

# Astrophysics

Lecture 12

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# Atomic Structure

## References

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- References for the atomic/molecular spectroscopy

Astronomical Spectroscopy [Jonathan Tennyson]

Physics and Chemistry of the Interstellar Medium [Sun Kwok]

Astrophysics of the Diffuse Universe [Michael A. Dopita & Ralph S. Sutherland]

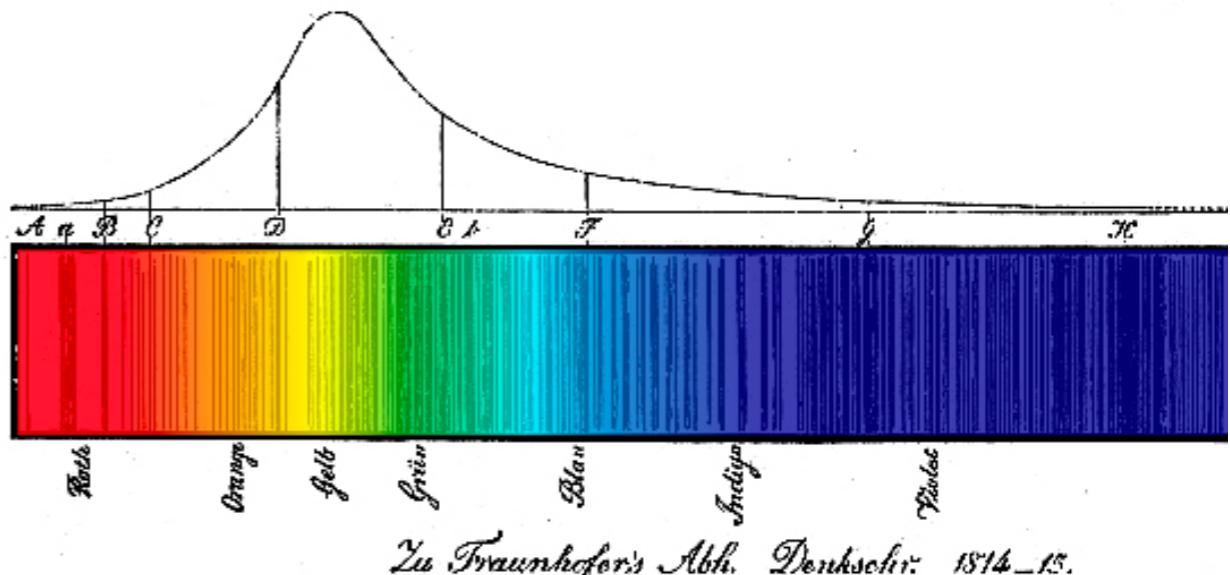
⇒ many typos

Atomic Spectroscopy and Radiative Processes [Egidio Landi Degl'Innocenti]

# History: Fraunhofer Lines

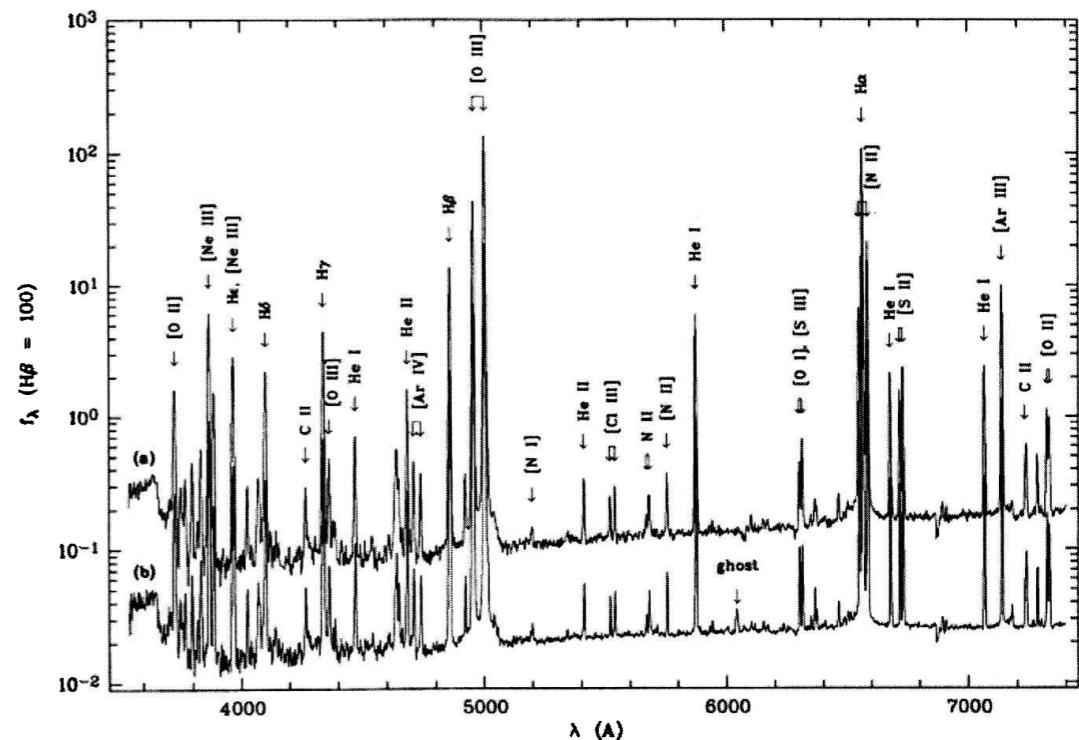
- In 1814, Joseph von Fraunhofer (1789-1826) used one of the high-quality prisms he had manufactured to diffract a beam of sunlight onto a whitewashed wall.
  - Besides the characteristic colors of the rainbow, he saw many dark lines.
  - He catalogued the exact wavelength of each dark line and labelled the strongest of them with letters. These are still known today as Fraunhofer lines. Many of these labels, such as the sodium D lines ( $5896\text{\AA}$ ,  $5890\text{\AA}$ ; Na I  $D_1$ ,  $D_2$ ) are still used today.
  - He did not know what caused the dark lines he observed.
  - However, he performed a similar experiment using light from the nearby star Betelgeuse and found that the pattern of dark lines changed significantly. He concluded correctly that most of those features were somehow related to the composition of the object.
  - The first real step in understanding Fraunhofer's observations came in the middle of the 19th century with the experiments of Gustav Kirchhoff (1824-1887) and Robert Bunsen (1811-1891). They studied the color of the light emitted when metals were burnt in flames. In certain cases, the wavelength of the emitted light gave an exact match with the Fraunhofer lines. These experiments demonstrated that the Fraunhofer lines were a direct consequence of the atomic composition of the Sun.
  - In fact, some of the lines were due to the Earth's atmosphere, the so-called telluric lines.

The solar spectrum as recorded by Fraunhofer (color overlaid).



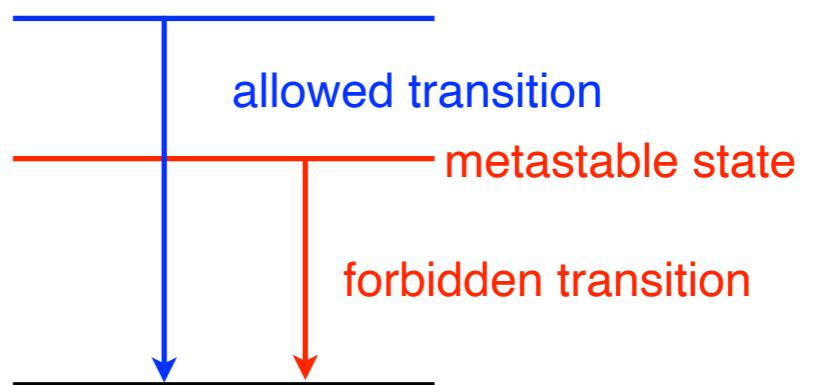
# History: Nebulium?

- In 1918, extensive studies of the emission spectra of nebulae found a series of lines which had not been observed in the laboratory.
  - Particularly strong were features at 4959Å and 5007Å. For a long time, this pair could not be identified and these lines were attributed to a new element, '**nebulium**'.
- In 1927, Ira Bowen (1898-1973) discovered that the lines were not really due to a new chemical element but instead **forbidden lines from doubly ionized oxygen** [O III].
- He realized that in the diffuse conditions found in nebulae, atoms and ions could survive a long time without undergoing collisions. Indeed, ***under typical nebula conditions the mean time between collisions is in the range 10-10,000 secs.*** This means that there is sufficient time for excited, metastable states to decay via weak, forbidden line emissions.
- The forbidden lines could not be observed in the laboratory where it was not possible to produce collision-free conditions over this long timeframe.
- Other 'nebulium' lines turned out to be forbidden lines originating from singly ionized oxygen [O II] and nitrogen [N II].



Optical spectra of NGC 6153, Liu et al. (2000, MNRAS)

[O III], [O II], [N II], etc:  
We use a pair of square  
brackets for a forbidden line.



# Quantum Mechanics

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- The classical theory of radiation is unable to treat physical processes in which the interaction between matter and radiation takes place by means of single (or a few) photons.

We have already dealt with some elementary aspects of this interaction when we discussed the Planck law and the Einstein coefficients.

However, to really solve problems we need to find explicit expressions for the A and B coefficients or equivalents.

This must involve detailed investigation of the structure of the matter that interacts with the radiation, its energy levels, and other physical properties.

- Astrophysical spectral lines offer two important insights into the workings of our Universe.

First, they are probes of the fundamental (QM) nature of matter because they originate from subatomic, atomic and molecular systems.

Second, they provide, via the Doppler effect, critical dynamical information on astrophysical systems ranging in scale from planetary system to superclusters of galaxies.

# Schrödinger Equation

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- A good starting point for a quantum mechanical understanding of spectral lines is the hydrogen atom, which is the simplest of all atoms, consisting of one proton and one electron.
- Since the H atom consists of only a proton and an electron, the Coulomb field experienced by the electron is spherically symmetric. The time-dependent Schrödinger equation for a system with Hamiltonian  $H$ :

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

Often we are interested in the stationary solutions found by separating the time and space parts of the wave function, which is possible *if  $H$  is independent of time*:

- Then, the time-independent Schrödinger equation is obtained:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{iEt/\hbar} \longrightarrow H\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$H = \frac{p^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

momentum operator:

$$\mathbf{p} = \frac{\hbar}{i}\nabla$$

Here, in the spherical coordinates, the Laplace operator is given by

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \mathcal{R} + \frac{1}{r^2} \mathcal{L}^2 \end{aligned}$$

- 
- Separation of variables: Since  $V(r)$  depends only on  $r$ , we can try something like

$$\phi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Then, the Schrödinger equation becomes

$$\left[ -\frac{\hbar^2}{2m} \mathcal{R}R(r) \right] Y(\theta, \phi) - \frac{\hbar^2}{2mr^2} [\mathcal{L}^2 Y(\theta, \phi)] R(r) + V(r)R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi)$$

→  $\frac{r^2 \mathcal{R}R(r)}{R(r)} + \frac{2mr^2}{\hbar^2} [E - V(r)] = -\frac{\mathcal{L}^2 Y(\theta, \phi)}{Y(\theta, \phi)} = \Lambda \text{ (a constant)}$

→ 
$$\begin{aligned} \mathcal{R}R(r) + \frac{2m}{\hbar^2} [E - V(r)] R(r) &= \frac{\Lambda}{r^2} R(r) \\ \mathcal{L}^2 Y(\theta, \phi) &= -\Lambda Y(\theta, \phi) \end{aligned}$$

The solution of the second equation is known to be the spherical harmonics.

$$Y(\theta, \phi) = Y_{\ell m}(\theta, \phi) \text{ and } \Lambda = \ell(\ell + 1)$$

The solution for the radial component is given by the associated Laguerre polynomials.

$$R_{n\ell}(r) = -2 \left( \frac{1}{na_0} \right)^{3/2} \sqrt{\frac{(n - \ell - 1)!}{n [(n + \ell)!]^3}} \left( \frac{2r}{na_0} \right)^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1} \left( \frac{2r}{na_0} \right)$$

# Summary of the Hydrogen atom

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- momentum operator  $\mathbf{p} = \frac{\hbar}{i}\nabla$
- Hamiltonian operator  $H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V$
- Expectation value of an operator

$$\langle F \rangle = \int \psi^* F \psi d^3x$$

- Wavefunction for a hydrogen-like atom:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

radial function:

$$R_{nl}(r) = - \left[ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right]^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

$$\rho = \frac{2Z}{na_0}r, \quad a_0 \equiv \frac{\hbar^2}{m_e c^2} = 0.529\text{\AA} \text{ (Bohr radius)},$$

$L_{n+l}^{2l+1}$  = associated Laguerre polynomial

spherical harmonics

$$Y_{lm}(\theta, \phi) = (-1)^{(m+|m|)/2} \left[ \frac{(l-|m|)!}{(l+|m|)!} \frac{2l+1}{4\pi} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{im\phi} \quad P_l^{|m|} = \text{associated Legendre function}$$

- $n = 1, 2, 3, \dots$  : principal quantum number
- $l = 0, 1, 2, \dots, n-1$  : orbital quantum number
- $m = -l, -l+1, \dots, 0, \dots, l-1, l$  : magnetic quantum number

- 
- Wavefunctions for a hydrogen-like atom

$$R_{1,0} = \left( \frac{Z}{a_0} \right)^{3/2} 2 e^{-\rho}$$

$$R_{2,0} = \left( \frac{Z}{2a_0} \right)^{3/2} 2 (1 - \rho) e^{-\rho}$$

$$R_{2,1} = \left( \frac{Z}{2a_0} \right)^{3/2} \frac{2}{\sqrt{3}} \rho e^{-\rho}$$

$$R_{3,0} = \left( \frac{Z}{3a_0} \right)^{3/2} 2 \left( 1 - 2\rho + \frac{2}{3}\rho^2 \right) e^{-\rho}$$

$$R_{3,1} = \left( \frac{Z}{3a_0} \right)^{3/2} \frac{4\sqrt{2}}{3} \rho \left( 1 - \frac{1}{2}\rho \right) e^{-\rho}$$

$$R_{3,2} = \left( \frac{Z}{3a_0} \right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \rho^2 e^{-\rho}$$

Normalisation:  $\int_0^\infty R_{n,l}^2 r^2 dr = 1$

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

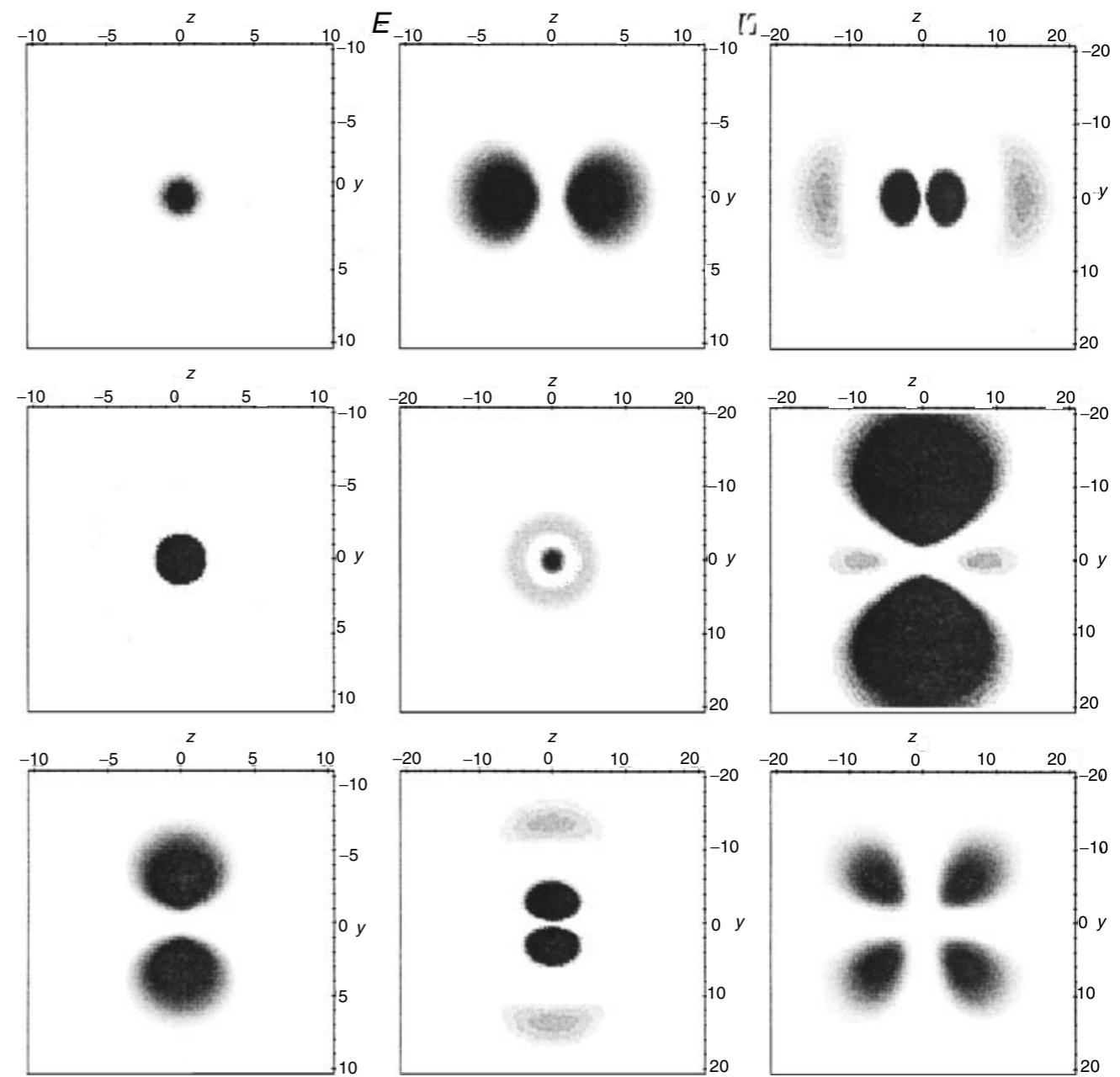
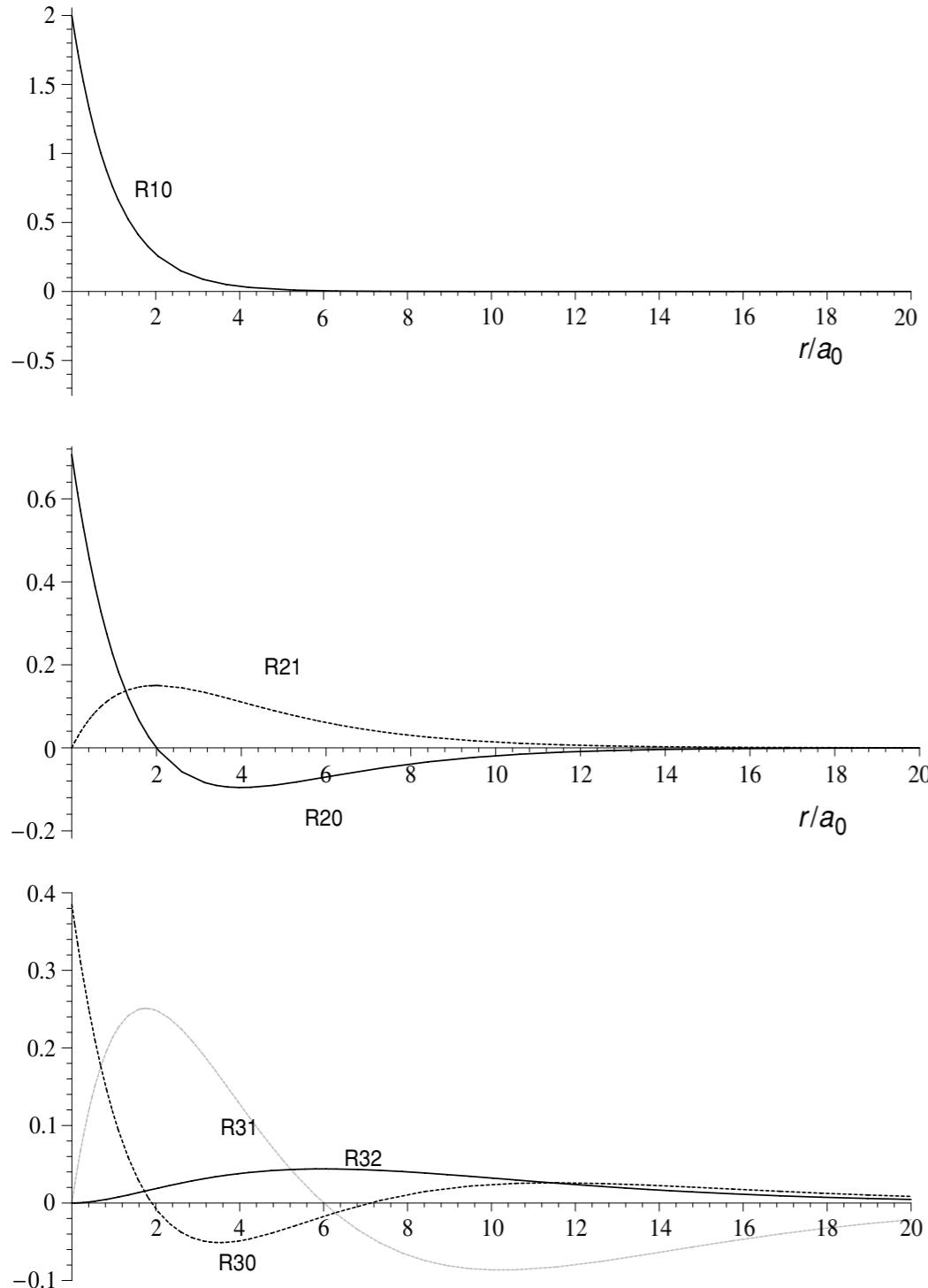
$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

Normalisation:  $\int_0^{2\pi} \int_0^\pi |Y_{l,m}|^2 \sin \theta d\theta d\phi = 1$



[Left] from top to bottom, 1s, 2s, 2p0  
 [Center] 2p1, 3s, 3p0  
 [Right] 3p1, 3d0, 3d1

- The spherical harmonics are eigenfunctions of the orbital angular momentum operator  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$

$$\mathbf{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, \quad L_z Y_{lm} = m\hbar Y_{lm}$$

- The sizes of the angular moment and z-component are  $|\mathbf{L}| = \sqrt{l(l+1)}\hbar, \quad |L_z| = m\hbar$
- Wavefunction (with  $l = 0$ ) at  $r = 0$

$$R_{10}(r) = \frac{2}{(a_0/Z)^{3/2}} e^{-r/(a_0/Z)}$$

$$R_{20}(r) = \frac{1}{(2a_0/Z)^{3/2}} \left(2 - \frac{r}{a_0/Z}\right) e^{-r/(2a_0/Z)}$$

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{1}{4\pi}}$$

$$|\psi_{n,l=0}(0)|^2 = \frac{1}{\pi} \left(\frac{Z}{na_0}\right)^3 \neq 0$$

This indicates that the electron can interact with the nucleus  $\rightarrow$  hyperfine structure!

- Probability:

$$|\psi(r, \theta, \phi)|^2 d^3x = R_{nl}^2(r) |Y_{lm}(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$$

- Properties of the spherical harmonics:

$$\int_0^\pi \int_0^{2\pi} |Y_{lm}(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1$$

$$\sum_{m=-l}^l |Y_{lm}(\theta, \phi)|^2 = \frac{2l+1}{4\pi}$$

- This implies that **closed shells are spherically symmetric and have very little interaction with external electrons.**

- Degeneracy for a given  $n$ .

$$2 \times \sum_{l=0}^{N-1} (2l + 1) = 2n^2$$

$n = 1, 2, 3, \dots$  : principal quantum number

$l = 0, 1, 2, \dots, n-1$  : orbital quantum number

$m = -l, -l+1, \dots, 0, \dots, l-1, l$  : magnetic quantum number

- Spin

The electron possesses an intrinsic angular momentum with the magnitude of  $|s| = \frac{1}{2}$ .

There are two states,  $m_s = \pm \frac{1}{2}$ , for the spin.

# Many electron systems

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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 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 solvable, even for the simplest case, the helium atom for which  $N = 2$ .

# Many-Electron Systems - [Central Field Approximation]

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- 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:

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

Note the average sign to make the potential angle-independent.

**Orbitals:** 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.

$$E = \sum_i E_i$$

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

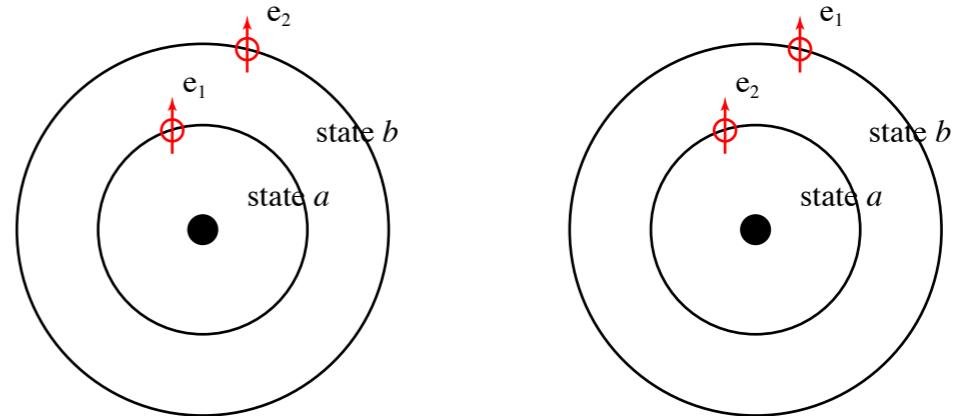
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dots\phi_N(\mathbf{r}_N)$$

## [Indistinguishable Particles]

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- 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

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



Particles 1 and 2 are indistinguishable.

The equation has two possible solutions:

- symmetric solution       $\Psi(a_1, b_2) = \Psi(a_2, b_1)$
- antisymmetric solution     $\Psi(a_1, b_2) = -\Psi(a_2, b_1)$

**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

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

**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]

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- **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  $2l+1$  different  $m$  values, each with two possible values of  $s_z$ . 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”.

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.

# [Electron Configuration]

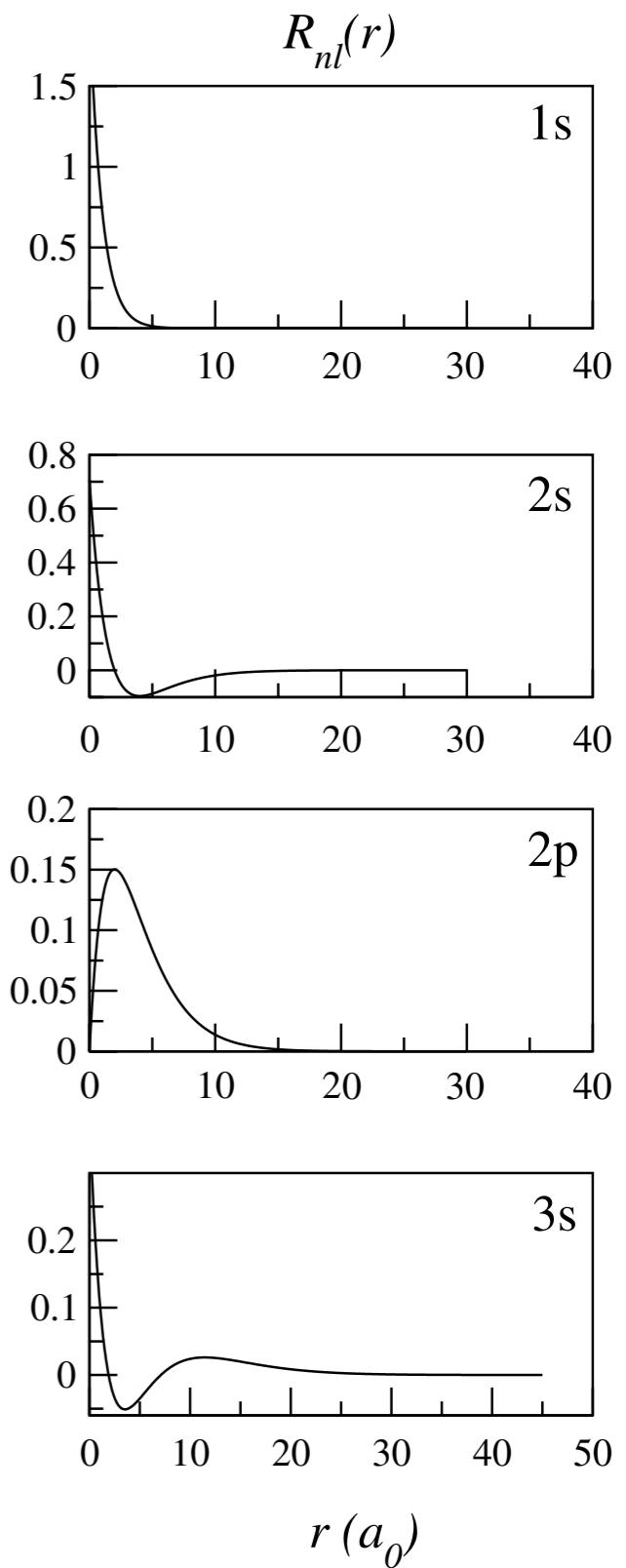
- **Energy ordering:**

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

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

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.

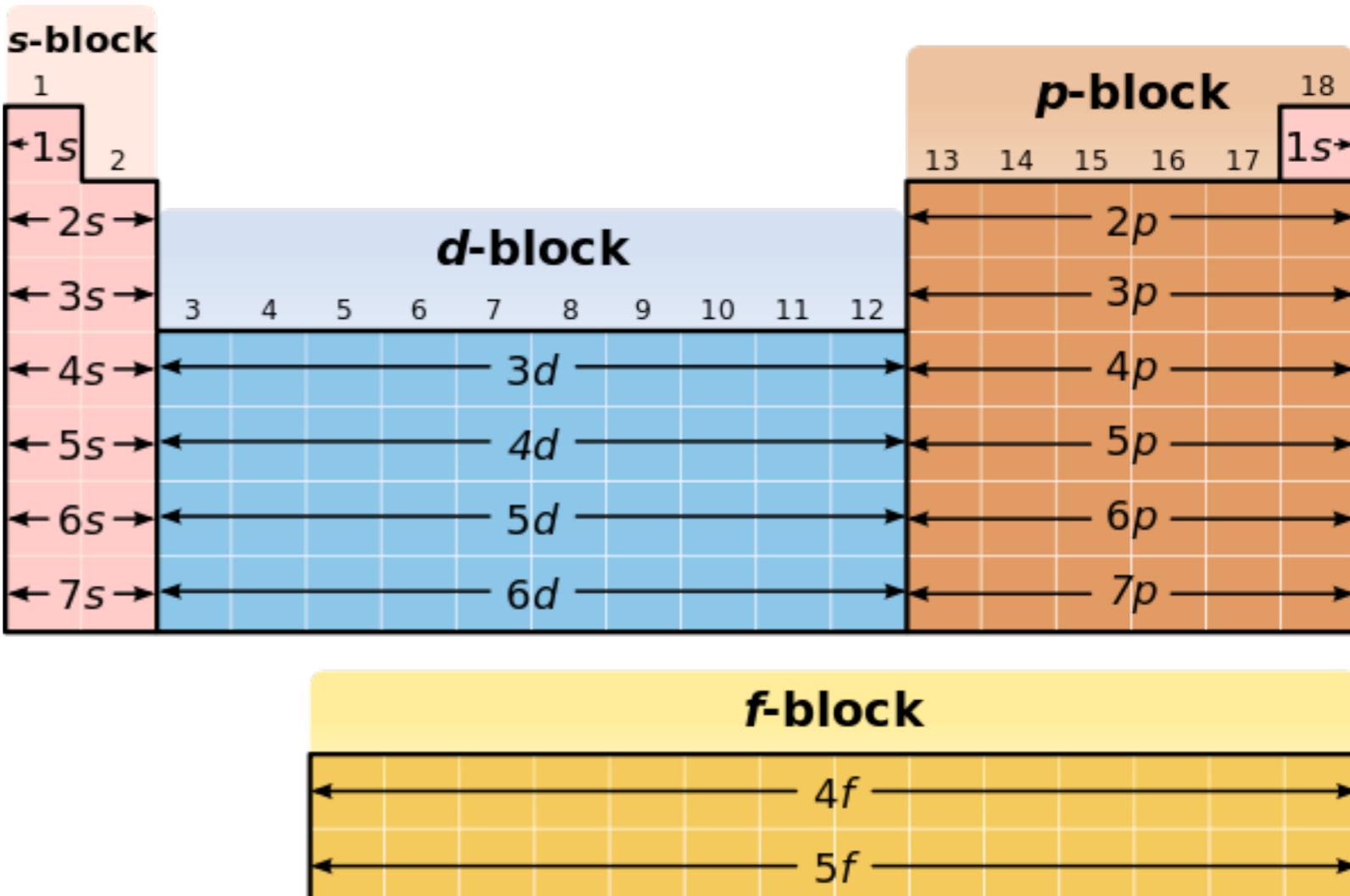
$$E(1s) < E(2s) < E(2p) < E(3s) < E(3p) < E(3d) \simeq E(4s) \dots$$



Atom	K	L	M	N	O	Ground level	
	1s	2s 2p	3s 3p 3d	4s 4p 4d	5s		
H	1	1				$^2S_1$	
He	2	2				$^1S_0$	
Li	3	2	1			$^2S_1$	
Be	4	2	2			$^1S_0$	
B	5	2	2 1			$^2P_1^0$	
C	6	2	2 2			$^3P_0$	
N	7	2	2 3			$^4S_1^0$	
O	8	2	2 4			$^3P_1$	
F	9	2	2 5			$^2P_1^0$	
Ne	10	2	2 6			$^1S_0$	
Na	11	2	2 6	1		$^2S_1$	
Mg	12			2		$^1S_0$	
Al	13			2 1		$^2P_1^0$	
Si	14	10		2 2		$^3P_0$	
P	15			2 3		$^4S_1^0$	
S	16	Ne core		2 4		$^3P_2$	
Cl	17			2 5		$^2P_1^0$	
Ar	18			2 6		$^1S_0$	
K	19	2	2 6	2 6	1	$^2S_1$	
Ca	20				2	$^1S_0$	
Sc	21			1	2	$^2D_{11}$	
Ti	22			2	2	$^3F_2$	
V	23	18		3	2	$^4F_{11}$	
Cr	24			5	1	$^7S_3$	
Mn	25	A core		5	2	$^6S_{21}$	
Fe	26			6	2	$^5D_4$	
Co	27			7	2	$^4F_{41}$	
Ni	28			8	2	$^3F_4$	
Cu	29	2	2 6	2 6	10	1	$^2S_1$
Zn	30	2	2 6			2	$^1S_0$

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 (noble gas) with a closed sub shell  $3p^6$ . The next element potassium (K) ( $Z = 19$ ), begins by filling in the 4s, instead of 3d.



# [The Electrostatic Interaction, LS coupling, Terms]

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- **The Electrostatic Interaction**

The specification of the electron configuration (the  $n, l$  values 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 Hamiltonian is

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

where  $V_i(r_i) = -\frac{Ze^2}{r_i} + \sum_{j \neq i} \left\langle \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right\rangle$

$H_0 \equiv$  central field approximation

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

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

The term  $H_{\text{es}}$  represent the residual electrostatic interaction between electrons after the averaged central field has been subtracted.

- **LS coupling (Russell-Saunders coupling): Spectroscopic Terms**

- The electrostatic interaction is the dominant splitting interaction of a configuration for many atoms (especially of low Z).
- The individual orbital angular momenta will not remain constant under this interaction, although their total  $L = \sum_i l_i$  will be constant.  
Also the sum of the spin angular momenta,  $S = \sum_i s_i$ , will be constant.
- 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 split into **terms** with particular values of L and S.
- Physical origin of the electrostatic splitting: 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.*
  - ◆ A large spin implies that the individual spins are aligned in the same direction. Then, the electrons will be further apart on the average by the nature of the Pauli principle.
  - ◆ There is a similar effect regarding the orbital angular moment. This effect is usually smaller than for the spin.

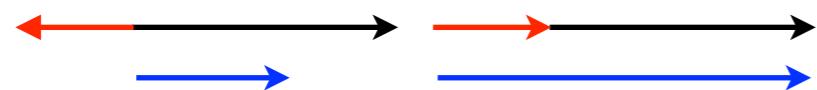
# Angular Momentum Coupling

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- Atoms contain several sources of angular momentum.
  - electron orbital angular momentum  $L$
  - electron spin angular momentum  $S$
  - nuclear spin angular momentum  $I$
  - The nuclear spin arises from the spins of nucleons. Protons and neutrons both have an intrinsic spin of a half.
- As in classical mechanics, only the total angular momentum is a conserved quantity.
  - It is therefore necessary to combine angular momenta together.
- Addition of two angular momenta:
  - The orbital and spin angular momenta are added vectorially as  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ . This gives the total electron angular momentum.
  - One then combines the total electron and nuclear spin angular momenta to give the final angular momentum  $\mathbf{F} = \mathbf{J} + \mathbf{I}$ .

- In classical mechanics, adding vector  $a$  and vector  $b$  gives a vector  $c$ , whose length must lie in the range

$$|a - b| \leq c \leq a + b \quad \text{Here, } a, b, c \text{ are the lengths of their respective vectors.}$$



$$c = |a - b| \quad c = a + b$$

- In quantum mechanics, a similar rule applies except that the results are quantized. The allowed values of the quantized angular momentum,  $c$ , span the range from the sum to the difference of  $a$  and  $b$  in steps of one:

$$c = |a - b|, |a - b| + 1, \dots, a + b - 1, a + b$$

- For example, add the two angular momenta  $L_1 = 2$  and  $L_2 = 3$  together to give  $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ . The result is

$$L = 1, 2, 3, 4, 5.$$

## [Spin-Orbit interaction, Levels, Fine Structure splitting]

---

- The fact that the remaining spin-orbit splitting is much smaller makes the LS coupling scheme a very useful one.
- 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.
- When the electron will move around the nucleus with a non relativistic velocity  $\mathbf{v}$ , the electric field exerting on the electron will be  $\mathbf{E} = Ze\frac{\mathbf{r}}{r^3}$ . (Note that the nucleus has a positive charge  $Ze$ .)

In the electron rest frame, this electric field will be perceived as a magnetic field

$$\mathbf{B}' = \mathbf{B}_\perp = \gamma(\mathbf{B}_\perp - \boldsymbol{\beta} \times \mathbf{E}) = -\frac{\mathbf{v}}{c} \times \mathbf{E}$$

$$= -\frac{Ze}{c} \frac{\mathbf{v} \times \mathbf{r}}{r^3}$$

$$= \frac{Ze}{m_e c r^3} \boldsymbol{\ell}$$

Here, the magnetic field is perpendicular to the electron's orbital plane.

(where  $\boldsymbol{\ell} \equiv \mathbf{r} \times \mathbf{p} = m_e \mathbf{r} \times \mathbf{v}$  is the electron's orbital angular momentum of electron)

- This magnetic field will interact with the electron's **magnetic moment**, which is

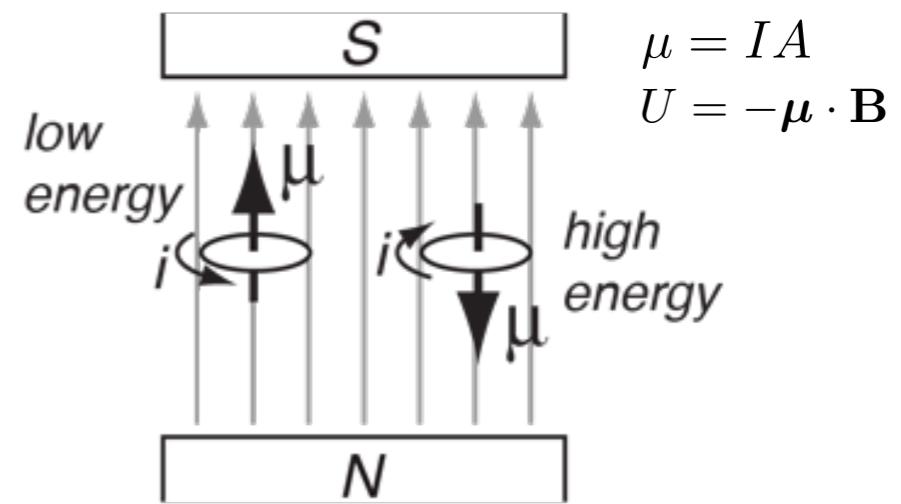
$$\boldsymbol{\mu} = -\frac{e}{m_e c} \mathbf{s}$$

- Then, the interaction energy is

$$U = -\mu \cdot \mathbf{B} = \frac{Ze^2}{m_e^2 c^2 r^3} \mathbf{s} \cdot \boldsymbol{\ell}$$

- For the sum of the interactions of all electrons will be

$$H_{\text{so}} = \sum_i \xi_i (\mathbf{s}_i \cdot \boldsymbol{\ell}_i)$$



The individual spin and orbital angular momenta may be averaged over in such a way that an equivalent interaction is simply

$$H_{\text{so}} = \xi (\mathbf{S} \cdot \mathbf{L}) \quad \text{where } \mathbf{S} = \sum_i \mathbf{s}_i, \quad \mathbf{L} = \sum_i \boldsymbol{\ell}_i$$

From the relation  $\mathbf{J}^2 = |\mathbf{L} + \mathbf{S}|^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{S} \cdot \mathbf{L}$  we obtain

$$H_{\text{so}} = \frac{1}{2} \xi (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

The eigen energy of the operator is given by  $E_{\text{so}} = \frac{1}{2} C [J(J+1) - L(L+1) - S(S+1)]$

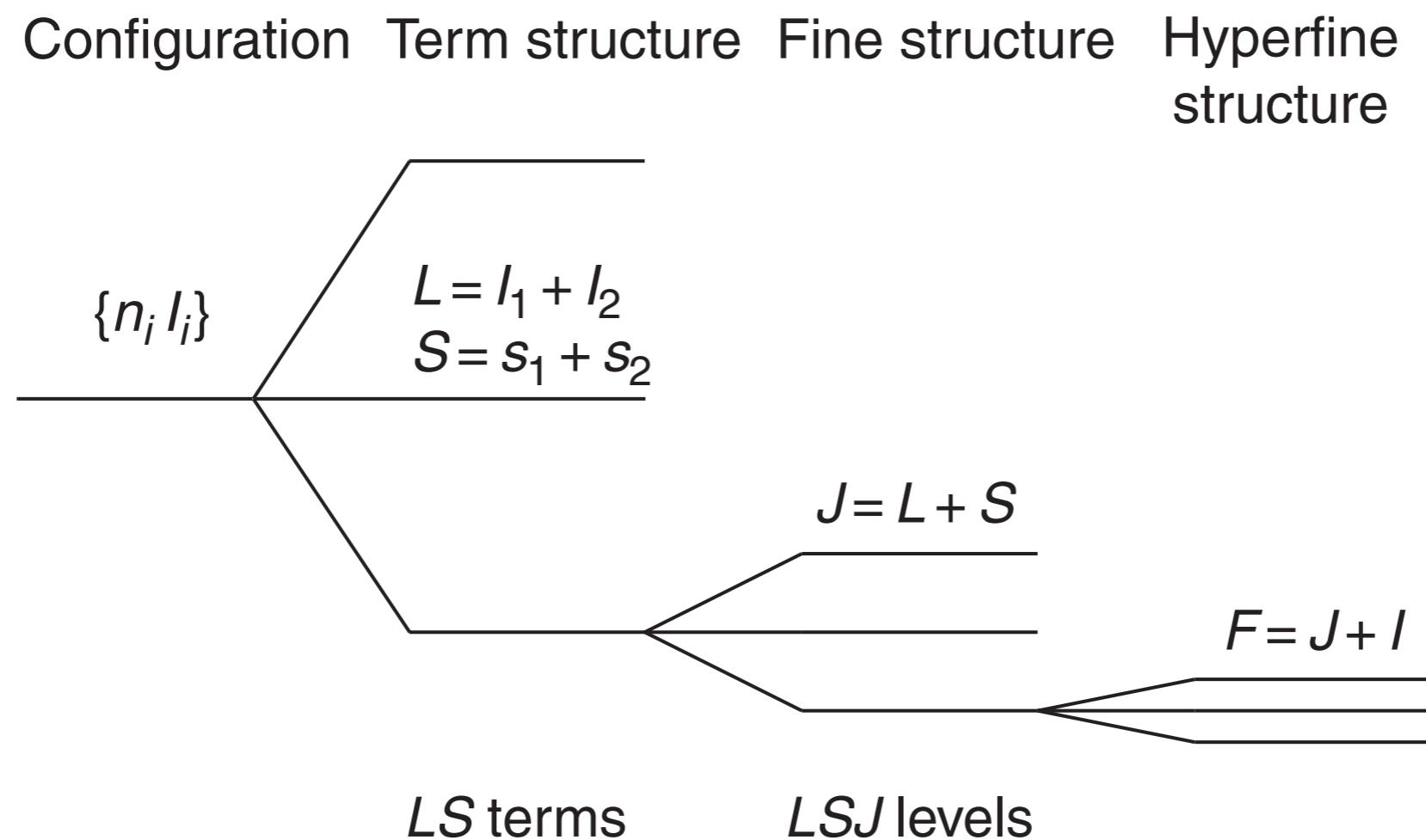
Thus, the energy difference due to the spin-orbit interaction is given by

$$\Delta E_{\text{so}} \equiv E_{\text{so}}(J+1) - E_{\text{so}}(J) = C(J+1)$$

**Lande interval rule:** the spacing between two consecutive levels of a term is proportional to the larger of the two J values involved.

- Electronic configuration and energy level splitting

Configurations  $\Rightarrow$  Terms  $\Rightarrow$  Fine Structure (Spin-Orbit Interaction)  $\Rightarrow$  Hyperfine Structure (Interaction with Nuclear Spin)



- **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.
- **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.

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

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

# [Spectroscopic Notation]

- Spectroscopic Notation

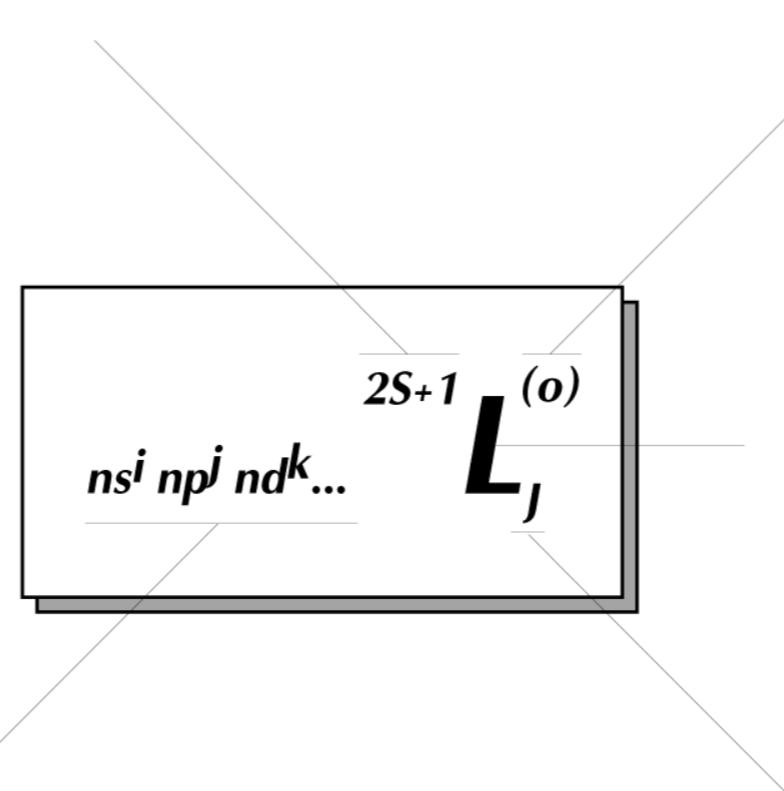
**Total Term Spin Multiplicity:**

$S$  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.

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,...

## [LS combinations]

- 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.

- For instance, consider the combination of two  $p$  electrons.

(2) If two  $p$  electrons have the same  $n$  values and thus equivalent. Then all the 36 states are not available: some are ruled out by the Pauli exclusion principle, and some are ruled out because they are not distinguishable from others.

We can find there are 15 distinguishable states allowed.

- If they have different values of  $n$  (i.e., nonequivalent electrons).

$$\begin{aligned} S = 0, 1, \quad L = 0, 1, 2 &\rightarrow {}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D \\ &\rightarrow 6 \text{ spectroscopic terms} \\ &\rightarrow 1 + 3 + 5 + 3 + 9 + 15 = 36 \\ &= (3^2 \times 2^2) \text{ distinguishable states} \end{aligned}$$

$m_{l1}$	$m_{l2}$	$m_{s1}$	$m_{s2}$	Label	$m_{l1}$	$m_{l2}$	$m_{s1}$	$m_{s2}$	Label
+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	OUT	0	-1	+	+	11
		+	-	1			+	-	12
		-	+	1			-	+	13
		-	-	OUT			-	-	14
+1	0	+	+	2	-1	+1	+	+	6
		+	-	3			+	-	8
		-	+	4			-	+	7
		-	-	5			-	-	9
+1	-1	+	+	6	-1	0	+	+	11
		+	-	7			+	-	13
		-	+	8			-	+	12
		-	-	9			-	-	14
0	+1	+	+	2	-1	-1	+	+	OUT
		+	-	4			+	-	15
		-	+	3			-	+	15
		-	-	5			-	-	OUT
0	0	+	+	OUT					
		+	-	10					
		-	+	10					
		-	-	OUT					

OUT : Pauli excluded states.

Only distinguishable states are labelled.

Label	$M_S$	$M_L$	$M_J$	Level
1	0	+2	+2	(1) $^1D_2$
2	+1	+1	+2	(2) $^3P_2$
3	0	+1	+1	(1) $^1D_2$
4	0	+1	+1	(2) $^3P_2$
5	-1	+1	0	(2) $^3P_2$
6	+1	0	+1	(3) $^3P_1$
7	0	0	0	(1) $^1D_2$
8	0	0	0	(3) $^3P_1$
9	-1	0	-1	(3) $^3P_1$
10	0	0	0	(5) $^1S_0$
11	+1	-1	0	(4) $^3P_0$
12	0	-1	-1	(1) $^1D_2$
13	0	-1	-1	(2) $^3P_2$
14	-1	-1	-2	(2) $^3P_2$
15	0	-2	-2	(1) $^1D_2$

Recall that **the total eigenfunction must be antisymmetric with respect to the exchange of two particles**. Therefore, we can have two distinct cases:

- (a) symmetric function for the spin + antisymmetric function for the orbital angular momentum  $\Rightarrow ^3P$
- (c) antisymmetric function for the spin + symmetric function for the orbital angular momentum  $\Rightarrow ^1S, ^1D$

- We must now compare these states with the states expected in the  $LS$  multiplet:  $^1S_0, ^1P_1, ^1D_2, ^3S_1, ^3P_{0,1,2}, ^3D_{1,2,3}$ .
- Of these, we immediately see that  $^3D_3$  state cannot be present, since this would require  $M_J$  values of +3 and -3. This in turn rules out the presence of  $^3D_2$  and  $^3D_1$ , since if one possible combination of a given  $L$  and  $S$  is present, all must be.
- State 1 can come only from an  $LS$  term having  $L \geq 2$  and  $S \geq 0$ ; from this we conclude that the  $^1D_2$  term must be present.
- State 2 requires the present of an  $LS$  term with  $L \geq 1$  and  $S \geq 1$ . Of the available combinations, this requires that  $^3P_{0,1,2}$  be present.
- We now found how many independent  $LS$  terms are known to be present. We have from  $^3P_{0,1,2}$ ,  $1+3+5 = 9$  states; from  $^1D_2$ , 5 states; a total of 14.
- Those states require  $M_J$  values of +2, +1, 0, -1, -2; +1, 0, -1; 0; and +2, +1, 0, -1, -2, respectively.
- These account for all of the  $M_J$  values in the table except for one, whose  $M_J$  value is zero. This then requires  $^1S_0$ , to be present.  
 $\Rightarrow$  Finally, we obtain  $^1S_0, ^1D_2, ^3P_{0,1,2}$ .

(Example 1)  $4p4d$  electron configuration

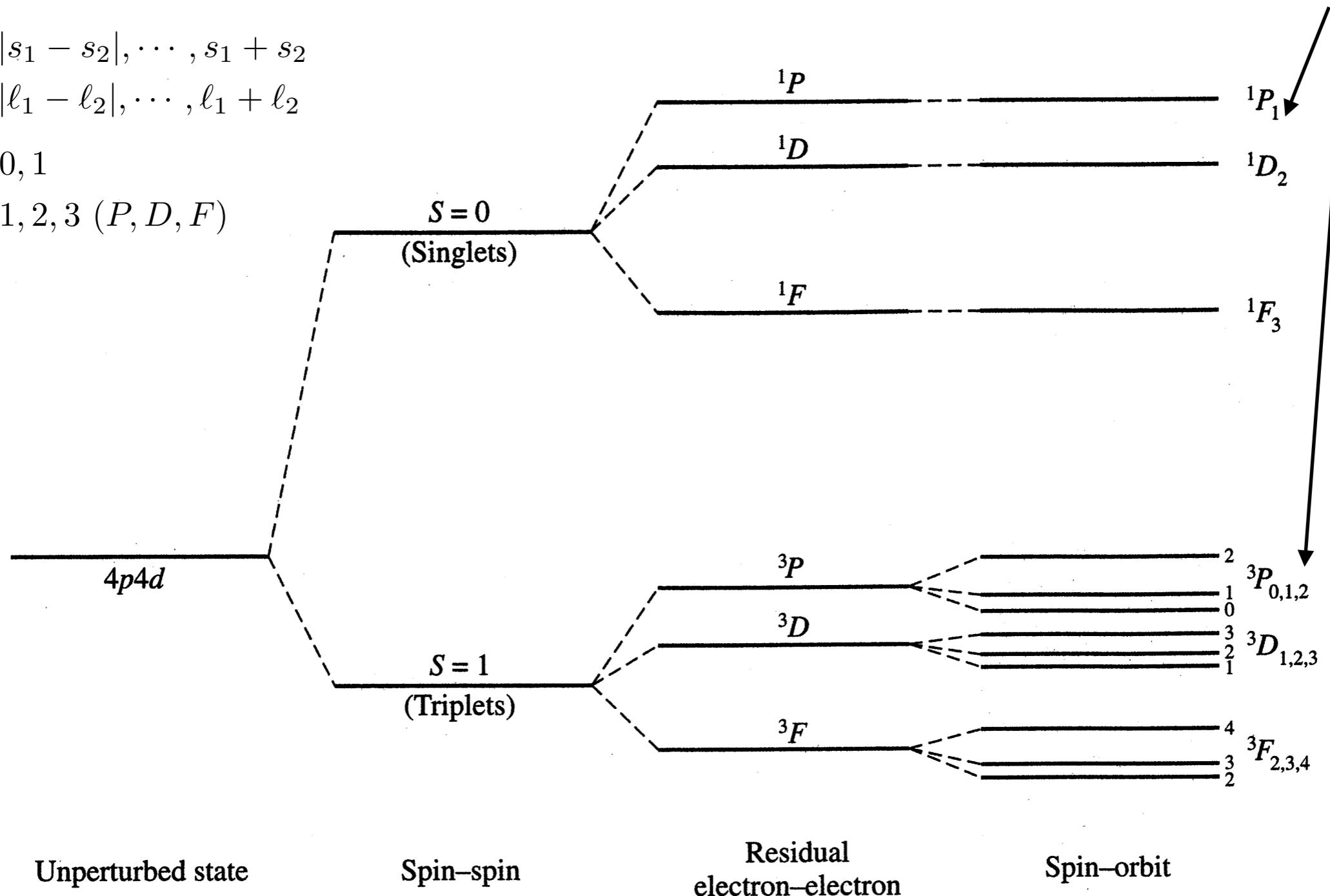
$$J = |L - S|, \dots, L + S$$

$$S = |s_1 - s_2|, \dots, s_1 + s_2$$

$$L = |\ell_1 - \ell_2|, \dots, \ell_1 + \ell_2$$

$$S = 0, 1$$

$$L = 1, 2, 3 \ (P, D, F)$$



(Example 2)  $nnp'p$  electron configuration

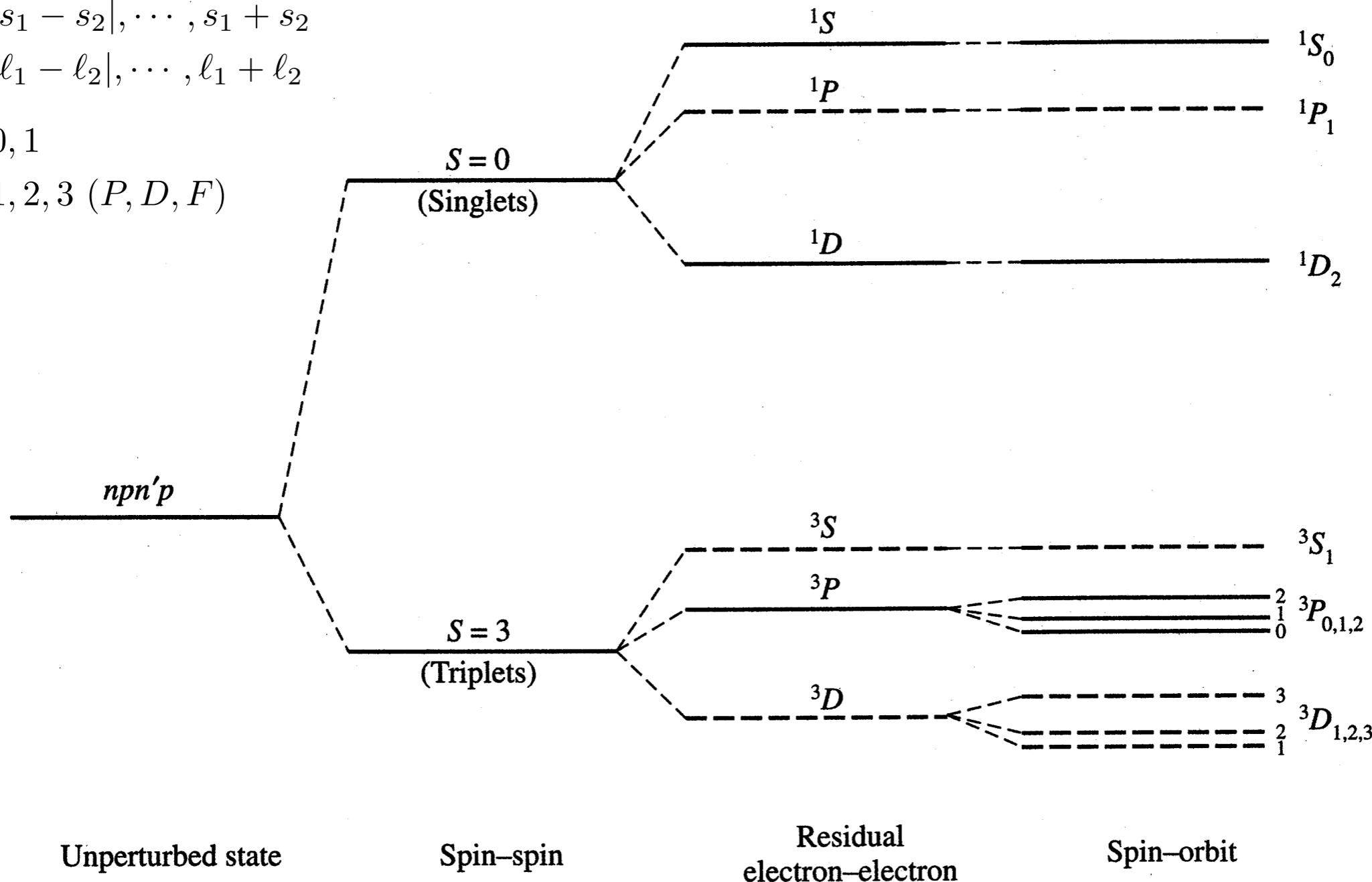
The dashed levels are missing if the two electrons are equivalent ( $n = n'$ )

$$S = |s_1 - s_2|, \dots, s_1 + s_2$$

$$L = |\ell_1 - \ell_2|, \dots, \ell_1 + \ell_2$$

$$S = 0, 1$$

$$L = 1, 2, 3 \text{ } (P, D, F)$$



[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	$^2P_{3/2}^o$
Ar	18			2	6	$^1S_0$
K	19	2	2	6	2	$^2S_{1/2}$
Ca	20				2	$^1S_0$
Sc	21				1	2
Ti	22				2	2
V	23		18	3	2	$^4F_{1/2}$
Cr	24			5	1	$^7S_3$
Mn	25		A core	5	2	$^6S_{2/1}$
Fe	26			6	2	$^5D_4$
Co	27			7	2	$^4F_{3/2}$
Ni	28			8	2	$^3F_4$
Cu	29	2	2	6	10	$^2S_{1/2}$
Zn	30				2	$^1S_0$

Blue: No fine structure in the ground state.

## [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.

$${}^3P_0 < {}^3P_1 < {}^3P_2 \text{ for carbon } (1s^2 2s^2 2p^2)$$

$${}^3P_2 < {}^3P_1 < {}^3P_0 \text{ for oxygen } (1s^2 2s^2 2p^4)$$

- 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.

- 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  ${}^1S$ , 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 atomic 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  ${}^3S$  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.

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:  ${}^3P_0^o$ ,  ${}^3P_1^o$  and  ${}^3P_2^o$ .

---

- O III

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:

$J = \underline{L} + \underline{S} \Rightarrow$	$L$	$S$	$J$	Level
	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	${}^3F_2^o, {}^3F_3^o, {}^3F_4^o$

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

=> 6 terms and 12 levels

## [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. e.g., C IV 1548, 1550 Å
- (2) Intercombination lines violate rule 4. e.g., C III] 1908.7 Å
- (3) Forbidden lines violate rule 5 and/or 6. Electric quadrupole and magnetic dipole transitions are also described as forbidden. e.g., [N II] 6585 Å, [S II] 6716 Å, [C II] 157 μm

---

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 $\Delta n$ any $\Delta l = \pm 1$	One or no electron jumps $\Delta n$ 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 $L = 0 - 0, 0 - 1$	$\Delta L = 0$

---

## [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  $1s^2 2s^2 2p^6 3s^1$  .

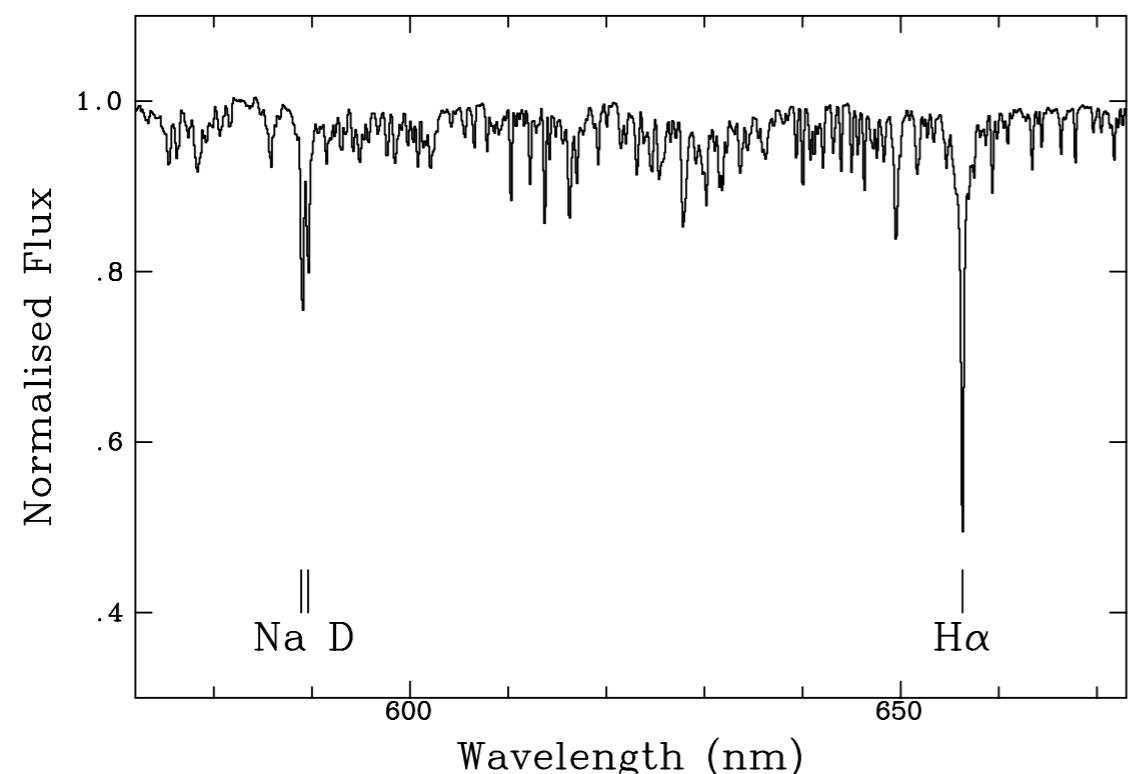
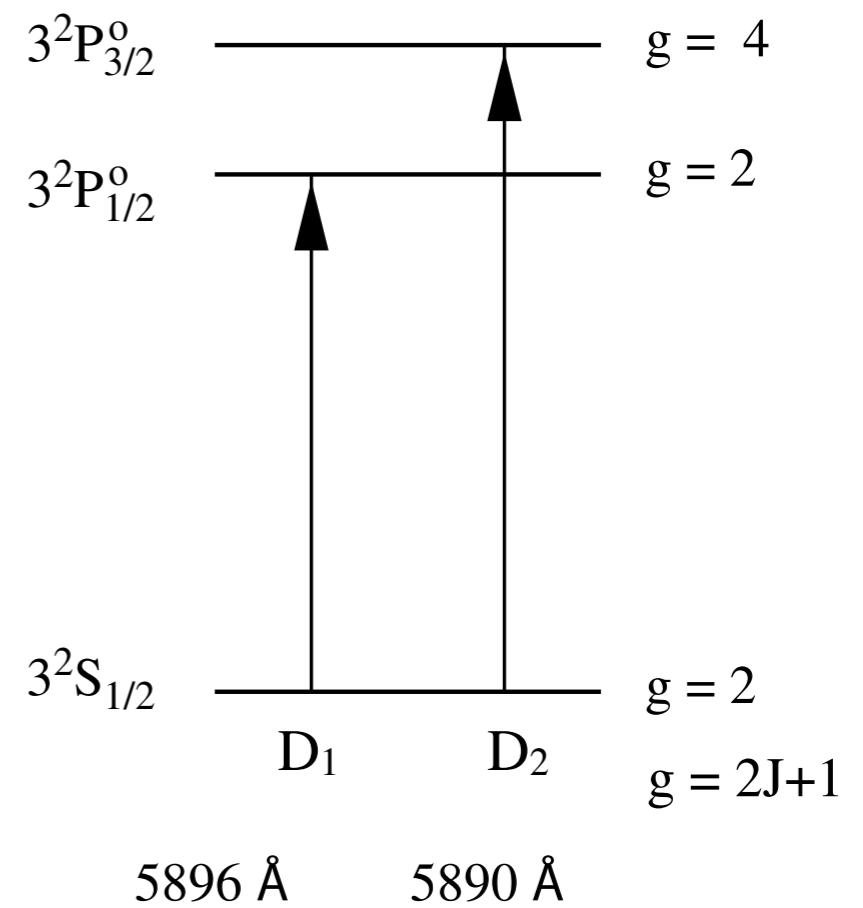


Fig. 6.6. A solar spectrum reflected from the Moon just before a lunar eclipse taken at the University of London Observatory. (S.J. Boyle, private communication.)



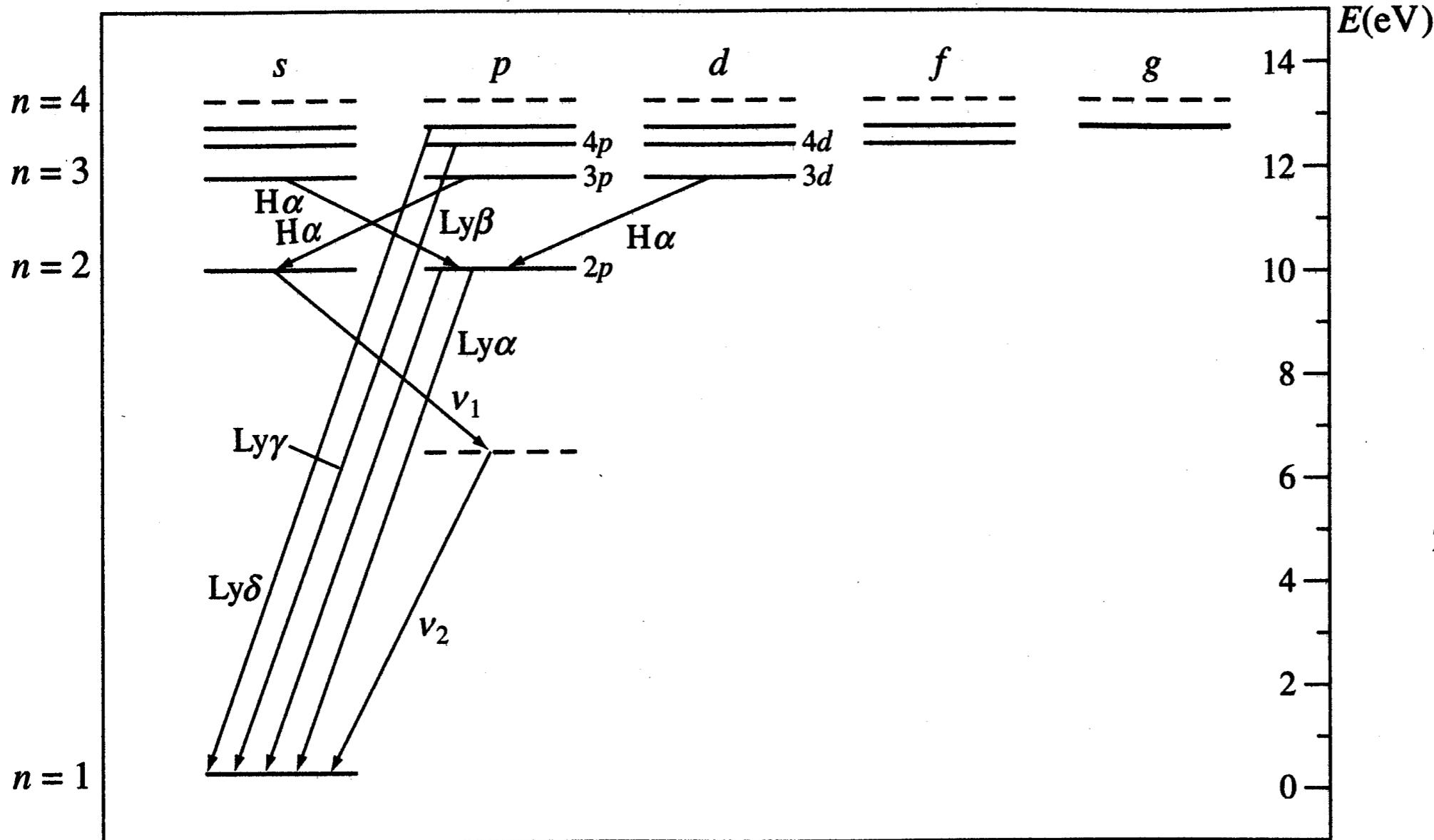
**Na D lines:**

$$\begin{aligned} \text{D}_1 \text{ } 5896 \text{ } \text{\AA} \text{ line} &: 3^2S_{1/2} - 3^2P_{1/2} \\ \text{D}_2 \text{ } 5890 \text{ } \text{\AA} \text{ line} &: 3^2S_{1/2} - 3^2P_{3/2} \end{aligned}$$

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

# [Hydrogen]

- Hydrogen



Lyman series:

$$n' = 2 \rightarrow n < 2 \quad \alpha : n' - n = 1$$

Balmer series:

$$n' = 3 \rightarrow n < 3 \quad \beta : n' - n = 2$$

Paschen series:

$$n' = 4 \rightarrow n < 4 \quad \gamma : n' - n = 3$$

Brackett series:

$$n' = 5 \rightarrow n < 5 \quad \delta : n' - n = 4$$

Pfund series:

$$n' = 6 \rightarrow n < 6 \quad \epsilon : n' - n = 5$$

Humphreys series:

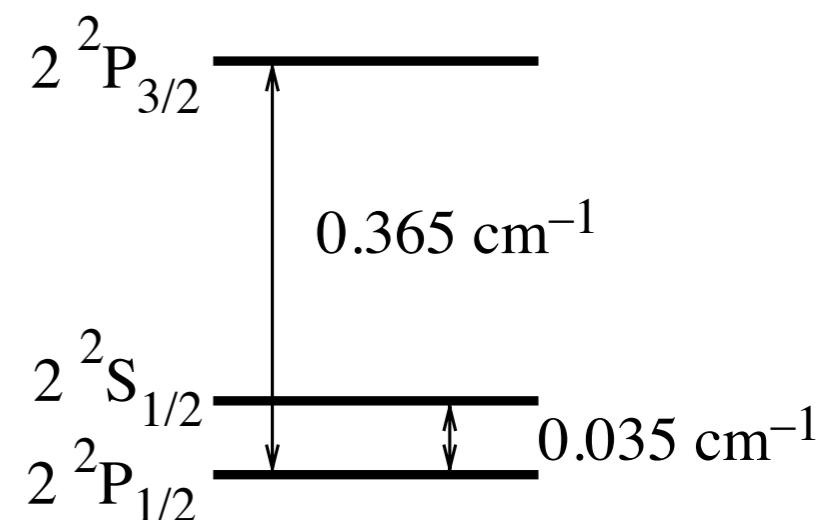
$$n' = 7 \rightarrow n < 7 \quad 41$$

- Fine structure of the hydrogen atom

**Relativistic QM (Dirac's eq)**

configuration	L	S	J	term	level	
$ns$	0	$1/2$	$1/2$	$^2S$	$^2S_{1/2}$	$2^2P_{3/2}$ —————
$np$	1	$1/2$	$1/2, 3/2$	$^2P^o$	$^2P_{1/2}^o, ^2P_{3/2}^o$	$2^2S_{1/2} = 2^2P_{1/2}$ —————
$nd$	2	$1/2$	$3/2, 5/2$	$^2D$	$^2D_{3/2}, ^2D_{5/2}$	
$nf$	3	$1/2$	$5/2, 7/2$	$^2F^o$	$^2F_{5/2}^o, ^2D_{7/2}^o$	
						$1^2S_{1/2}$ —————

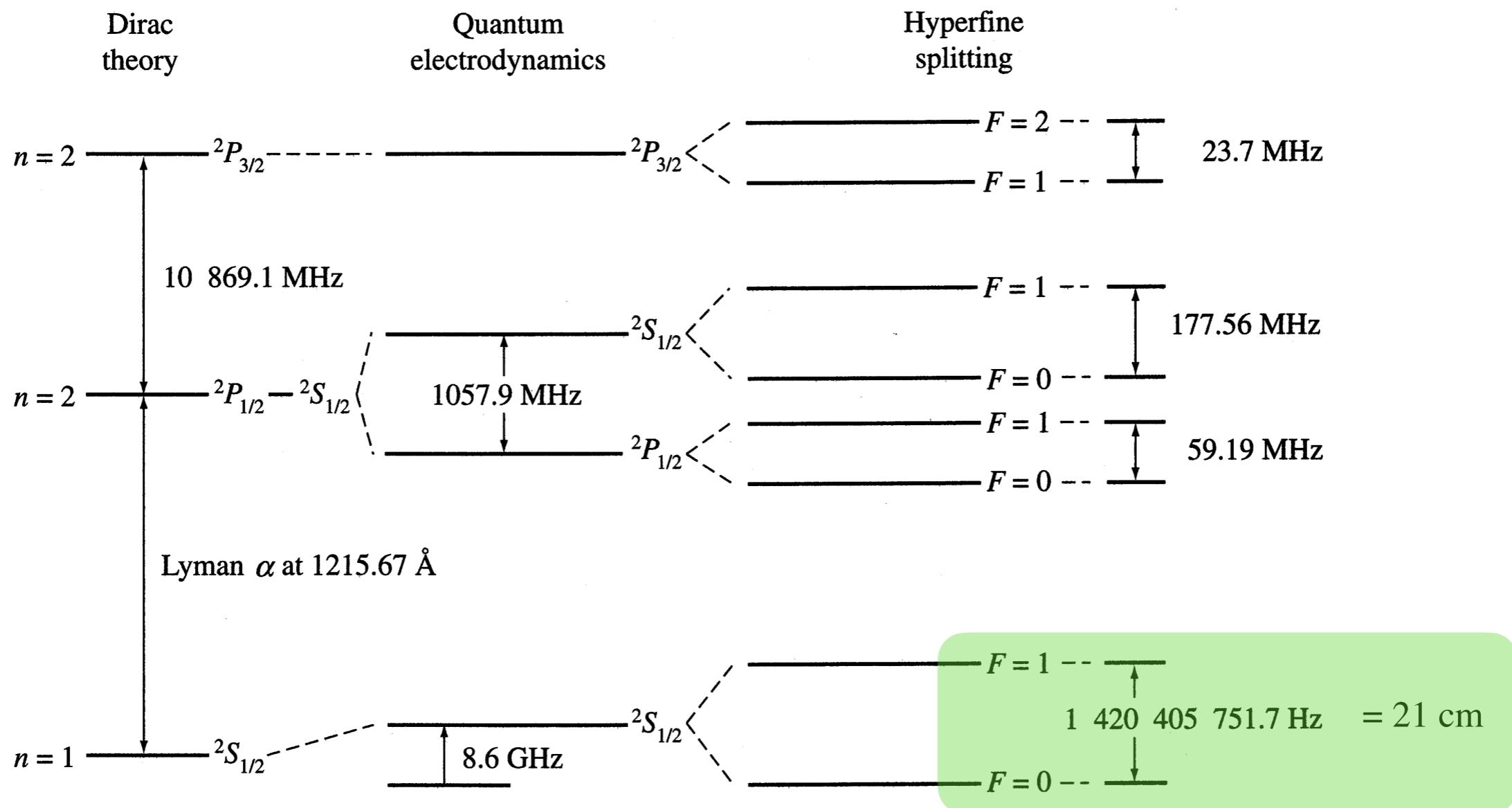
- Splitting in the  $n = 2$  levels of atomic hydrogen. The larger splitting is the fine structure and the smaller one the Lamb shift.  
According to the Dirac equation, the  $^2S_{1/2}$  and  $^2P_{1/2}$  orbitals should have the same energies. However, the interaction between the electron and the vacuum (which is not accounted for by the Dirac equation) causes a tiny energy shift on  $^2S_{1/2}$ . (Quantum electrodynamics effect)

**Quantum Electrodynamics**


- 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: 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 shown, a few times  $10^{-9}$  s.

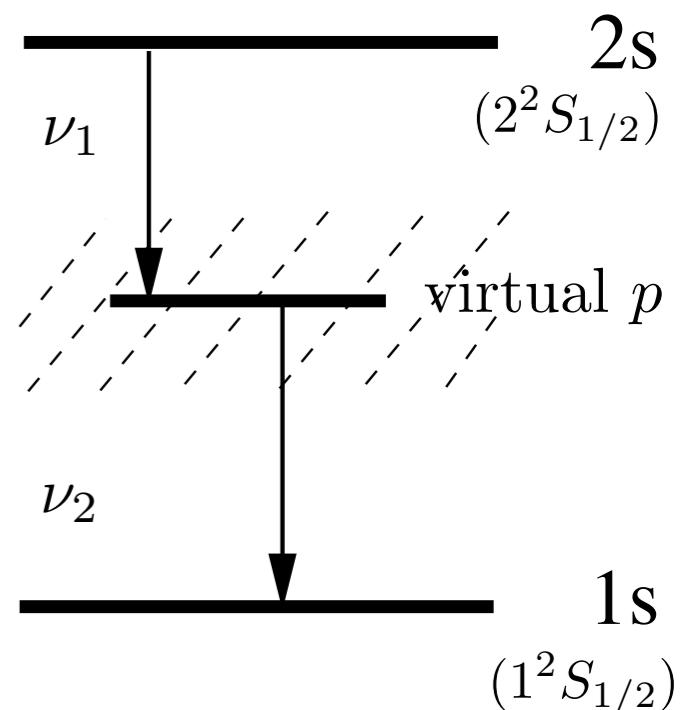
However, the lifetime for the (2s)  $2^2S_{1/2}$  level is  $\sim 0.14$  s, which is  $10^8$  times longer than the 2p states. (The level is called to be metastable.)

- Two-photon radiation

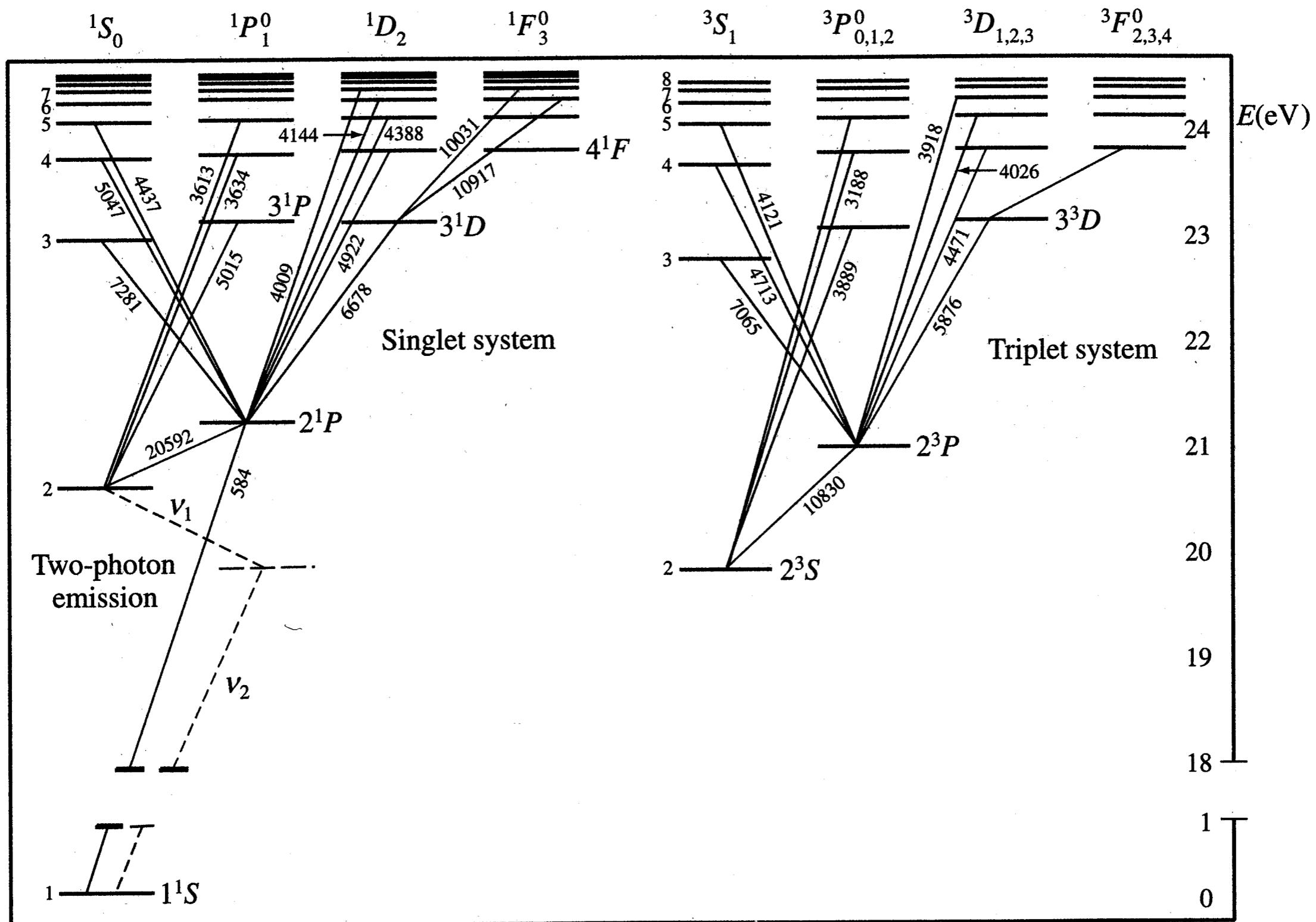
In low-density environments, an electron in the  $2^2S_{1/2}$  level can jump to a virtual  $p$  state, which lies between  $n = 1$  and  $n = 2$  levels. The electron then jumps from this virtual state to the ground state, in the process emitting two photons with total frequency .

$$\nu_1 + \nu_2 = \nu_{\text{Ly}\alpha}$$

Since this virtual  $p$  state can occur anywhere between  $n = 1$  and  $n = 2$ , continuum emission longword of Ly $\alpha$  will result.



- Helium (Grotrian diagram)



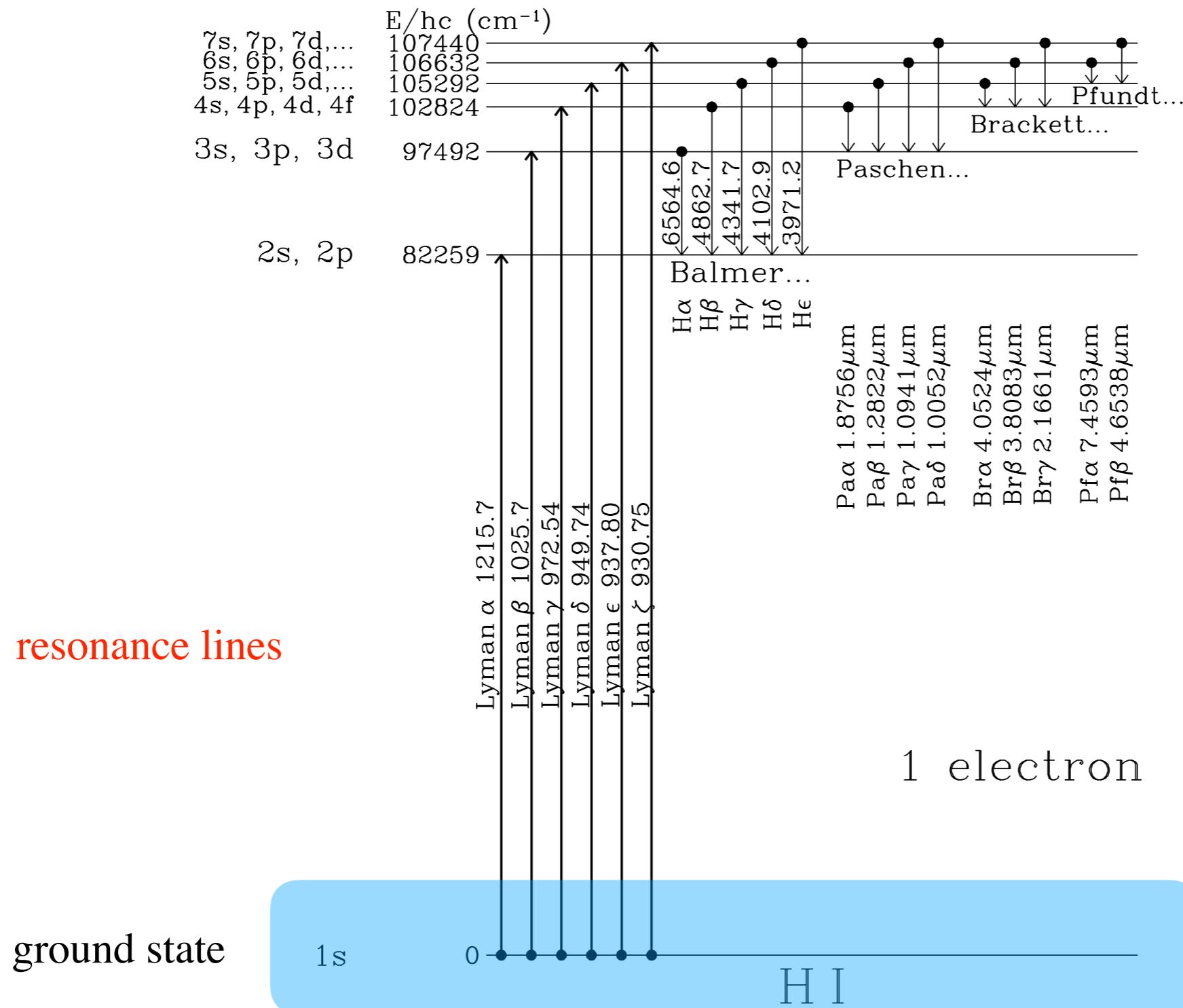
## [Notations]

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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 and cannot be 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> ( $C^{+2} + e^- \rightarrow C^{+2*} + e^- \rightarrow C^{+2} + e^- + h\nu$ ) or by recombination of C<sup>+3</sup> ( $C^{+3} + e^- \rightarrow C^{+2} + h\nu$ ). 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.

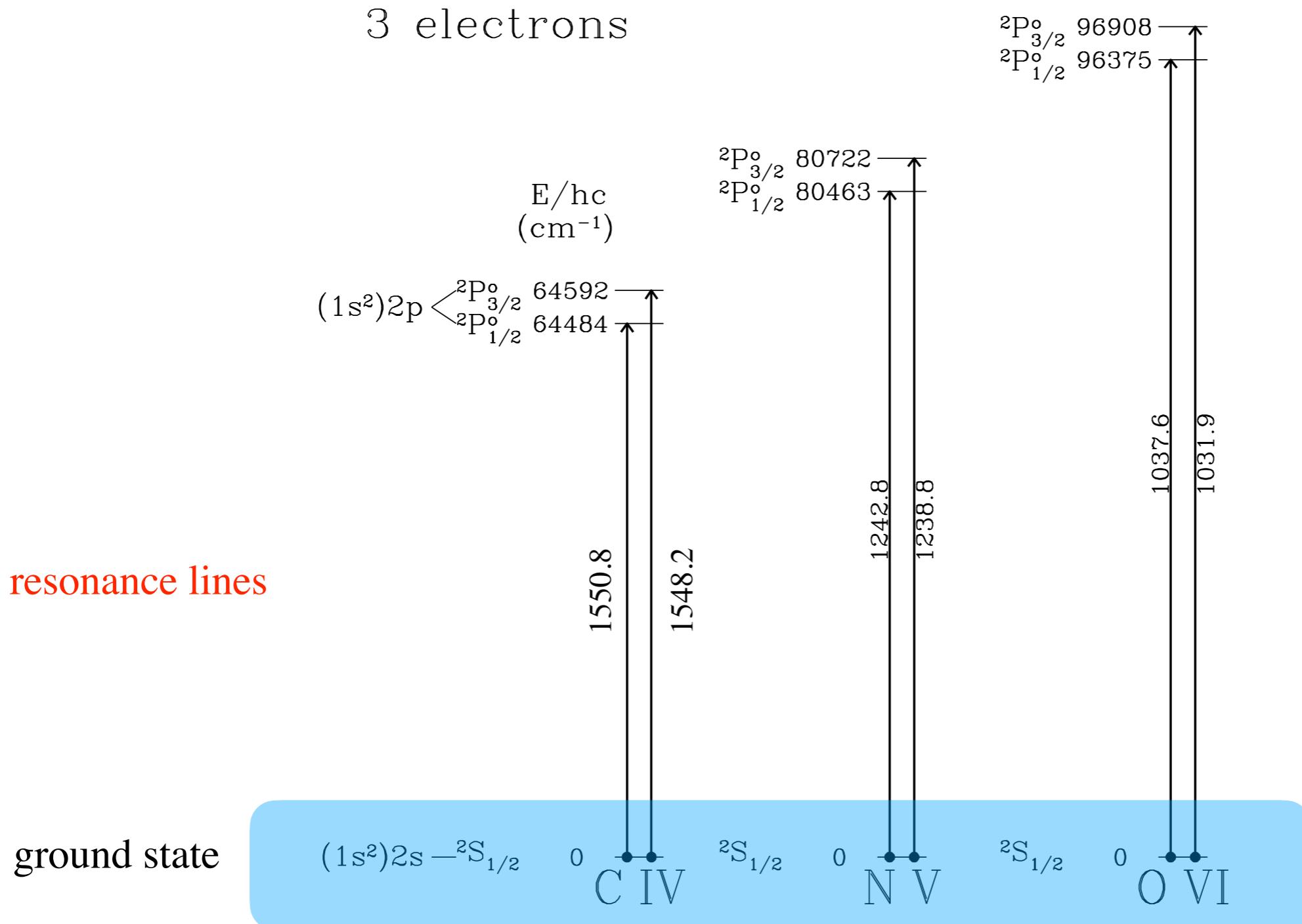
# [Energy Level Diagrams]

- 1 electron



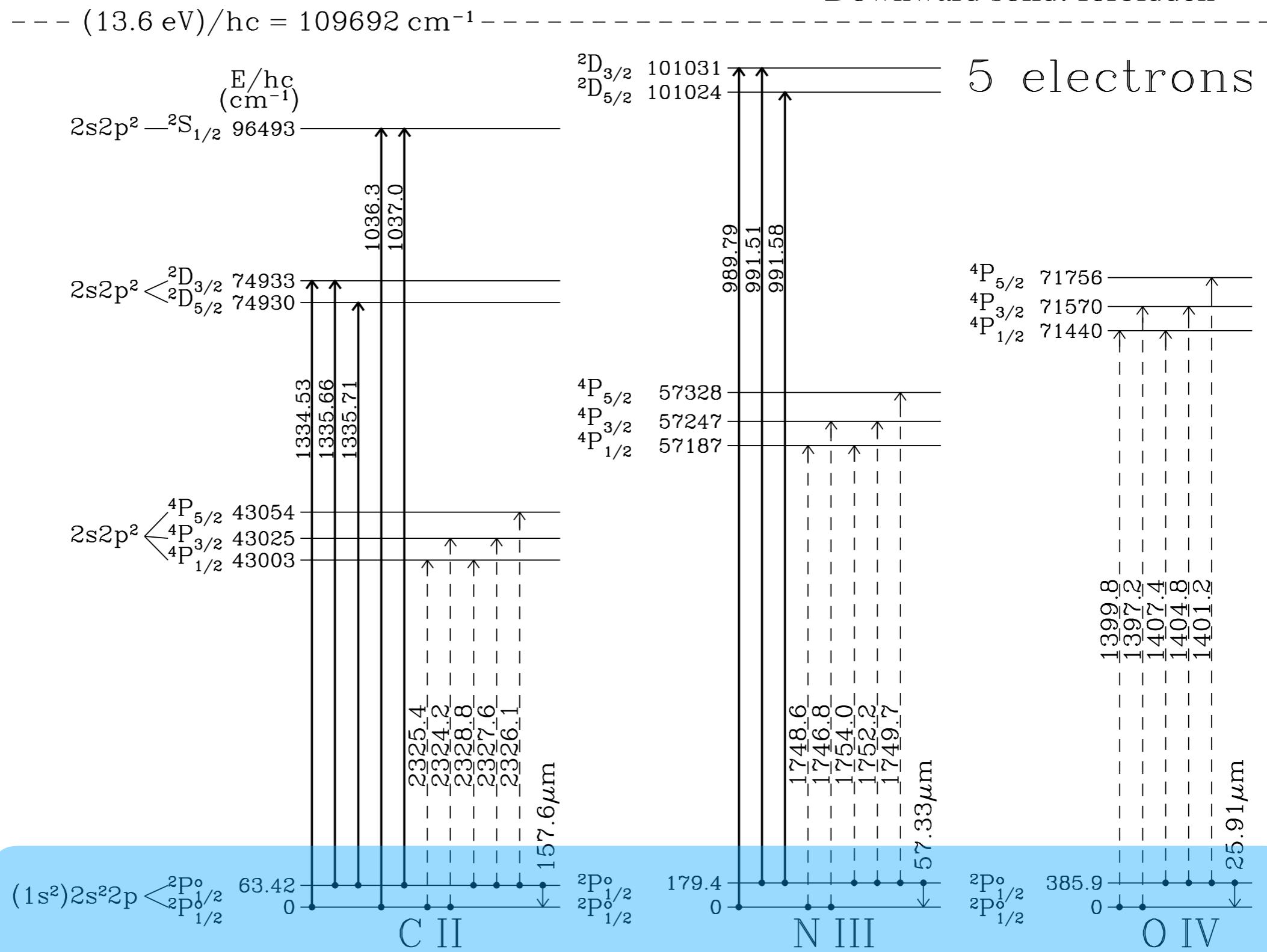
- 3 electrons (Lithium-like ions)

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



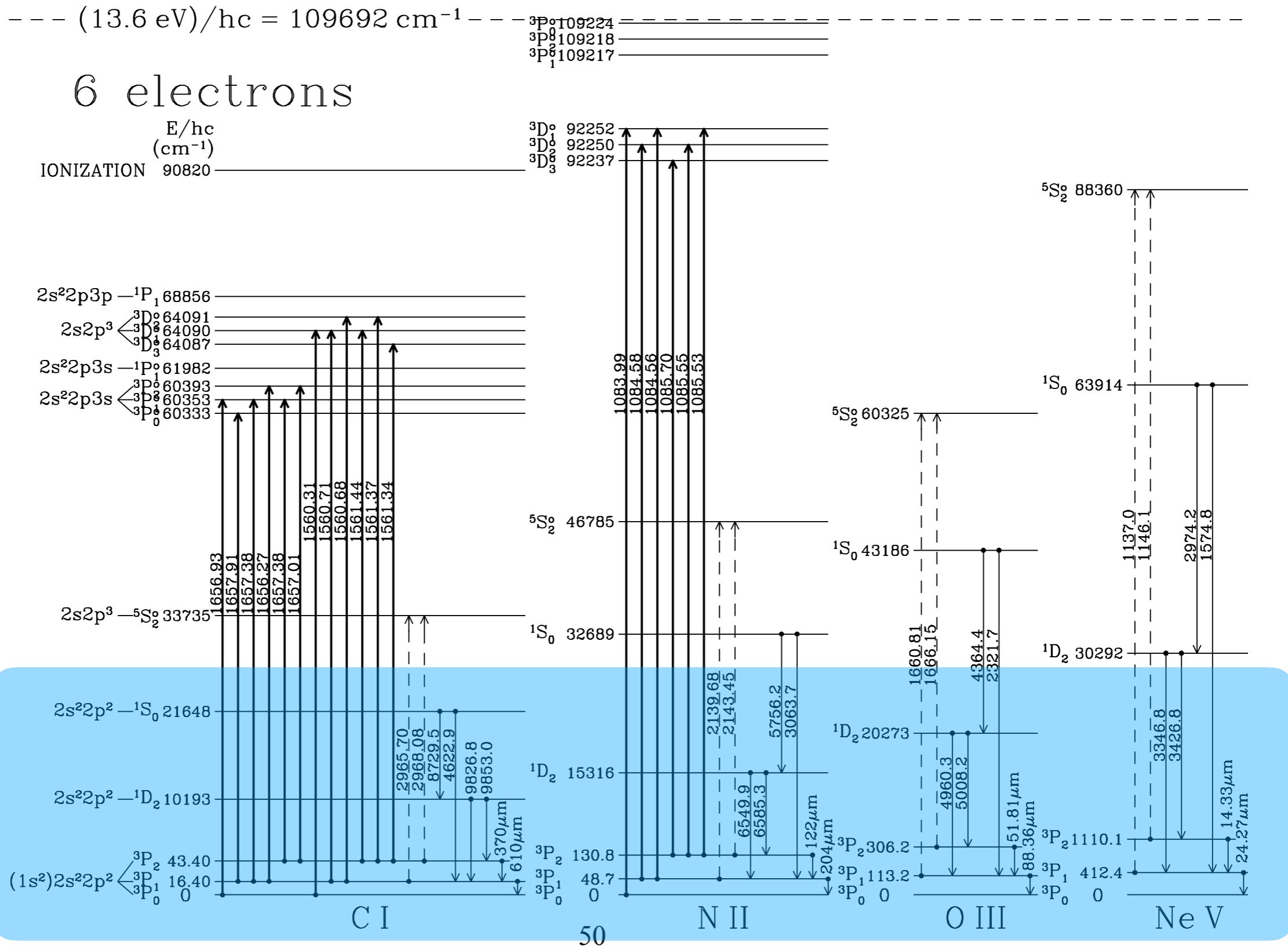
- 5 electrons

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



- 6 electrons

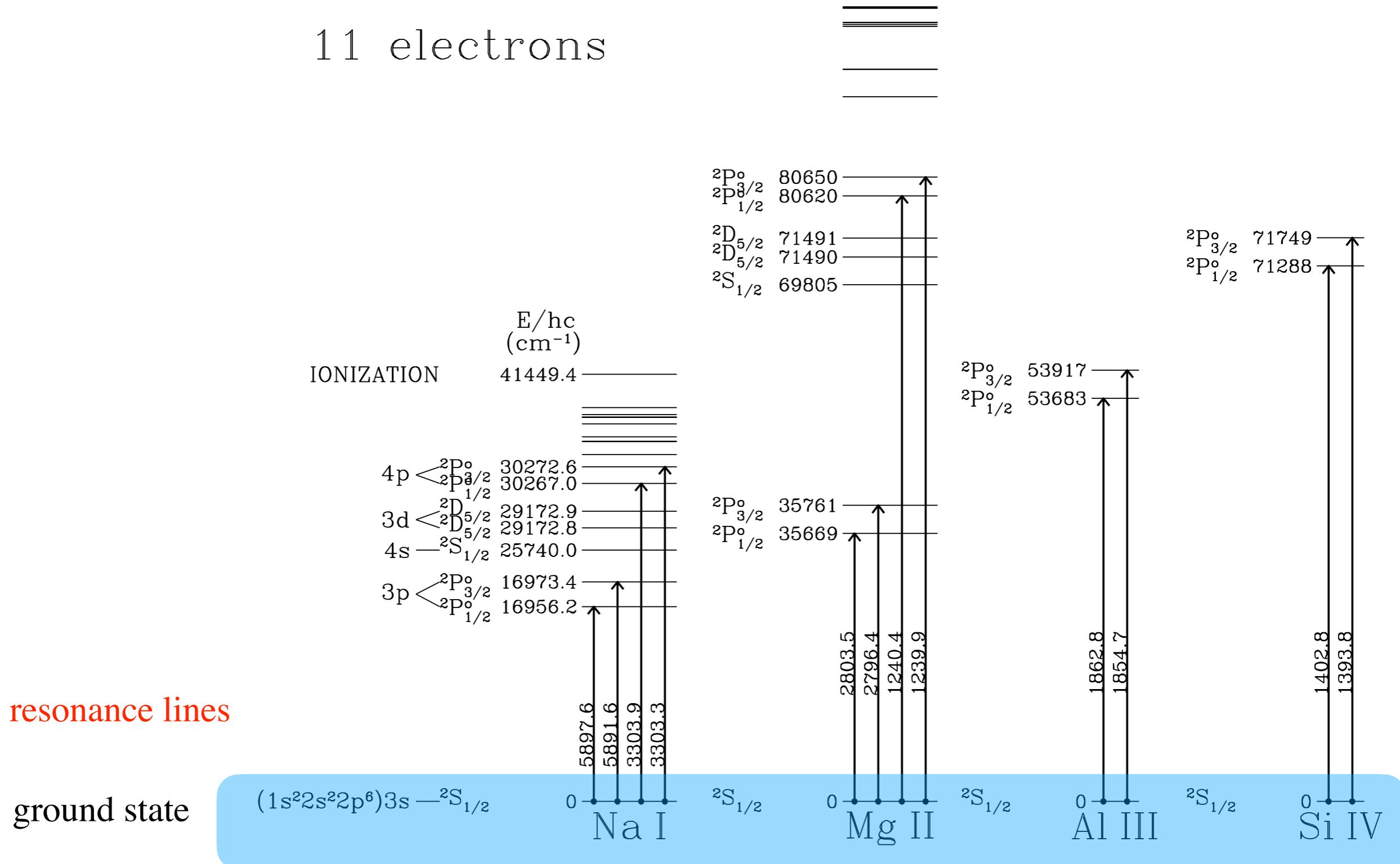
Upward heavy: resonance, Upward Dashed: intercombination  
Downward solid: forbidden



- 11 electrons

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

11 electrons



- 15 electrons

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

