

# 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

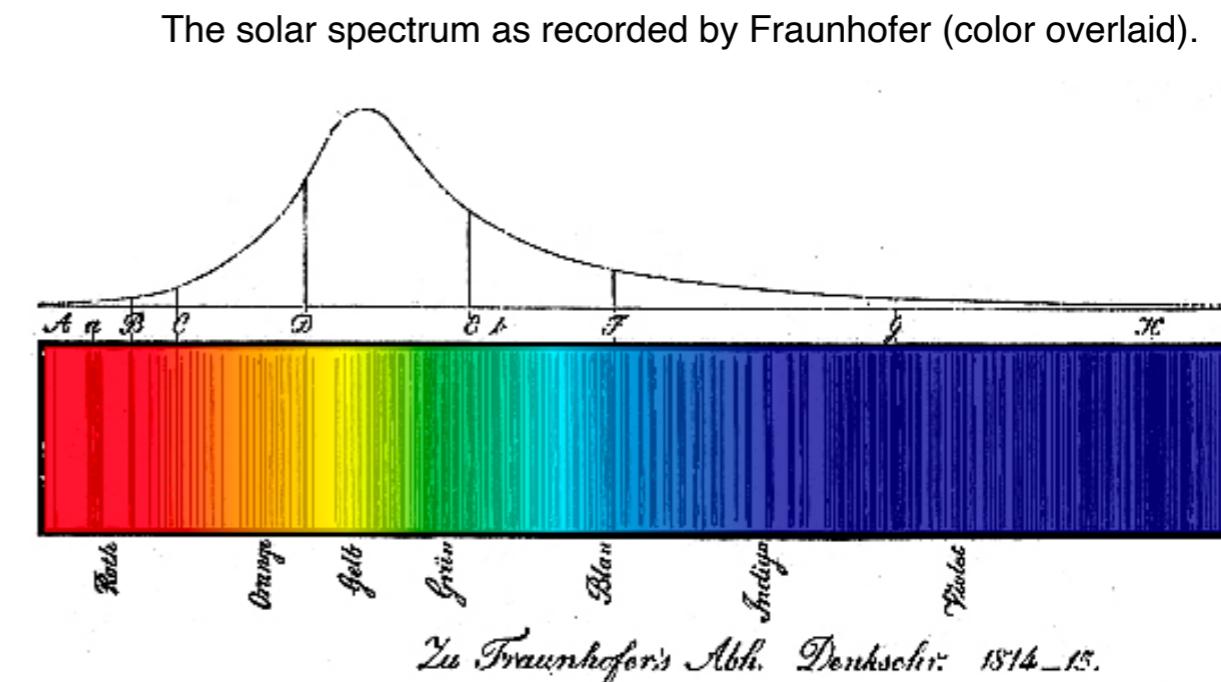
Atomic Spectroscopy and Radiative Processes [Egidio Landi Degl'Innocenti]

Atomic Astrophysics and Spectroscopy [Pradhan, A. K., & Nahar, S. N.]

# History: Fraunhofer Lines

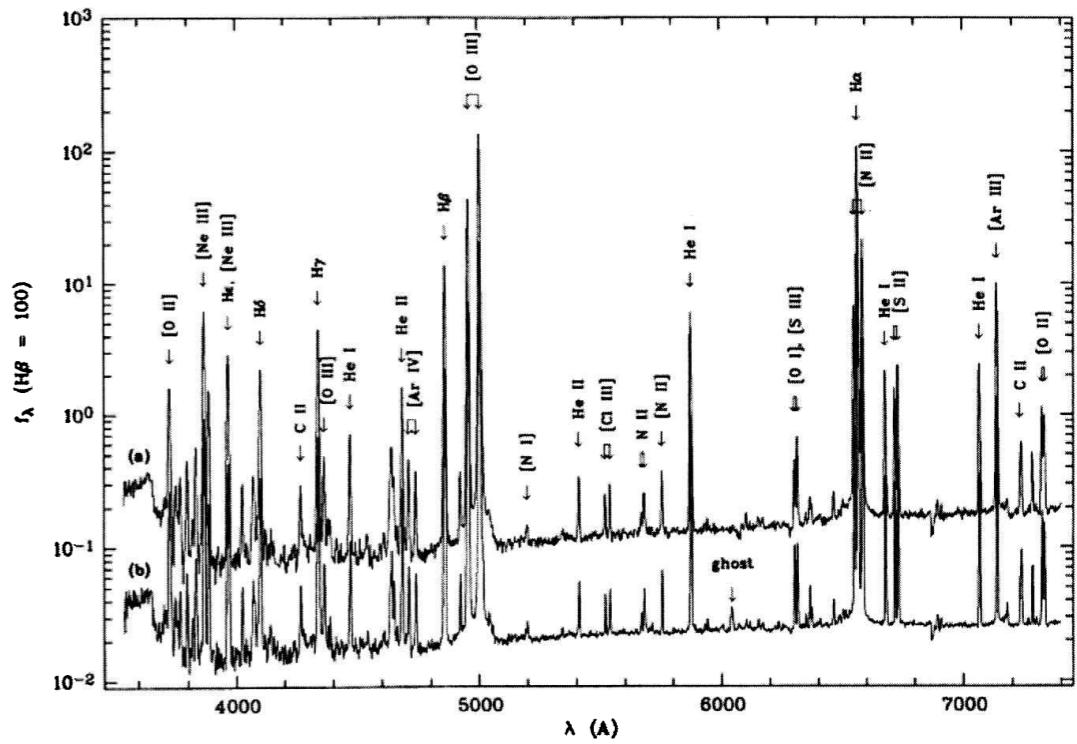
- In 1814, Joseph von Fraunhofer (1789-1826) used one of the high-quality prisms he had manufactured to diffract a beam of sunlight onto a whitewashed wall.
  - Besides the characteristic colors of the rainbow, he saw many dark lines.
  - He catalogued the exact wavelength of each dark line and labelled 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<sub>1</sub>, D<sub>2</sub>) 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.



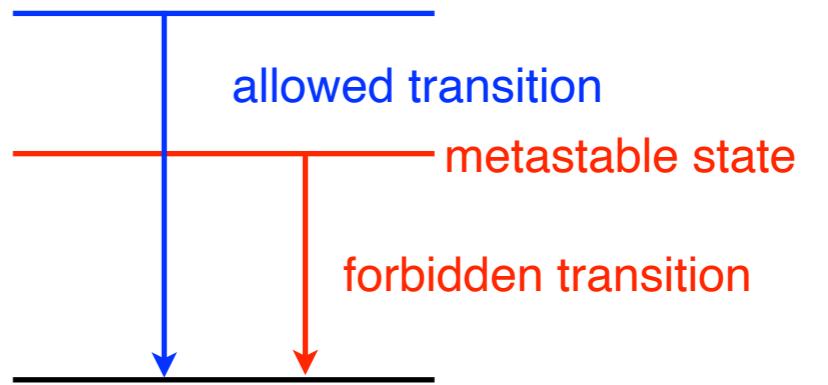
# History: Nebulium?

- 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  $4959\text{\AA}$  and  $5007\text{\AA}$ . 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 III].



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*:

- The time-independent Schrödinger equation is obtained as follows:

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

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

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

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

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

$$\mathcal{R}R(r) + \frac{2m}{\hbar^2} [E - V(r)] R(r) = \frac{\Lambda}{r^2} R(r)$$

$$\mathcal{L}^2 Y(\theta, \phi) = -\Lambda Y(\theta, \phi)$$

The left side depends only on  $r$  and the right side on  $\theta$  and  $\phi$ . Therefore, they should be a constant.

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

- 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

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

- Wavefunction for a hydrogen-like atom:

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

radial function:

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

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

$L_{n+l}^{2l+1}$  = 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 angular momentum quantum number**
- **$m = -l, -l+1, \dots, 0, \dots, l-1, l$  : magnetic quantum number**

bra-ket notation (Dirac notation)

ket vector :  $|\psi\rangle$

bra vector :  $\langle\phi| = |\psi\rangle^\dagger$

( $\dagger$  denotes the conjugate transpose)

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

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

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

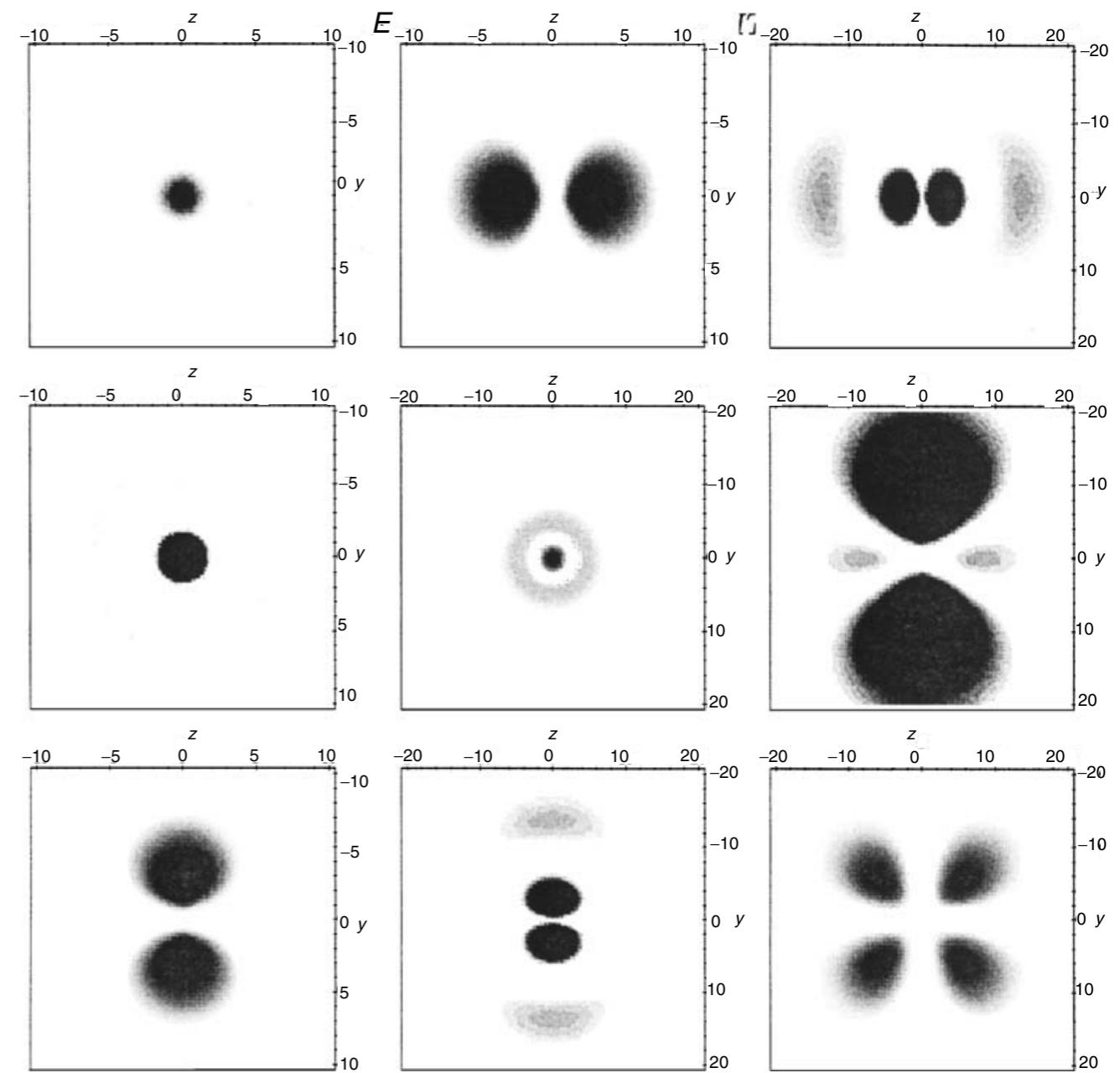
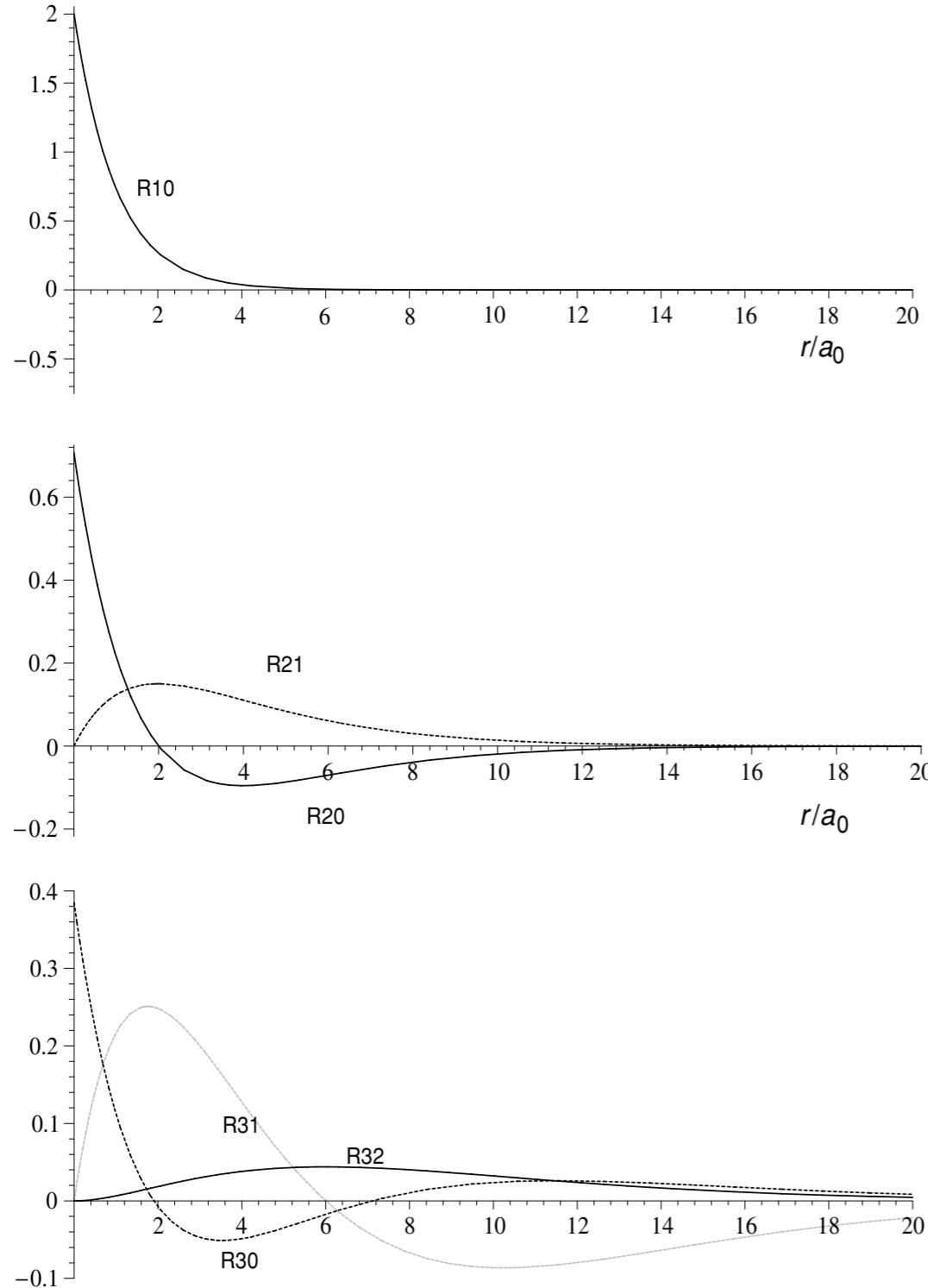
$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

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

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

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

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



Probability distributions (per unit volume). A slice through the  $\phi = 0$  plane. The darker the shading the greater the probability density.

[Left] 1s, 2s, 2p0      from top to bottom  
 [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 of being located within a volume  $d^3x = |\psi(r, \theta, \phi)|^2 d^3x = R_{nl}^2(r) |Y_{lm}(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$

- Properties of the spherical harmonics:

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

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

No dependency on  $\phi$ .

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

- Orthonormality

$$\int d\Omega Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) = \delta_{\ell, \ell'} \delta_{m, m'}$$

$$\int_0^\infty R_{n\ell}(r) R_{n'\ell'}(r) dr = \delta_{n, n'}$$

- Energy

$$E_n = -Z^2/2n^2$$

- 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 angular momentum 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.

Wavefunctions:

$$\left| \frac{1}{2} \right\rangle \equiv \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \left| -\frac{1}{2} \right\rangle \equiv \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

To incorporate spin into the theory in a completely satisfactory way one should use the relativistic Dirac equation.

# 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]

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

**Hartree-Fock approximation (or 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.

$$E = \sum_i E_i$$

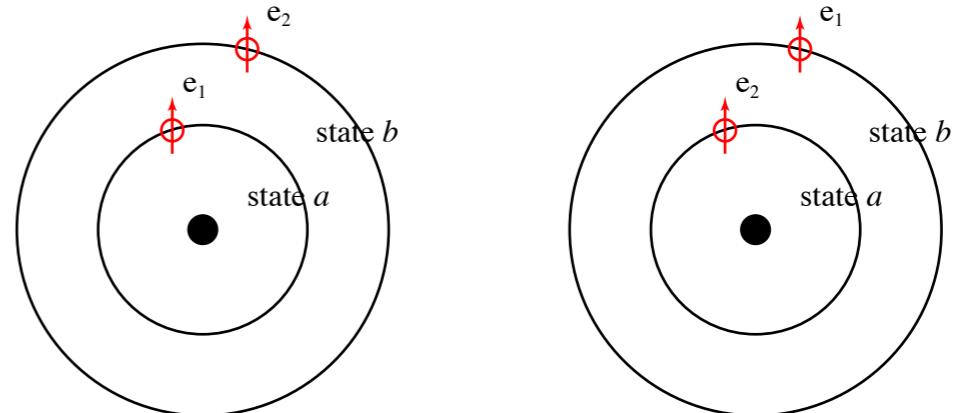
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

**However, this wave function fails to satisfy a basic principle of quantum mechanics that one cannot distinguish between electron  $i$  and electron  $j$ .**

## [Indistinguishable Particles]

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

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



The equation has two possible solutions:

- symmetric solution

$$\Psi(a_1, b_2) = \Psi(a_2, b_1)$$

- antisymmetric solution

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

Particles 1 and 2 are indistinguishable.

**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 state.**"

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  $2l+1$  different  $m$  values, each with two possible values of  $s_z$  ( $= \pm 1/2$ ).

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.

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

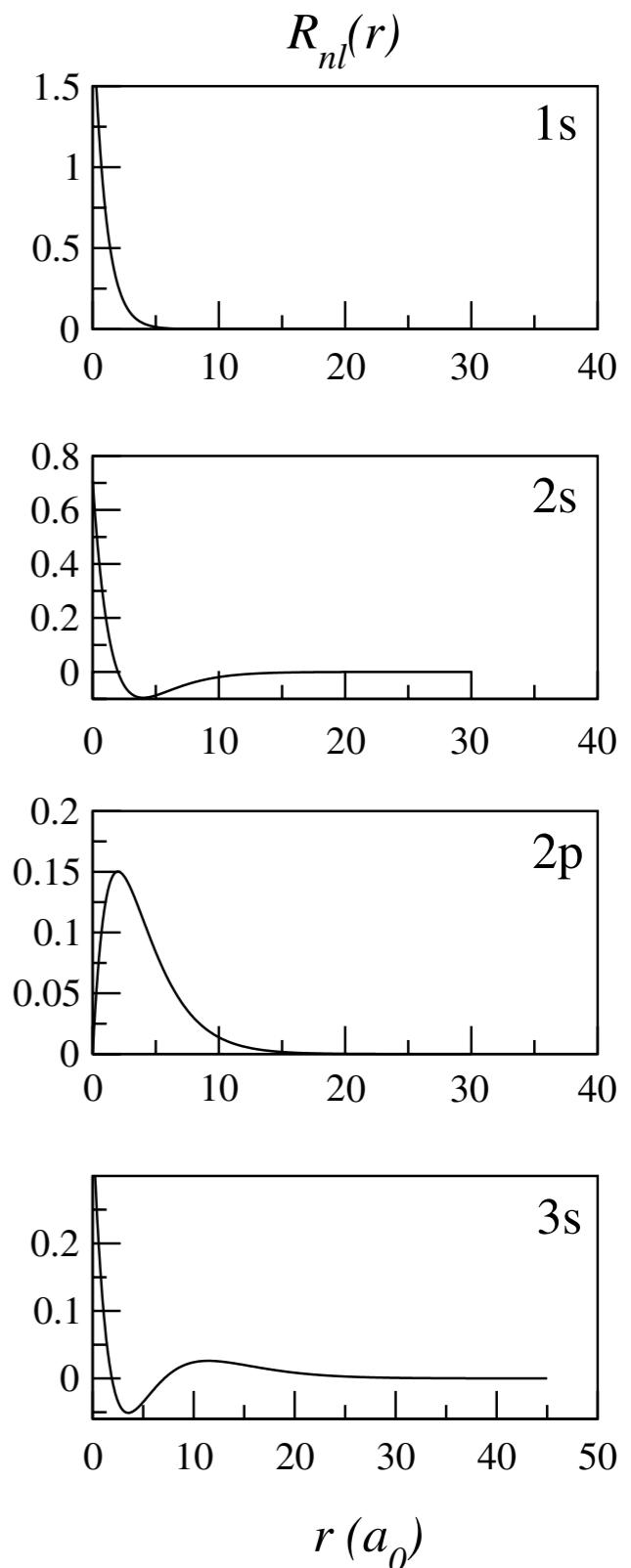
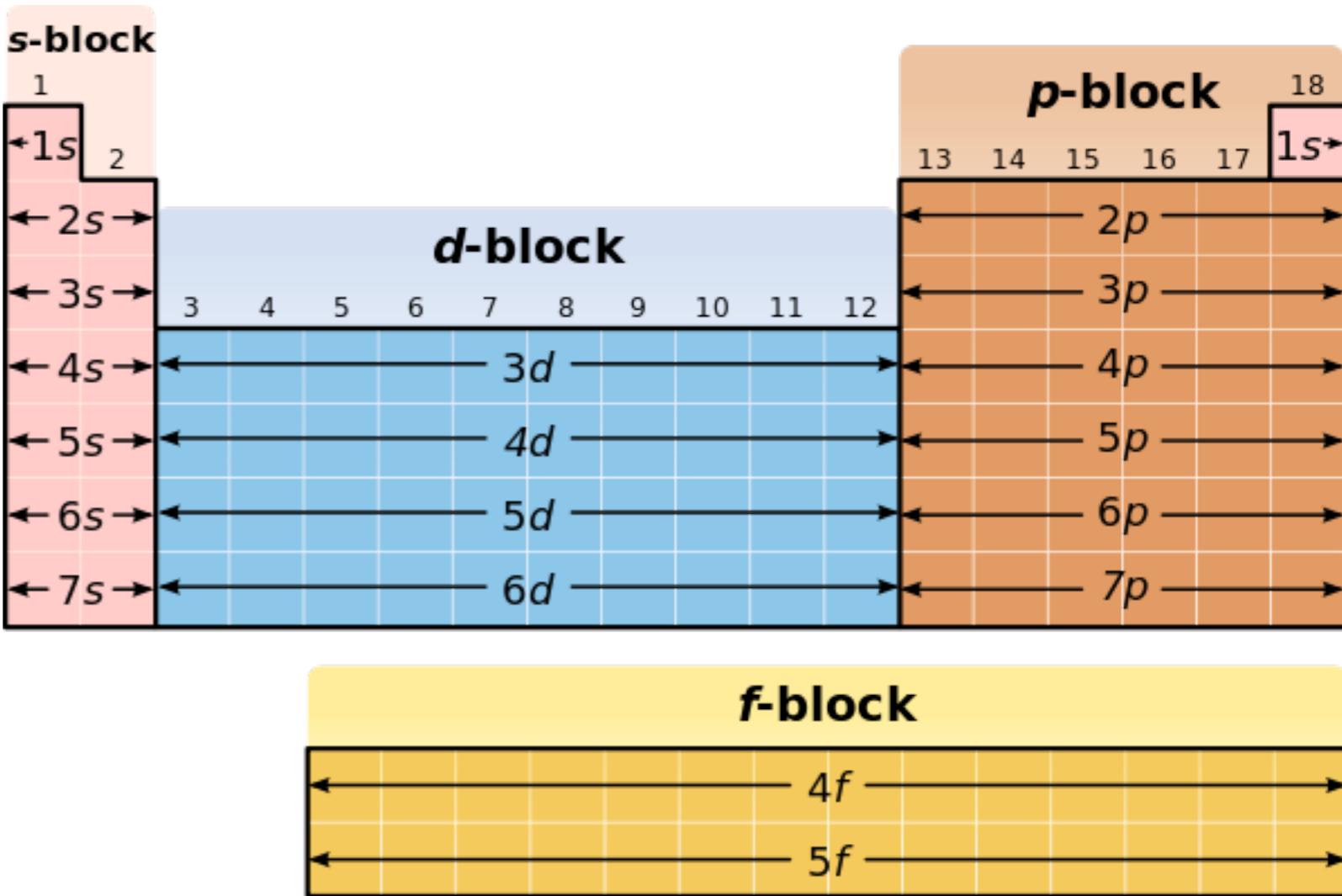


표 9.2 원자의 전자 배열과 전리 에너지(Kramida et al. 2018)

원소/ 원자번호	K		L		M			N				바닥상태 준위	전리 에너지(eV)	
	1s	2s 2p	3s 3p	3d	4s	4p	4d	4f					I → II	II → III
H	1	1							$^2S_{1/2}$		13.598			
He	2	2							$^1S_0$		24.587		54.418	
Li	3	2	1						$^2S_{1/2}$		5.392		75.640	
Be	4	2	2						$^1S_0$		9.323		18.211	
B	5	2	2	1					$^2P_{1/2}^o$		8.298		25.155	
C	6	2	2	2					$^3P_0$		11.260		24.385	
N	7	2	2	3					$^4S_{3/2}^o$		14.534		29.601	
O	8	2	2	4					$^3P_2$		13.618		35.121	
F	9	2	2	5					$^2P_{3/2}^o$		17.423		34.971	
Ne	10	2	2	6					$^1S_0$		21.565		40.963	
Na	11			1					$^2S_{1/2}$		5.139		47.286	
Mg	12			2					$^1S_0$		7.646		15.035	
Al	13		2	1					$^2P_{1/2}^o$		5.986		18.829	
Si	14	Neon	2	2					$^3P_0$		8.152		16.346	
P	15	배열	2	3					$^4S_{3/2}^o$		10.487		19.769	
S	16		2	4					$^3P_2$		10.360		23.338	
Cl	17		2	5					$^2P_{3/2}^o$		12.968		23.814	
Ar	18		2	6					$^1S_0$		15.760		27.630	
K	19			-	1				$^2S_{1/2}$		4.341		31.625	
Ca	20			-	2				$^1S_0$		6.113		11.872	
Sc	21		1	2					$^2D_{3/2}$		6.561		12.800	
Ti	22		2	2					$^3F_2$		6.828		13.576	
V	23		3	2					$^4F_{3/2}$		6.746		14.634	
Cr	24		5	1					$^7S_3$		6.767		16.486	
Mn	25		5	2					$^6S_{5/2}$		7.434		15.640	
Fe	26		6	2					$^5D_4$		7.902		16.199	
Co	27	Argon	7	2					$^4F_{9/2}$		7.881		17.084	
Ni	28	배열	8	2					$^3F_4$		7.640		18.169	
Cu	29		10	1					$^2S_{1/2}$		7.726		20.292	
Zn	30		10	2					$^1S_0$		9.394		17.964	
Ga	31		10	2	1				$^2P_{1/2}^o$		5.999		20.515	
Ge	32		10	2	2				$^3P_0$		7.899		15.935	
As	33		10	2	3				$^4S_{3/2}^o$		9.789		18.589	
Se	34		10	2	4				$^3P_2$		9.752		21.196	
Br	35		10	2	5				$^2P_{3/2}^o$		11.814		21.591	
Kr	36		10	2	6				$^1S_0$		14.000		24.360	

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  $\ell$ .

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 exact Hamiltonian can be written as

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

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

The term  $H_{\text{so}}$  is the spin-orbit interaction, which causes the fine structure splitting.

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- **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.
- According to perturbation theory, the configurations split into terms with particular values of L and S. These terms then split further by the action of the spin-orbit interaction.
- 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 (positive) 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. Terms with larger spin tend to lie lower in energy because of lower, positive electrostatic energies.
  - ◆ There is a similar effect regarding the orbital angular moment. This effect is usually smaller than for the spin.
  - ◆ ⇒ The above two properties give rise to the so called Hund's rule.

# Angular Momentum Coupling

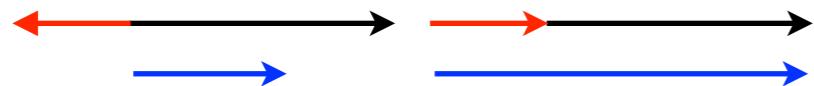
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- Atoms contain several sources of angular momentum.
  - electron orbital angular momentum  $L$
  - electron spin angular momentum  $S$
  - nuclear spin angular momentum  $I$
  - The nuclear spin arises from the spins of nucleons. Protons and neutrons 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  $\mathbf{F} = \mathbf{J} + \mathbf{I}$ .

# Addition of two angular momenta

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

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



$$c = |\mathbf{a} - \mathbf{b}| \quad c = \mathbf{a} + \mathbf{b}$$

- 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

$$\begin{aligned}\mathbf{B}' &= \mathbf{B}'_{\perp} = \gamma(\mathbf{B}_{\perp} - \boldsymbol{\beta} \times \mathbf{E}) = -\frac{\mathbf{v}}{c} \times \mathbf{E} \\ &= -\frac{Ze}{c} \frac{\mathbf{v} \times \mathbf{r}}{r^3} \\ &= \frac{Ze}{m_e c r^3} \boldsymbol{\ell}\end{aligned}$$

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)

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

$$\boldsymbol{\mu} = -\frac{e}{m_e c} \mathbf{s} = 2\boldsymbol{\mu}_{\text{classical}}$$

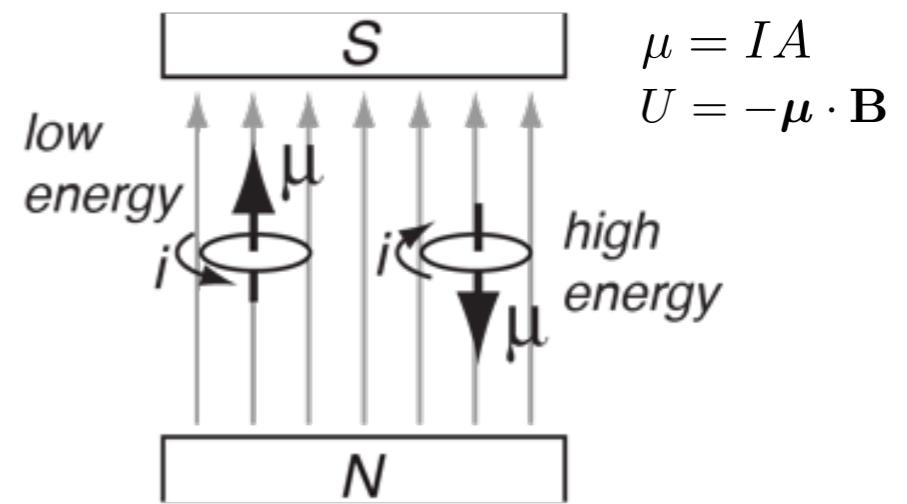
definition of magnetic moment:  $\boldsymbol{\mu} = \frac{1}{2c} \int_V \mathbf{x}' \times \mathbf{J} d^3x'$

- 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.

$$\Delta E_{\text{so}}(J+1 \leftrightarrow J) > \Delta E_{\text{so}}(J \leftrightarrow J-1)$$

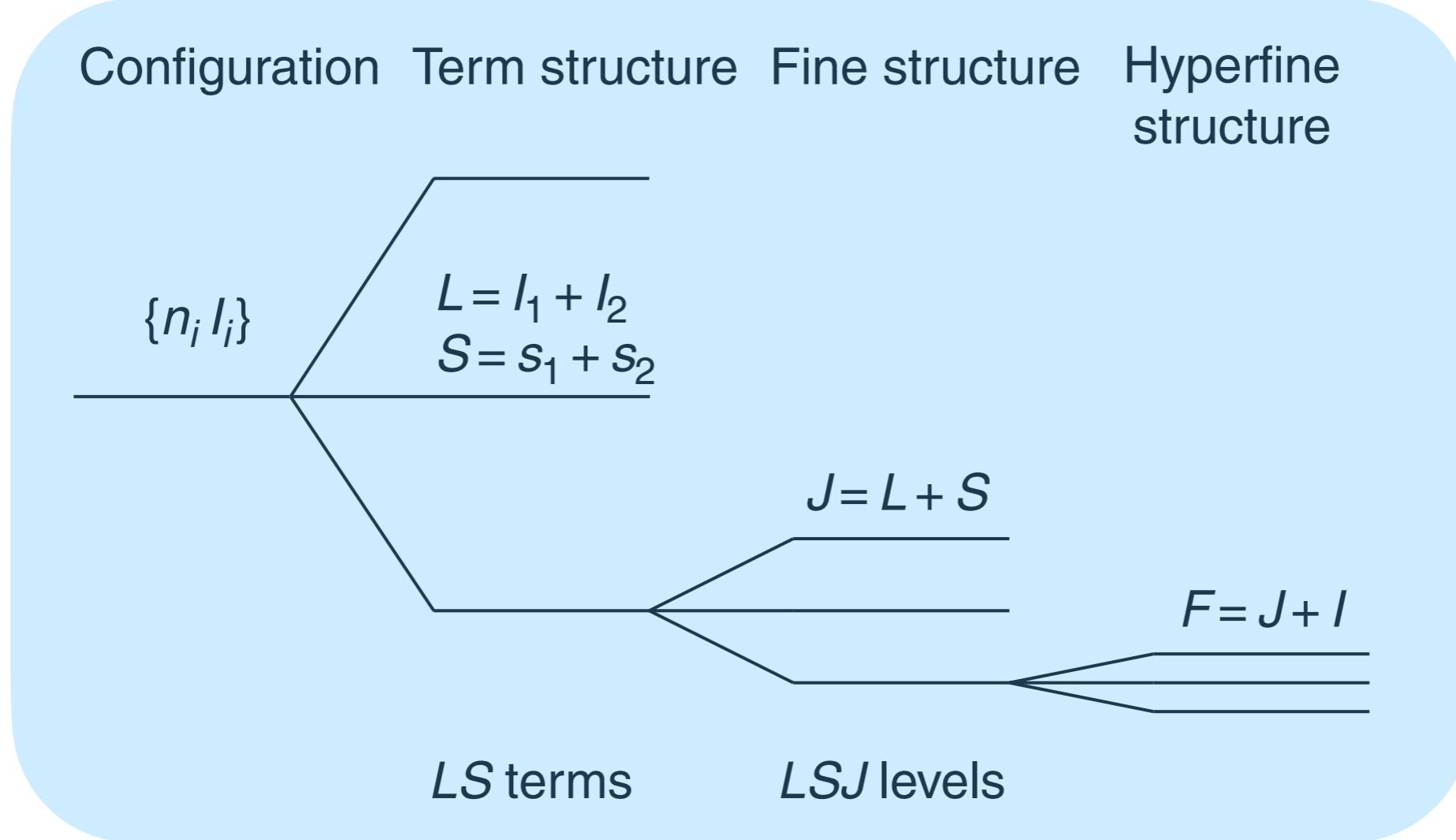
Note that

$$E_{\text{so}} = 0 \text{ for } L = 0 \text{ because } J = S$$

Therefore, there will be no fine structure for  $L = 0$ .

- 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.

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

**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  $2S+1 = 1$ .
  - ▶  $J = L$  (singlet)
- A state with  $S = 1/2$  is a ‘doublet’ as  $2S+1 = 2$ 
  - ▶  $J = L - 1/2, L + 1/2$  (doublet if  $L \geq 1$ )
- One with  $S = 1$  is a ‘triplet’ as  $2S+1 = 3$ 
  - ▶  $J = L - 1, L, L + 1$  (triplet  $L \geq 1$ )

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

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

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

sharp, principal, diffuse, fundamental,...

## LS Terms: (1) Nonequivalent Electrons, 2p3p

---

- **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.

- **Consider the combination of two p electrons.**

(1) **2p3p** - Two electrons are nonequivalent.

***In this nonequivalent case, all possible spectroscopic combinations are available.***

$$S = 0, 1, \quad L = 0, 1, 2 \quad \rightarrow \quad ^1S, ^1P, ^1D, ^3S, ^3P, ^3D$$

→ 6 spectroscopic terms

$$\rightarrow \quad ^1S_0, ^1P_1, ^1D_2, ^3S_1, ^3P_{0,1,2}, ^3D_{1,2,3}$$

→ 10 spectroscopic levels

We can have  $(2J+1)$  states for each  $J$  value.

Therefore, 36 distinguishable states are available in total.

$$\rightarrow \quad 1 + 3 + 5 + 3 + 9 + 15 = 36$$

There are two possible states  $m_s = \pm 1/2$  for spin of each electron, and three states  $m_l = -1, 0, 1$  for orbital angular momentum of each electron.

Thus, we expect that there will be  $2^2 \times 3^2 = 36$  distinguishable states.

## (2) Equivalent Electrons, $2p^2$

---

(2)  $2p^2$  - Two electrons are equivalent.

Then, *all the 36 states are not available. Some are ruled out by Pauli exclusion principle, and some are ruled out because they are not distinguishable from others.*

Table 1

Label	$m_l$	$m_s$
a	+1	+1/2
b	0	+1/2
c	-1	+1/2
d	+1	-1/2
e	0	-1/2
f	-1	-1/2

- The first step is to make a table to label the states for a single electron (e.g., a, b, c, d, e, f), as shown in Table 1.

Table 2

	States	$M_L$	$M_S$
1	ab	1	1
2	ac	0	1
3	ad	2	0
4	ae	1	0
5	af	0	0
6	bc	-1	1
7	bd	1	0
8	be	0	0
9	bf	-1	-1
10	cd	0	0
11	ce	-1	0
12	cf	-2	0
13	de	1	-1
14	df	0	-1
15	ef	-1	-1

- Next step is to make a table for the combination of  $(M_L, M_S)$  of two electrons, as shown in Table 2. Here,  $M_L = m_{l1} + m_{l2}$ , and  $M_S = m_{s1} + m_{s2}$ .
  - According to Pauli's exclusion principle, the states that have two identical states (aa, bb, cc, dd, ee, and ff) are not allowed.
  - Notice also that "ab" and "ba" states are identical and thus the "ba" state is ignored. Other identical combinations are also ignored.
- Following the above two rules, we construct Table 2 which contains 15 distinguishable states.

Table 3

States	$M_L$	$M_S$	Term 1	Term 2	Term 3
ab	1	1		$^3P$	
ac	0	1		$^3P$	
ad	2	0	$^1D$		
ae	1	0	$^1D$		
af	0	0	$^1D$		
bd	1	0		$^3P$	
be	0	0		$^3P$	
cd	0	0			$^1S$

- In addition to the above two rules, we can recognize that every “negative” values have always their “positive” counterparts.
  - Therefore, it is more convenient to remove the states with negative values. This gives us Table 3, which contains only 8 states.
- Now, we pick the states starting with the largest  $M_L$  and then the largest  $M_S$ .
  - (ad)  $M_L = 2$  and  $M_S = 0$ : The presence of the  $M_L = 2, M_S = 0$  indicates that a  $^1D$  term is among the possible terms. To this term we must further assign states with  $M_L = 1,0$  and  $M_S = 0$  (ae, af). What is left?
  - (ab)  $M_L = 1$  and  $M_S = 1$ : This is the next largest values. The combination  $M_L = 1, M_S = 1$  indicates that a  $^3P$  term is among the possible terms. To this term we must further assign states with  $M_L = 1,0$  and  $M_S = 1,0$  (ac, bd, be). What is left?
  - (cd)  $M_L = 0$  and  $M_S = 0$ : This is the only remaining combination. This implies that a  $^1S$  term is among the possible terms.
  - Finally, we obtain 3 terms  $^1D$ ,  $^3P$ , and  $^1S$ .
  - The 3 terms are split into 5 levels :  $^1D_2$ ,  $^3P_{0,1,2}$ , and  $^1S_0$ .

### (3) Equivalent Electrons, $2p^3$

(3)  $2p^3$  - Three electrons are equivalent.

- According to Pauli's exclusion principle, any states that include two identical states (aaa, aab, aac, add, bbc, bbd, etc) are not allowed.
- We have only seven states that have non-negative values, as shown in Table 4.

Table 4

States	$M_L$	$M_S$	Term 1	Term 2	Term 3
abc	0	3/2			$^4S$
abd	2	1/2	$^2D$		
abe	1	1/2	$^2D$		
abf	0	1/2	$^2D$		
acd	1	1/2		$^2P$	
ace	0	1/2		$^2P$	
bcd	0	1/2			$^4S$

Table 1

Label	$m_L$	$m_S$
a	+1	+1/2
b	0	+1/2
c	-1	+1/2
d	+1	-1/2
e	0	-1/2
f	-1	-1/2

- Now, we pick the states starting with the largest  $M_L$  and then the largest  $M_S$ .
  - (abd)  $M_L = 2$  and  $M_S = 1/2$ : This indicates that a  $^2D$  term is among the possible terms. To this term we must further assign states with  $M_L = 1, 0$  and  $M_S = 1/2$  (abe, abf). What is left?
  - (acd)  $M_L = 1$  and  $M_S = 1/2$ : This indicates the presence of a  $^2P$  term. To this term we must further assign states with  $M_L = 0$  and  $M_S = 1/2$  (ace). What is left?
  - (abc)  $M_L = 0$  and  $M_S = 3/2$ : This indicates the presence of a  $^4S$  term.
  - **Finally, we obtain three terms ( $^2D$ ,  $^2P$ , and  $^4S$ ) and five levels :  $^2D_{3/2, 5/2}$ ,  $^2P_{1/2, 3/2}$ , and  $^4S_{3/2}$ .**

## (4) Another method for $2p^2$

---

**When we have only two electrons, we can use the Pauli principle to obtain the terms.**

This method is much simpler than the above method. However, this method is not easy to apply to the case of three electrons.

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

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

Note that among the six terms  ${}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D$ , the following terms are all excluded.

${}^1P$  is antisymmetric for both spin and orbital angular momenta

${}^3S$  is symmetric for both spin and orbital angular momenta

${}^3D$  is also symmetric for both spin and orbital angular momenta

Because

- |   |  |
|---|--|
| $S = 0 \rightarrow s_1 = 1/2, s_2 = -1/2$ | : Product of two spin functions are antisymmetric w.r.t. the exchange  |
| $S = 1 \rightarrow s_1 = 1/2, s_2 = 1/2$  | : Product of two spin functions are symmetric.   |
| $L = 1 \rightarrow l_1 = 1, l_2 = 0$      | : The first wavefunction is antisymmetric and the second one is symmetric.<br>Therefore, their product is antisymmetric w.r.t. the exchange. |
| $L = 2 \rightarrow l_1 = 1, l_2 = 1$      | : Both are antisymmetric. Therefore, their product is symmetric.   |

# Example: Helium

---

- (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

---

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: 4p4d

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(Example) 4p4d electron configuration

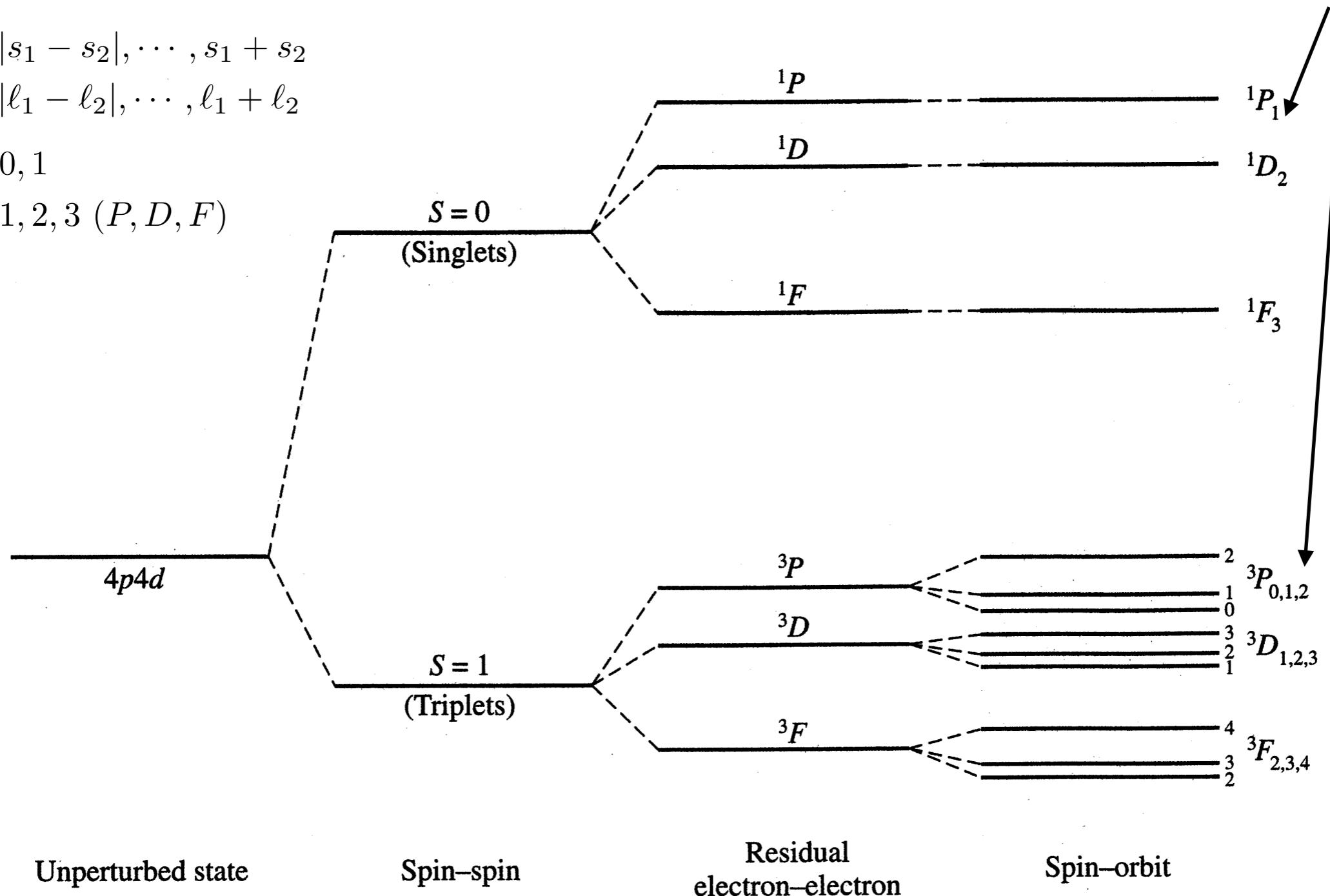
$$J = |L - S|, \dots, L + S$$

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

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

$$S = 0, 1$$

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



# Example npn'p

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(Example)  $nnp'n'p$  electron configuration

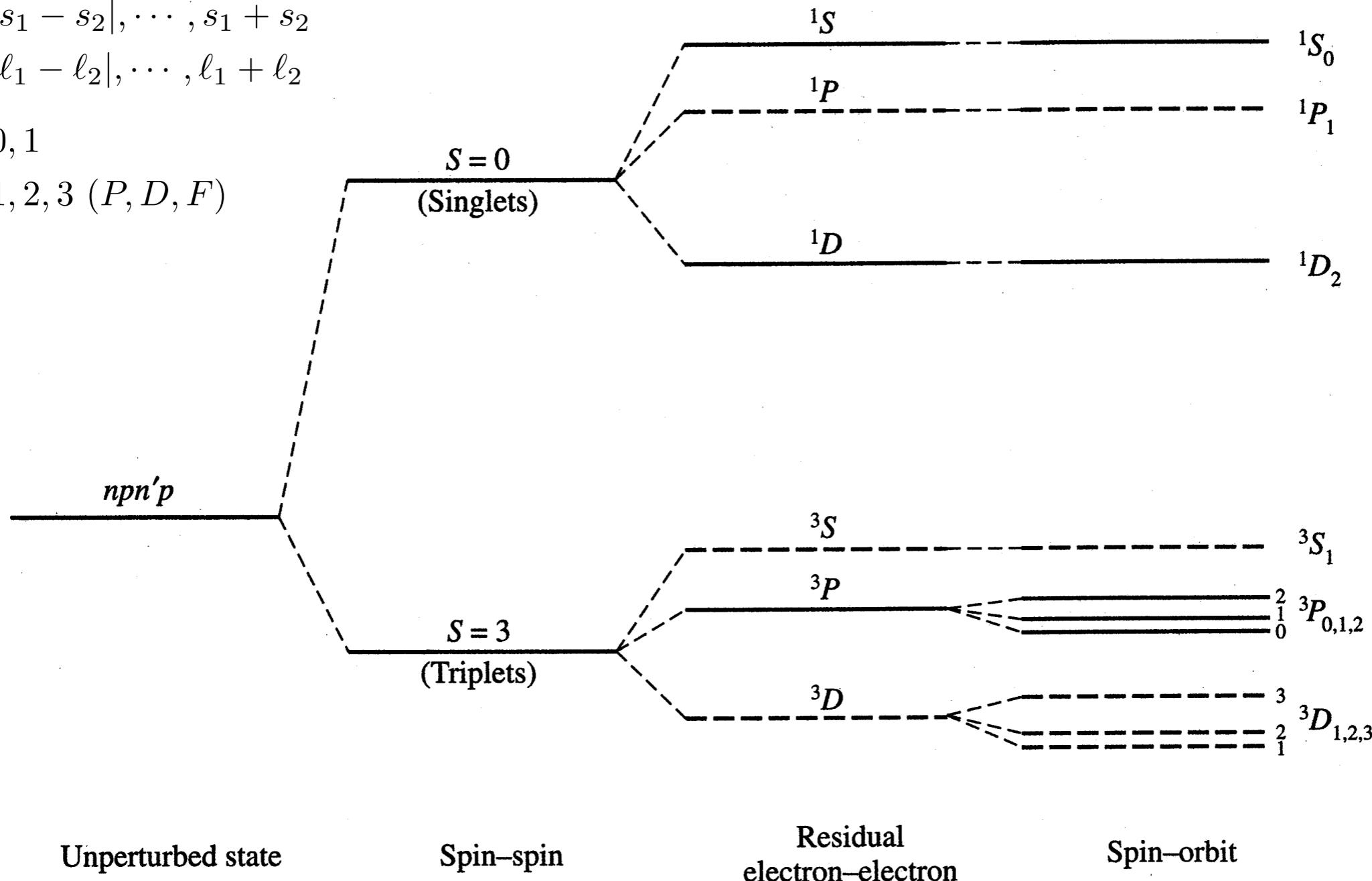
The dashed levels are missing if the two electrons are equivalent ( $n = n'$ )

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

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

$$S = 0, 1$$

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



[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

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

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

- (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.

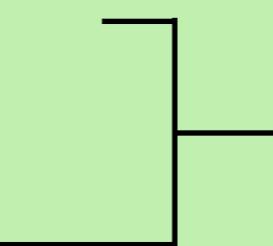
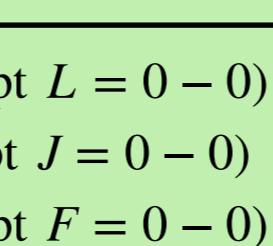
The normal case is a shell which is less than half filled. The inverted case is a shell which is more than half full such as the ground state of atomic oxygen.



- The Hund's rules are only applicable within 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

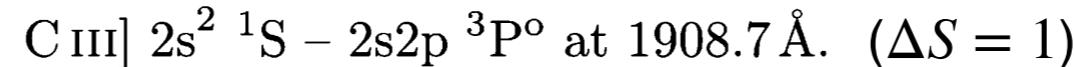
- **Selection Rules**

- |  |  |
|--|--|
| (1) one electron jumps<br>(2) $\Delta n$ any<br>(3) $\Delta l = \pm 1$<br>(4) parity change<br>(5) $\Delta S = 0$<br>(6) $\Delta L = 0, \pm 1$ (except $L = 0 - 0$ )<br>(7) $\Delta J = 0, \pm 1$ (except $J = 0 - 0$ )<br>(8) $\Delta F = 0, \pm 1$ (except $F = 0 - 0$ ) | <br>selection rule for configuration                            |
|  | <br><i>intercombination</i> line if only this rule is violated. |
|  | It is only rarely necessary to consider this.  |

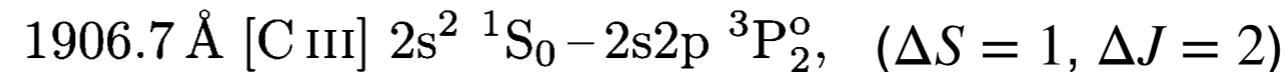
- ***Allowed = Electric Dipole*** : Transitions which satisfy all the above selection rules are referred to as ***allowed transitions***. These transitions are strong and have a typical lifetime of  $\sim 10^{-8}$  s. Allowed transitions are denoted without square brackets.

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.

# Forbidden Lines

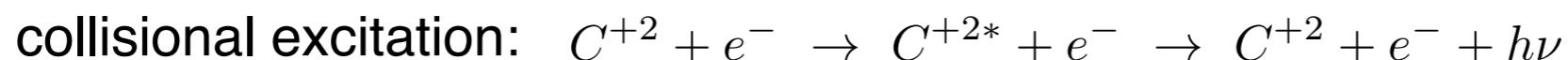
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- Forbidden lines are often difficult to study in the laboratory as collision-free conditions are needed to observe metastable states.
  - In this context, it must be remembered that laboratory ultrahigh vacuums are significantly denser than so-called 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 enough 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 up to 90% of the total visual brightness of objects such as emission nebulae.*

## [Notations]

---

- 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>.



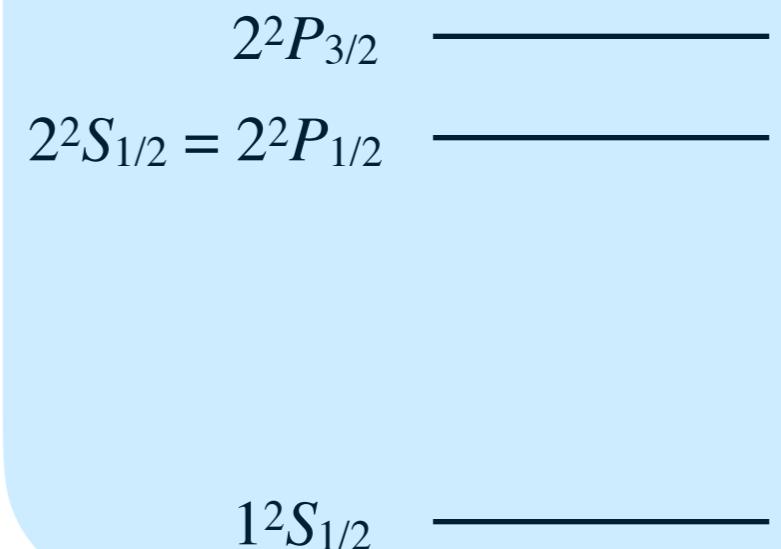
- There is no ambiguity in absorption line studies - only C<sup>+2</sup> can produce a C III absorption line. This had caused many people to think that C III refers to the matter rather than the spectrum.
- But this notation is ambiguous in the case of emission lines.

# Hydrogen Atom : Fine Structure

- Fine structure of the hydrogen atom

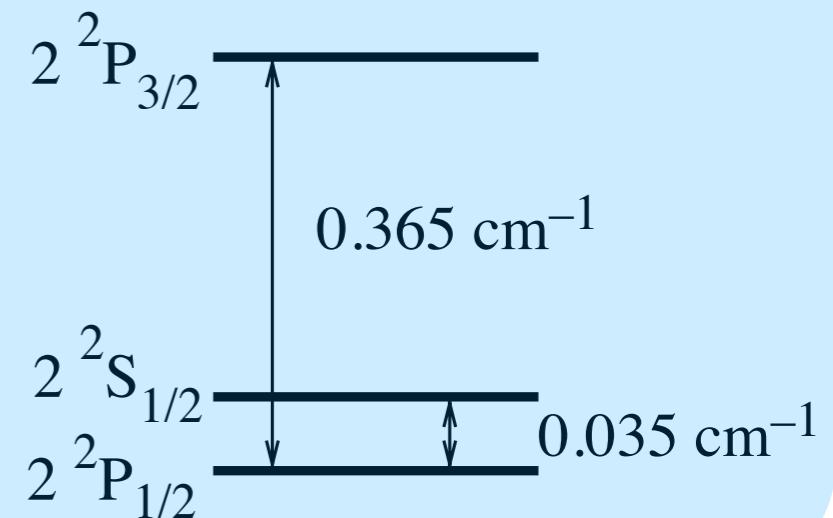
configuration	L	S	J	term	level
$ns$	0	$1/2$	$1/2$	$^2S$	$^2S_{1/2}$
$np$	1	$1/2$	$1/2, 3/2$	$^2P^o$	$^2P_{1/2}^o, ^2P_{3/2}^o$
$nd$	2	$1/2$	$3/2, 5/2$	$^2D$	$^2D_{3/2}, ^2D_{5/2}$
$nf$	3	$1/2$	$5/2, 7/2$	$^2F^o$	$^2F_{5/2}^o, ^2D_{7/2}^o$

## Relativistic QM (Dirac's eq)



- 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

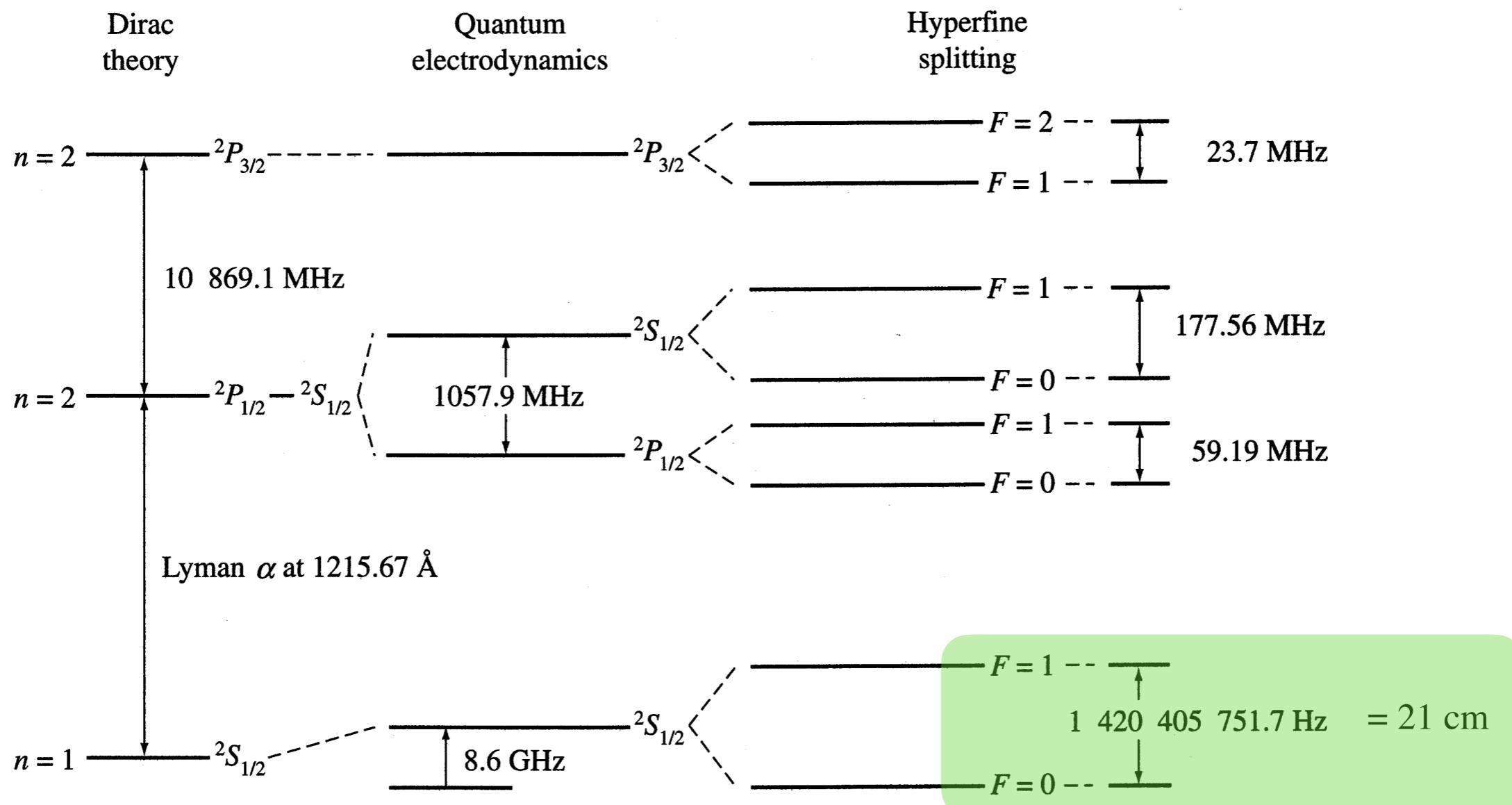


# Hydrogen Atom : Hyperfine Structure

- 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

$\Delta l = \pm 1$

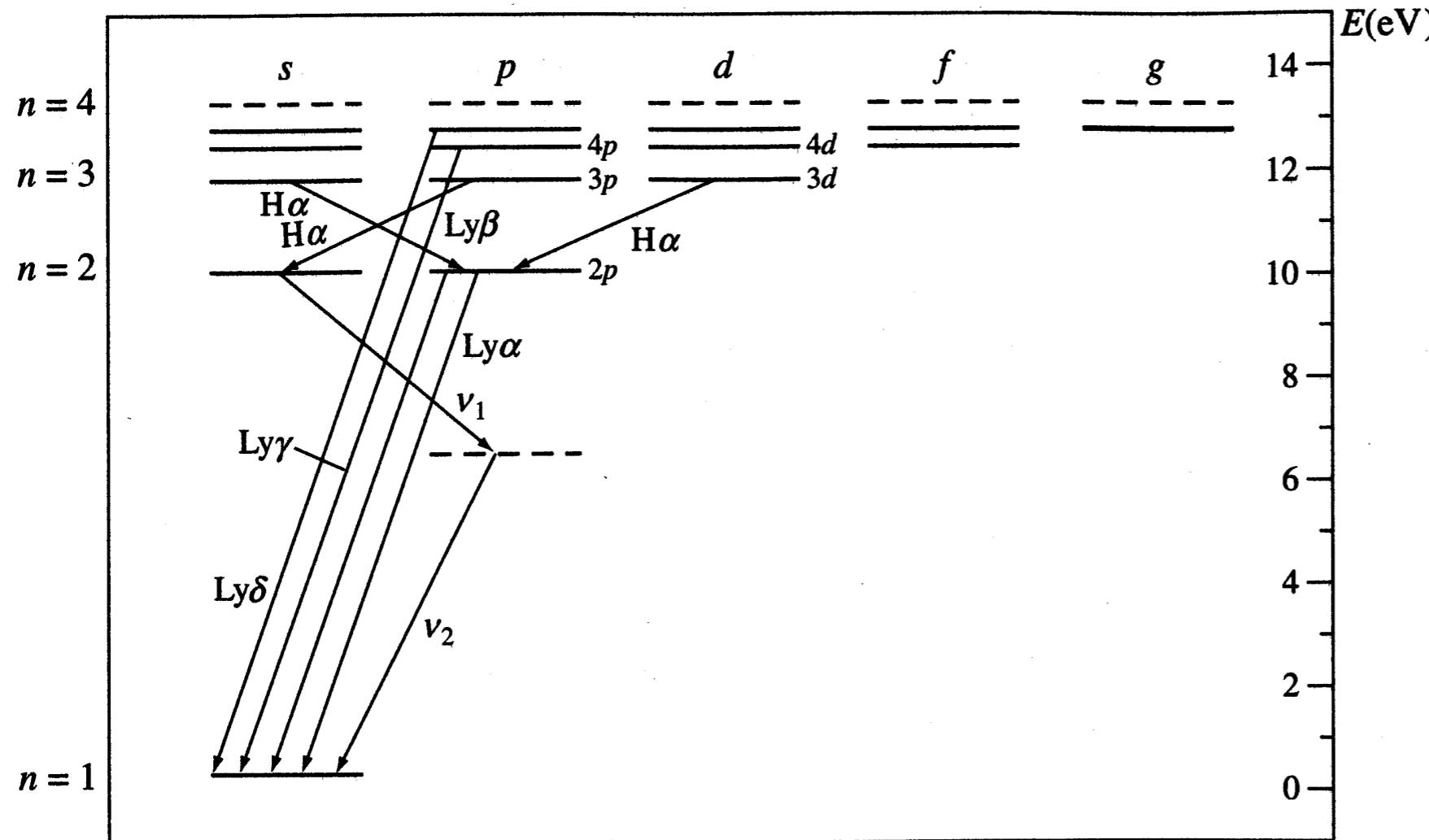
$\Delta S = 0$   For H atom, this is always satisfied as  $S = 1/2$  for all states.

$\Delta L = 0, \pm 1$  (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.

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

$- 3p_{3/2}$  is allowed;

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

$- 3s_{1/2}$  is allowed;

$- 3d_{3/2}$  is allowed;

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

$- 3d_{3/2}$  is allowed;

$- 3d_{5/2}$  is allowed .

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

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

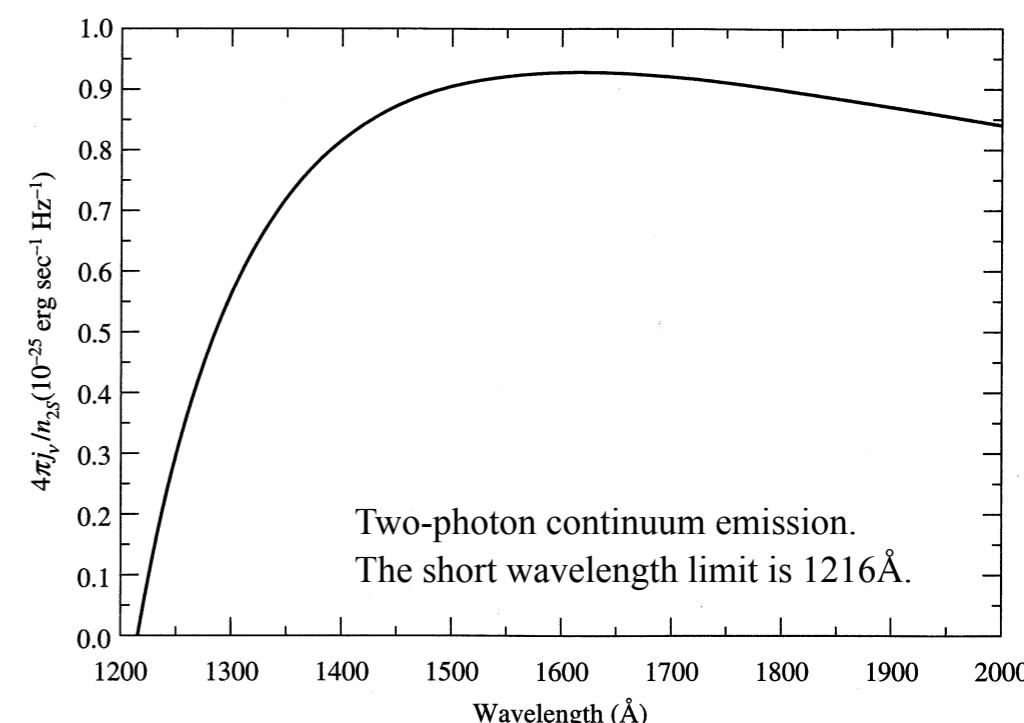
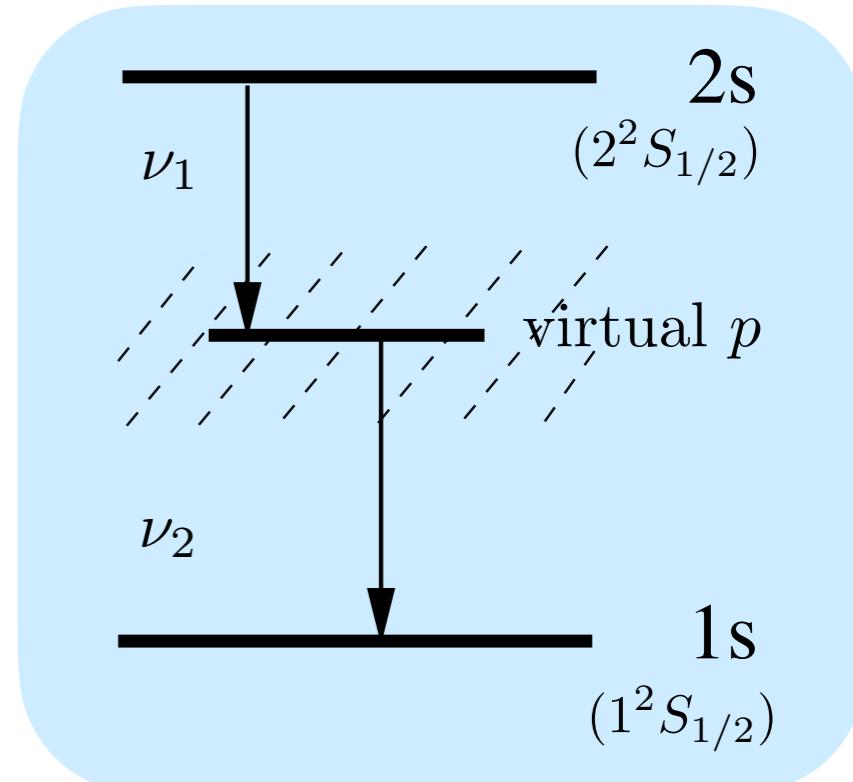
$$\tau_i = \left( \sum_j A_{ij} \right)^{-1} \quad \text{where } A_{ij} \text{ is the Einstein A coefficient}$$

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

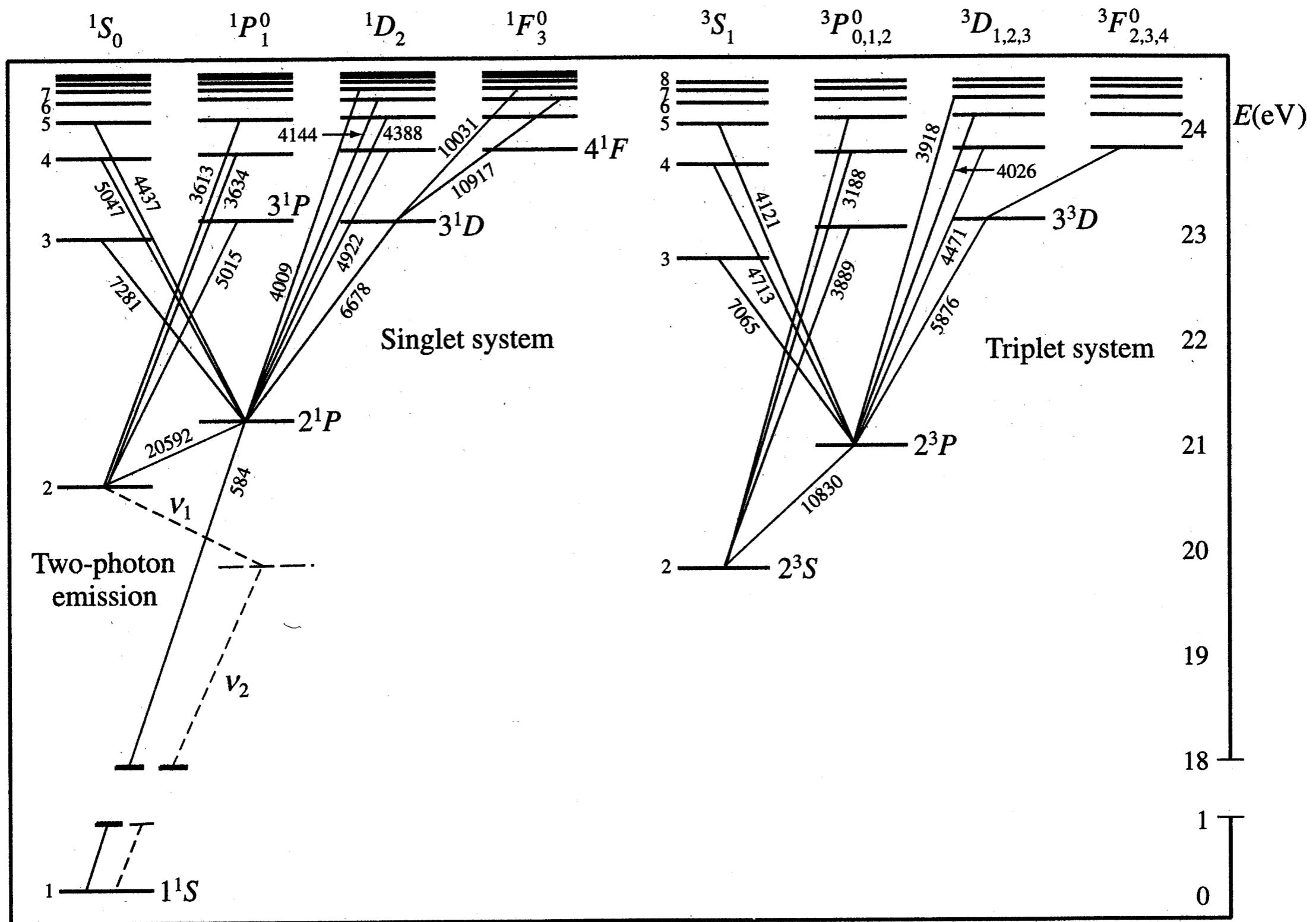
- Lifetimes for allowed transitions are short, a few times  $10^{-9}$  s.
- However, the lifetime for the (2s)  $2^2S_{1/2}$  level is  $\sim 0.14$  s, which is  $10^8$  times longer than the 2p states. (***The level is called to be metastable.***)

- Two-photon continuum radiation***

- In low-density environments (e.g., ISM), 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 ISM, the radiative decay is in general faster than the collisional depopulation process.



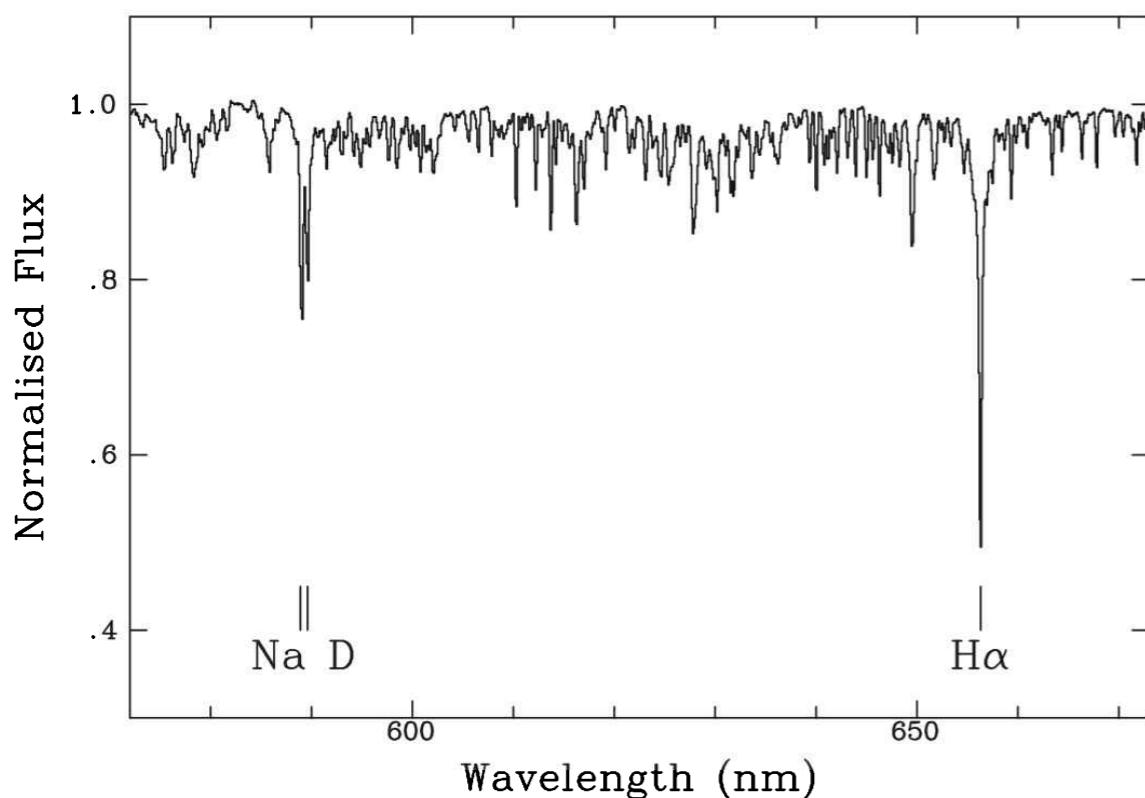
- Helium (Grotrian diagram)



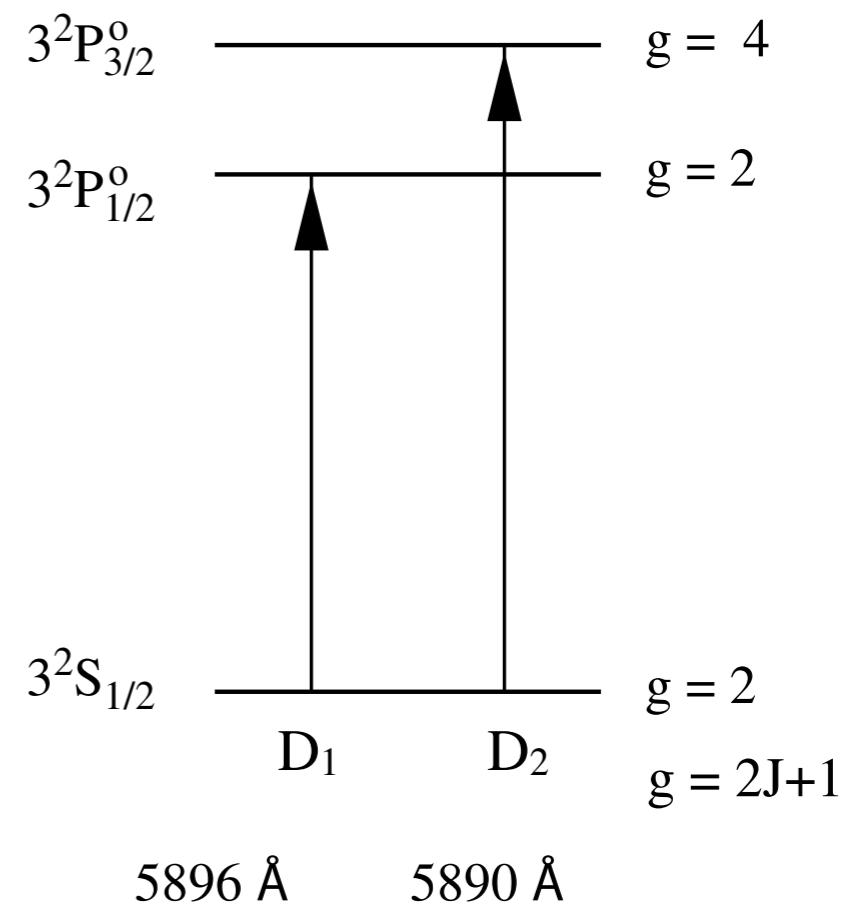
## [Alkali Atoms]

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- 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  $1s^2 2s^2 2p^6 3s^1$  .



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



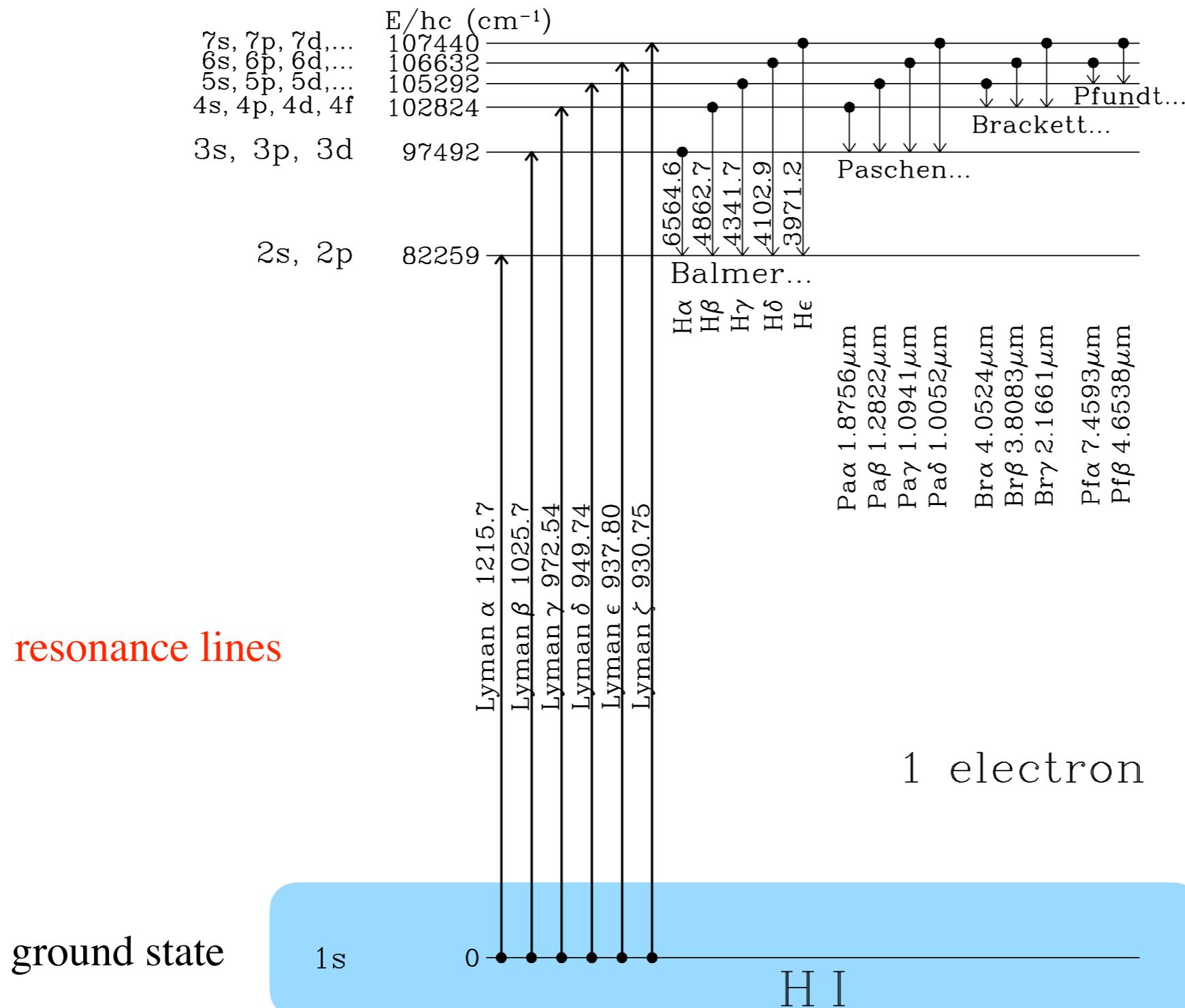
Na D lines:

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

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

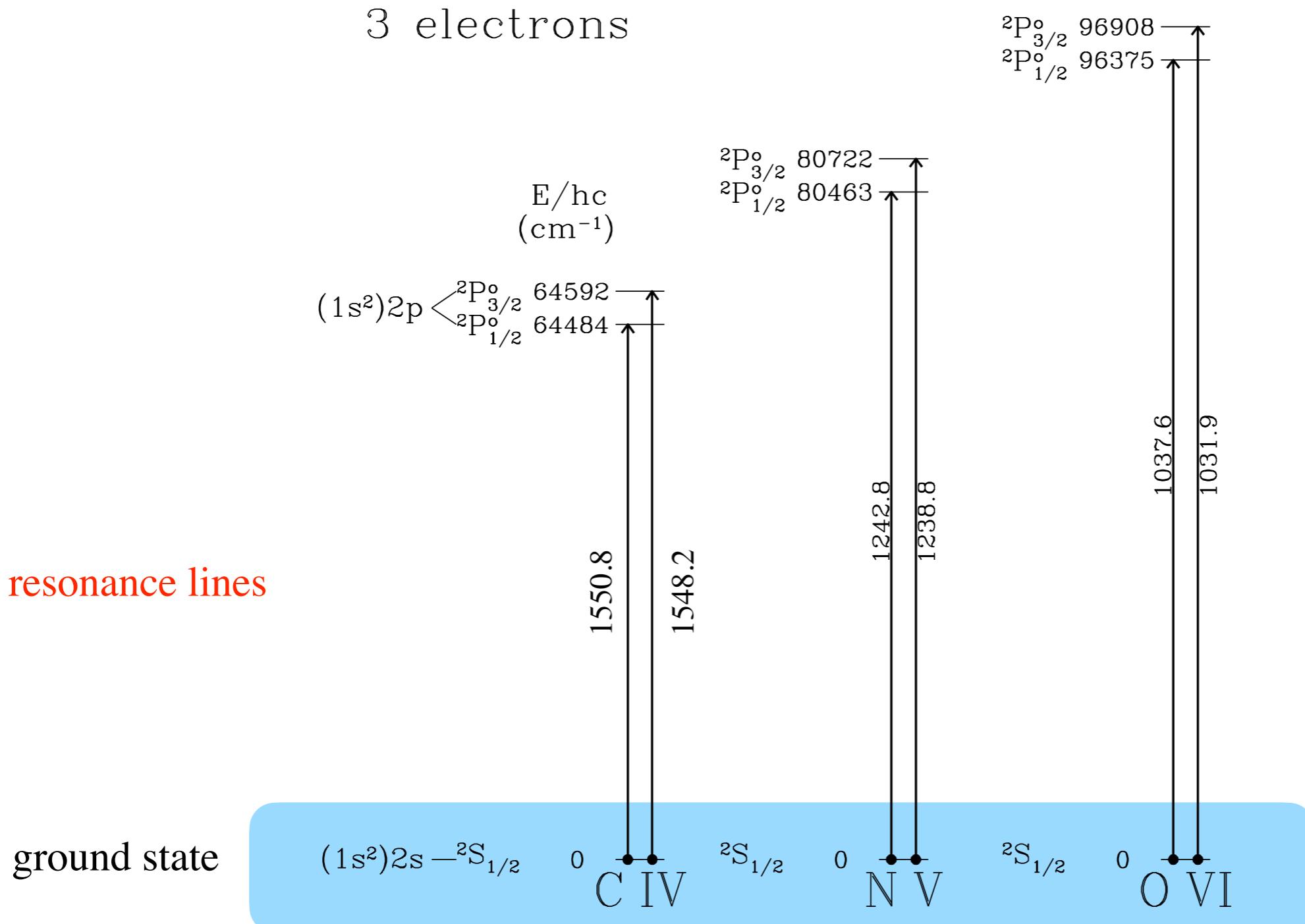
# [Energy Level Diagrams]

- 1 electron



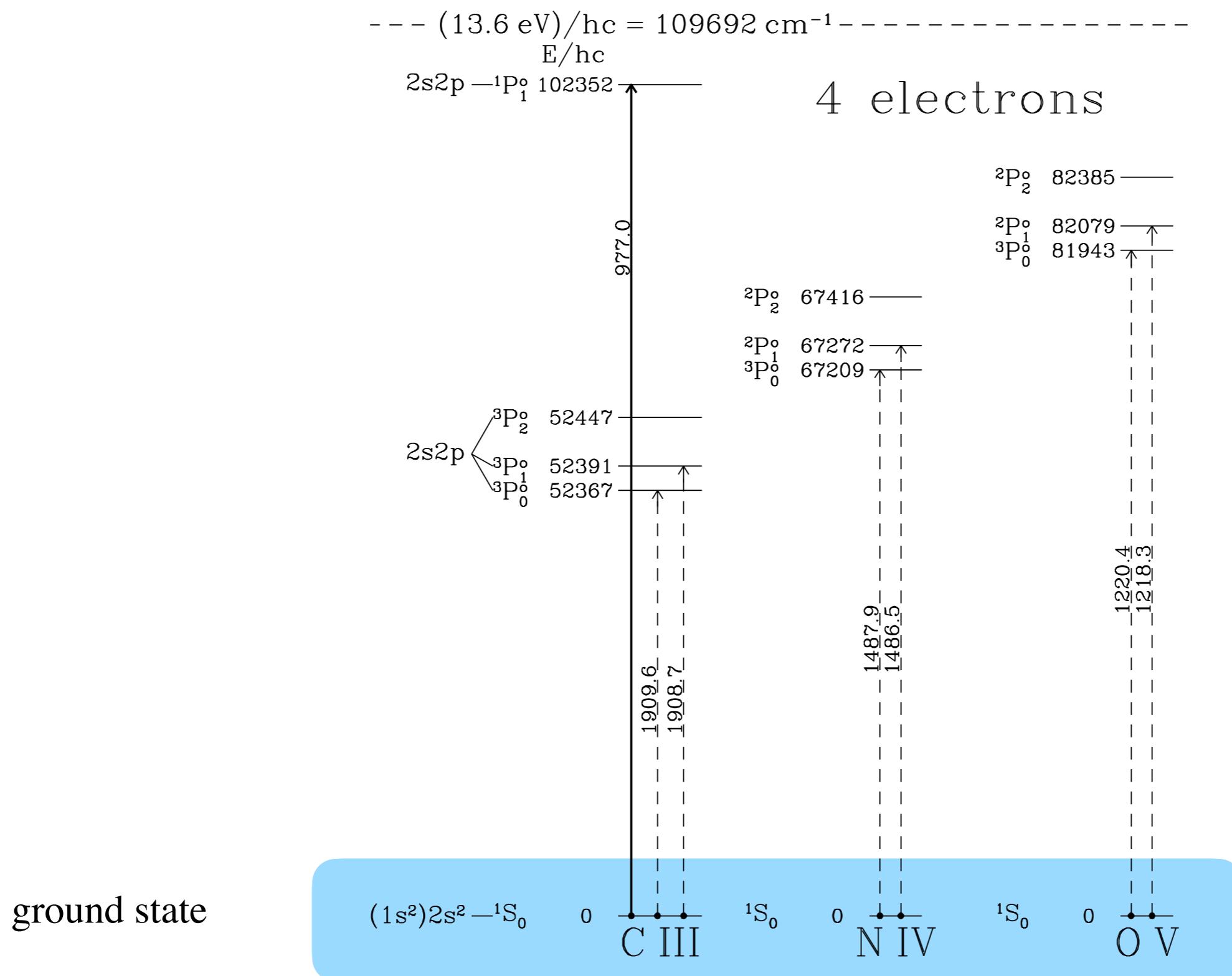
- 3 electrons (Lithium-like ions)

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



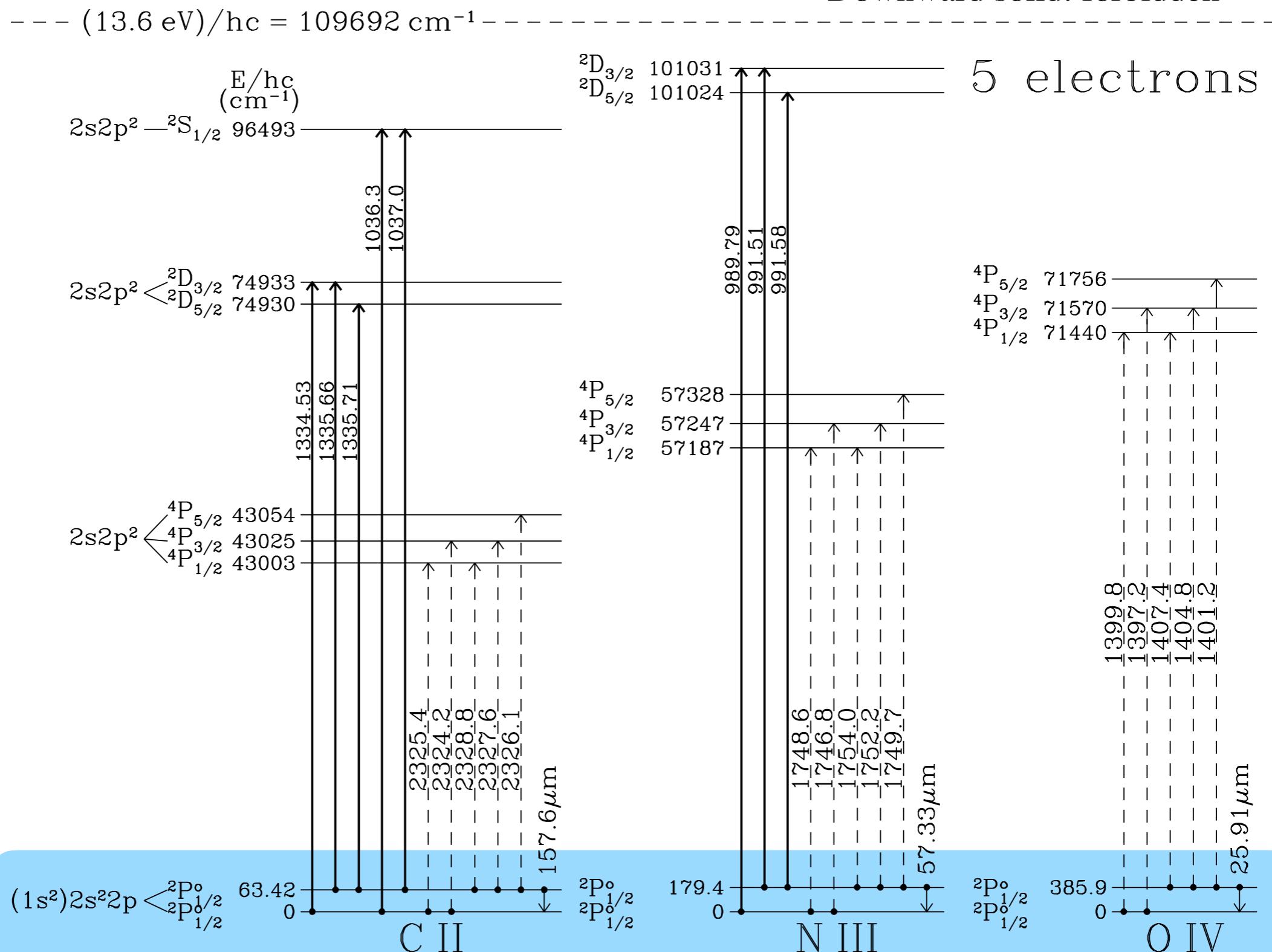
- 4 electrons

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



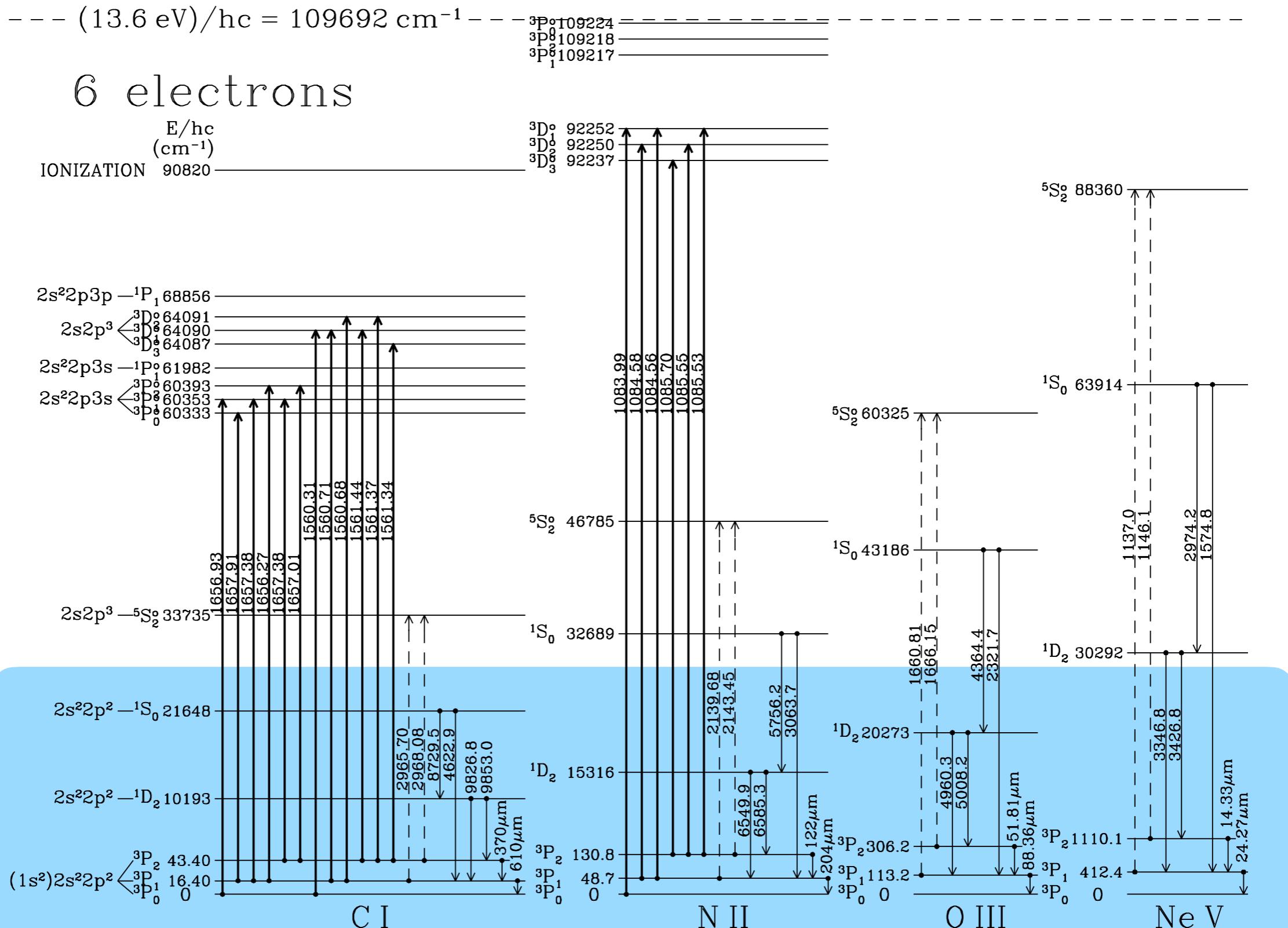
- 5 electrons

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



- 6 electrons

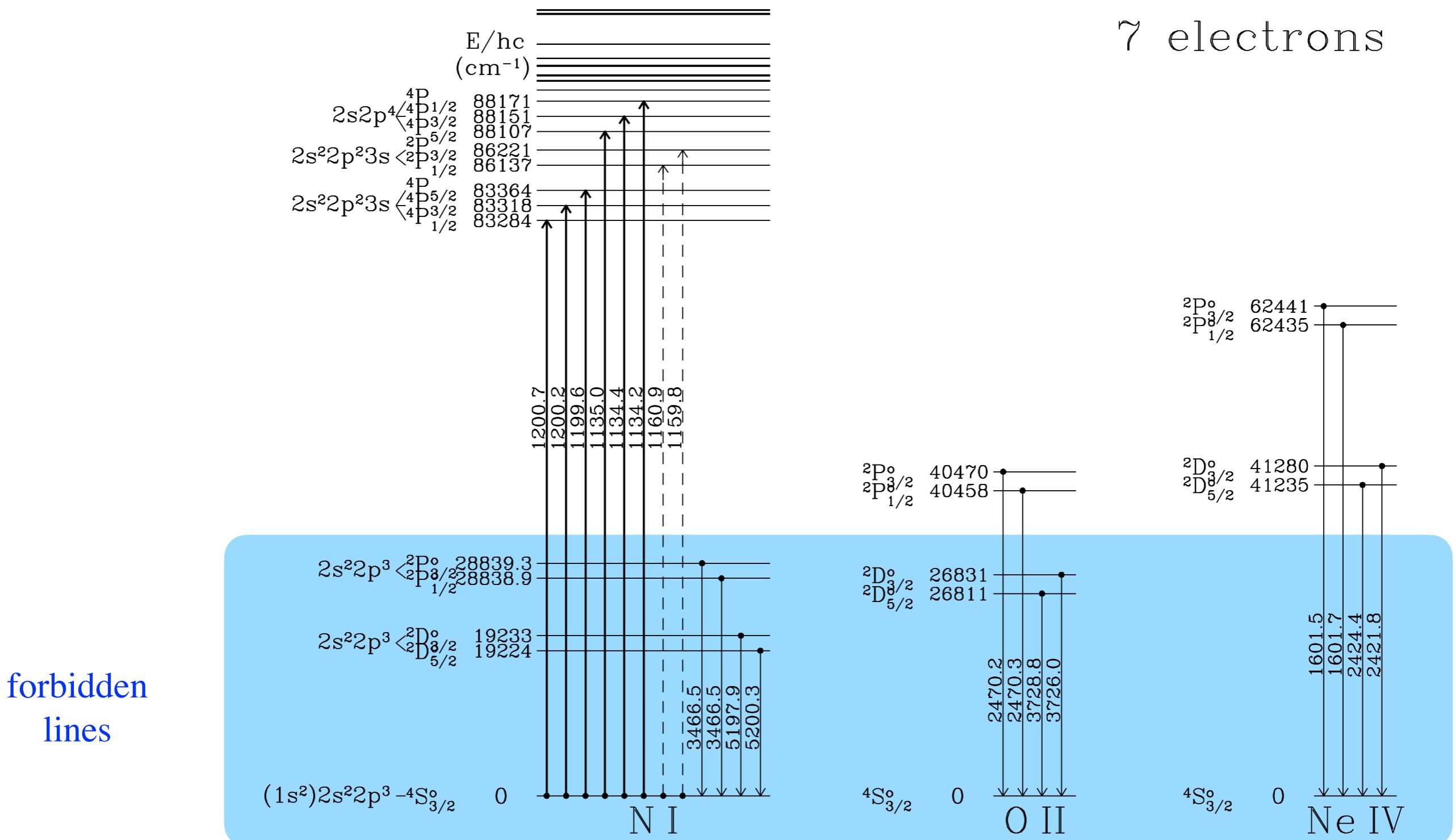
Upward heavy: resonance, Upward Dashed: intercombination  
Downward solid: forbidden



- 7 electrons

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

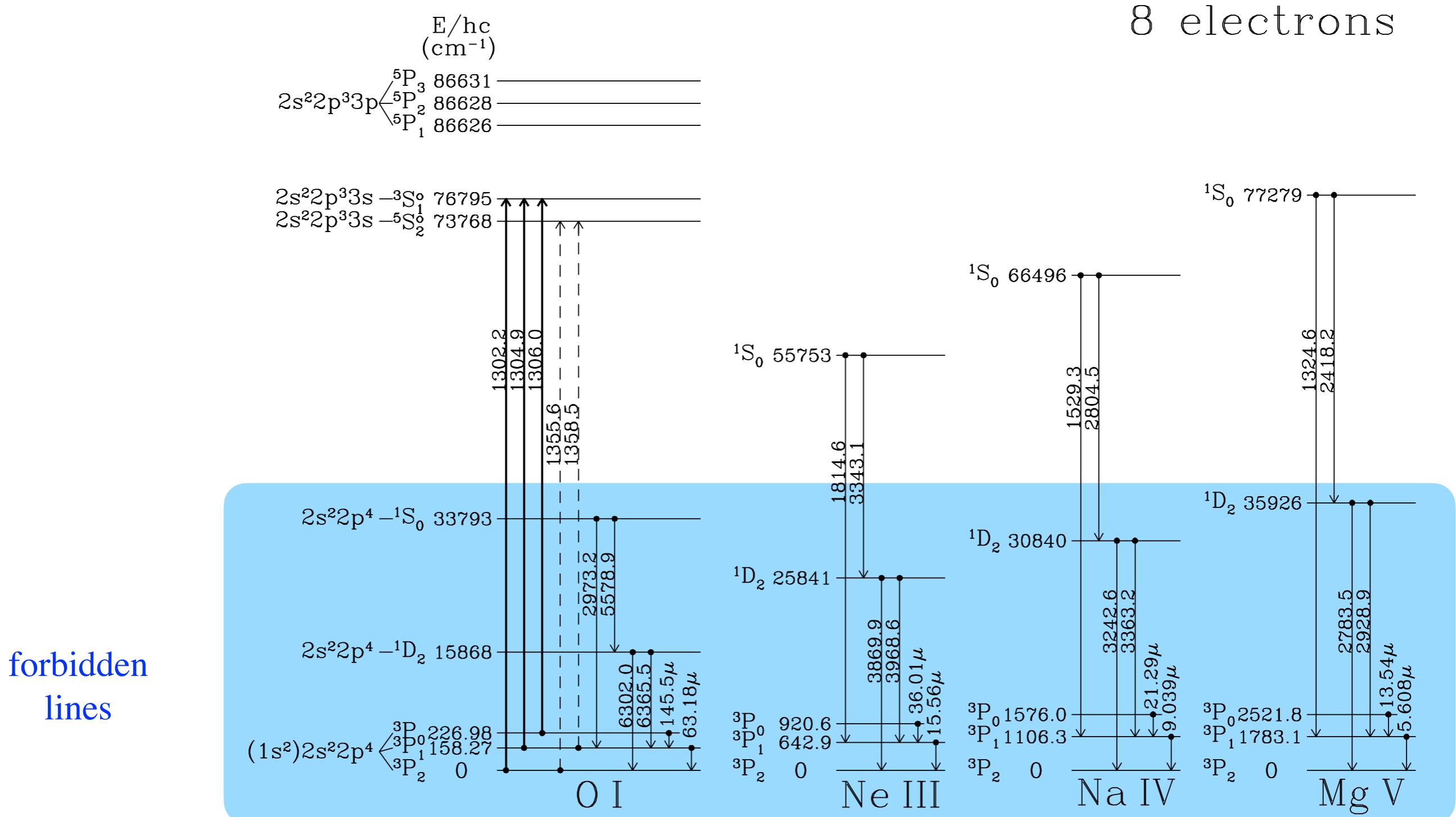
$$\text{---} (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{---} \text{---} \text{---}$$



- 8 electrons

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

--- (13.6 eV)/hc = 109692 cm<sup>-1</sup> -----



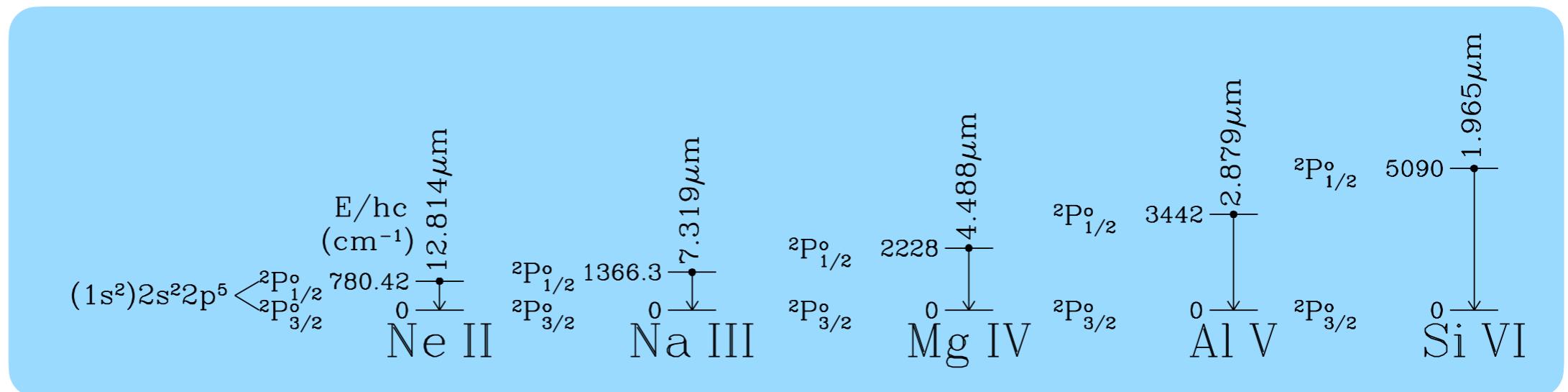
- 9 electrons

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

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

9 electrons

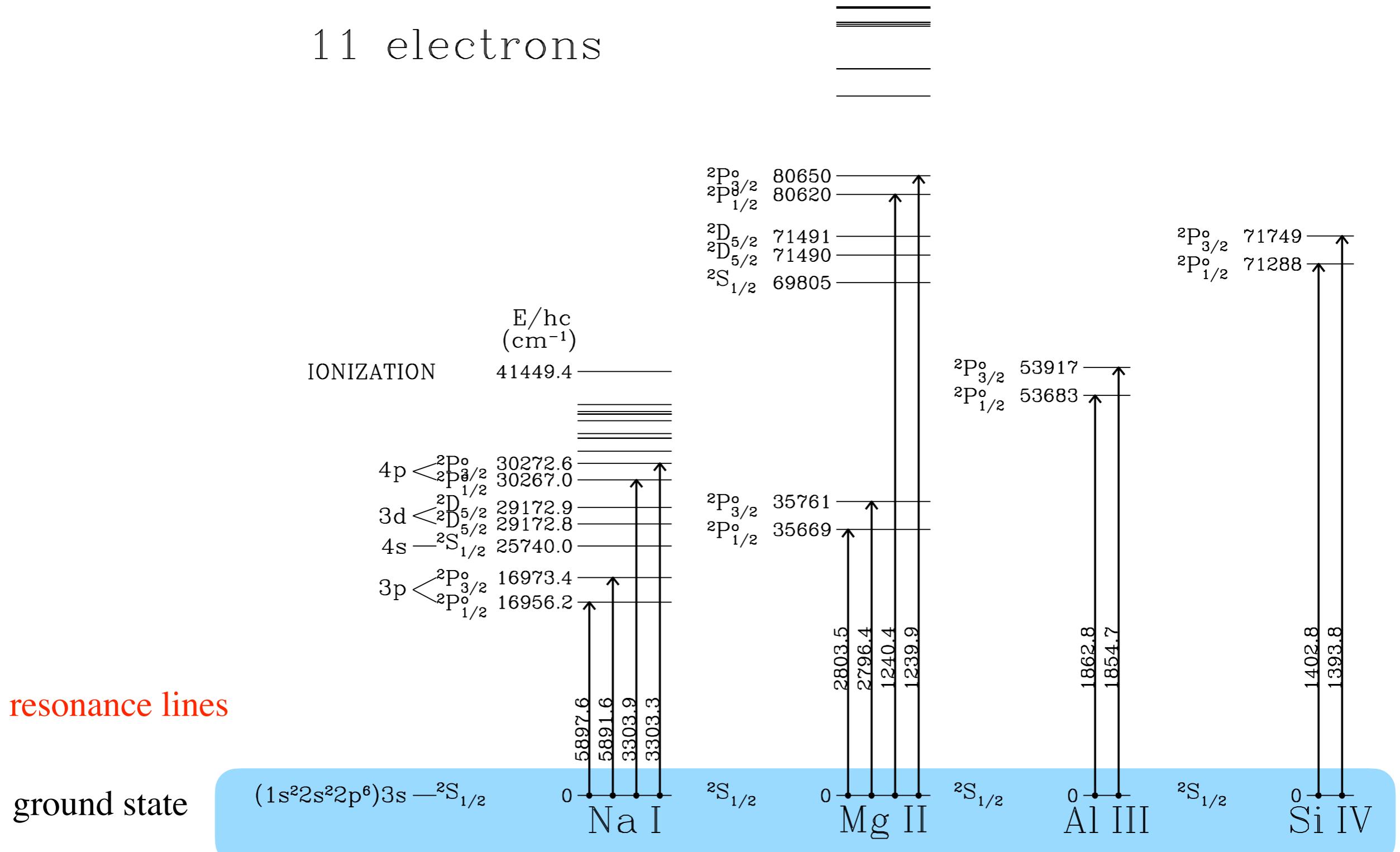
forbidden  
lines



- 11 electrons

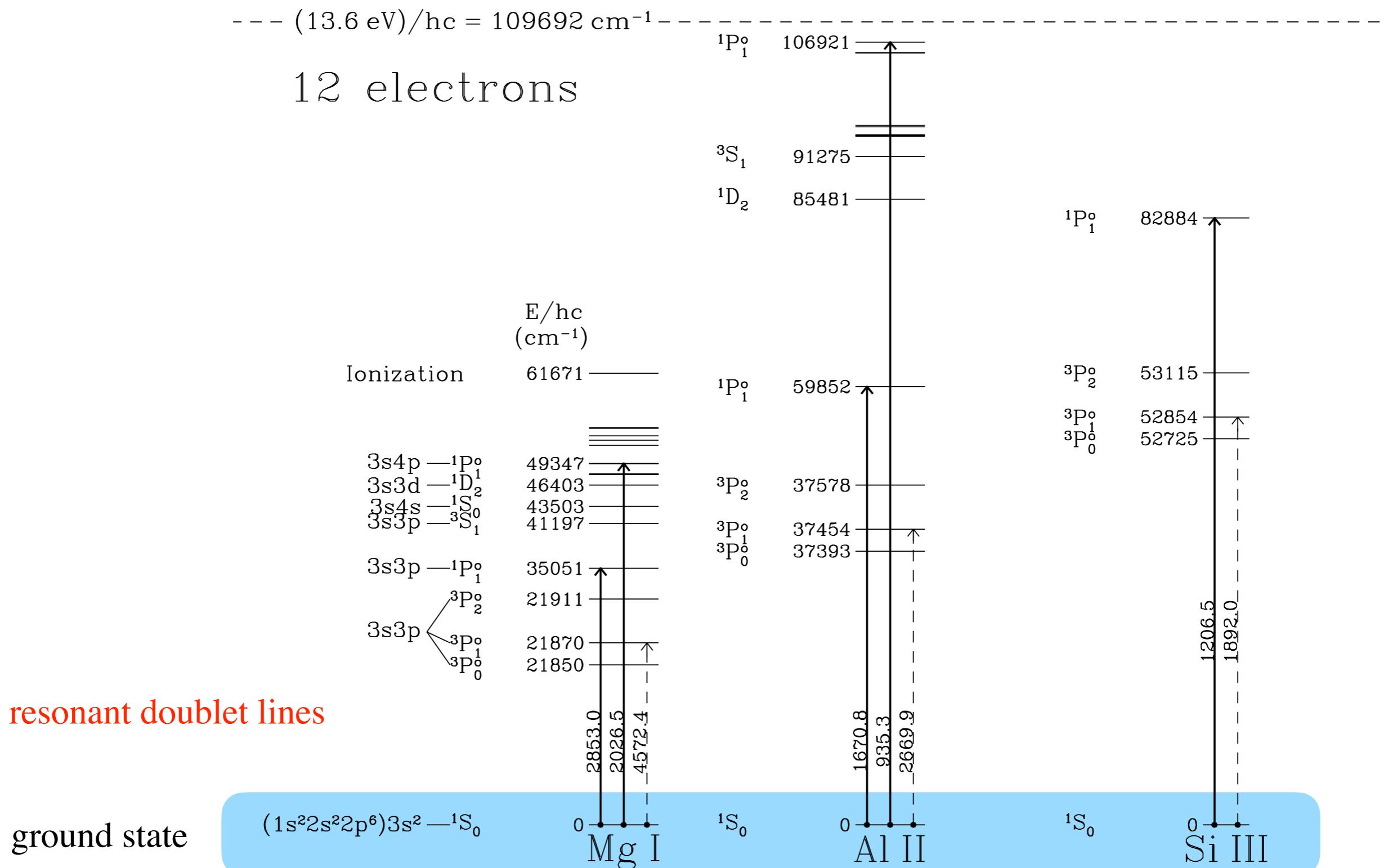
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{ --- }$$

11 electrons



- 12 electrons

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

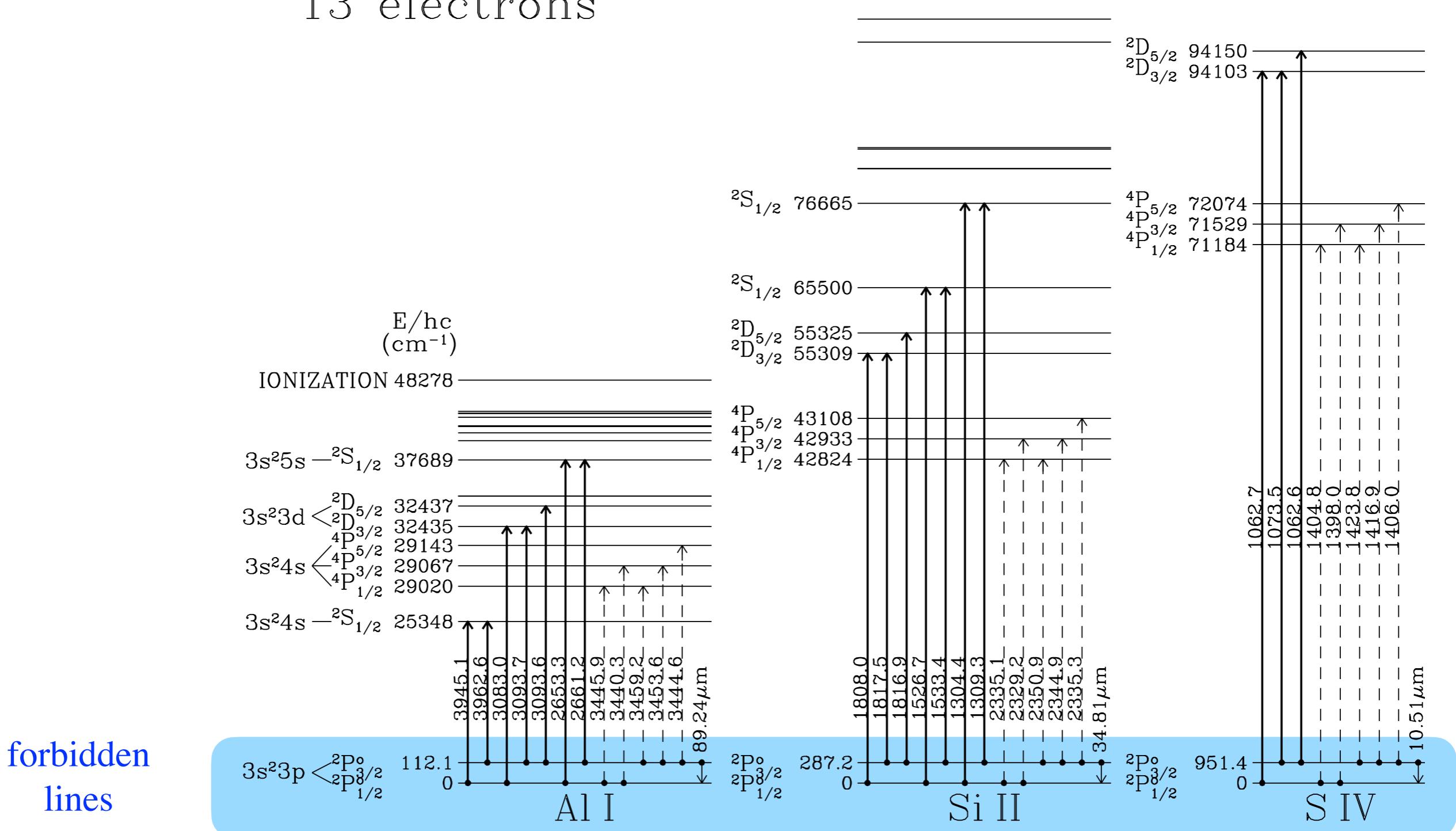


- 13 electrons

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

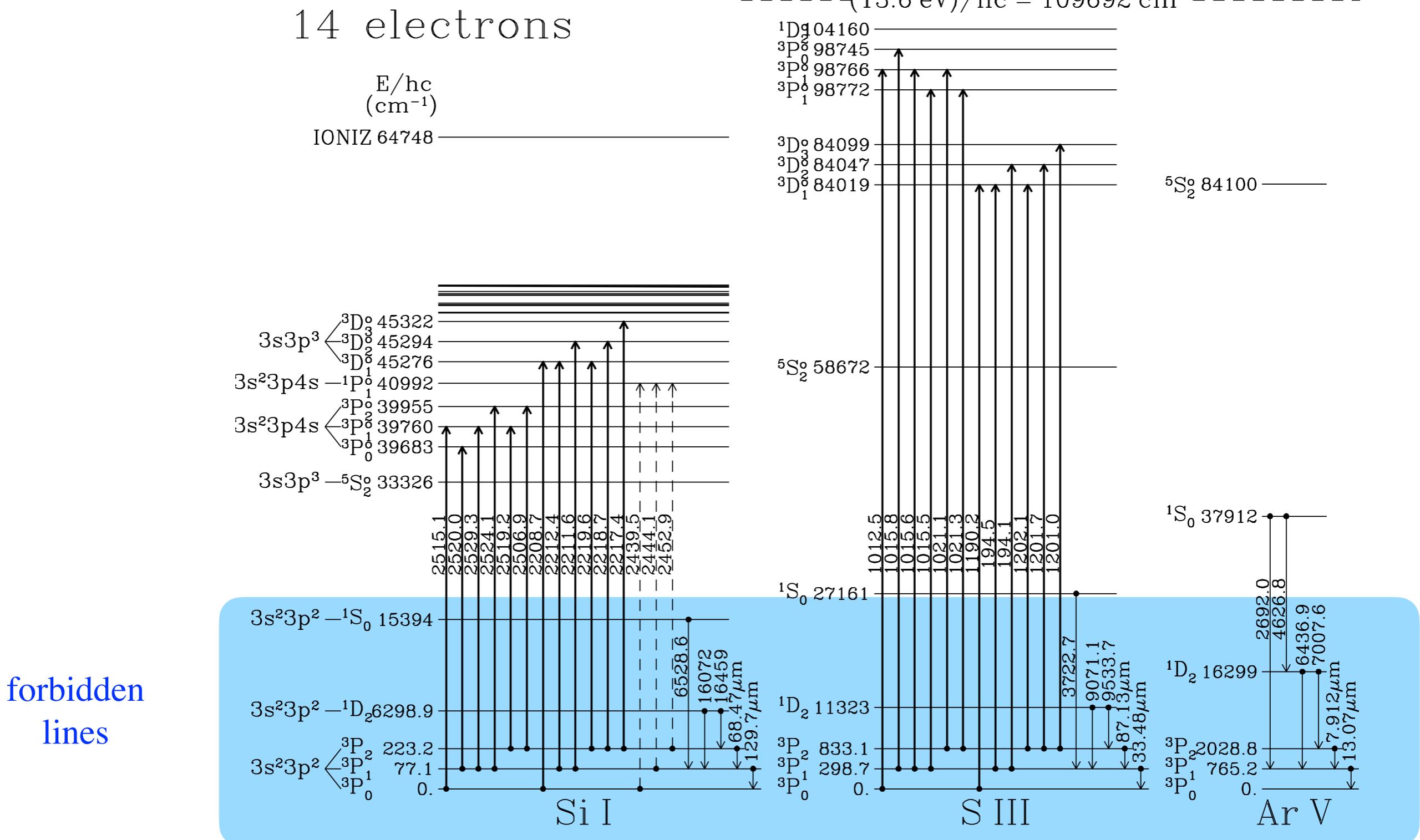
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1}$$

13 electrons



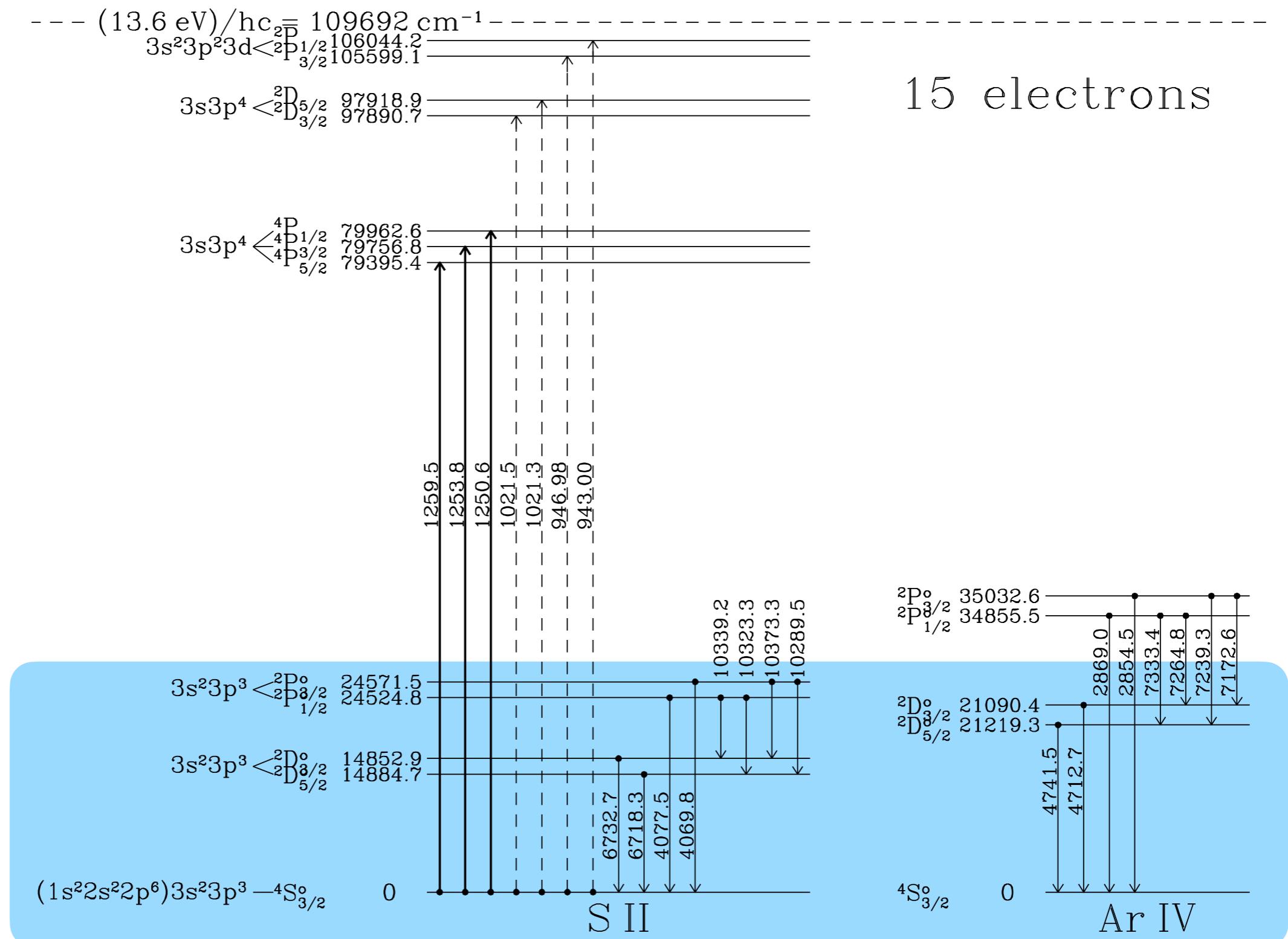
- 14 electrons

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



- 15 electrons

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



# Homework

Deadline: 2022, Dec. 07 (Wed)

1. 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?
2. 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.
3. Give the spectroscopic terms arising from the following configurations, using L-S coupling. Include parity and J values. Give your arguments in detail for deriving these results
  - (a)  $2s^2$
  - (b)  $2p3s$
  - (c)  $3p4p$
  - (d)  $2p^43p$

4. 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?

5. The right 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.

