

# **KAIST Astrophysics (PH481) - Part 1**

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**Kwang-il Seon (선광일)**  
Korea Astronomy & Space Science Institute (KASI)  
University of Science and Technology (UST)

# Complex Atoms : Schrödinger Equation

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

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

where  $\mathbf{r}_i$  is the coordinate of the  $i$ th 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 the electron and the nucleus.
- The second term contains the electron-electron Coulomb repulsion term.
- The equation is not analytically solvable, even for the simplest case, the helium atom for which  $N = 2$ .

# Complex Atoms : Central Field Approximation

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- **Central field approximation (or orbital approximation):**

- We assume that ***each electron moves in the potential of the nucleus plus the averaged potential due to the other N - 1 electrons.***
- Within this model, the Schrodinger equation can be separated into  $N$  single electron equations:

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

- The solutions of the above equations are known as ***orbitals***. The total wave function would be written as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

- Within this approximation, each atomic orbital can be written as the product of a radial and an angular function, as to H atom.
  - ▶ The angular part is independent of the other electrons and is therefore simply a spherical harmonic.
  - ▶ However, the radial function is different from that for H atom.
- It provides a useful classification of atomic states and also a starting point.
- It is standard to use the hydrogen atom orbital labels,  $n$ ,  $l$  and  $m$ , to label the orbitals. This is called the ***configuration*** of electrons.

# Central Field Approximation: Electron Configuration

- **The configuration** is the distribution of electrons of an atom in atomic **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  $l$ .
- Each orbital labelled  $nl$  actually consists of orbitals with  $2l + 1$  different  $m$  values, each with two possible values of  $m_s$ . Thus the  $nl$  orbital can hold a maximum  $2(2l + 1)$  electrons.

- **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”.

- **open shell configuration, closed shell configuration:**

- open shell = shell that is not completely filled with electrons: For instance, the ground state configuration of carbon, which has six electrons:  $1s^2 2s^2 2p^2$
- closed shell = shell of which orbitals are fully occupied: For example, the ground state configuration of neon atom, which has ten electrons:  $1s^2 2s^2 2p^6$

- **Active electrons:** 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.***

- **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.

# Indistinguishable Particles & Parity

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

$$|\Psi(a_1, b_2)|^2 = |\Psi(a_2, b_1)|^2$$

- **Pauli exclusion principle:** 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.
  - **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.
- $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \pm \Psi(-\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_N)$
- 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.
- $$\text{parity} = (-1)^{l_1+l_2+\dots+l_N}$$
- As closed shells and sub-shells have an even number of electrons, ***it is only necessary to explicitly consider the active electrons.***

# Energy ordering & Periodic Table

- **Energy ordering for configuration:**

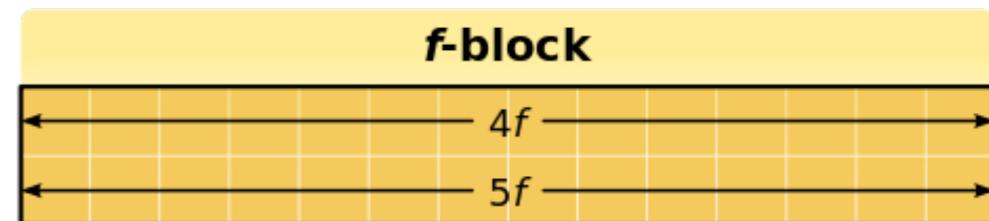
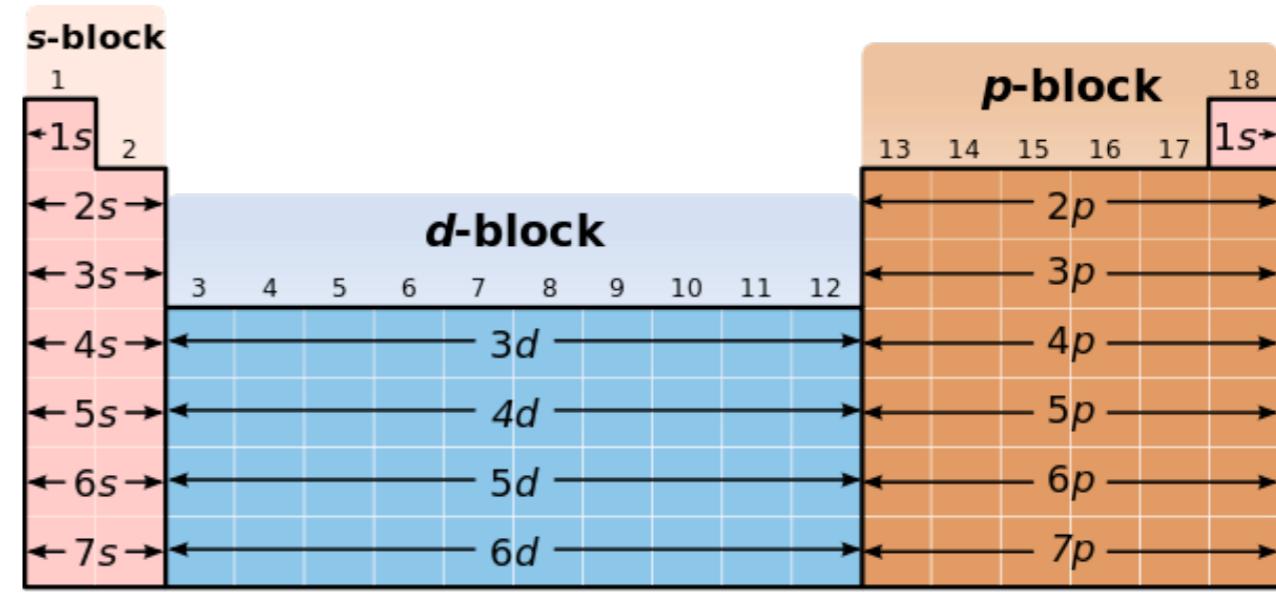
- For a H atom, the energy of the individual orbitals is determined only by principal quantum number  $n$ .
- For complex atoms, the degeneracy on the orbital angular momentum quantum number  $l$  is lifted.
- Electrons in low  $l$  orbits ‘penetrate’, i.e., get inside orbitals with lower  $n$ -values. 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.

- **Periodic Table**

- The subshell structure of elements up to argon ( $Z = 18$ ) is filled up in a naturally straightforward manner, first according to  $n$  and then according to  $l$ .
- The  $3p$  subshell is all occupied in **argon** (Ar; noble gas) with a closed subshell  $3p^6$ . The next element **potassium** (K;  $Z = 19$ ), begins by filling in the  $4s$ , instead of  $3d$ .

The orbitals of complex atoms follow a revised energy ordering:

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



Atom	Z	Configuration
hydrogen	H	1 1s
helium	He	2 1s <sup>2</sup>
lithium	Li	3 K 2s
beryllium	Be	4 K 2s <sup>2</sup>
boron	B	5 K 2s <sup>2</sup> 2p
carbon	C	6 K 2s <sup>2</sup> 2p <sup>2</sup>
nitrogen	N	7 K 2s <sup>2</sup> 2p <sup>3</sup>
oxygen	O	8 K 2s <sup>2</sup> 2p <sup>4</sup>
fluorine	F	9 K 2s <sup>2</sup> 2p <sup>5</sup>
neon	Ne	10 K 2s <sup>2</sup> 2p <sup>6</sup>
sodium	Na	11 K L 3s
magnesium	Mg	12 K L 3s <sup>2</sup>
aluminium	Al	13 K L 3s <sup>2</sup> 3p
silicon	Si	14 K L 3s <sup>2</sup> 3p <sup>2</sup>
phosphorus	P	15 K L 3s <sup>2</sup> 3p <sup>3</sup>
sulphur	S	16 K L 3s <sup>2</sup> 3p <sup>4</sup>
chlorine	Cl	17 K L 3s <sup>2</sup> 3p <sup>5</sup>
argon	Ar	18 K L 3s <sup>2</sup> 3p <sup>6</sup>
potassium	K	19 K L 3s <sup>2</sup> 3p <sup>6</sup> 4s
calcium	Ca	20 K L 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup>

# Angular Momentum

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- There are two coupling schemes or ways of summing the individual electron angular momentum to give the total angular momentum.
- $L$ - $S$  coupling (Russell-Saunders coupling):
  - The orbital and spin angular momenta are added separately to give the total angular momentum  $\mathbf{L}$  and the total spin angular momentum  $\mathbf{S}$ . These are then added to give  $\mathbf{J}$ .

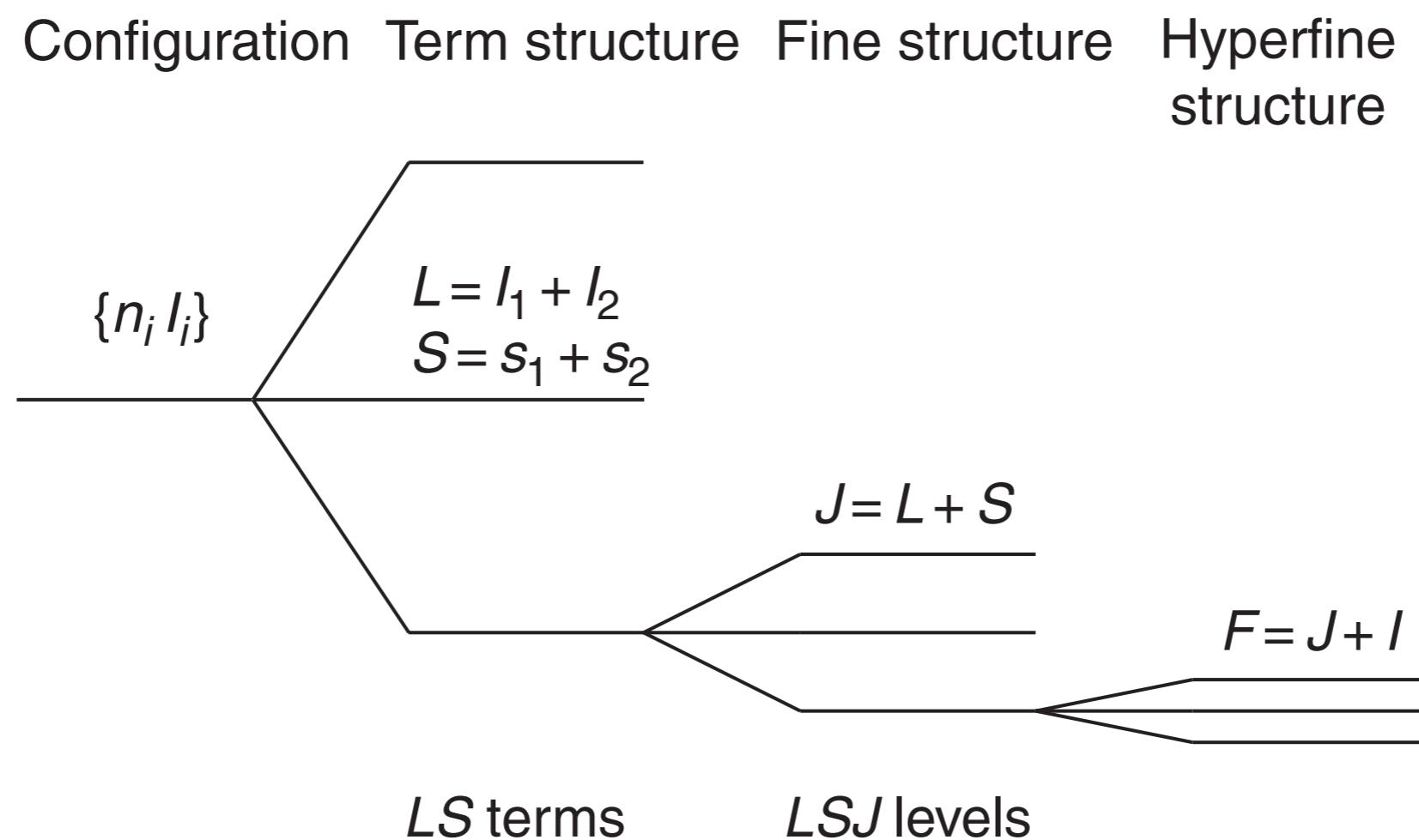
$$\mathbf{L} = \sum_i \mathbf{l}_i, \quad \mathbf{S} = \sum_i \mathbf{s}_i \quad \rightarrow \quad \mathbf{J} = \mathbf{L} + \mathbf{S}$$

- The configurations split into **terms** with particular values of  $\mathbf{L}$  and  $\mathbf{S}$ .
- $j$ - $j$  coupling
  - An alternative scheme is to consider the total angular momentum  $\mathbf{j}_i$  for each electron by combining  $\mathbf{l}_i$  and  $\mathbf{s}_i$  and then coupling these  $\mathbf{j}$ 's together to give the total angular momentum.

$$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i \quad \rightarrow \quad \mathbf{J} = \sum_i \mathbf{j}_i$$

- Why two coupling schemes?
  - They give the same results for  $\mathbf{J}$ .
  - For light atoms (lighter than iron), the values of  $\mathbf{L}$  and  $\mathbf{S}$  are approximately conserved quantities, and the  $L$ - $S$  coupling scheme is the most appropriate.
  - For heavy atoms (beyond iron),  $\mathbf{L}$  and  $\mathbf{S}$  are no longer conserved quantities and  $j$ - $j$  coupling is more appropriate.

- Electronic configuration and energy level splitting
  - Configurations  $\Rightarrow$  Terms  $\Rightarrow$  Fine Structure (Spin-Orbit Interaction)  $\Rightarrow$  Hyperfine Structure (Interaction with Nuclear Spin)



# Spectroscopic Notation

- Spectroscopic Notation**

**Total Term Spin Multiplicity:**

$S$  is vector sum of electron spins ( $\pm 1/2$  each)

Inner full shells sum to 0

**Term Parity:**

$o$  for odd, nothing for even



**Total Term Orbital Angular Momentum:**

Vector sum of contributing electron orbitals.

Inner full shells sum to 0.

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

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

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

- A state with  $S = 0$  is a ‘singlet’ as  $2S+1 = 1$ .
- A state with  $S = 1/2$  is a ‘doublet’ as  $2S+1 = 2$
- One with  $S = 1$  is a ‘triplet’ as  $2S+1 = 3$

$$n = 1, 2, 3, 4, 5 \dots \rightarrow K, L, M, N, O, \dots$$

$$\ell = 0, 1, 2, 3, 4 \dots \rightarrow s, p, d, f, g, \dots$$

$$L = 0, 1, 2, 3, 4 \dots \rightarrow S, P, D, F, G, \dots$$

sharp, principal, diffuse, fundamental,...

[Kowk, Physics and Chemistry of the ISM]

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.

[Draine, Physics of the ISM and IGM]

**Table 4.1** Terms for  $ns$  and  $np$  Subshells

Ground configuration	Terms (in order of increasing energy)	Examples
$\dots ns^1$	$^2S_{1/2}$	HI, He II, C IV, N V, O VI
$\dots ns^2$	$^1S_0$	He I, C III, N IV, O V
$\dots np^1$	$^2P_{1/2,3/2}^o$	C II, N III, O IV
$\dots np^2$	$^3P_{0,1,2}, ^1D_2, ^1S_0$	CI, N II, O III, Ne V, S III
$\dots np^3$	$^4S_{3/2}^o, ^2D_{3/2,5/2}^o, ^2P_{1/2,3/2}^o$	NI, O II, Ne IV, S II, Ar IV
$\dots np^4$	$^3P_{2,1,0}, ^1D_2, ^1S_0$	O I, Ne III, Mg V, Ar III
$\dots np^5$	$^2P_{3/2,1/2}^o$	Ne II, Na III, Mg IV, Ar IV
$\dots np^6$	$^1S_0$	Ne I, Na II, Mg III, Ar III

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

Blue: No fine structure in the ground state.

# Energy ordering for Terms and Levels

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

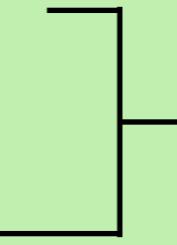
- (1) **S-rule:** For a given configuration, the state with the maximum spin multiplicity is lowest in energy. The electrons repel each other, and therefore their mutual electrostatic energy is positive. The farther away the electrons get, the lower will be the contribution of the electrostatic energy 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.



- The Hund's rules are only applicable within  $L$ - $S$  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

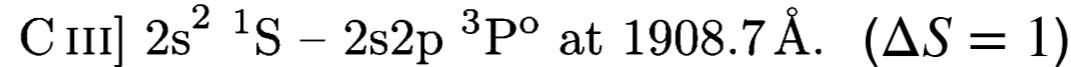
- **Selection Rules**

- |  |   |  |
|--|---|--|
| (1) one electron jumps                       |  | selection rule for configuration                               |
| (2) $\Delta n$ any                           |   |  |
| (3) $\Delta l = \pm 1$                       |   |  |
| (4) parity change                            |   |  |
| (5) $\Delta S = 0$                           |  | <i>intercombination</i> line if<br>only this rule is violated. |
| (6) $\Delta L = 0, \pm 1$ (not $L = 0 - 0$ ) |   |  |
| (7) $\Delta J = 0, \pm 1$ (not $J = 0 - 0$ ) |   |  |
| (8) $\Delta F = 0, \pm 1$ (not $F = 0 - 0$ ) |   |  |
- It is only rarely necessary to consider this.

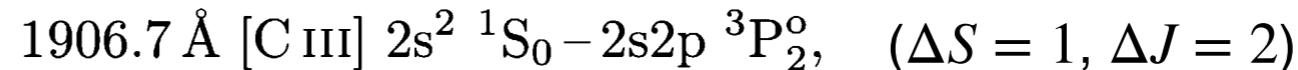
- **Allowed = Electric Dipole** : Transitions which satisfy all the above selection rules are referred to as ***allowed transitions***. These transitions are strong and have a typical lifetime of  $\sim 10^{-8}$  s. Allowed transitions are denoted without square brackets.

e.g., C IV 1548, 1550 Å

- Photons do not change spin, so transitions usually occur between terms with the same spin state ( $\Delta S = 0$ ). However, relativistic effects mix spin states, particularly for high  $Z$  atoms and ions. As a result, one can get (weak) spin changing transitions. These are called ***intercombination (semi-forbidden or intersystem) transitions*** or lines. They have a typical lifetime of  $\sim 10^{-3}$  s. An intercombination transition is denoted with a single right bracket.



- If any one of the rules 1-4, 6-8 are violated, they are called ***forbidden transitions*** or lines. They have a typical lifetime of  $\sim 1 - 10^3$  s. A forbidden transition is denoted with two square brackets.



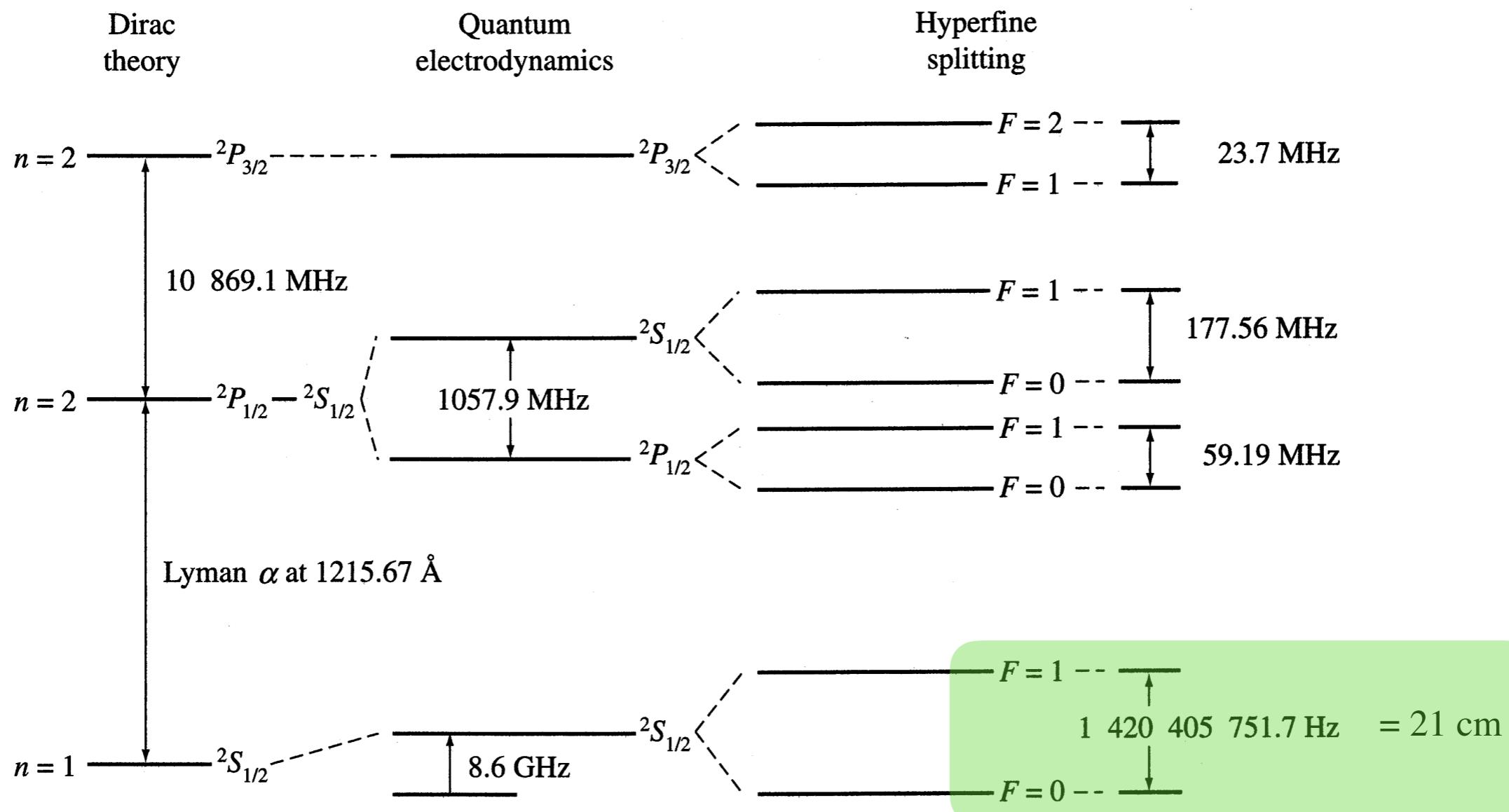
- ***Resonance line*** denotes the longest wavelength, dipole-allowed transition arising from the ground state of a particular atom or ion.

# Hydrogen Atom : Hyperfine Structure

- 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

$$F = J + I = J \pm \frac{1}{2}$$



# Hydrogen Atom : Allowed Transitions

- **Selection Rules**

- Transitions are governed by selection rules which determine whether they can occur.

$\Delta n$  any  selection rule for configuration

$\Delta l = \pm 1$

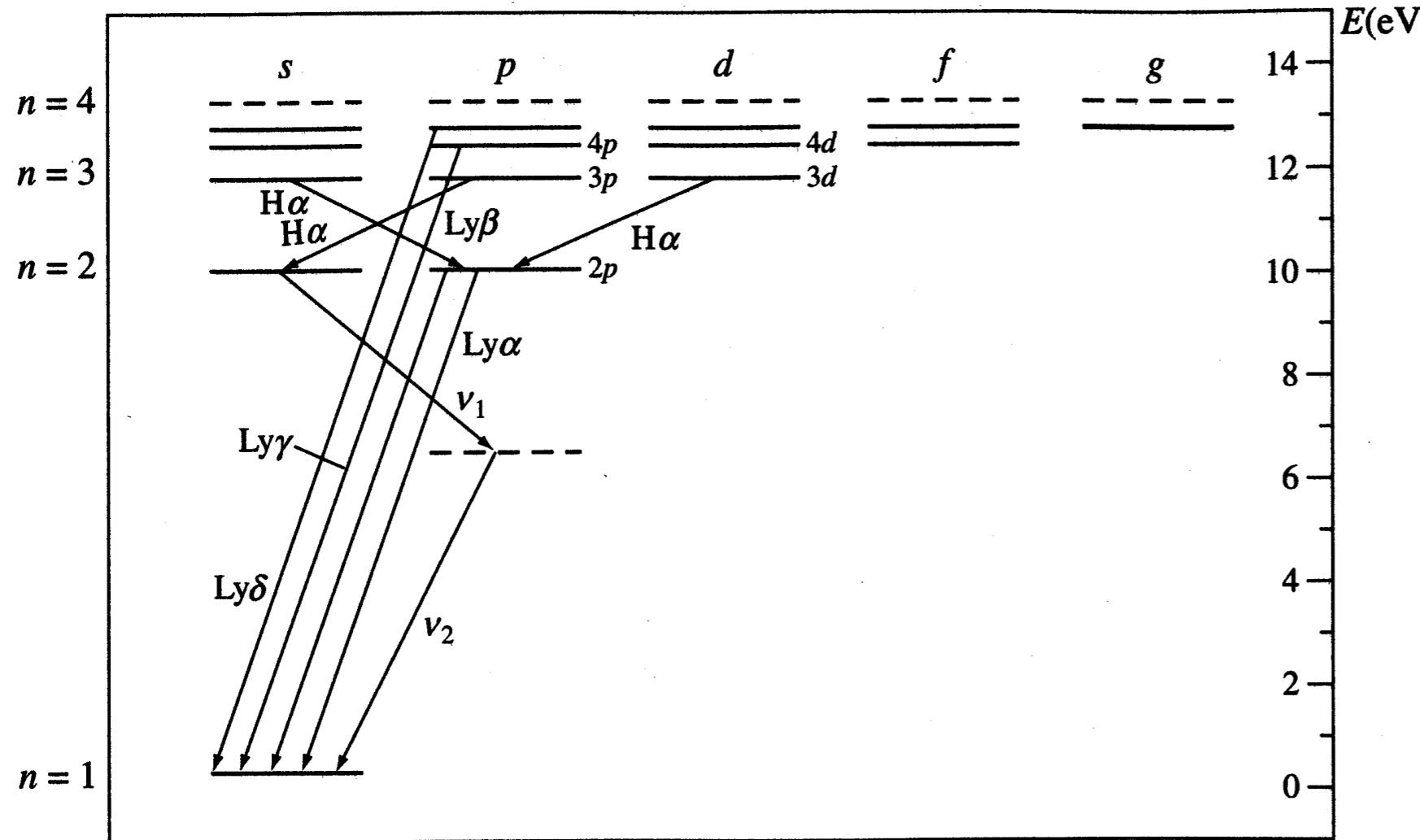
$\Delta S = 0$   For H atom, this is always satisfied as  $S = 1/2$  for all states.

$\Delta L = 0, \pm 1$  (not  $L = 0 - 0$ )

$\Delta J = 0, \pm 1$  (not  $J = 0 - 0$ )

For H-atom,  $l$  and  $L$  are equivalent since there is only one electron.

**For  $H\alpha$  transitions:**



Not all  $H\alpha$  transitions which correspond to  $n = 2 - 3$  are allowed.

$2s_{\frac{1}{2}} - 3p_{\frac{1}{2}}$  is allowed;

$- 3p_{\frac{3}{2}}$  is allowed;

$2p_{\frac{1}{2}} - 3d_{\frac{5}{2}}$  is not allowed; ( $\Delta J = 2$ )

$- 3s_{\frac{1}{2}}$  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 .

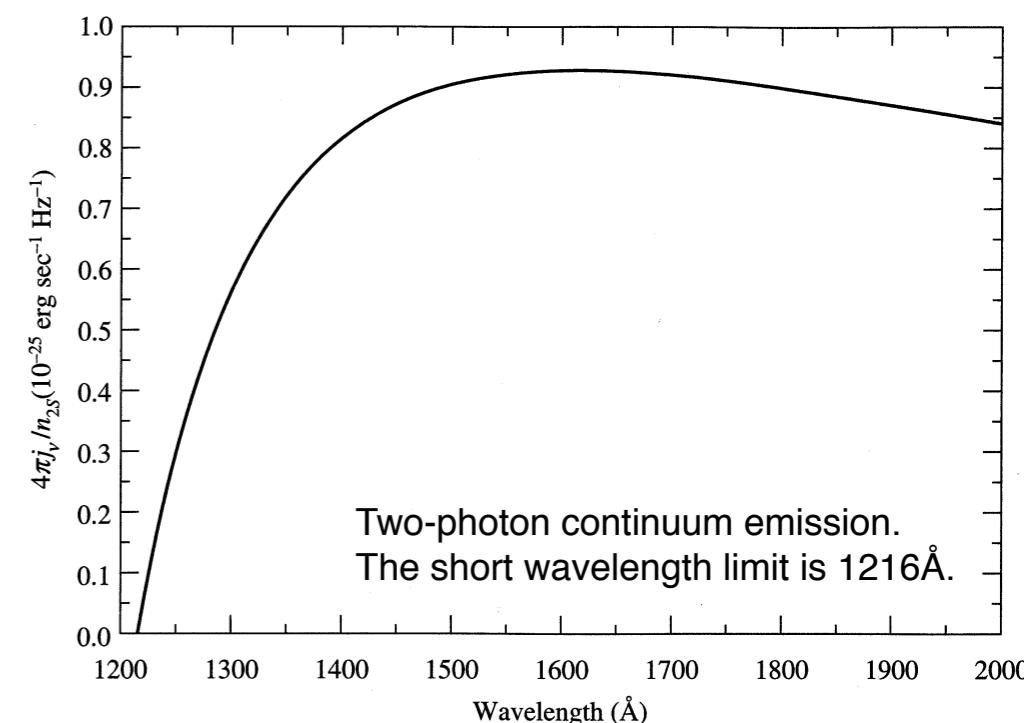
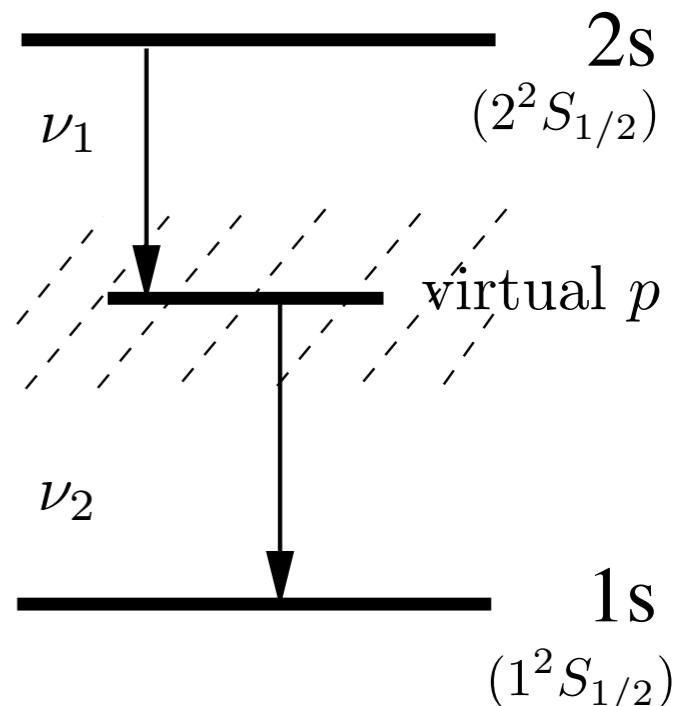
***The transition between  $2s - 1s$  is not allowed ( $\Delta l = 0$ ).***

- Hydrogen: ***lifetime of excited states***

$$\tau_i = \left( \sum_j A_{ij} \right)^{-1} \quad \text{where } A_{ij} \text{ is the Einstein A coefficient}$$

Level	2s	2p	3s	3p	3d
$\tau/\text{s}$	0.14	$1.6 \times 10^{-9}$	$1.6 \times 10^{-7}$	$5.4 \times 10^{-9}$	$2.3 \times 10^{-7}$

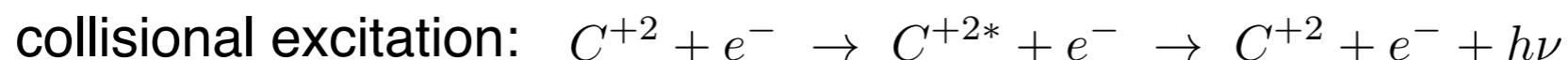
- Lifetimes for allowed transitions are short, a few times  $10^{-9}$  s.
- However, the lifetime for the (2s)  $2^2S_{1/2}$  level is  $\sim 0.14$  s, which is  $10^8$  times longer than the 2p states. (**The level is called to be metastable.**)
- Two-photon continuum radiation**
  - In low-density environments (e.g., interstellar medium), an electron in the  $2^2S_{1/2}$  level can jump to a virtual  $p$  state, which lies between  $n = 1$  and  $n = 2$  levels. The electron then jumps from this virtual state to the ground state, in the process emitting two photons with total frequency  $\nu_1 + \nu_2 = \nu_{\text{Ly}\alpha}$ .
  - Since this virtual  $p$  state can occur anywhere between  $n = 1$  and  $n = 2$ , continuum emission longward of Ly $\alpha$  will result.
  - Because the radiative lifetime of the 2s level is long, we need to consider the possibility for collisions with electrons and protons to depopulate 2s level before a spontaneous decay occurs. However, the critical density at which deexcitation by electron and proton collision is equal to the radiative decay rate is  $n_{\text{crit}} \approx 1880 \text{ cm}^{-3}$ . In the interstellar medium, the radiative decay is in general faster than the collisional depopulation process.



# Notations

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- Notations for Spectral Emission Lines and for Ions
  - There is a considerable confusion about the difference between these two ways of referring to a spectrum or ion, for example, C III or C<sup>+2</sup>. These have very definite different physical meanings. However, in many cases, they are used interchangeably.
  - C<sup>+2</sup> is a baryon and C III is a set of photons.
  - C<sup>+2</sup> refers to carbon with two electrons removed, so that is doubly ionized, with a net charge of +2.
  - C III is the spectrum produced by carbon with two electrons removed. The C III spectrum will be produced by impact excitation of C<sup>+2</sup> or by recombination of C<sup>+3</sup>. So, depending on how the spectrum is formed. C III may be emitted by C<sup>+2</sup> or C<sup>+3</sup>.



- There is no ambiguity in absorption line studies - only C<sup>+2</sup> 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.

# Example : Helium

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- (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  ${}^1S$ , and level  ${}^1S_0$ .

S	L	J
0	0	0

$${}^1S \rightarrow {}^1S_0$$

- (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.

S	L	J
0	0	0
1	0	1

$$\begin{aligned} {}^1S &\rightarrow {}^1S_0 \\ {}^3S &\rightarrow {}^3S_1 \end{aligned}$$

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

So the  ${}^3S$  term ( ${}^3S_1$  level) is lower in energy than the  ${}^1S$  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.

S	L	J
0	1	1
1	1	0, 1, 2

$$\begin{aligned} {}^1P^o &\rightarrow {}^1P_1^o \\ {}^3P^o &\rightarrow {}^3P_0^o < {}^3P_1^o < {}^3P_2^o \end{aligned}$$

Following the rule above, the  ${}^3P^o$  term is lower in energy than the  ${}^1P^o$  term, in this case by 0.25 eV.

## Example : Doubly Ionized Oxygen, O III

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Consider O III with the configuration:  $1s^2 2s^2 2p3d$ .

$1s^2$  and  $2s^2$  are closed, so they 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  $s_2 = \frac{1}{2}$ .

$$\underline{L} = \underline{l}_1 + \underline{l}_2 \Rightarrow L = 1, 2, 3;$$

$$\underline{S} = \underline{s}_1 + \underline{s}_2 \Rightarrow S = 0, 1.$$

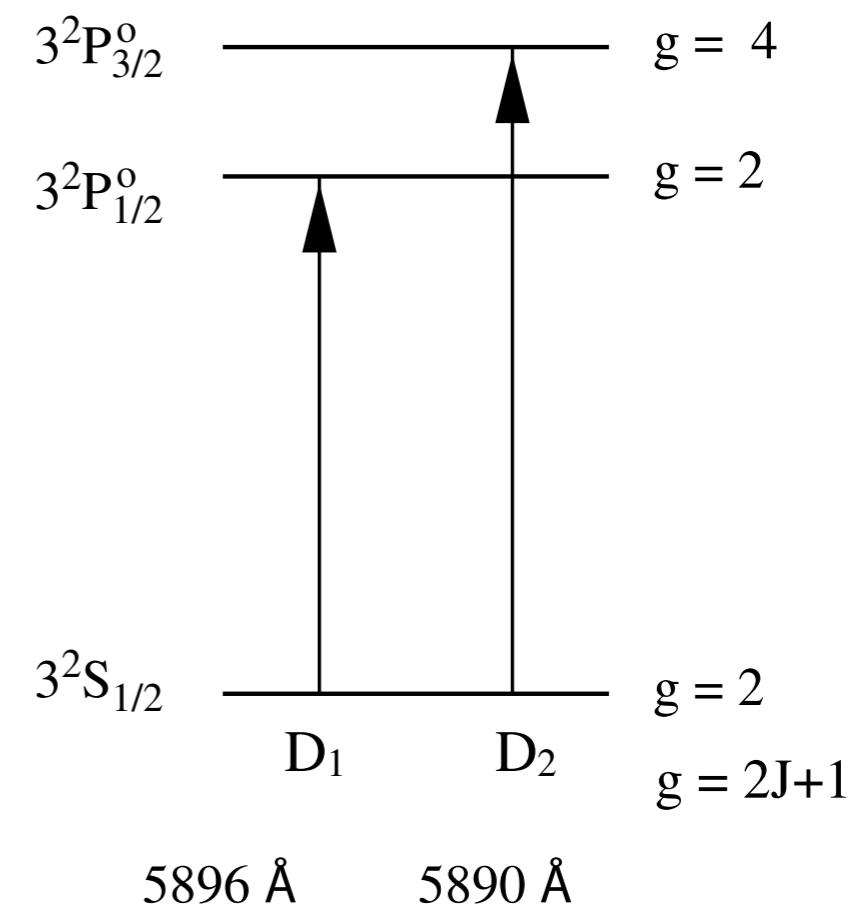
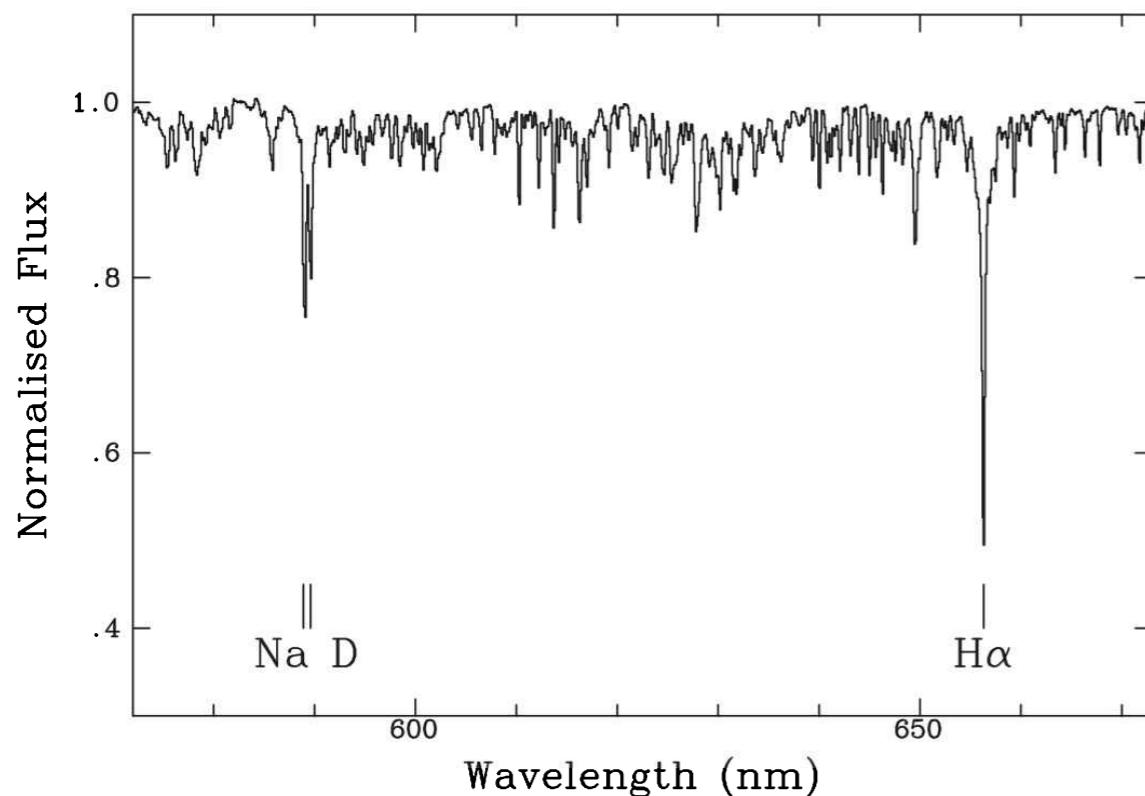
Combining these using all possible combinations of  $L$  and  $S$ , and the rules of vector addition, gives:

	$L$	$S$	$J$	Level
$\underline{J} = \underline{L} + \underline{S} \Rightarrow$	1	0	1	${}^1P_1^o$
	1	1	0, 1, 2	${}^3P_0^o, {}^3P_1^o, {}^3P_2^o$
	2	0	2	${}^1D_2^o$
	2	1	1, 2, 3	${}^3D_1^o, {}^3D_2^o, {}^3D_3^o$
	3	0	3	${}^1F_3^o$
	3	1	2, 3, 4	${}^3F_2^o, {}^3F_3^o, {}^3F_4^o$ .

In total, 6 terms and 12 levels.

## Example : Alkali Atoms

- Alkali atoms: Lithium, sodium, potassium and rubidium all have ground state electronic structures which consist of one electron in an  $s$  orbital outside a closed shell.
- Sodium (Na) : Sodium has  $Z = 11$  and a ground state configuration of  $1s^2 2s^2 2p^6 3s^1$ .



Na D lines:

$$\begin{aligned} D_1 \text{ } 5896 \text{ } \text{\AA} \text{ line} &: 3^2S_{1/2} - 3^2P_{1/2} \\ D_2 \text{ } 5890 \text{ } \text{\AA} \text{ line} &: 3^2S_{1/2} - 3^2P_{3/2} \end{aligned}$$

- 
- **Ca II (potassium-like calcium)**

H 3968.47 Å line :  $4\ ^2S_{1/2} - 4\ ^2P_{1/2}^o$

K 3933.66 Å line :  $4\ ^2S_{1/2} - 4\ ^2P_{3/2}^o$
  - **Mg II (sodium-like magnesium)**

2802.7 Å line :  $3\ ^2S_{1/2} - 3\ ^2P_{1/2}^o$

2795.5 Å line :  $3\ ^2S_{1/2} - 3\ ^2P_{3/2}^o$
  - **C IV (lithium-like carbon)**

1550.8 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{1/2}^o$

1548.2 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$
  - **N V (lithium-like nitrogen)**

1242.8 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{1/2}^o$

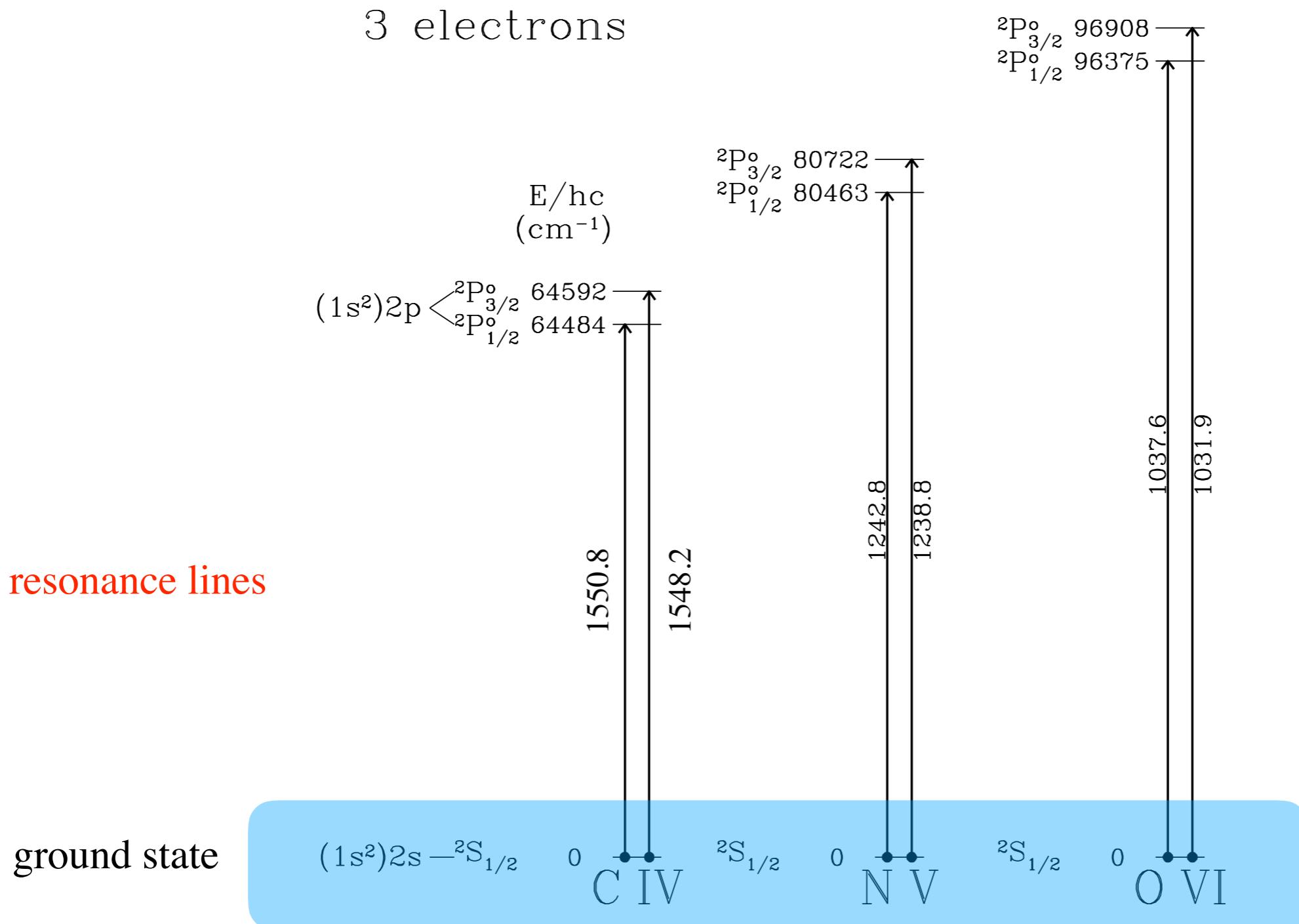
1238.8 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$
  - **O VI (lithium-like oxygen)**

1037.6 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{1/2}^o$

1031.9 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$
- 8498.0 Å line :  $4\ ^2P_{3/2}^o - 3\ ^2D_{3/2}$   
 8542.1 Å line :  $4\ ^2P_{3/2}^o - 3\ ^2D_{5/2}$   
 8662.1 Å line :  $4\ ^2P_{1/2}^o - 3\ ^2D_{3/2}$   
 (Note that  $^2P_{1/2}^o - ^2D_{5/2}$  is forbidden because  $\Delta J = 2$ .)
- 1240.4 Å line :  $3\ ^2S_{1/2} - 4\ ^2P_{1/2}^o$   
 1239.9 Å line :  $3\ ^2S_{1/2} - 4\ ^2P_{3/2}^o$

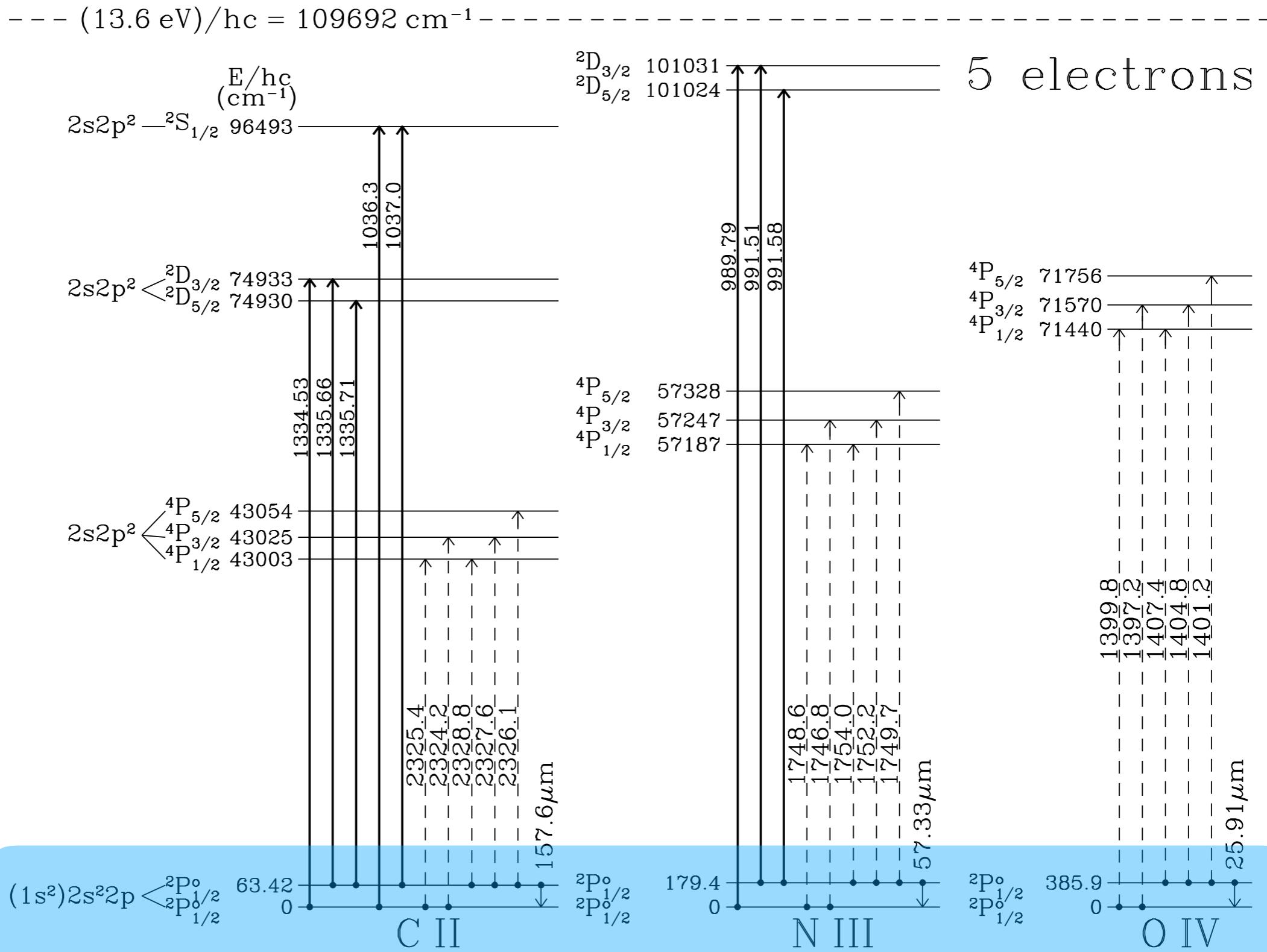
- 3 electrons (Lithium-like ions)

$$\dots (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \dots$$



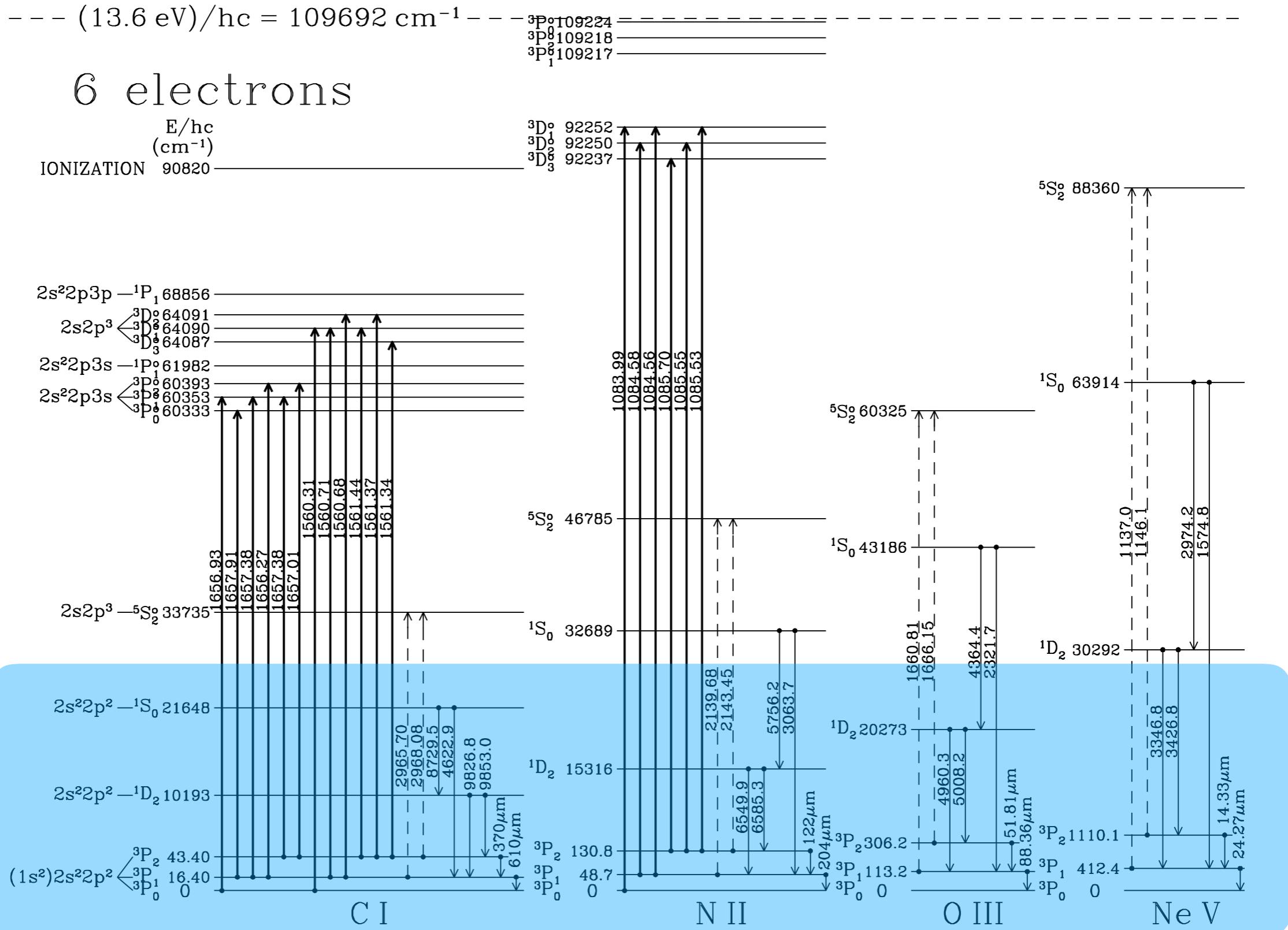
- 5 electrons

Upward heavy: resonance, Upward Dashed: intercombination  
Downward solid: forbidden



- 6 electrons

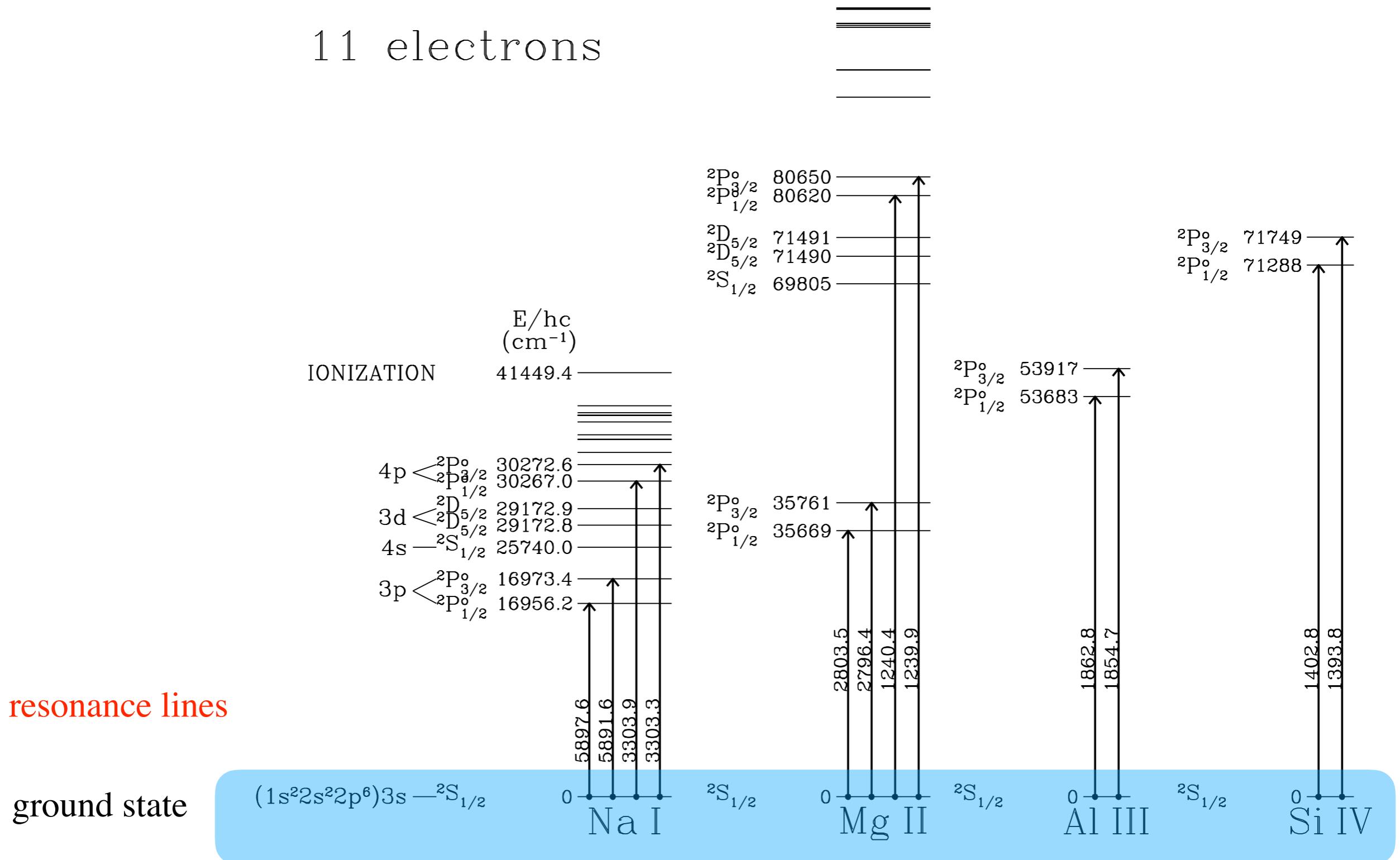
Upward heavy: resonance, Upward Dashed: intercombination  
Downward solid: forbidden



- 11 electrons

$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{ --- }$$

11 electrons



# Forbidden Lines

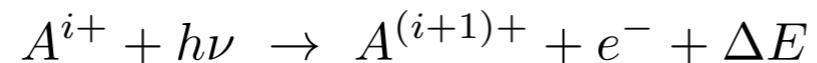
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- Forbidden lines are often difficult to study in the laboratory as collision-free conditions are needed to observe metastable states.
  - In this context, it must be remembered that laboratory ultrahigh vacuums are significantly denser than so-called dense interstellar molecular clouds.
  - ***Even in the best vacuum on Earth, frequent collisions knock the electrons out of these orbits (metastable states) before they have a chance to emit the forbidden lines.***
  - In astrophysics, low density environments are common. In these environments, the time between collisions is very long and an atom in an excited state has time to radiate even when it is metastable.
  - Forbidden lines of nitrogen ([N II] at 654.8 and 658.4 nm), sulfur ([S II] at 671.6 and 673.1 nm), and oxygen ([O II] at 372.7 nm, and [O III] at 495.9 and 500.7 nm) are commonly observed in astrophysical plasmas. ***These lines are important to the energy balance of planetary nebulae and H II regions.***
  - ***The forbidden 21-cm hydrogen line is particularly important for radio astronomy as it allows very cold neutral hydrogen gas to be seen.***
  - Since metastable states are rather common, forbidden transitions account for a significant percentage of the photons emitted by the ultra-low density gas in Universe.
  - ***Forbidden lines can account for 90% or more of the total visual brightness of objects such as emission nebulae.***

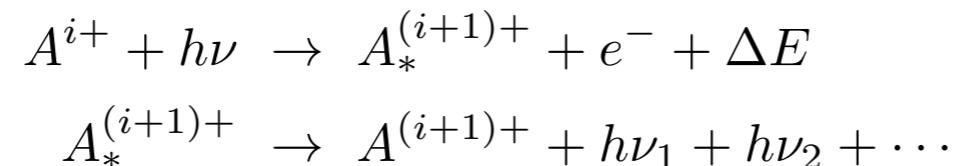
# Atomic Processes - Photoionization

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- 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.
- From the Outer Shells
  - Photoionization is the inverse process to radiative recombination.



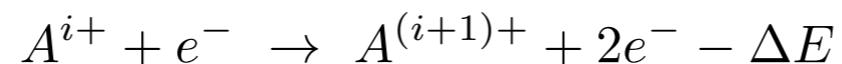
- If the incoming photon has sufficient energy, it may leave the ionized species in an excited state.



# Collisional Ionization & Recombination

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



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



- ▶ 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**.

# Ionization Equilibrium

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- Collisional Ionization Equilibrium (CIE) or coronal equilibrium
  - 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.
  - In this equilibrium, effectively, all ions are in their ground state.
- Photoionization Equilibrium:
  - dynamic balance between photo-ionization and the process of recombination.
- Ionization balance under conditions of local thermodynamic equilibrium (LTE)
  - The ionization equilibrium in LTE is described by the Saha equation.
  - In LTE, the excited states are all populated according to Boltzmann's law.

# Collisional Excitation

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- Under the conditions of very low density and weak radiation fields, as in the Interstellar Medium.
  - **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, which is frequently the case for the forbidden transitions observed in ionized astrophysical plasmas.
  - Flux of an emission line  $\propto$  Flux number of collisions  $\propto$  Product of the number densities of the two colliding species.
  - 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  $E_{12} < kT$ .  
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.
- At high enough densities,
  - The collisional timescales are shorter than the spontaneous radiative decay timescale.
  - The population in any upper level is set by the balance between collisional excitation, and the collisional de-excitation out of these levels, and are governed by the Boltzmann equilibrium.

# Emission Line Mechanisms

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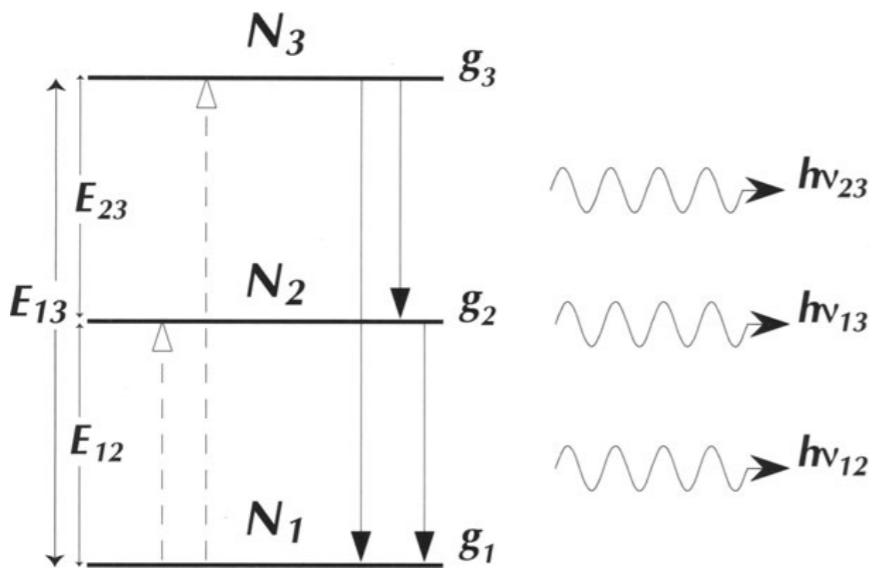
- There are three types of mechanism to create emission lines.
- ***Collisional Excitation:*** electron collisions largely populate low-lying excited states. Excitations depend on the electron temperature.
- ***Radiative Recombination:*** the cascade of emissions following the recombination of an electron with an ion leads to emissions from more highly-excited states than collisional excitations.
- ***Optical Pumping:*** this is the process of excitation from a lower level  $\ell$  by absorption of a (continuum or line) photon to an upper level  $u$ .
  - Resonance fluorescence (Bowen fluorescence): (H and He) resonance-line photons can pump other species when there is an accidental coincidence with a resonance line, resulting in specific longer-wavelength lines as part of the radiative decay cascade from the pumped level.

# Nebular Diagnostics

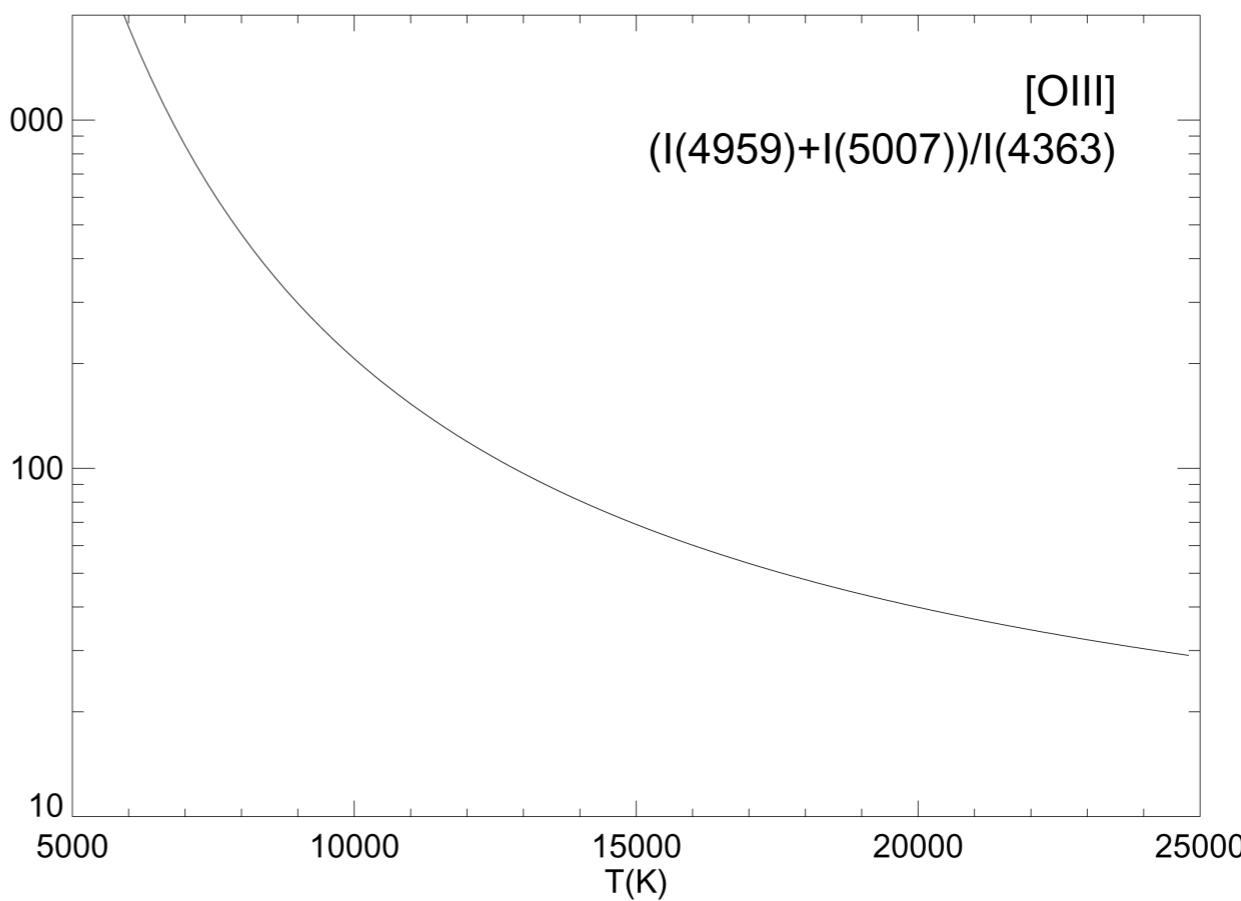
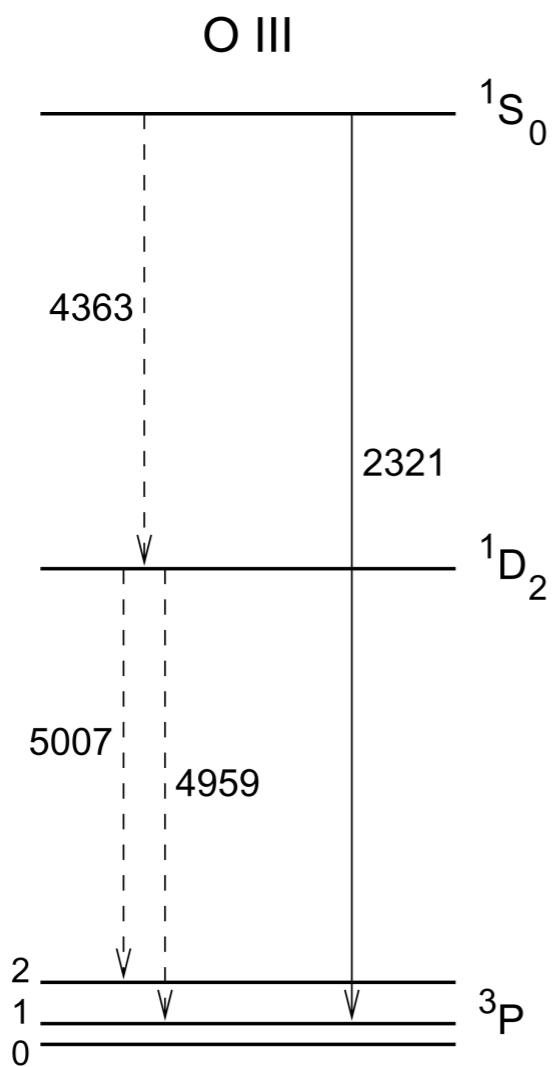
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- The populations of excited states of atoms and ions depend on the local density and temperature. Therefore, if we can determine the level populations from observations, we can use atoms and ions as probes of the interstellar space.
  - To be a useful probe, an atom or ion must be sufficiently abundant to observe, must have energy levels that are at suitable energies, and must have radiative transitions that allow us to probe these levels, either through emission lines or absorption lines.
- There are two principal type of nebular diagnostics.
  - **Temperature:** The first type uses ions with two excited levels that are both “energetically accessible” at the temperatures of interest, but ***with an energy difference between them that is comparable to  $kT$*** , so that the populations of these levels are sensitive to the gas temperature.
  - **Density:** The second type uses ions with two or more “energetically accessible” ***energy levels that are at nearly the same energy***, so that the relative rates for populating these levels by collisions are nearly independent of temperature.
    - ▶ The ratio of the level populations will have one value in the low-density limit, where every collisional excitation is followed by spontaneous radiative decay, and another value in the high-density limit, where the levels are populated by the balance between the collisional excitation and deexcitation. If the relative level populations in these two limits differ (in general, they do), then the relative level populations (determined by observed emission line ratios) can be used to determine the density in the emission region.

# Electron Temperature

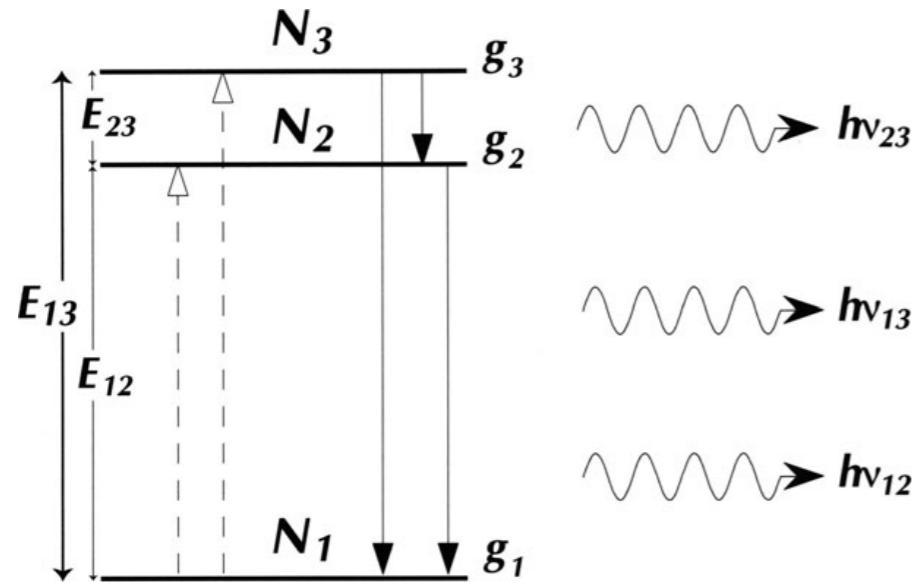


Choose an atom with two levels with different excitation energy, i.e.,  $E_{12} < E_{13}$ , but  $E_{23} \sim kT$ .

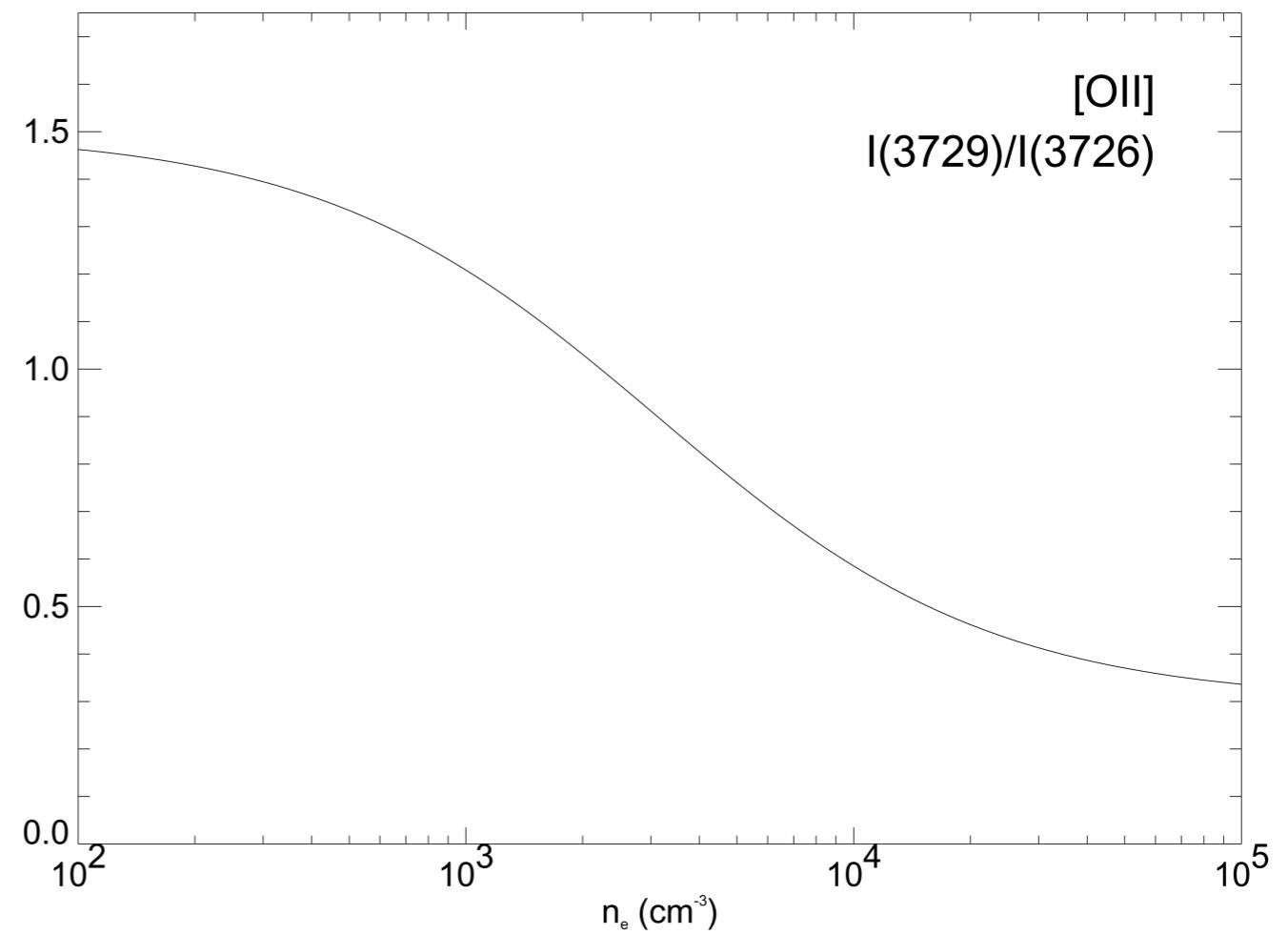
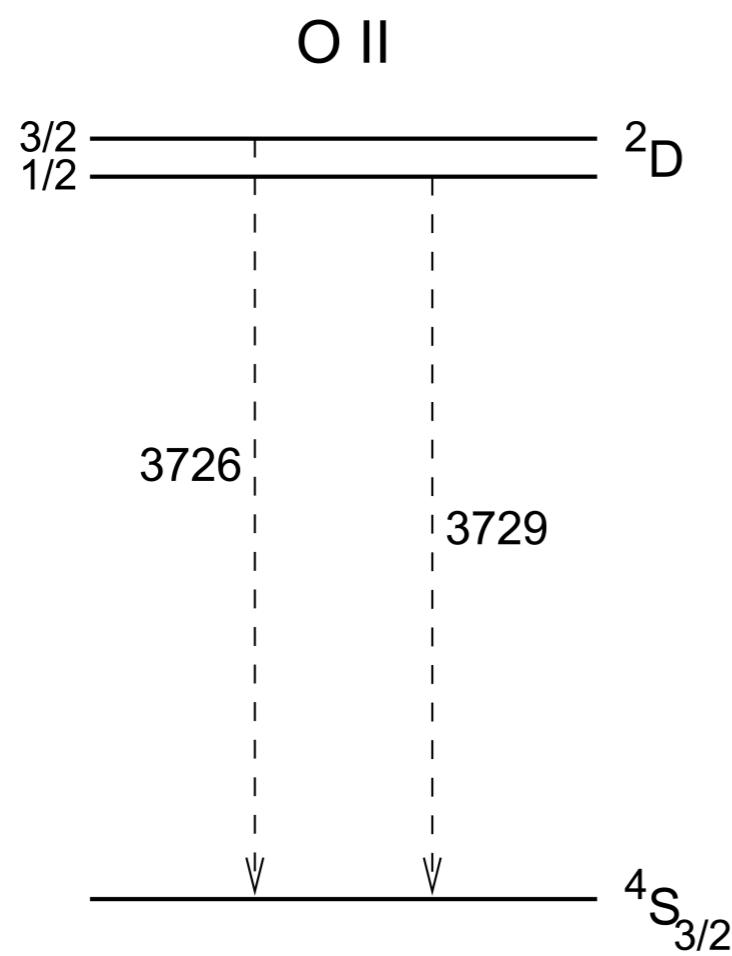


$$\frac{I(4959 + 5007)}{4363} = \frac{7.7 \exp(3.29 \times 10^4 / T)}{1 + 4.5 \times 10^{-4} n_e T^{-1/2}}$$

# Electron Density

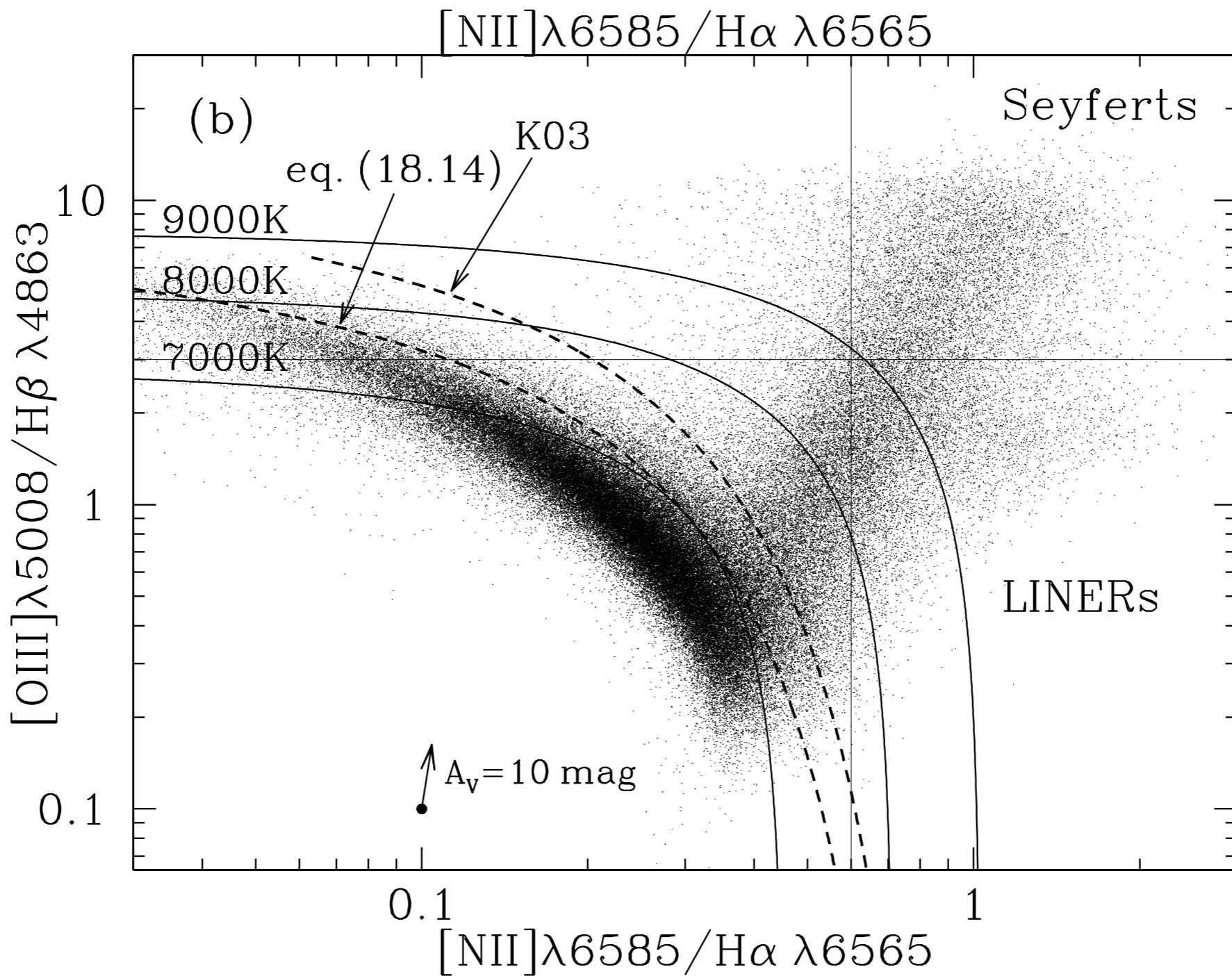


Choose an atom with two levels with almost same excitation energy i.e.,  $E_{12} \sim E_{13}$ .



# BPT diagram

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



# Homework

Deadline: 2019, Sep. 25 (Wed)

- What is the ground-state configuration, term and level of the beryllium atom, Be? One of the outer electrons in Be is promoted to the 3rd orbital. What terms and levels can this configuration have?
- Symbols for particular levels of three different atoms are written as  $^1D_1$ ,  $^0D_{3/2}$  and  $^3P_{3/2}$ . Explain in each case why the symbol must be wrong.
- The lithium atom, Li, has three electrons. Consider the following configurations of Li: (a)  $1s^22p$ , (b)  $1s2s3s$ , (c)  $1s2p3p$ . By considering the configuration only, state which of the three sets of transitions between the configuration (a), (b) and (c) are allowed and forbidden transitions?
- The figure shows the term diagram for helium-like oxygen, O VII, showing transitions from the  $1s2l$  states. Explain why  $22.1\text{\AA}$  line is an intercombination line and why  $22.8\text{\AA}$  is a forbidden line.

