both electrons have precisely the same quantum numbers.

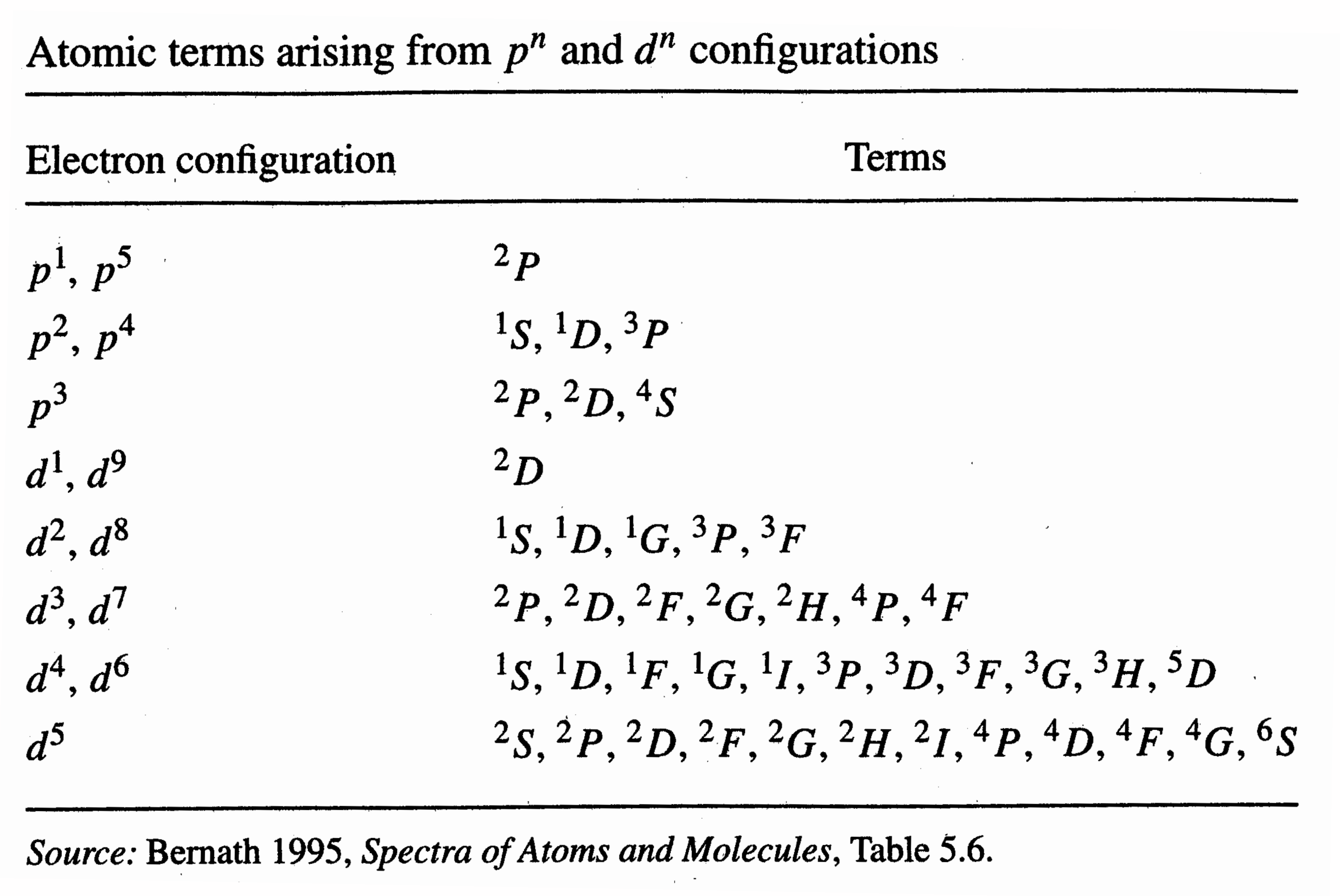
$$^1S, {}^3S, {}^1P, {}^3P, {}^1D, {}^3D \rightarrow {}^1S, {}^3P, {}^1D \quad \text{are only valid terms.}$$

There are general methods of determining which terms are allowed for a configuration with a multiply occupied open shell [see Bransden and Joachain (2003) in further reading]. However there is a rule of thumb which suffices for present purposes. It turns out that for systems with equivalent electrons, that is, electrons which have the same n and l values, then the sum $L + S$ for these electrons must be even for the Pauli Principle to be satisfied.

The ground state configuration of carbon, C I, thus gives terms ^{1}S, ^{3}P and ^{1}D. The ^{3}P term has the highest spin and is thus the ground state term. The other two terms have however, the same spin multiplicity, so which is lower in energy? Hund's second rule states:

For a given configuration and spin multiplicity, the state with the maximum orbital angular momentum is the lowest in energy.

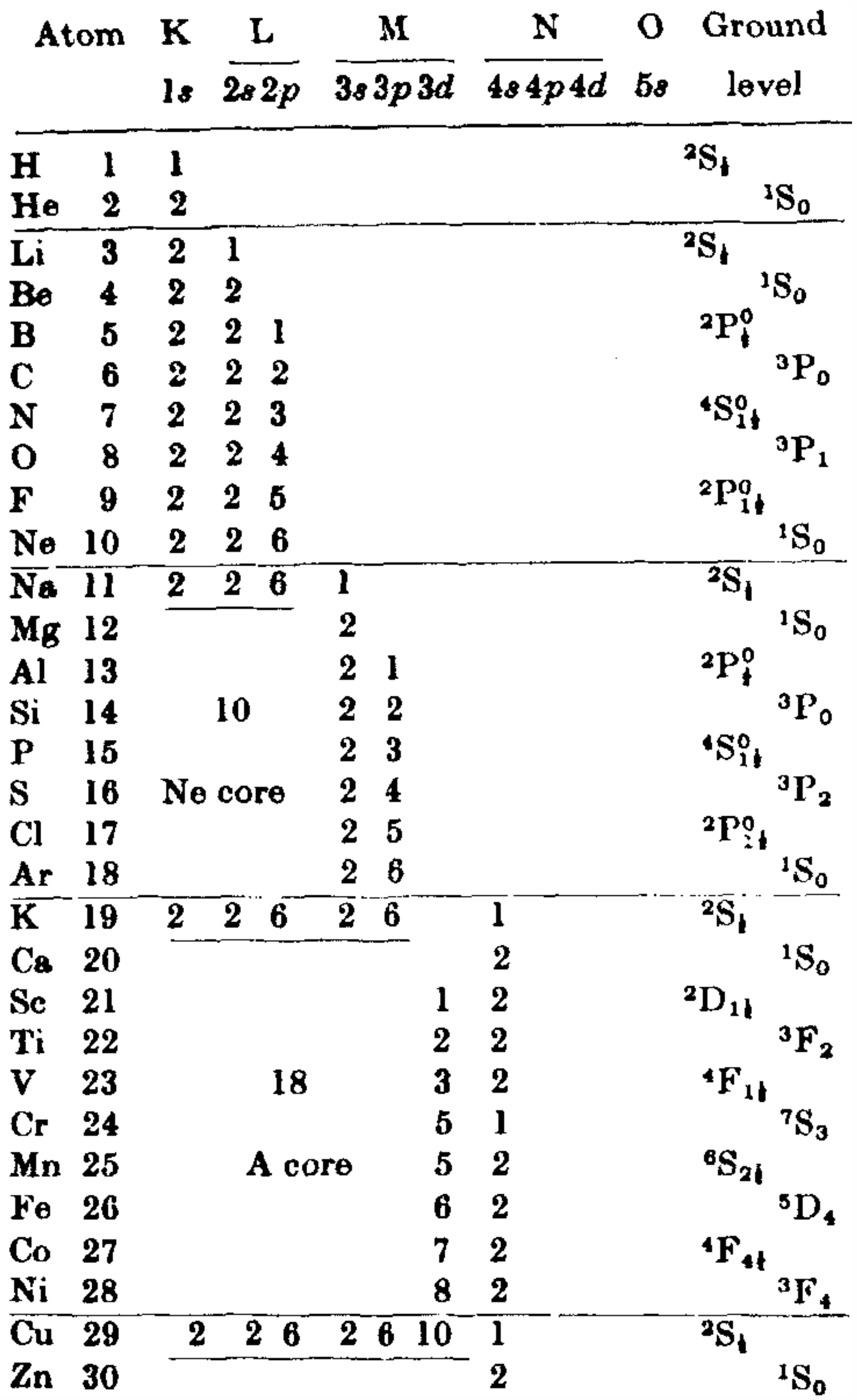
In the case of the ground state configuration of carbon, the ^{1}D state lies 1.42 eV lower in energy than the ^{1}S state, but is 1.26 eV above the ^{3}P state.



Atomic terms arising from p^n and d^n configurations

Electron configuration	Terms
p^1, p^5	^2P
p^2, p^4	$^1S, ^1D, ^3P$
p^3	$^2P, ^2D, ^4S$
d^1, d^9	^2D
d^2, d^8	$^1S, ^1D, ^1G, ^3P, ^3F$
d^3, d^7	$^2P, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$
d^4, d^6	$^1S, ^1D, ^1F, ^1G, ^1I, ^3P, ^3D, ^3F, ^3G, ^3H, ^5D$
d^5	$^2S, ^2P, ^2D, ^2F, ^2G, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

Source: Bernath 1995, *Spectra of Atoms and Molecules*, Table 5.6.



Atom		K	L		M			N			O	Ground
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	5*s*	level
H	1	1										$^2S_{\frac{1}{2}}$
He	2	2										$^1S_0$
Li	3	2	1									$^2S_{\frac{1}{2}}$
Be	4	2	2									$^1S_0$
B	5	2	2	1								$^2P^0_{\frac{1}{2}}$
C	6	2	2	2								$^3P_0$
N	7	2	2	3								$^4S^0_{1\frac{1}{2}}$
O	8	2	2	4								$^3P_1$
F	9	2	2	5								$^2P^0_{1\frac{1}{2}}$
Ne	10	2	2	6								$^1S_0$
Na	11	2	2	6	1							$^2S_{\frac{1}{2}}$
Mg	12				2							$^1S_0$
Al	13				2	1						$^2P^0_{\frac{1}{2}}$
Si	14		10		2	2						$^3P_0$
P	15				2	3						$^4S^0_{1\frac{1}{2}}$
S	16		Ne core		2	4						$^3P_2$
Cl	17				2	5						$^2P^0_{1\frac{1}{2}}$
Ar	18				2	6						$^1S_0$
K	19	2	2	6	2	6		1				$^2S_{\frac{1}{2}}$
Ca	20							2				$^1S_0$
Sc	21						1	2				$^2D_{1\frac{1}{2}}$
Ti	22						2	2				$^3F_2$
V	23			18			3	2				$^4F_{1\frac{1}{2}}$
Cr	24						5	1				$^7S_3$
Mn	25			A core			5	2				$^6S_{2\frac{1}{2}}$
Fe	26						6	2				$^5D_4$
Co	27						7	2				$^4F_{4\frac{1}{2}}$
Ni	28						8	2				$^3F_4$
Cu	29	2	2	6	2	6	10	1				$^2S_{\frac{1}{2}}$
Zn	30							2				$^1S_0$

[Hund's rules]

- **Energy ordering: Hund's rules**

  (1) **S-rule**: For a given configuration, the state with the maximum spin multiplicity is lowest in energy.

  The electrons repel each other, and therefore their mutual electrostatic energy is positive. The farther away the electrons get, the lower will be the contribution of the electrostatic energy to the total energy.

  (2) **L-rule**: For a given configuration and spin multiplicity, the state with the maximum orbital angular momentum is the lowest in energy.

  (3) **J-rule**: The lowest energy is obtained for lowest value of *J* in the normal case and for highest *J* value in the inverted case.

  The normal case is a shell which is less than half filled. The inverted case is a shell which is more than half full such as the ground state of atomic oxygen.

$$
\begin{aligned}
&{}^3P_0 < {}^3P_1 < {}^3P_2 \quad \text{for} \quad \text{carbon}\ (1\text{s}^2 2s^2 2p^2) \\
&{}^3P_2 < {}^3P_1 < {}^3P_0 \quad \text{for} \quad \text{oxygen}\ (1\text{s}^2 2s^2 2p^4)
\end{aligned}
$$

- The Hund's rules are only applicable within LS coupling. They are only rigorous for ground states. However, they are almost always useful for determining the energy ordering of excited states. The rules show increasing deviations with higher nuclear charge.

[Selection Rules]

- **Selection Rules**

Laporte rule: All electric dipole transitions connect states of opposite parity.

Resonance line: denote the longest wavelength, dipole-allowed transition arising from the ground state of a particular atom or ion.

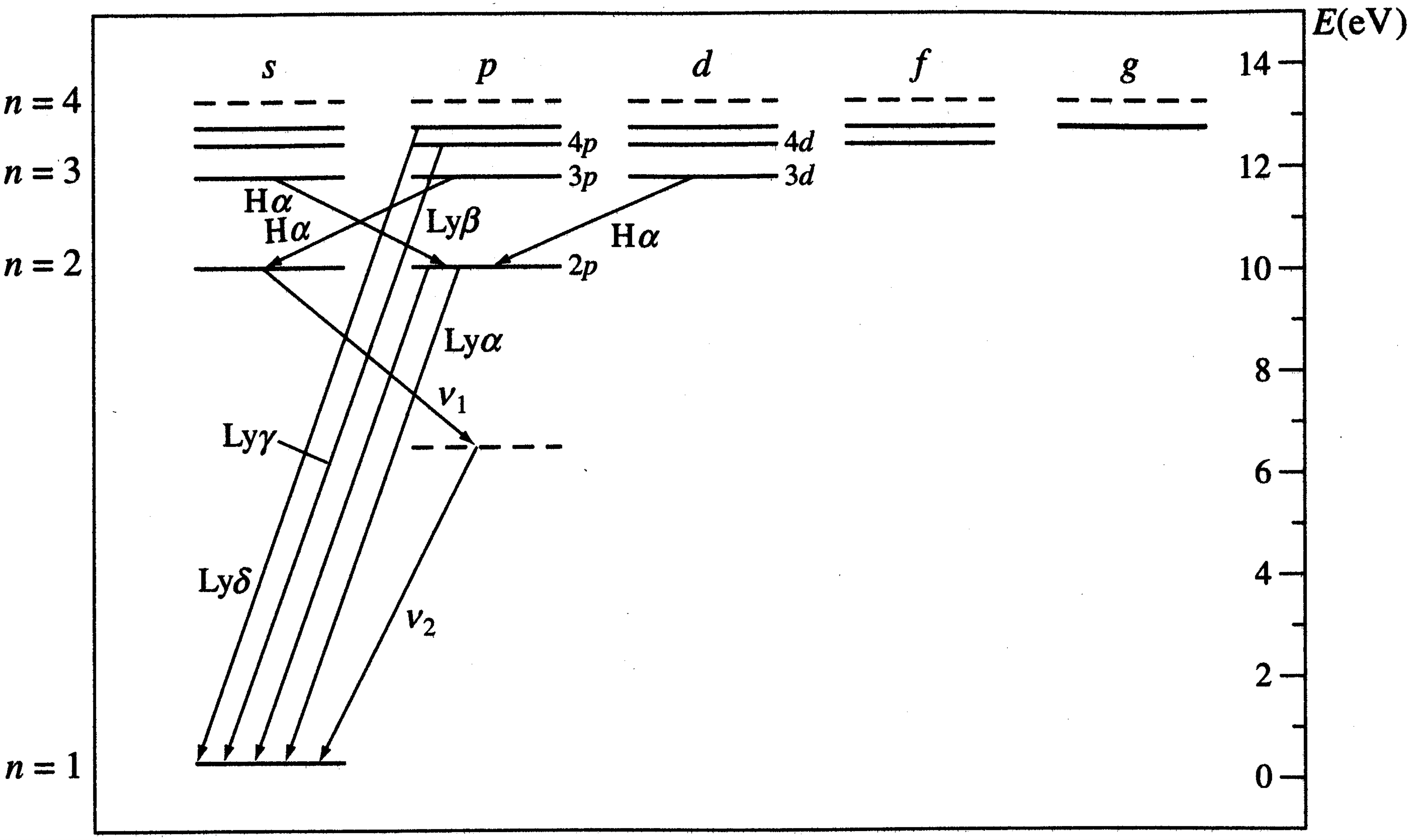
(1) For electric dipole transitions, Rules 1, 2 and 3 must always be obeyed.

(2) Intercombination lines violate rule 4.

(3) Forbidden lines violate rule 5 and/or 6. Electric quadrupole and magnetic dipole transitions are also described as forbidden.

	Electric dipole	Electric quadrupole	Magnetic dipole
1.	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$	$\Delta J = 0, \pm 1, \pm 2$ Not $J = 0 - 0, \frac{1}{2} - \frac{1}{2}, 0 - 1$	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$
2.	$\Delta M_J = 0, \pm 1$	$\Delta M_J = 0, \pm 1, \pm 2$	$\Delta M_J = 0, \pm 1$
3.	Parity changes	Parity unchanged	Parity unchanged
4.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
5.	One electron jumps Δn any $\Delta l = \pm 1$	One or no electron jumps Δn any $\Delta l = 0, \pm 2$	No electron jumps $\Delta n = 0$ $\Delta l = 0$
6.	$\Delta L = 0, \pm 1$ Not $L = 0 - 0$	$\Delta L = 0, \pm 1, \pm 2$ Not $L = 0 - 0, 0 - 1$	$\Delta L = 0$

- Hydrogen


E(eV)
s
p
d
f
g
n = 4
n = 3
n = 2
n = 1
4p
3p
2p
4d
3d
Hα
Hα
Hα
Lyβ
Lyα
Lyγ
Lyδ
ν_1
ν_2
14
12
10
8
6
4
2
0

- Hydrogen

$H\alpha$ transitions

$2s_{\frac{1}{2}} - 3p_{\frac{1}{2}}$ is allowed;
$- 3p_{\frac{3}{2}}$ is allowed;
$2p_{\frac{1}{2}} - 3d_{\frac{5}{2}}$ is not allowed;
$- 3s_{\frac{1}{2}}$ is allowed;
$- 3d_{\frac{3}{2}}$ is allowed;
$2p_{\frac{3}{2}} - 3s_{\frac{1}{2}}$ is allowed;
$- 3d_{\frac{3}{2}}$ is allowed;
$- 3d_{\frac{5}{2}}$ is allowed .

The lifetime of excited state i is given by

$$\tau_i = \left(\sum_j A_{ij}\right)^{-1},$$

where A_{ij} is the Einstein A coefficient

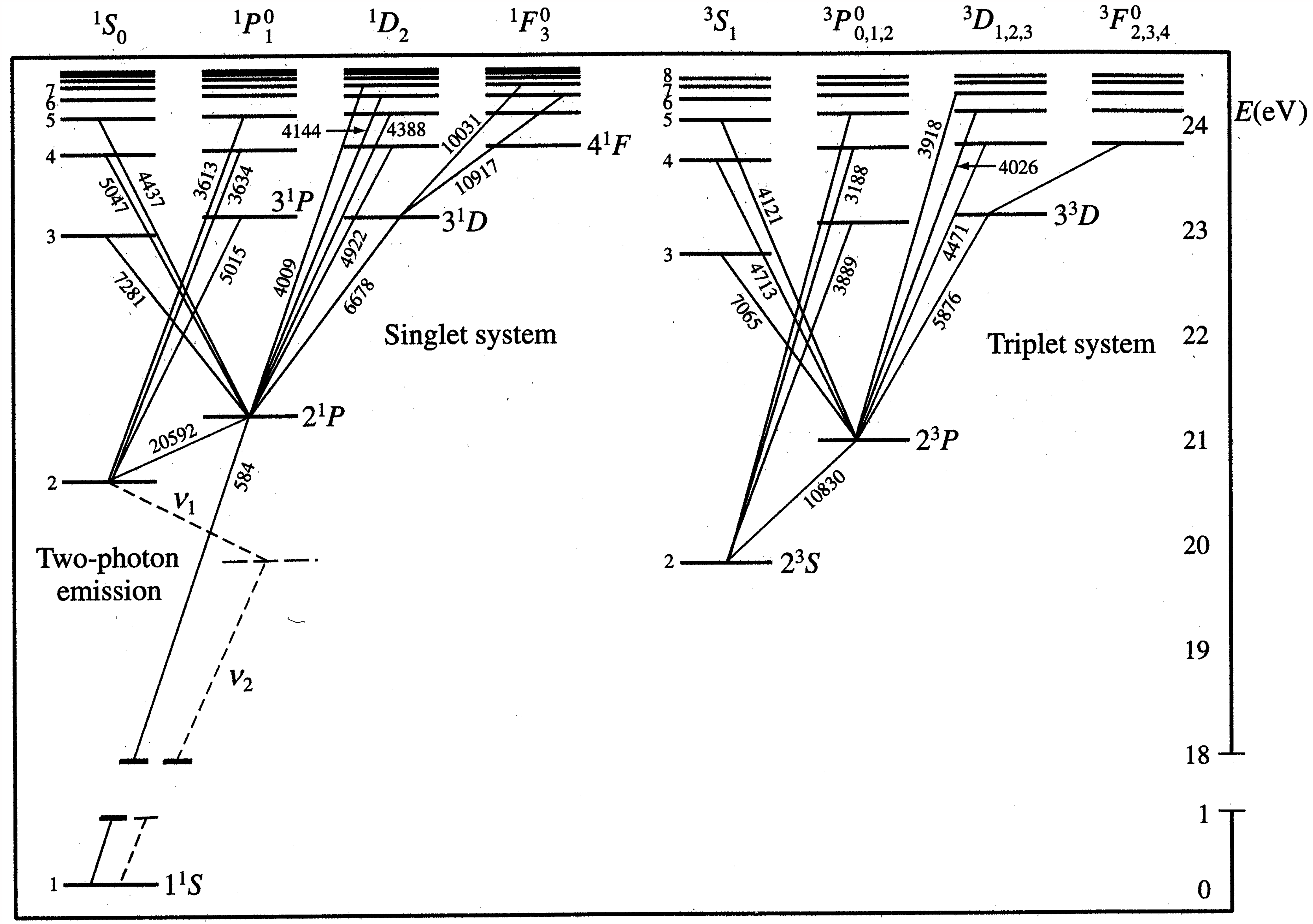
Table 3.6. Lifetimes, τ, for decay by spontaneous emission for low-lying excited states of the hydrogen atom.

Level	2s	2p	3s	3p	3d
τ/s	0.14	1.6×10^{-9}	1.6×10^{-7}	5.4×10^{-9}	2.3×10^{-7}

Lifetimes for allowed atomic transitions are short, perhaps a few times 10^{-9} s. Table 3.6 gives some examples for the H atom. A glaring exception in Table 3.6 is the lifetime of the 2s level of H. This state has a lifetime of $\sim$0.14 s, i.e. it lives 10^8 times longer than the 2p state. This is because the transition 2s $\rightarrow$ 1s is strongly forbidden. The 2s state is metastable which means that on the atomic scale, it is long-lived.

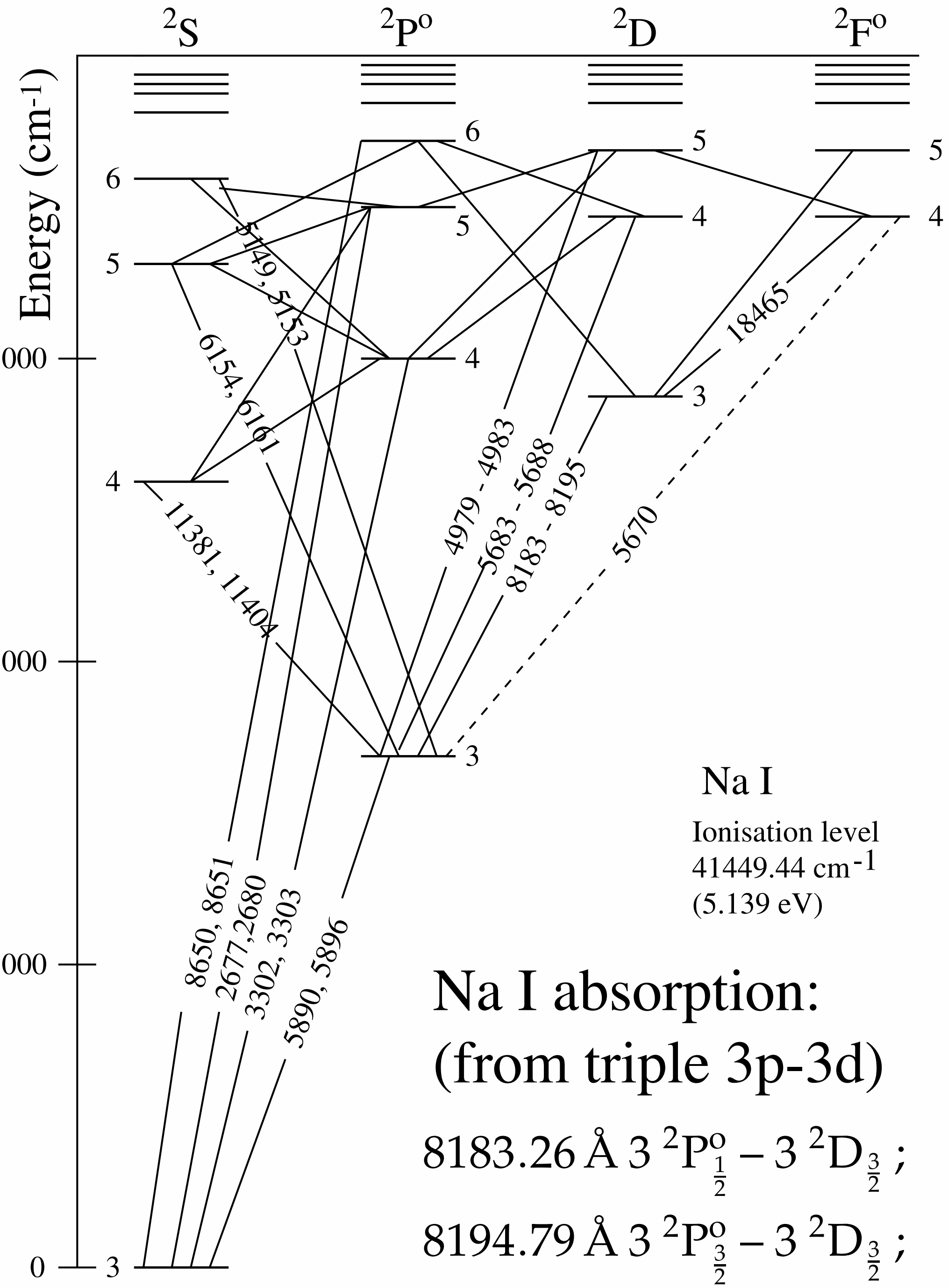
So how does the 2s state decay? By the process of two-photon emission, which is an inefficient process and in this case has an Einstein A coefficient of $7\,\mathrm{s}^{-1}$ which can be compared to $A(2p \rightarrow 1s) = 6.3 \times 10^8\,\mathrm{s}^{-1}$. The combined energy of the photons emitted must correspond to the energy difference $E(2s) - E(1s)$ but the photons themselves can take any energy within this constraint (see Fig. 3.23). The photons thus appear as continuous emission radiation. Indeed the two-photon decay of the H 2s state is responsible for approximately one half the continuum emission observed from H II regions.

- Helium (Grotrian diagram)



- Sodium (Na)

Sodium has Z = 11 and a ground state configuration of $1s^2 2s^2 2p^6 3s^1$.



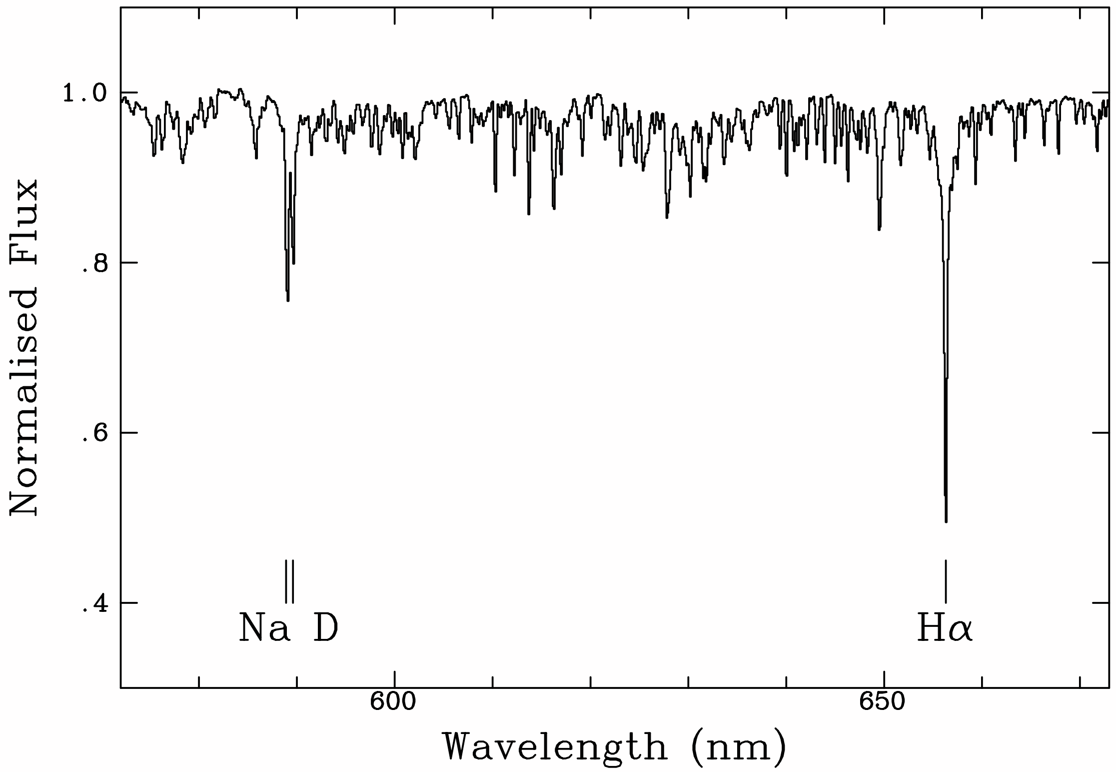


Fig. 6.6. A solar spectrum reflected from the Moon just before a lunar eclipse taken at the University of London Observatory. (S.J. Boyle, private communication.)

Na I absorption:
(from triple 3p-3d)

$$8183.26\,\text{Å}\ 3\,{}^2P^o_{\frac{1}{2}} - 3\,{}^2D_{\frac{3}{2}}\ ;$$

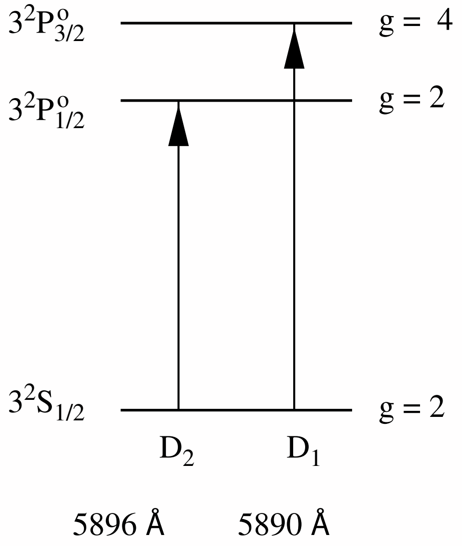
$$8194.79\,\text{Å}\ 3\,{}^2P^o_{\frac{3}{2}} - 3\,{}^2D_{\frac{3}{2}}\ ;$$

$$8194.82\,\text{Å}\ 3\,{}^2P^o_{\frac{3}{2}} - 3\,{}^2D_{\frac{5}{2}}\ .$$

Na D lines:

$$D_2\ 5890\,\text{Å}\ 3p-3s\ 3\,{}^2P_{\frac{3}{2}} - 3\,{}^2S_{\frac{1}{2}}\ ,$$

$$D_1\ 5896\,\text{Å}\ 3p-3s\ 3\,{}^2P_{\frac{1}{2}} - 3\,{}^2S_{\frac{1}{2}}\ .$$



g = 2J+1

[Notations]

1. Notations for Spectral Emission Lines and for Ions
   - (a) There is considerable confusion about the difference between these two ways of referring to a spectrum or ion, for example C III or C^{+2}. These have very definite different physical meanings and cannot be used interchangeably.
   - (b) C^{+2} is a baryon and C III is a set of photons.
   - (c) C^{+2} refers to carbon with two electrons removed, so that it is doubly ionized, with a net charge of $+2$.
   - (d) C III is the spectrum produced by carbon with two electrons removed. The C III spectrum will be produced by impact excitation of C^{+2} ($\mathrm{C}^{+2} + \mathrm{e}^- \longrightarrow \mathrm{C}^{+2*} + \mathrm{e}^- \longrightarrow \mathrm{C}^{+2} + \mathrm{e}^- + h\nu$) or by recombination of C^{+3} ($\mathrm{C}^{+3} + \mathrm{e}^- \longrightarrow \mathrm{C}^{+2} + h\nu$). So, depending on how the spectrum is formed, C III may be emitted by C^{+2} or C^{+3}.
   - (e) There is no ambiguity in absorption line studies - only C^{+2} can produce a C III absorption line. This had caused many people to think that C III refers to the matter rather than the spectrum. But this notation is ambiguous in the case of emission lines.

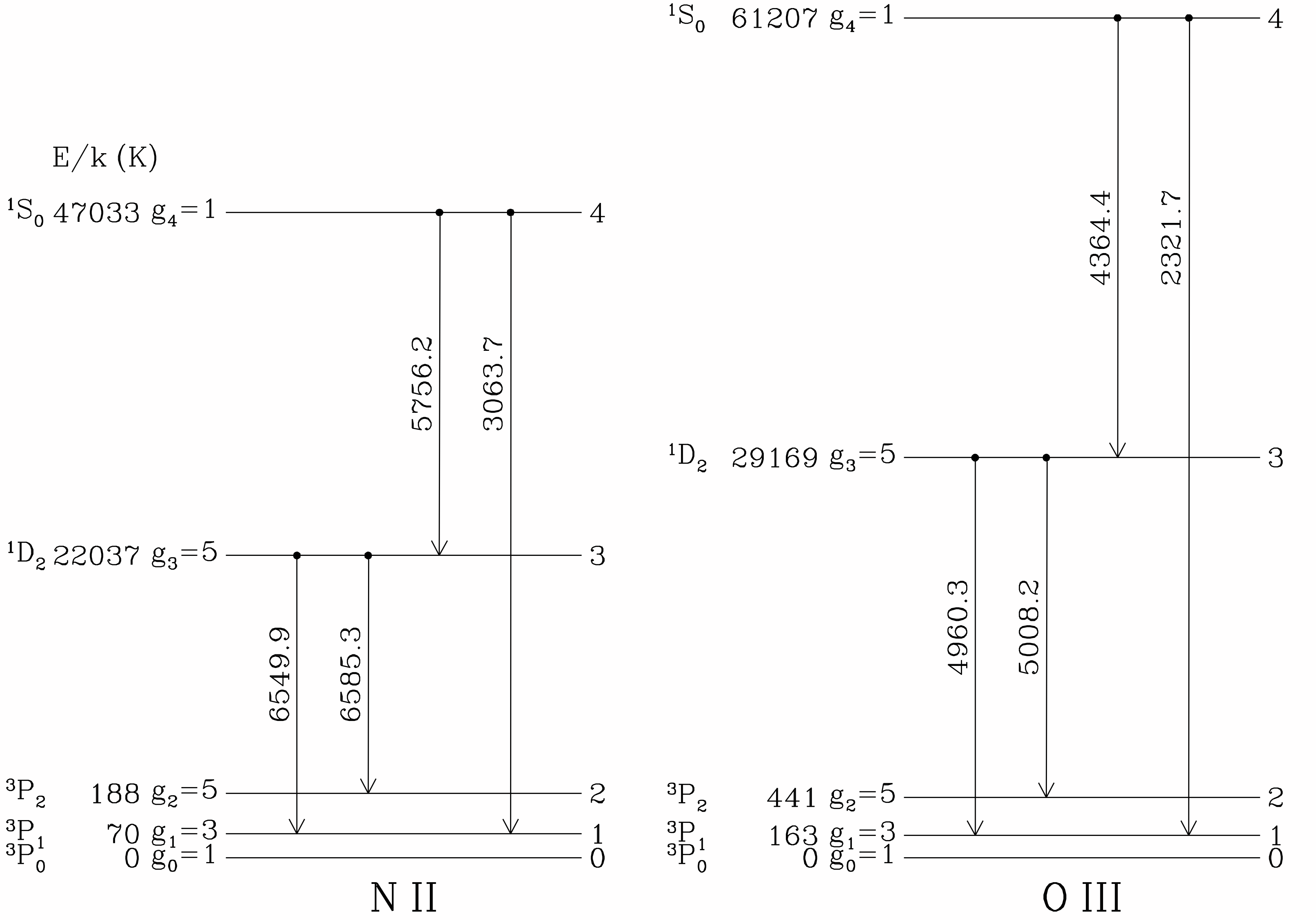


Figure 18.1 Energy levels for temperature diagnostic $2p^2$ ions N II and O III. Transitions are labeled by vacuum wavelength (Å).

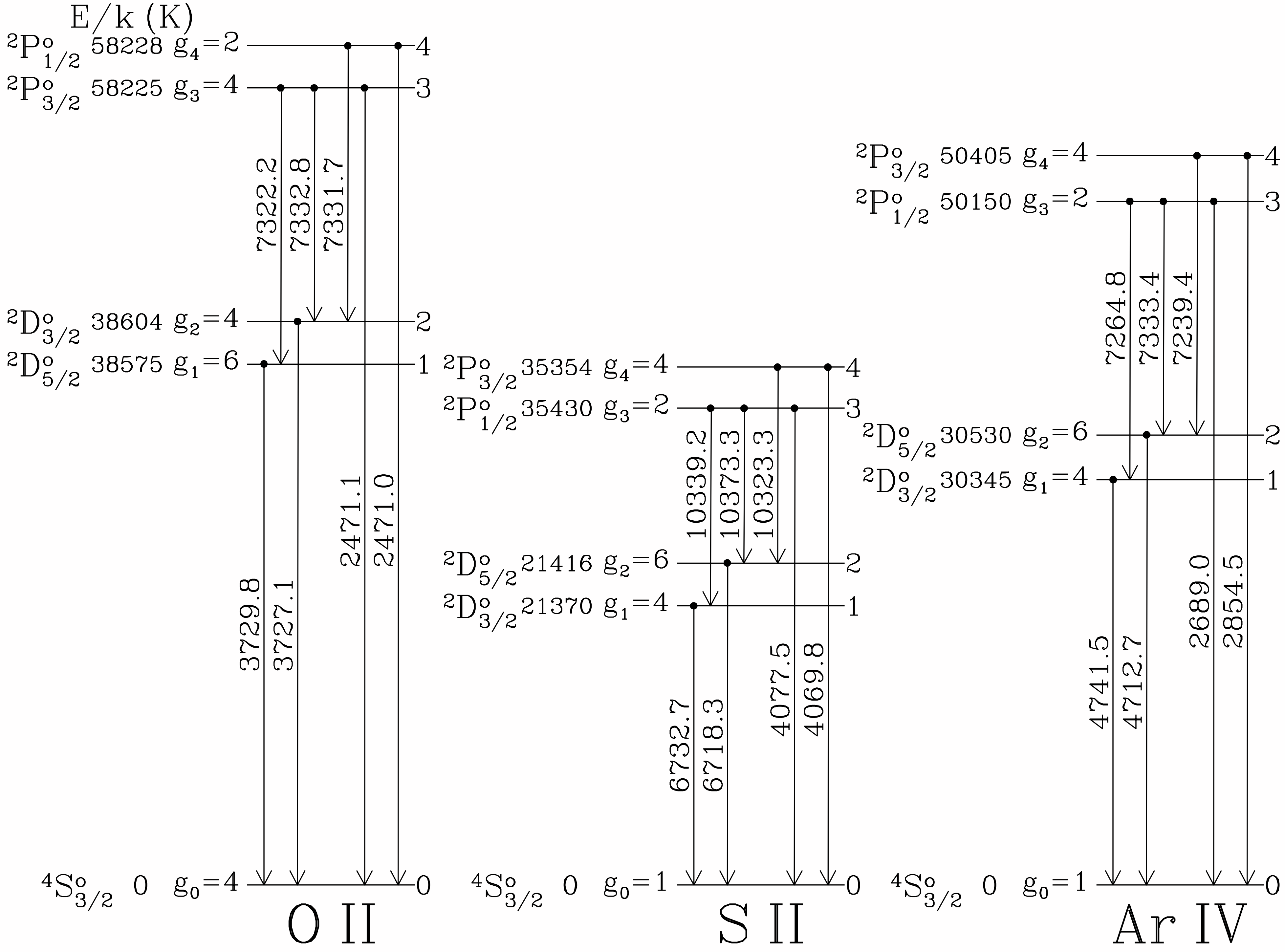
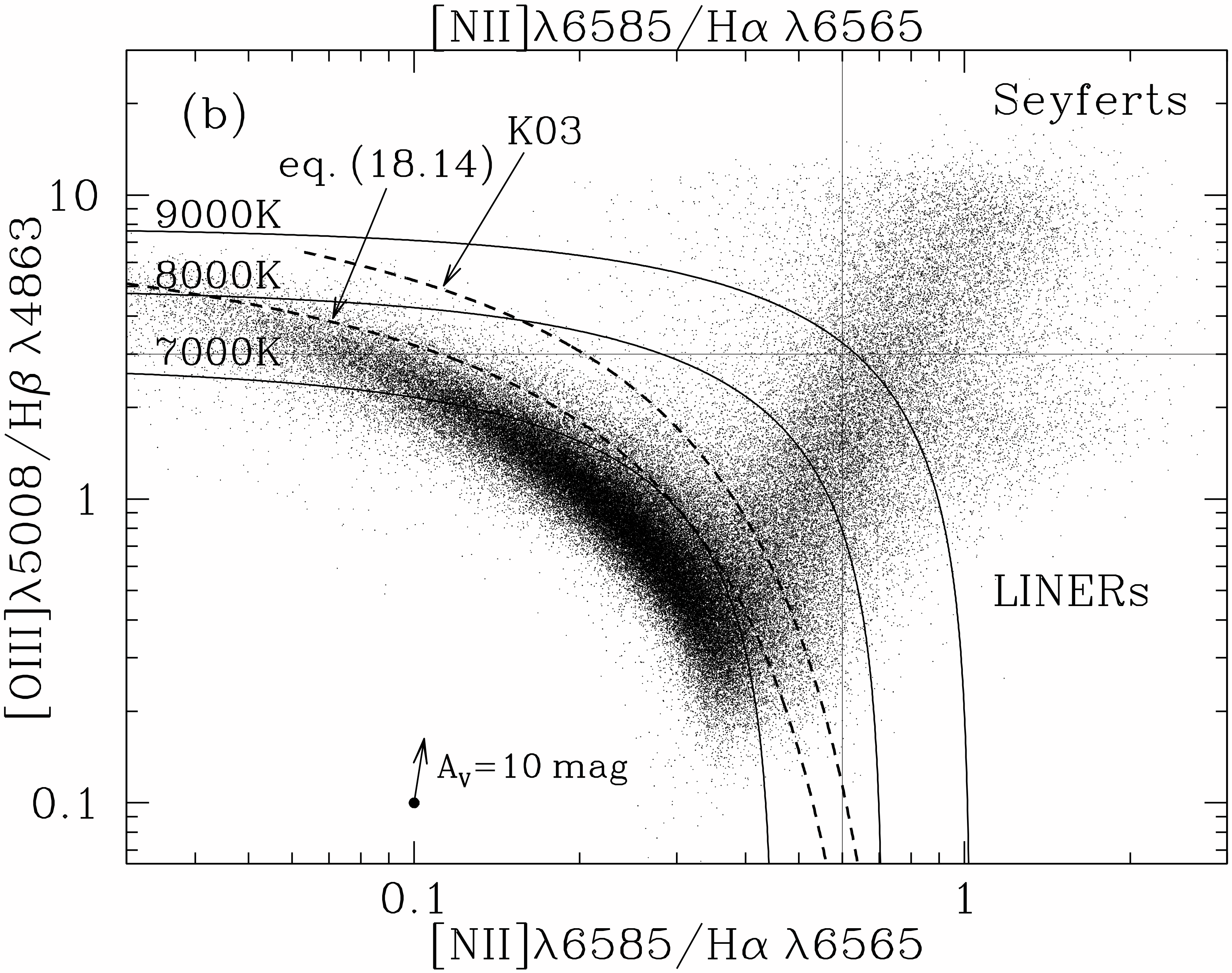


Figure 18.3 First five energy levels of the $2p^3$ ion O II, and the $3p^3$ ions S II and Ar IV. Transitions are labeled by wavelength in vacuo.

- BPT diagram

Baldwin, Phillips & Terlevich (1981, PASP, 93, 5)



2.3 Atomic processes

1. Ionization
   (a) Photoionization and Auger-ionization
   (b) Collisional Ionization (direct ionization and excitation-autoionization)
2. Recombination
   (a) radiative recombination $\Longleftrightarrow$ photoionization
   (b) dielectronic recombination
   (c) three-body recombination $\Longleftrightarrow$ direct collisional ionization
3. Charge exchange

4. Excitation and de-excitation
   (a) Collisional excitation
   (b) Collisional de-excitation
   (c) Radiative de-excitation (spontaneous emission)

2.4 Photoionization

Interstellar medium (ISM) is transparent to $h\nu < 13.6$ eV photons, but is very opaque to ionizing photons. In fact, the ISM does not become transparent until $h\nu \sim 1$ keV. Sources of ionizing photons include massive, hot young stars, hot white dwarfs, and supernova remnant shocks.

1. From the Outer Shells
   (a) Photoionization is the inverse process to radiative recombination.

$$A^{i+} + h\nu \rightarrow A^{(i+1)+} + e^{-} + \Delta E$$

   (b) If the incoming photon has sufficient energy, it may leave the ionized species in an excited state.

$$\begin{aligned} A^{i+} + h\nu &\rightarrow A_{*}^{(i+1)+} + e^{-} + \Delta E \\ A_{*}^{(i+1)+} &\rightarrow A^{(i+1)+} + h\nu_1 + h\nu_2 + \cdots \end{aligned}$$

2. Inner Shell Photoionization

   (a) If the energy of the incoming photon still higher, it becomes possible to remove one of the inner shell electrons which also results in a change in the electron configuration in the excited species. This may be followed by a radiative readjustment back to the ground state.

   (b) However, in this case, Auger ionization becomes more probable. High frequency photons may eject an inner shell electron from an ion or atom, and the resulting ion may then fill the gap in its inner shell with an outer electron, ejecting another outer electron to remove the energy in a radiationless transition called an Auger transition. Such a process will produce very energetic electrons which will lose their energy in heating up the gas.

$$
\begin{aligned}
A^{i+} + h\nu &\rightarrow A_{**}^{(i+1)+} + e^- + \Delta E_1, \\
A_{**}^{(i+1)+} &\rightarrow A_{*}^{(i+m+1)+} + me^- + \Delta E_2, \ \text{(radiationless autoionization, } m \succeq 1\text{)} \\
A_{*}^{(i+m+1)+} &\rightarrow A^{(i+m+1)+} + h\nu_1 + h\nu_2 + \cdots
\end{aligned}
$$

2.5 Collisional Ionization

1. Direct collisional ionization: The process whereby an electron strikes an ion A (with charge $i+$), with sufficient energy to strip out a bound electron:

$$A^{i+} + e^- \rightarrow A^{(i+1)+} + 2e^- - \Delta E.$$

2. Excitation-autoionization: At sufficiently high electron impact energies, more than one electron of the target nucleus may be excited, leaving the atom in an unstable state, which is stabilized by the radiationless ejection of an electron, possibly followed by a radiative decay of the ionized atom back to its ground state. This process is favored in heavy elements which have a large number of inner shell electrons and only one or two electrons in the outer shell.

$$\begin{aligned} A^{i+} + e^- &\rightarrow A_*^{i+} + e^- - E_1 \\ A_*^{i+} &\rightarrow A_*^{(i+1)+} + e^- + E_2 \\ A_*^{(i+1)+} &\rightarrow A^{i+} + h\nu \end{aligned}$$

3. For example, in collisions of Li-like ions, excitation and autoionization can occur via excitation of the 1s-electron into states with principal quantum numbers $n \geq 2$. After the decay of a doubly excited state, one has an additional electron in the final channel.

$$\begin{aligned} A^{i+}(1s^2 2s) + e^- &\rightarrow A^{i+}_{**}(1s2snl) + e^- - E_1 \\ &\rightarrow A^{(i+1)+}_{*}(1s^2) + (e^- + E_2) + (e^- - E_1) \end{aligned}$$

2.6 Recombination

1. Radiative recombination

   (a) Radiative recombination is the process of capture of an electron by an ion where the excess energy is radiated away in a photon.

   (b) The electron is captured into an excited state. The recombined but still excited ion radiates several photons in a radiative cascade, as it returns to the ground state:

   $$\begin{aligned} A^{i+} + e^- &\rightarrow A_*^{(i-1)+} + h\nu \\ A_*^{(i-1)+} &\rightarrow A^{(i-1)+} + h\nu_1 + h\nu_2 + h\nu_3 + \cdots \end{aligned}$$

   The photon in the first line represents a recombination continuum ($h\nu$) photon. However, photons ($h\nu_1, h\nu_2, h\nu_3$) represent quantized transitions and are therefore termed recombination lines.

   (c) The initial capture of the electron in recombination tends to occur into states of high angular momentum due to the initial orbital angular momentum of the electron around the ioni. Electrons which are initially in a state of high angular momentum tend to get trapped into the highest l state consistent with the principal quantum number.

   (d) The total effective recombination rate can be written as the sum of the recombination rate to each state.

2. Dielectronic recombination

   (a) Dielectronic recombination (DR) is a resonant two-step process in which a free electron is captured by the incident ion into an autoionizing state followed by a stabilizing radiation decay of the resulting ion in the second step. The DR is often more important than radiative recombination.

$$
\begin{aligned}
A^{i+}(1s,\ldots) + e^- &\rightarrow A_{**}^{(i-1)+}(n_1l_1;n_2l_2). \\
A_{**}^{(i-1)+}(n_1l_1;n_2l_2) &\rightarrow A_{*}^{(i-1)+}(n_3l_3;n_2l_2) + h\nu \\
A_{*}^{(i-1)+}(n_3l_3;n_2l_2) &\rightarrow A_{*}^{(i-1)+}(n_3l_3;n_2l_2) + h\nu_1 + h\nu_2 + \cdots
\end{aligned}
$$

   (b) The first step is a double-electron process, often called dielectronic capture, through which one free electron is captured and another core electron is simultaneously excited forming a doubly excited state. One of the electron is in an autoionizing state, n_1l_1, and the other is in an excited state, n_2l_2. In the second step, the ion in a doubly excited state emits a photon and decays into a stable state below the ionization limit.

   (c) There is a competitive process for the decay of the doubly excited ion. – the autoionization or Auger decay associated not with the radiative transition but with a change in ion charge.

2.7 Charge-Exchange

1. During the collision of two ionic species, the charge clouds surrouding each interact, and it is possible that an electron is exchanged bewteen them.

2. Since, in virtually all diffuse astrophysical plasmas, hydrogen and helium are overwhelmingly the most abundant species, the charge-exchange reactions which are significant to the ionization balance of the plasma are

$$A^{(i+1)+} + H^0 \rightleftarrows A^{i+} + H^+ + \Delta E,$$

$$A^{(i+1)+} + He^0 \rightleftarrows A^{i+} + He^+ + \Delta E.$$

2.8 Ionization Equilibrium

1. Collisional Ionization Equilibrium (CIE) or coronal equilibrium
   (a) dynamic balance at a given temperature between collisional ionization from the ground states of the various atoms and ions, and the process of recombination from the higher ionization stages.
   (b) In this equilibrium, effectively, all ions are in their ground state.
2. Photoionization Equilibrium: dynamic balance between photo-ionization and the process of recombination.
3. Ionization balance under conditions of local thermodynamic equilibrium (LTE)
   (a) The ionization equilibrieum in LTE is describted by the Saha equation.
   (b) In LTE, the excited states are all populated according to Boltzmann's law.

2.9 Collisional Excitation

1. Under the conditions of very low density and weak radiation fields,

   (a) The vast majority of the atoms reside in the ground state.

   collisional excitation timescale $\gg$ radiative decay time scale

   This condition will remain true even if the excited state has a radiative lifetime of several second. This is frequently the case for the forbidden transitions observed in ionized astrophysical plasmas.

   (b) flux of an emission line $\propto$ flux number of collisions

   $\propto$ product of the number densities of the two colliding species by the probability that a collision will produce a collisional excitation

   (c) If the energy gap between the ground state and the excited state, E_{12}, is much larger than the mean energy of the colliding species $\sim T$, then, because there are few very energetic collisions, relatively few collisional excitations can occur. Therefore, the resulting emission line will be very much weaker than when $E_{12} \leq kT$.

   $\Longrightarrow$ This gives us the possibility of measuring temperature from the relative strengths of lines coming from excited levels at different energies above the ground state.

2. At high enough densities,
   (a) The collisional timescales are short.
   (b) The population in any upper level is set by the balance between collisional excitation, and the collisional deexcitation out of these levels, and are governed by the Boltzmann equlibrium.

3. At intermediate densities,
   (a) The collisional rates and the radiative decay rates are compatible.
   (b) The intensity of an emission line is determined by both the temperature and the density.
   (c) If the temperature is known, the density can be determined from the intensity ratio of two such lines.

4. Collisional Rate (Two Level Atom)

(a) The collisional cross section is in general varying approximately inversely as the impact energy (because of the focusing effect of the Coulomb force).

$$\begin{aligned}
\sigma_{12}(v) &= \left(\pi a_0^2\right)\left(\frac{hR}{\frac{1}{2}m_e^2 v^2}\right)\frac{\Omega_{12}}{g_1}\ \text{cm}^2 \text{ for } \frac{1}{2}m_e^2 v^2 > E_{12} \\
&= \frac{\pi \hbar^2}{m_e^2 v^2}\frac{\Omega_{12}}{g_1} \\
\text{or } \sigma_{12}(E) &= \frac{h}{8\pi m_e E}\frac{\Omega_{12}}{g_1} \\
\text{where, } a_0 &= \frac{\hbar^2}{m_e e^2} = 5.12 \times 10^{13}\ \text{cm, Bohr radius} \\
R &= \frac{m_e e^4}{4\pi \hbar^3} = 109,737\ \text{cm}^{-1}\text{, Rydberg constant}
\end{aligned}$$

(b) The collision strength Ω_{12} is a function of electron velocity (or energy) but is often approximately constant near the threshold, g_1 is the statistical weight of the lower level.

(c) Advantage of using the collision strength

i. It removes the primary energy dependence for most atomic transitions.

ii. The symmetry between the upper and the lower states.

Using the principle of detailed balance, which states that in thermodynamic equilibrium each microscopic process is balanced by its inverse,

$$n_e n_1 v_1 \sigma_{12}\left(v_1\right) f\left(v_1\right) dv_1 = n_e n_2 v_2 \sigma_{21}\left(v_2\right) f\left(v_2\right) dv_2,$$

where v_1 and v_2 are related by $\frac{1}{2} m_e v_1^2 = \frac{1}{2} m_e v_2^2 + E_{12}$, and using the Boltzman equation of thermodynamic equilibrium,

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{kT}\right)$$

we derive the following relation

$$g_1 v_1^2 \sigma_{12}\left(v_1\right) = g_2 v_2^2 \sigma_{21}\left(v_2\right),$$

and the symmetry of the collision strength between levels

$$\Omega_{12} = \Omega_{21}.$$

(d) Collisional excitation and de-excitation rates

If Ω_{21} is a constant, the total collisional de-excitation rate per unit volume per unit time is

$$\begin{aligned} R_{21} &= n_e n_2 q_{21} \\ &= n_e n_2 \int_0^\infty v\sigma_{21}(v) f(v)\, dv \\ &= n_e n_2 \left(\frac{2\pi\hbar^4}{k m_e^2}\right)^{1/2} T^{-1/2}\frac{\Omega_{21}}{g_2}. \\ &= n_e n_2 \frac{8.62942\times 10^{-6}}{T^{1/2}}\frac{\Omega_{21}}{g_2}\ \mathrm{cm}^{-3}\mathrm{s}^{-1}, \end{aligned}$$

and the collisional excitation rate per unit volume per unit time is $R_{12} = n_e n_1 q_{12}$, where

$$\begin{aligned} q_{12} &= \int_{v_{\mathrm{min}}}^\infty v\sigma_{12}(v) f(v)\, dv \\ &= \left(\frac{2\pi\hbar^4}{k m_e^2}\right)^{1/2} T^{-1/2}\frac{\Omega_{12}}{g_1} \exp\left(-\frac{E_{12}}{kT}\right) \\ &= \frac{g_2}{g_1} q_{21} \exp\left(-\frac{E_{12}}{kT}\right). \end{aligned}$$

(e) Quantum mechanical sum rule for collision strengths for the case where one term consists of a single level and the second consists of a multiplet, if either $S = 0$ or $L = 0$,

$$\Omega_{(SLJ,S'L'J')} = \frac{(2J'+1)}{(2S'+1)(2L'+1)}\Omega_{(SL,S'L')}$$

Here, $(2J'+1)$ is the statistical weight of an individual level (or term) in the multiplet, and $(2S'+1)(2L'+1)$ is the statistical weight of the multiplet. We can regard the collision strength as "shared" amongst these levels in proportion to the statistical weights of the individual levels $(g_J = 2J+1)$.

i. C-like ions $\left(1s^2 2s^2 2p^2 \longrightarrow 1s^2 2s^2 2p^2, \text{ same electron configurations}\right) \longrightarrow$ forbidden or intercombination transitions.
ground states (triplet) – ${}^3P_0 :{}^3 P_1 :{}^3 P_2 = 1/9 : 3/9 : 5/9$
excited states (singlets) – ${}^1D_2,{}^1 S_1$

ii. Li-like ions $\left(1s^2 2s^1 \longrightarrow 1s^2 2p^1\right) \longrightarrow$ resonance transitions
ground state (single) – ${}^2S_{1/2}$
excited states (doublet) – ${}^2P_{3/2} :{}^2 P_{1/2} = 2/3 : 1/3$

(f) Limiting Cases

i. In the low density limit, the collisional rate between atoms and electrons is much slower than the radiative deexcitation rate of the excited level. Thus, we can balance the collisional feeding into level 2 by the rate of radiative transitions back down to level 1. The collision rate is

$$\begin{aligned} R_{12} &= A_{21} n_2, \\ n_2 &= \frac{n_e n_1 q_{12}}{A_{21}}, \end{aligned}$$

where A_{21} is the Einstein coefficient for spontaneous emission. Emission line flux is

$$\begin{aligned} F_{21} &= E_{12} A_{21} n_2 = E_{12} R_{12} \\ &= n_e n_1 E_{12} \frac{8.62942 \times 10^{-6}}{T^{1/2}} \left(\frac{\Omega_{12}}{g_1}\right) \exp\left(-\frac{E_{12}}{kT}\right) \text{ erg cm}^{-3}\text{ s}^{-1} \\ &\simeq \chi n_e^2 \beta E_{12} T^{-1/2} \left(\frac{\Omega_{12}}{g_1}\right) \exp\left(-\frac{E_{12}}{kT}\right) \end{aligned}$$

For low temperatures, the exponential term dominates. At high temperature, the $T^{-1/2}$ term controls the cooling rate.

ii. In high-density limt, the level populations are set by the Boltzman equilibrium,

$$\begin{aligned} F_{21} &= E_{12} A_{21} n_2 \\ &= n_1 E_{12} A_{21} \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{kT}\right) \\ &\simeq \chi n_e E_{12} A_{21} \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{kT}\right) \end{aligned}$$

iii. Critical density defined as the density where the radiative depopulation rate matches the collisional deexcitation for the excited state,

$$\begin{aligned} A_{21} n_2 &= R_{21} \\ A_{21} n_2 &= n_e n_2 \frac{\beta}{T^{1/2}} \frac{\Omega_{21}}{g_2} \\ n_{\text{crit}} &= \frac{A_{21} g_2 T^{1/2}}{\beta \Omega_{12}} \text{ cm}^{-3}. \end{aligned}$$

At around this density, the line emissivity plotted in log-scale changes slope from $+2$ to $+1$.

5. The Three-Level Atom (Line diagnostics)

   (a) Let C_{ij} be the collision rate ($C_{ij} = n_e q_{ij}$ s^{-1}) between any two levels. The equations of statistical equilibrium for a three level atom are

$$N_1 C_{13} + N_2 C_{23} = N_3 \left(C_{31} + C_{32} + A_{32} + A_{31}\right),$$
$$N_1 C_{12} + N_3 \left(C_{32} + A_{32}\right) = N_2 \left(C_{23} + C_{21} + A_{21}\right),$$
$$N_1 + N_2 + N_3 = 1.$$

   (b) Electron temperature

      i. Low-Density Limit; $E_{12} \sim E_{23}$

      ii. In this limit, $C_{31} \sim C_{32} \sim 0$. Also, because of the increasing threshold energies to excite each level, $N_3 \ll N_2 \ll N_1$ so that the equations are reduced to

$$N_3 = \frac{N_1 C_{13}}{\left(A_{32} + A_{31}\right)}$$
$$N_2 = \frac{N_1 C_{12}}{A_{21}}.$$

      If we now form the line intensity ratio for the 3 → 2 and 2 → 1 transitions, we have

$$\begin{aligned}\frac{F_{32}}{F_{21}} &= \frac{E_{23}N_3A_{32}}{E_{12}N_2A_{21}}\\ &= \frac{E_{23}A_{32}C_{13}}{E_{12}(A_{32}+A_{31})C_{12}}\\ &= \frac{E_{23}A_{32}q_{13}}{E_{12}A_{31}q_{12}}\\ &= \frac{E_{23}A_{32}\Omega_{13}}{E_{12}A_{31}\Omega_{12}}\exp\left(-\frac{E_{23}}{kT}\right).\end{aligned}$$

provided that A_{32} is very much less than A_{31}.

(c) Ions in which $E_{23} \ll E_{12}$

i. In low density limit

$$N_1 C_{13} = N_3 A_{31},$$
$$N_1 C_{12} = N_2 A_{21},$$

$$\frac{F_{31}}{F_{21}} = \frac{E_{31} A_{31} N_3}{E_{21} A_{21} N_2} = \frac{E_{31} C_{13}}{E_{21} C_{12}} \sim \frac{\Omega_{31}}{\Omega_{21}} \exp\left(-\frac{E_{23}}{kT}\right) \sim \frac{\Omega_{31}}{\Omega_{21}} = \frac{g_3}{g_2}.$$

using the quantum-mechanical sum rule for collision strengths.

ii. In high density limit, the upper levels are populated according to their Bolzmann ratios,

$$\frac{F_{31}}{F_{21}} = \frac{E_{31} A_{31} N_3}{E_{21} A_{21} N_2} \sim \frac{A_{31} g_3}{A_{21} g_2}$$

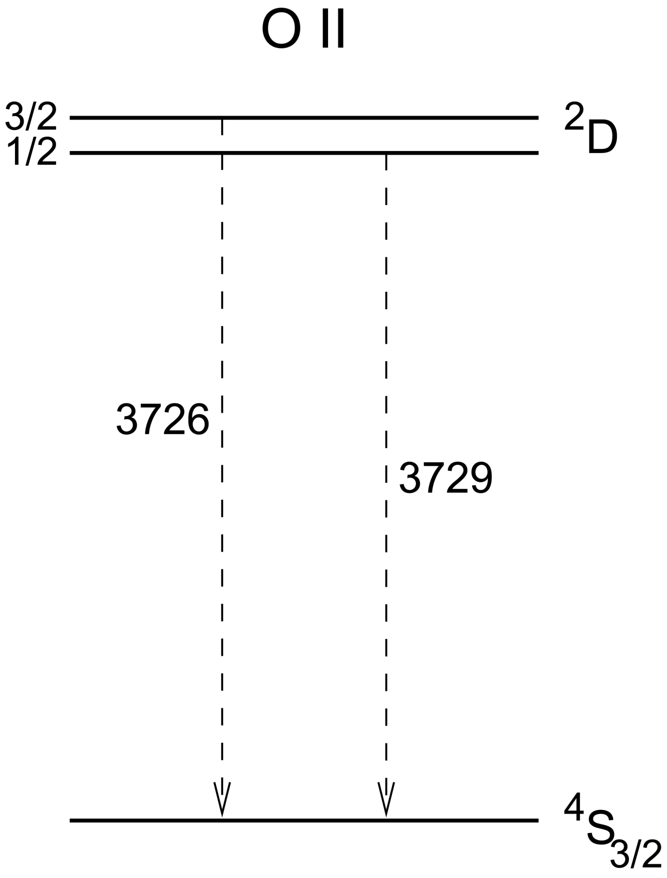
6. Examples of Line Diagnostics

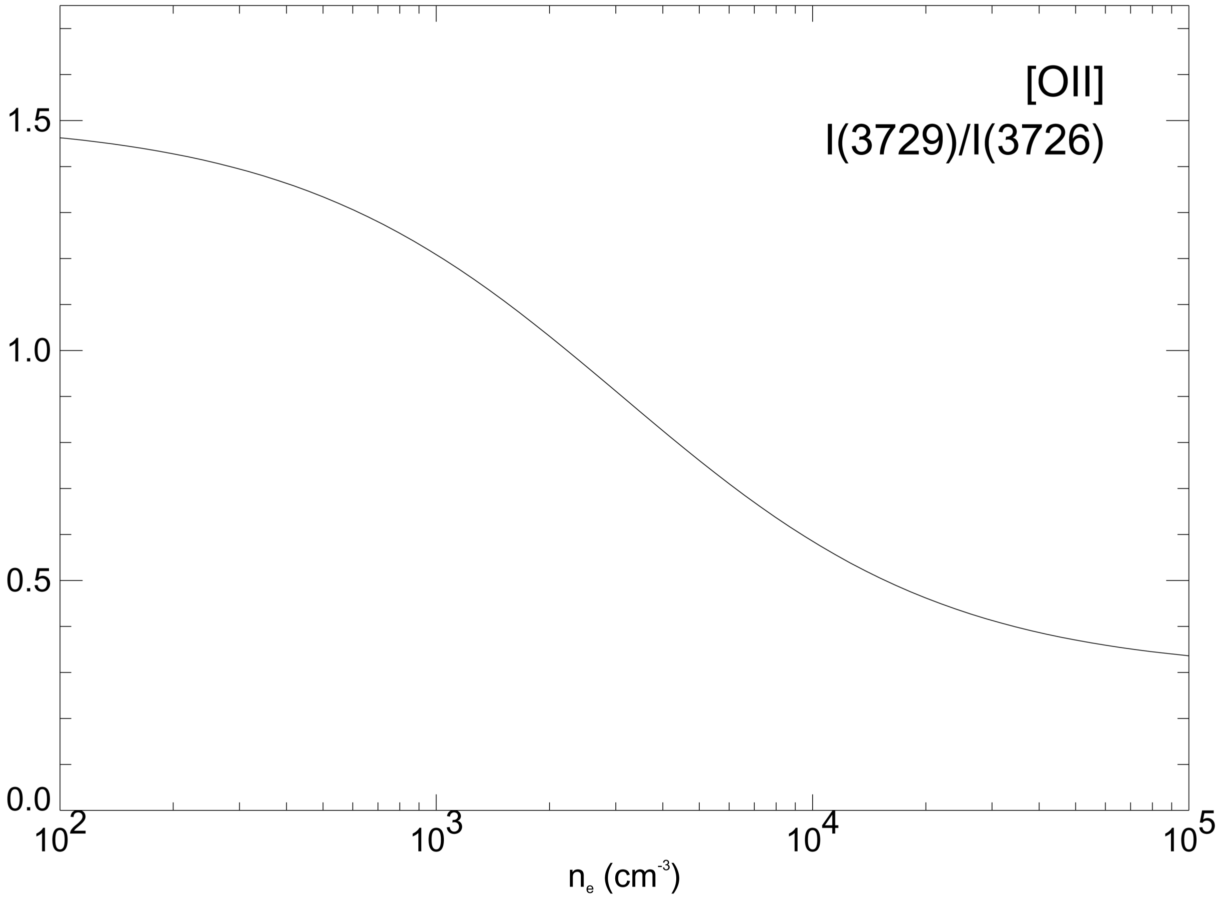
(a) Density: Choose atom with two levels with almost same excitation energy.

(b) Temperature: Use two levels with different excitation energy.

Density

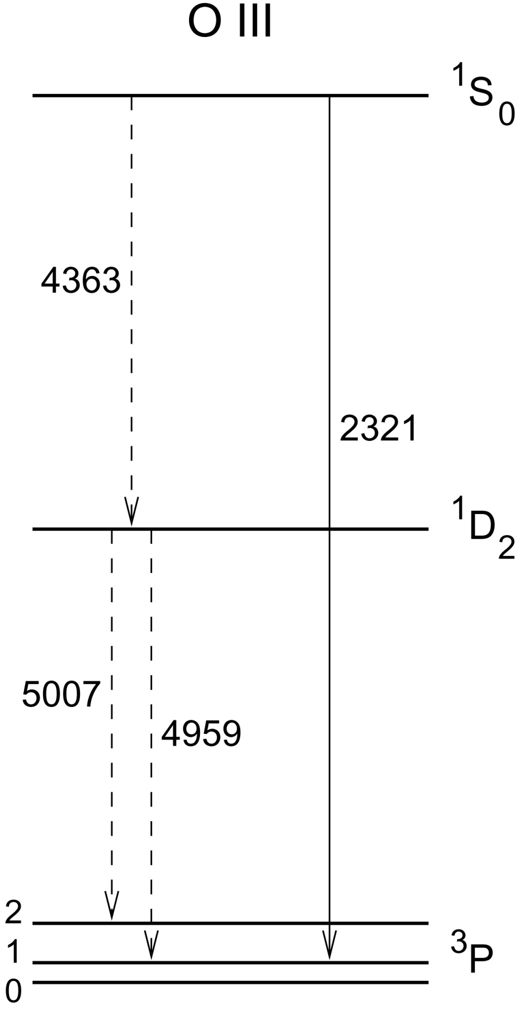
Choose atom with two levels with almost same excitation energy.

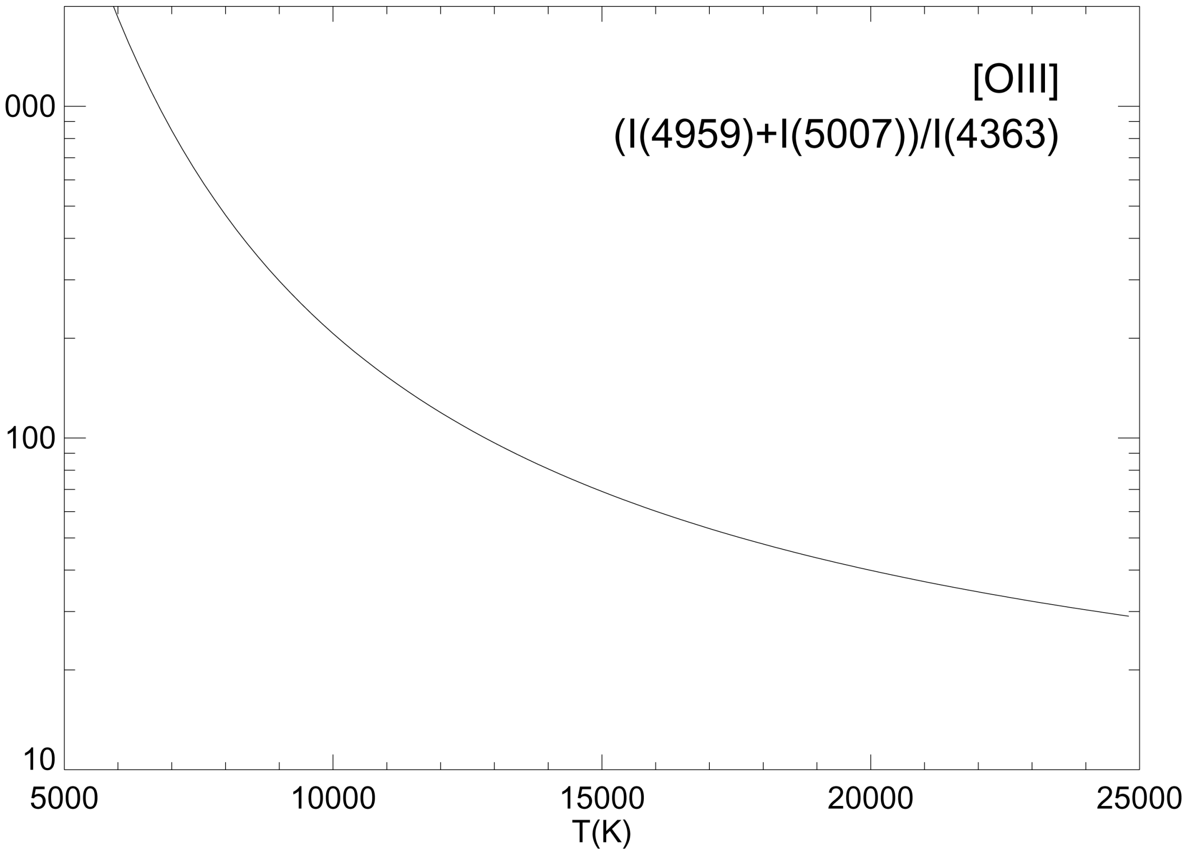




Temperature

Use two levels with different excitation energy.





$$\frac{I(4959+5007)}{4363} = \frac{7.7\exp(3.29\times 10^4/T)}{1+4.5\times 10^{-4} n_{\mathrm{e}} T^{-1/2}}$$