

Interstellar Medium (ISM)

Week 2

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Atomic Structure, Spectroscopy

References

- Books for atomic/molecular structure and spectroscopy
 - Astronomical Spectroscopy [Jonathan Tennyson]
 - Physics of the Interstellar and Intergalactic Medium [Bruce T. Draine]
⇒ see <https://www.astro.princeton.edu/~draine/> for errata
 - Astrophysics of the Diffuse Universe [Michael A. Dopita & Ralph S. Sutherland]
⇒ many typos
 - Physics and Chemistry of the Interstellar Medium [Sun Kwok]
 - Atomic Spectroscopy and Radiative Processes [Egidio Landi Degl'Innocenti]

Hydrogen Atom: Schrödinger Equation

- Momentum operator

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

- Hamiltonian operator

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

- The time-dependent Schrödinger equation for a system with Hamiltonian H:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad \xrightarrow{\hspace{1cm}} \quad i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) + V(r)\Psi(\mathbf{r}, t)$$

The time and space parts of the wave function can be separated:

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

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

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad \xrightarrow{\hspace{1cm}} \quad \frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

- 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

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

- Quantum Number

- $n = 1, 2, 3, \dots$: principal quantum number
- $l = 1, 2, \dots, n-1$: 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: $\int_0^{2\pi} \int_0^\pi |Y_{l,m}|^2 \sin \theta d\theta d\phi = 1$

- The spherical harmonics are eigenfunctions of the orbital angular momentum operator

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \frac{\hbar}{i} \mathbf{r} \times \nabla$$

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

- The sizes of the angular moment and z-component are

$$|\mathbf{L}| = \sqrt{l(l+1)}\hbar, \quad |L_z| = m\hbar$$

- 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
 - $l = 1, 2, \dots, n - 1$: 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 for the spin.

$$m_s = \pm \frac{1}{2}$$

Complex Atoms : Schrödinger Equation

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

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

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

- The first term contains a ***kinetic energy operator for the motion of each electron*** and the ***Coulomb attraction between the electron and the nucleus***.
- The second term contains the ***electron-electron Coulomb repulsion*** term.
- The equation is not analytically solvable, even for the simplest case, the helium atom for which $N = 2$.

Complex Atoms : Central Field Approximation

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

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

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

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

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

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

Central Field Approximation: Electron Configuration

- **The configuration** is the distribution of electrons of an atom in atomic **orbitals**.
 - The configuration of an atomic system is defined by specifying the nl values of all the electron orbitals: nl^x means x electrons in the orbital defined by n and l .
 - Each orbital labelled nl actually consists of orbitals with $2l + 1$ different m values, each with two possible values of m_s . Thus the nl orbital can hold a maximum $2(2l + 1)$ electrons.
- **shells, subshells:**
 - Shells correspond with the principal quantum numbers (1, 2, 3, ...). They are labeled alphabetically with letters used in the X-ray notation (K, L, M, ...).
 - Each shell is composed of one or more subshells. The first (K) shell has one subshell, called “1s”; The second (L) shell has two subshells, called “2s” and “2p”.
- **open shell configuration, closed shell configuration:**
 - open shell = shell that is not completely filled with electrons: For instance, the ground state configuration of carbon, which has six electrons: $1s^2 2s^2 2p^2$
 - closed shell = shell of which orbitals are fully occupied: For example, the ground state configuration of neon atom, which has ten electrons: $1s^2 2s^2 2p^6$
- **Active electrons:** As a result of the Pauli Principle, closed shells and sub-shells have both $L = 0$ and $S = 0$. This means that ***it is only necessary to consider ‘active’ electrons, those in open or partially-filled shells.***
- **Equivalent and Nonequivalent Electrons**
 - Nonequivalent electrons are those differing in either n or l values, whereas equivalent electrons have the same n and l values.

Indistinguishable Particles & Parity

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

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

- **Pauli exclusion principle:** The Pauli exclusion principle is summarized as “**No two electrons can occupy the same spin-orbital.**”
 - This exclusion provides the degeneracy pressure which holds up the gravitational collapse of white dwarfs and neutron stars.
 - **Parity of the wave function**
 - The parity of the wave function is determined by how the wave function behaves upon inversion. The square of the wave function, i.e., the probability distribution of the electrons, must be unchanged by the inversion operation.
- $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \pm \Psi(-\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_N)$
- Even parity states are given by “+” sign and odd parity states are given by “−” sign.
 - The parity arising from a particular configuration can be determined simply by summing the orbital angular momentum quantum numbers for each of the electrons.
- $$\text{parity} = (-1)^{l_1+l_2+\dots+l_N}$$
- As closed shells and sub-shells have an even number of electrons, ***it is only necessary to explicitly consider the active electrons.***

Energy ordering & Periodic Table

- **Energy ordering for configuration:**

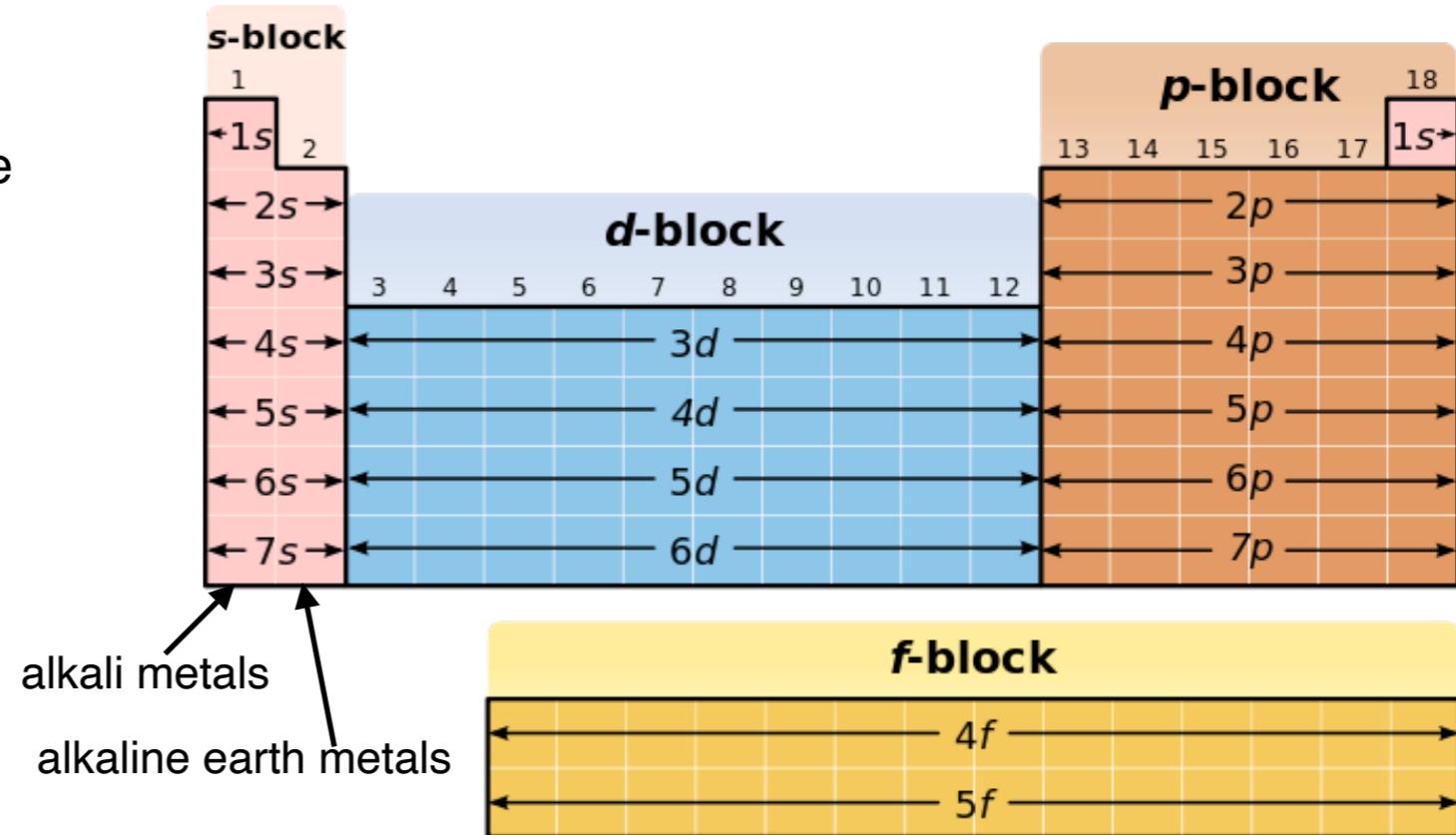
- For a H atom, the energy of the individual orbitals is determined only by principal quantum number n .
- For complex atoms, the degeneracy on the orbital angular momentum quantum number l is lifted.
- Electrons in low l orbits ‘penetrate’, i.e., get inside orbitals with lower n -values. Penetration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

- **Periodic Table**

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

The orbitals of complex atoms follow a revised energy ordering:

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



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

Lifting Degeneracy in Configuration: Angular Momentum Coupling, Terms

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

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

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

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

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

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 an electron moves around the nucleus with a non relativistic velocity \mathbf{v} , the electric field exerting on the electron will be $E = Ze\frac{\mathbf{r}}{r^3}$. (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 of electron)

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

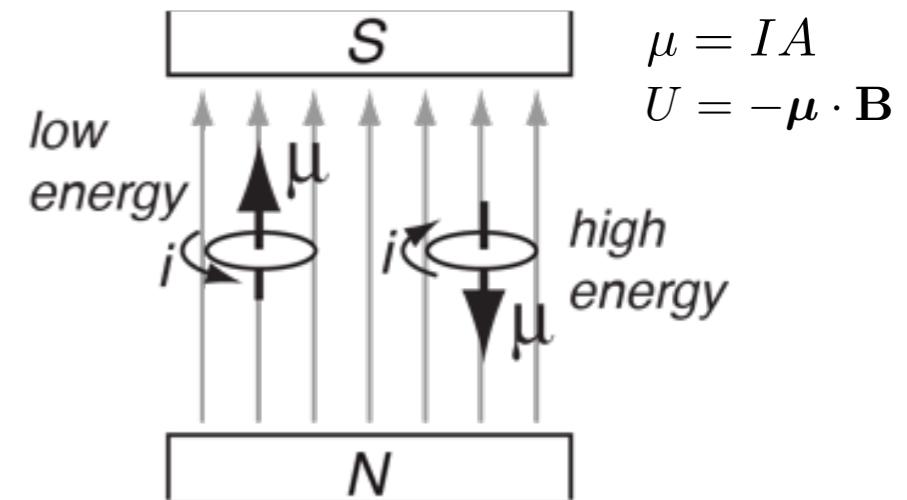
$$\boldsymbol{\mu} = -\frac{e}{m_e c} \mathbf{s}$$

- 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

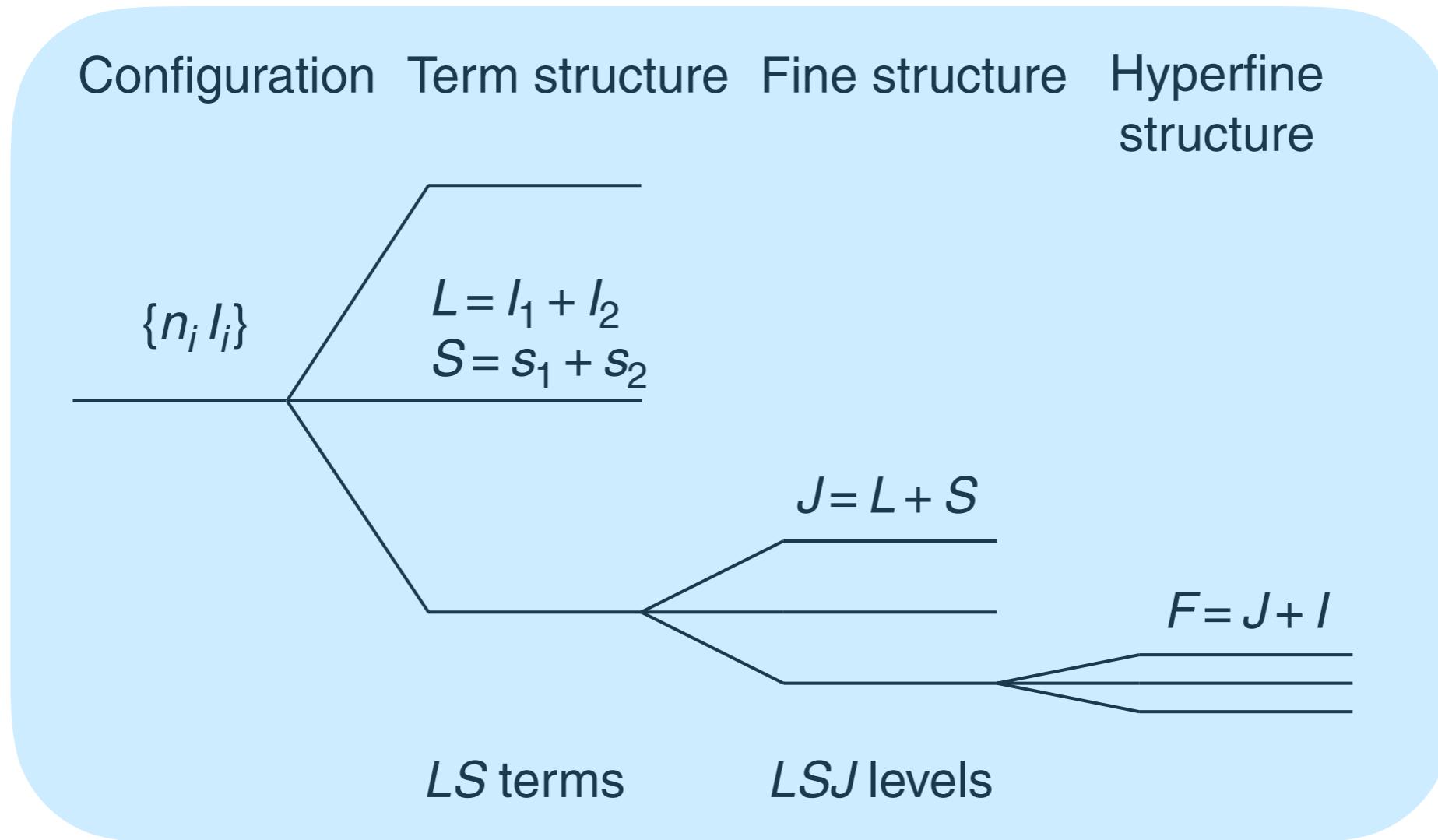
$$H_{\text{so}} = \frac{1}{2} \xi (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

- 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)

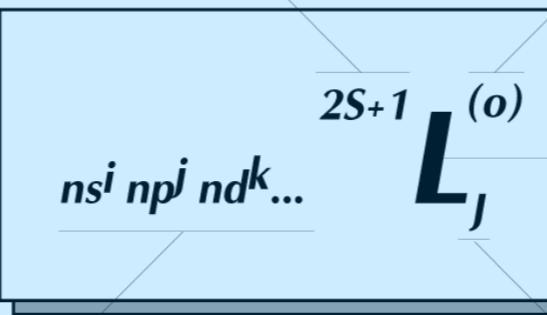


Spectroscopic Notation

- Spectroscopic Notation**

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

Term Parity:
 o for odd, nothing for even



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

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

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

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

- A state with $S = 0$ is a ‘singlet’ as $2S+1 = 1$.
 - ▶ $J = L$ (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,...

[Draine, Physics of the ISM and IGM]

Table 4.1 Terms for ns and np Subshells

Ground configuration	Terms / Levels (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
$\dots np^2$	$^3P_{0,1,2}^o, ^1D_2, ^1S_0$	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

[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.

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
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

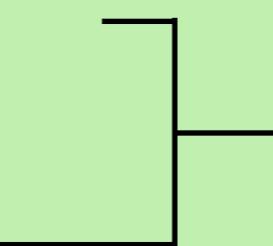
- **Energy ordering: Hund's rules**
 - (1) **S-rule:** For a given configuration, ***the state with the maximum spin multiplicity is lowest in energy.*** The electrons repel each other, and therefore their mutual electrostatic energy is positive. The farther away the electrons get, the lower will be the contribution of the electrostatic energy to the total energy.
 - (2) **L-rule:** For a given configuration and spin multiplicity, ***the state with the maximum orbital angular momentum is the lowest in energy.***
 - (3) **J-rule:** ***The lowest energy is obtained for lowest value of J in the normal case and for highest J value in the inverted case.***
 - The normal case is a shell which is less than half filled. The inverted case is a shell which is more than half full such as the ground state of atomic oxygen.



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

Selection Rules

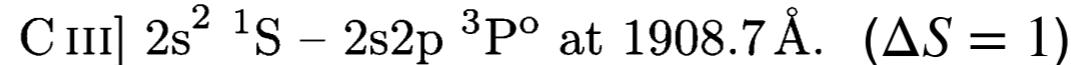
- **Selection Rules**

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

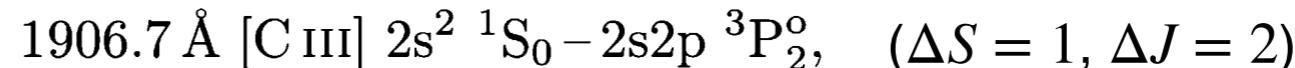
- ***Allowed = Electric Dipole*** : Transitions which satisfy all the above selection rules are referred to as ***allowed transitions***. These transitions are strong and have a typical lifetime of $\sim 10^{-8}$ s. Allowed transitions are denoted without square brackets.

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

- 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

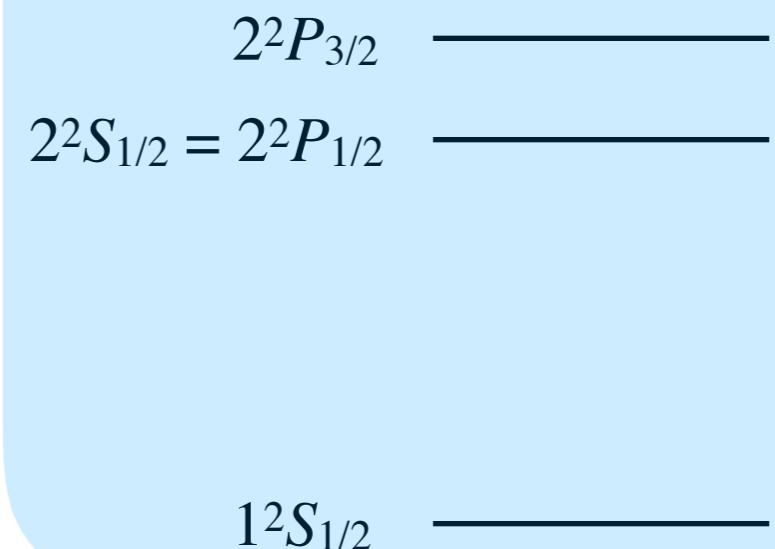
- Notations for Spectral Emission Lines and for Ions
 - There is a considerable confusion about the difference between these two ways of referring to a spectrum or ion, for example, C III or C⁺². These have very definite different physical meanings. However, in many cases, they are used interchangeably.
 - C⁺² is a baryon and C III is a set of photons.
 - C⁺² 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⁺² or by recombination of C⁺³. So, depending on how the spectrum is formed. C III may be emitted by C⁺² or C⁺³.
- collisional excitation: $C^{+2} + e^- \rightarrow C^{+2*} + e^- \rightarrow C^{+2} + e^- + h\nu$
- recombination: $C^{+3} + e^- \rightarrow C^{+2} + h\nu$
- There is no ambiguity in absorption line studies - only C⁺² can produce a C III absorption line. This had caused many people to think that C III refers to the matter rather than the spectrum.
- But this notation is ambiguous in the case of emission lines.

Hydrogen Atom : Fine Structure

- Fine structure of the hydrogen atom

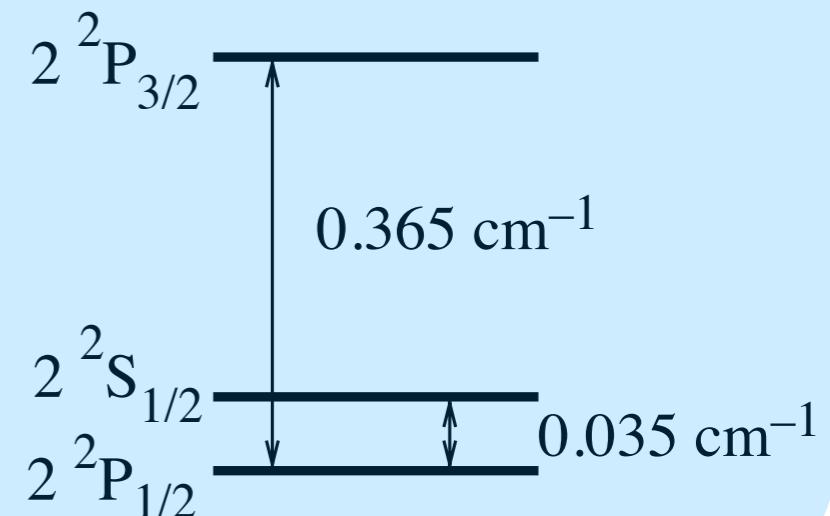
configuration	L	S	J	term	level
ns	0	$1/2$	$1/2$	2S	$^2S_{1/2}$
np	1	$1/2$	$1/2, 3/2$	$^2P^o$	$^2P_{1/2}^o, ^2P_{3/2}^o$
nd	2	$1/2$	$3/2, 5/2$	2D	$^2D_{3/2}, ^2D_{5/2}$
nf	3	$1/2$	$5/2, 7/2$	$^2F^o$	$^2F_{5/2}^o, ^2D_{7/2}^o$

Relativistic QM (Dirac's eq)



- Splitting in the $n = 2$ levels of atomic hydrogen.
 - 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 $^2S_{1/2}$.
 - This is called the Lamb shift (Quantum Electrodynamics effect).

Quantum Electrodynamics

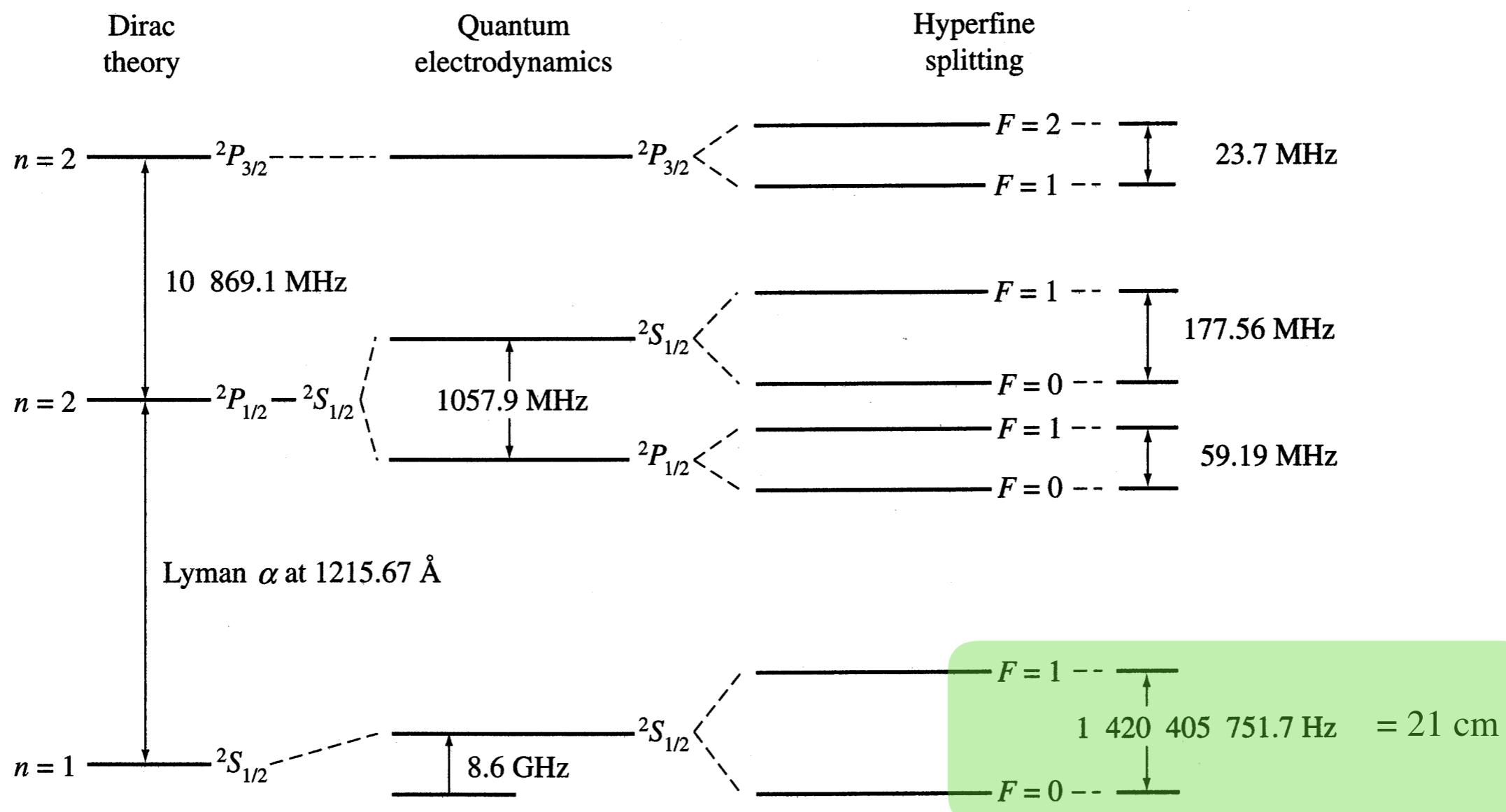


Hydrogen Atom : Hyperfine Structure

- 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.

Δn any → selection rule for configuration

$\Delta l = \pm 1$

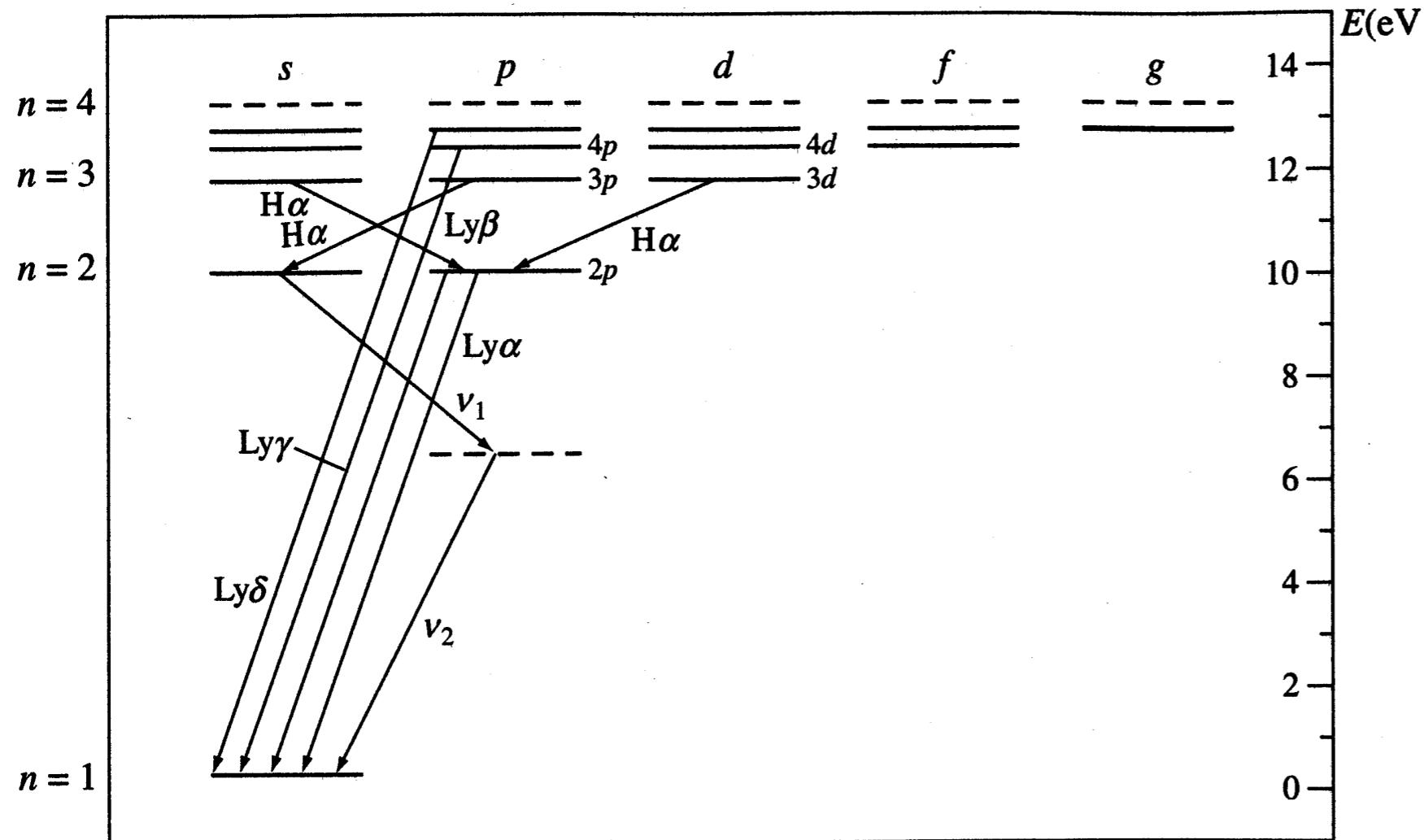
$\Delta S = 0$ → For H atom, this is always satisfied as $S = 1/2$ for all states.

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

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

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

For $H\alpha$ transitions:



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

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

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

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

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

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

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

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

$- 3d_{\frac{5}{2}}$ is allowed .

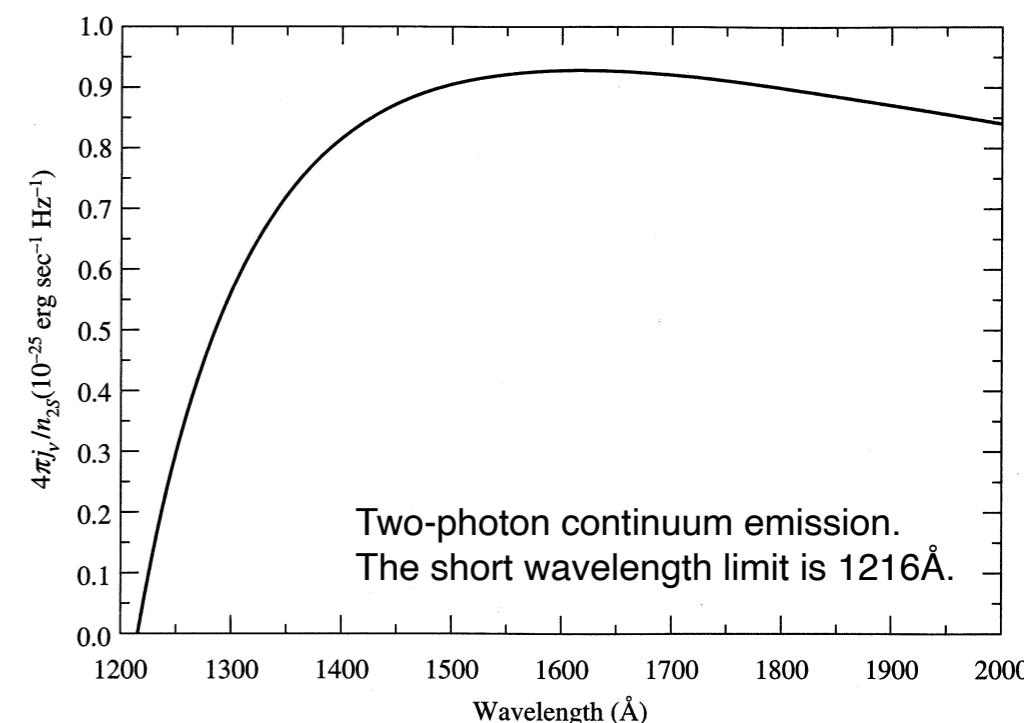
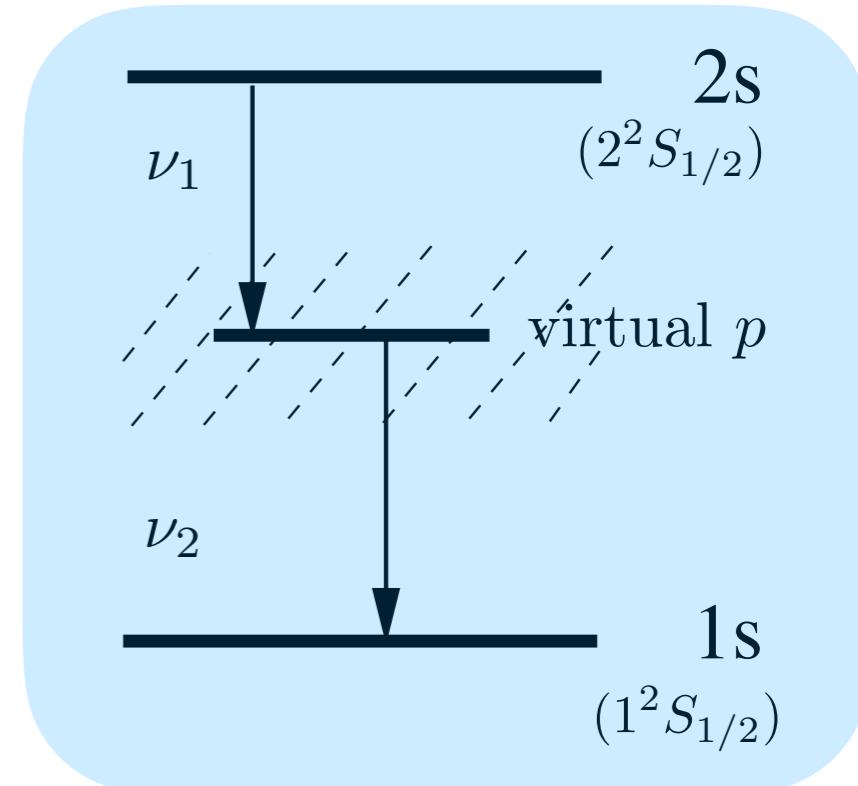
The transition between $2s - 1s$ is not allowed ($\Delta l = 0$).

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

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

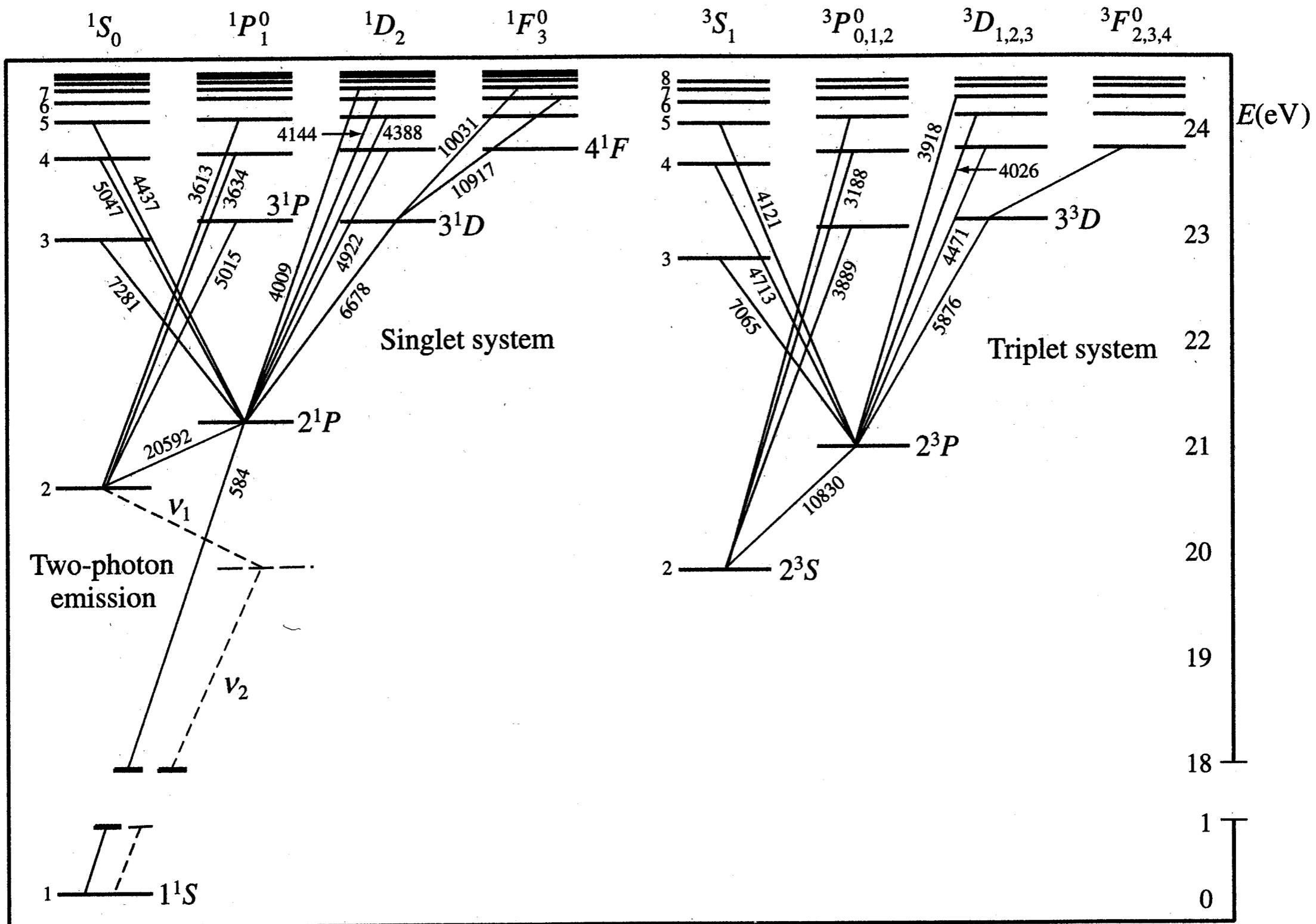
Level	2s	2p	3s	3p	3d
τ/s	0.14	1.6×10^{-9}	1.6×10^{-7}	5.4×10^{-9}	2.3×10^{-7}

- Lifetimes for allowed transitions are short, a few times 10^{-9} s.
- However, the lifetime for the (2s) $2^2S_{1/2}$ level is ~ 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 jumps 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 α 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 Atom : Energy Level Diagram

- Helium (Grotrian diagram)



LS Spectroscopic Terms: Example (1) 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 .

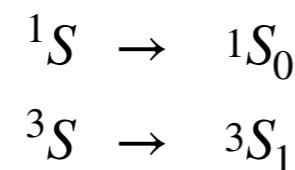
S	L	J
0	0	0

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

- (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



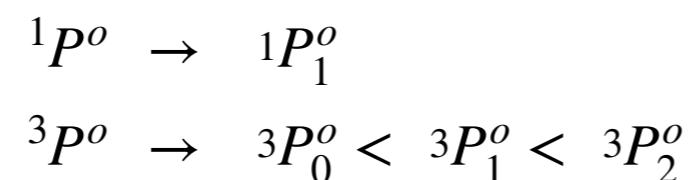
For a given configuration, the state with the maximum spin multiplicity is lowest in energy.

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



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 (2) Excited Configuration of O III

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 $s_2 = \frac{1}{2}$.

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

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

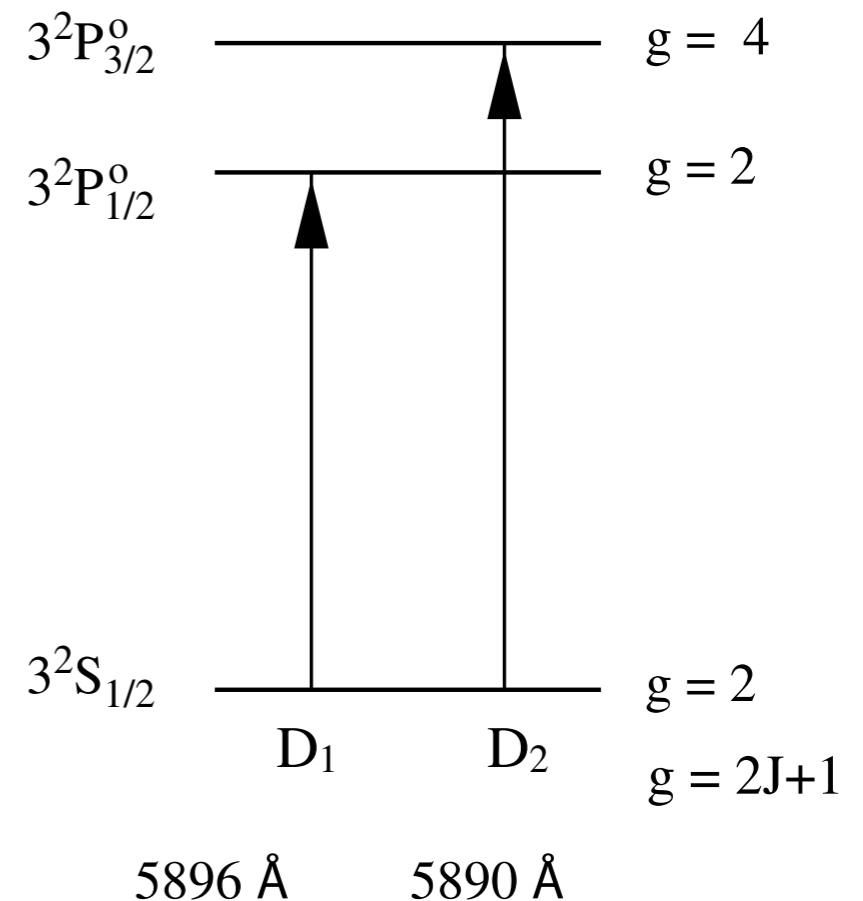
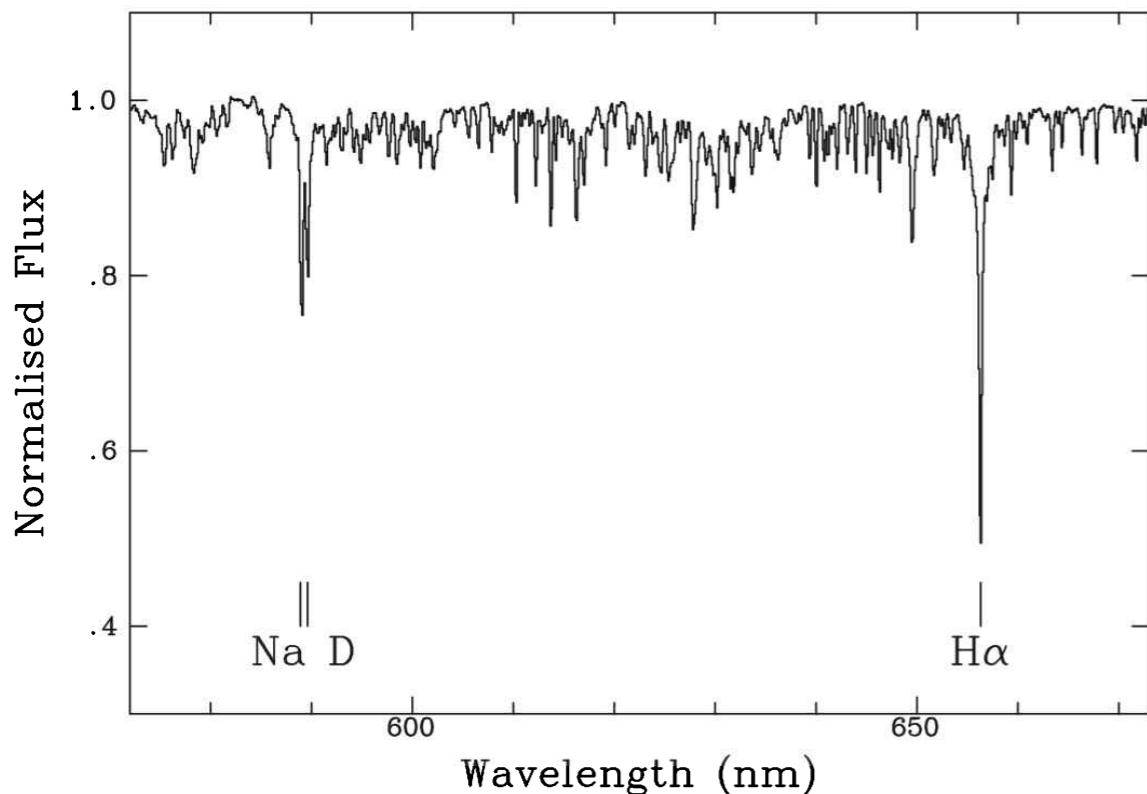
Combining these using all possible combinations of L and S , and the rules of vector addition, gives:

	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 (3) Alkali Atoms

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



Na D lines:

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

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

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

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

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

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

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

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

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

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

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

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

Example (4) 4p4d

4p4d electron configuration

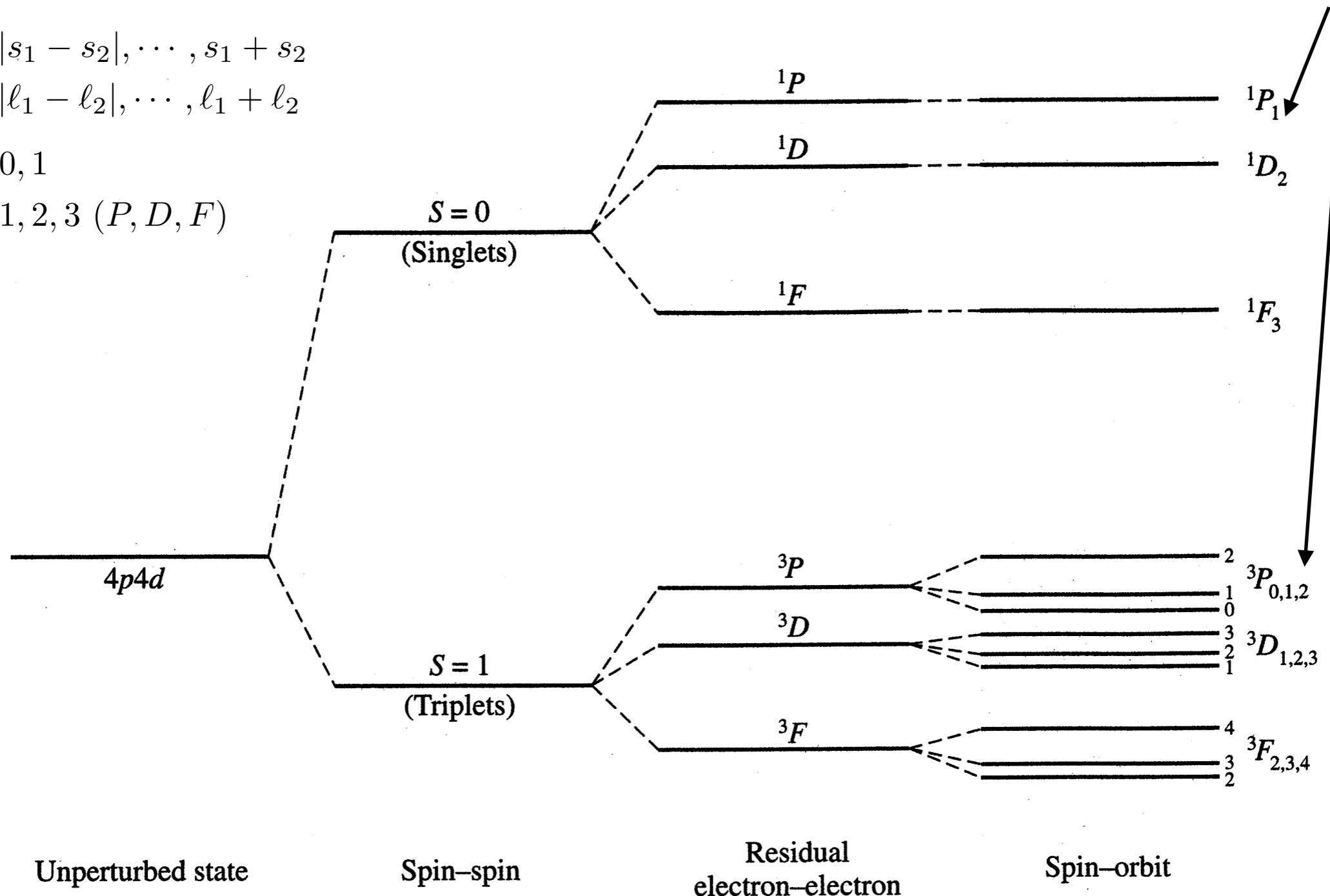
$$J = |L - S|, \dots, L + S$$

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

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

$$S = 0, 1$$

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



Example (5) npn'p

npn'p electron configuration

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

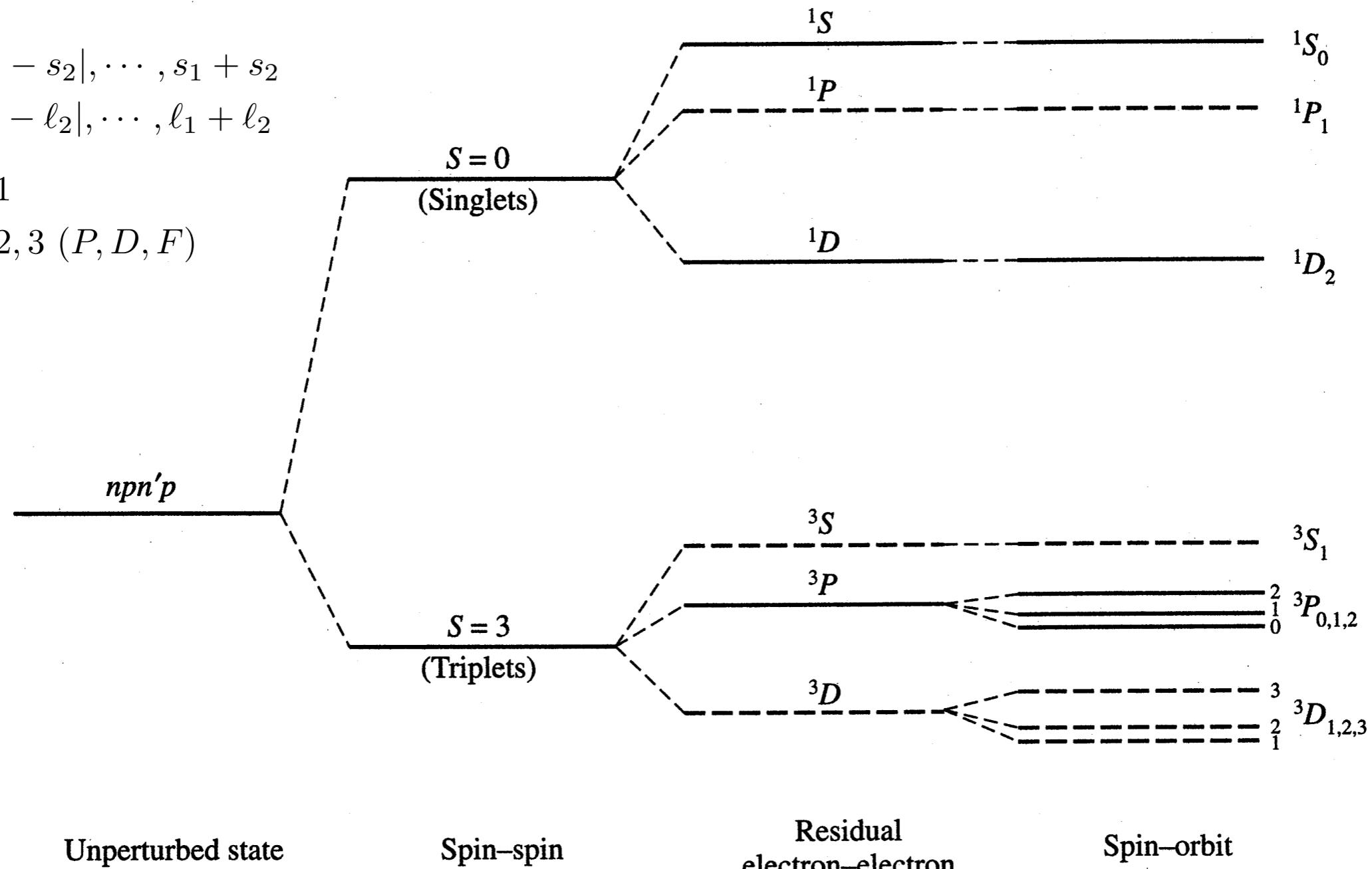
The levels for $n = n'$ will be explained in the next slides.

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

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

$$S = 0, 1$$

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



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

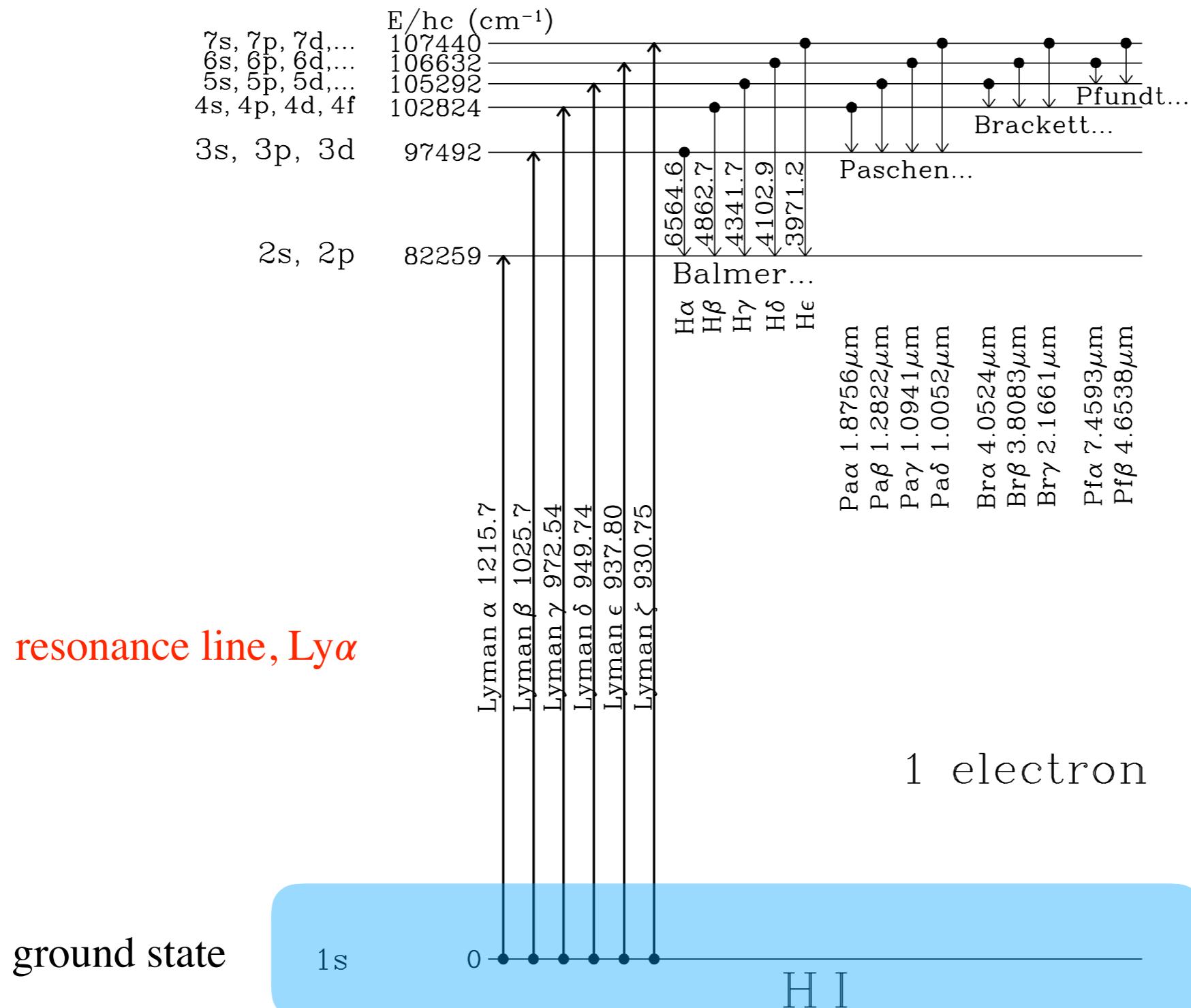
3D is also symmetric for both spin and orbital angular momenta

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.
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. |

Energy Level Diagrams

- 1 electron



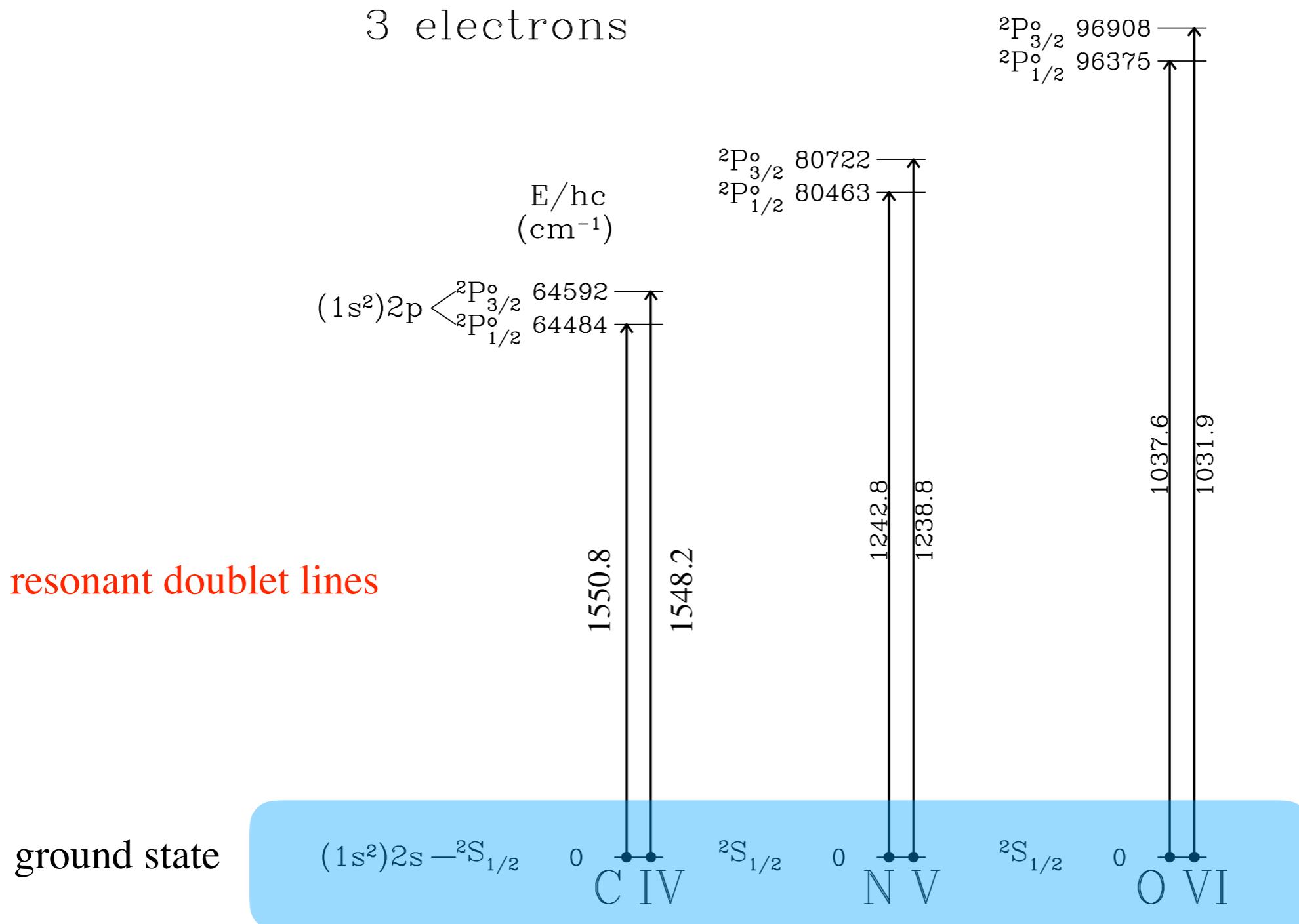
resonance line, $\text{Ly}\alpha$

1 electron

ground state

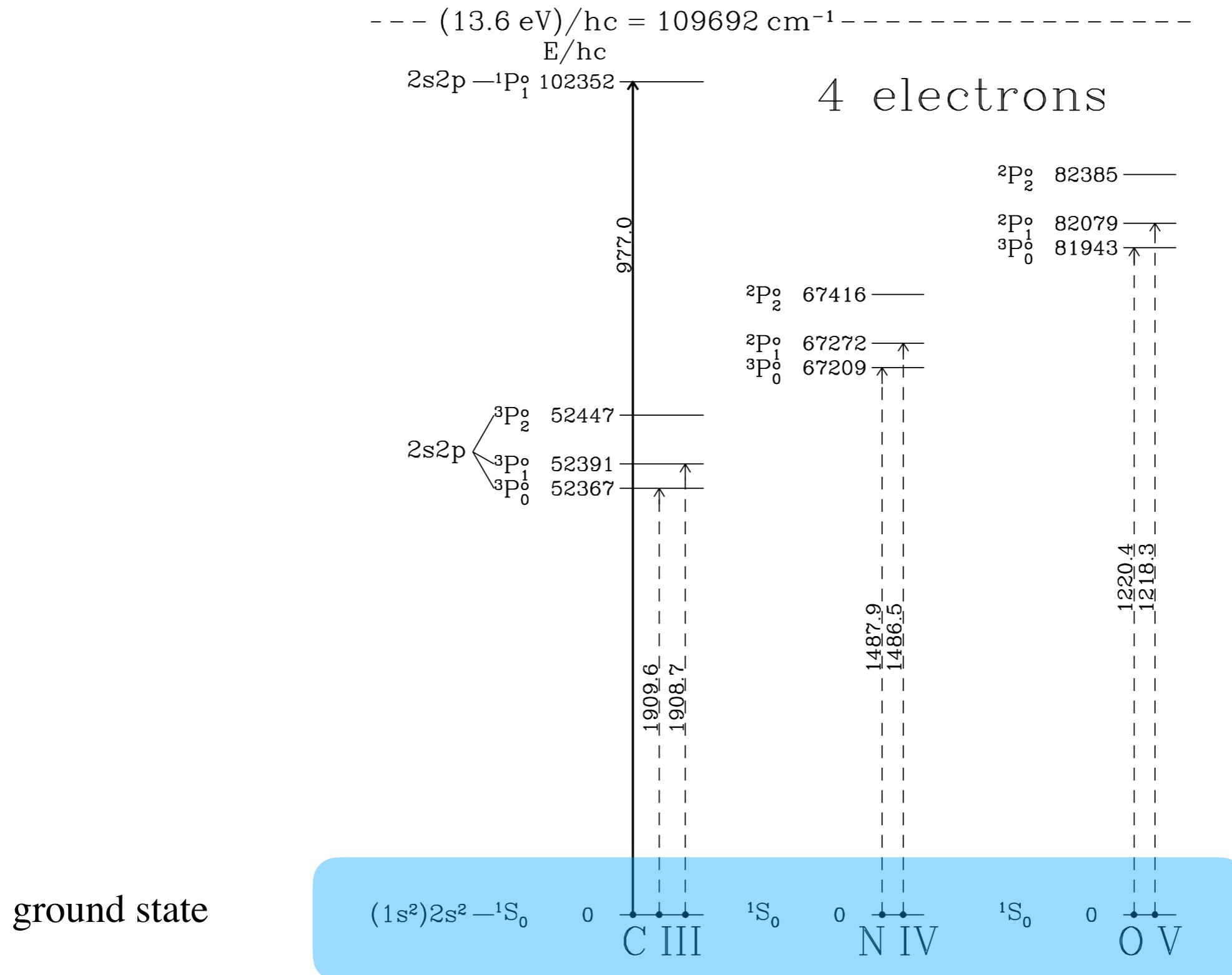
- 3 electrons (Lithium-like ions)

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



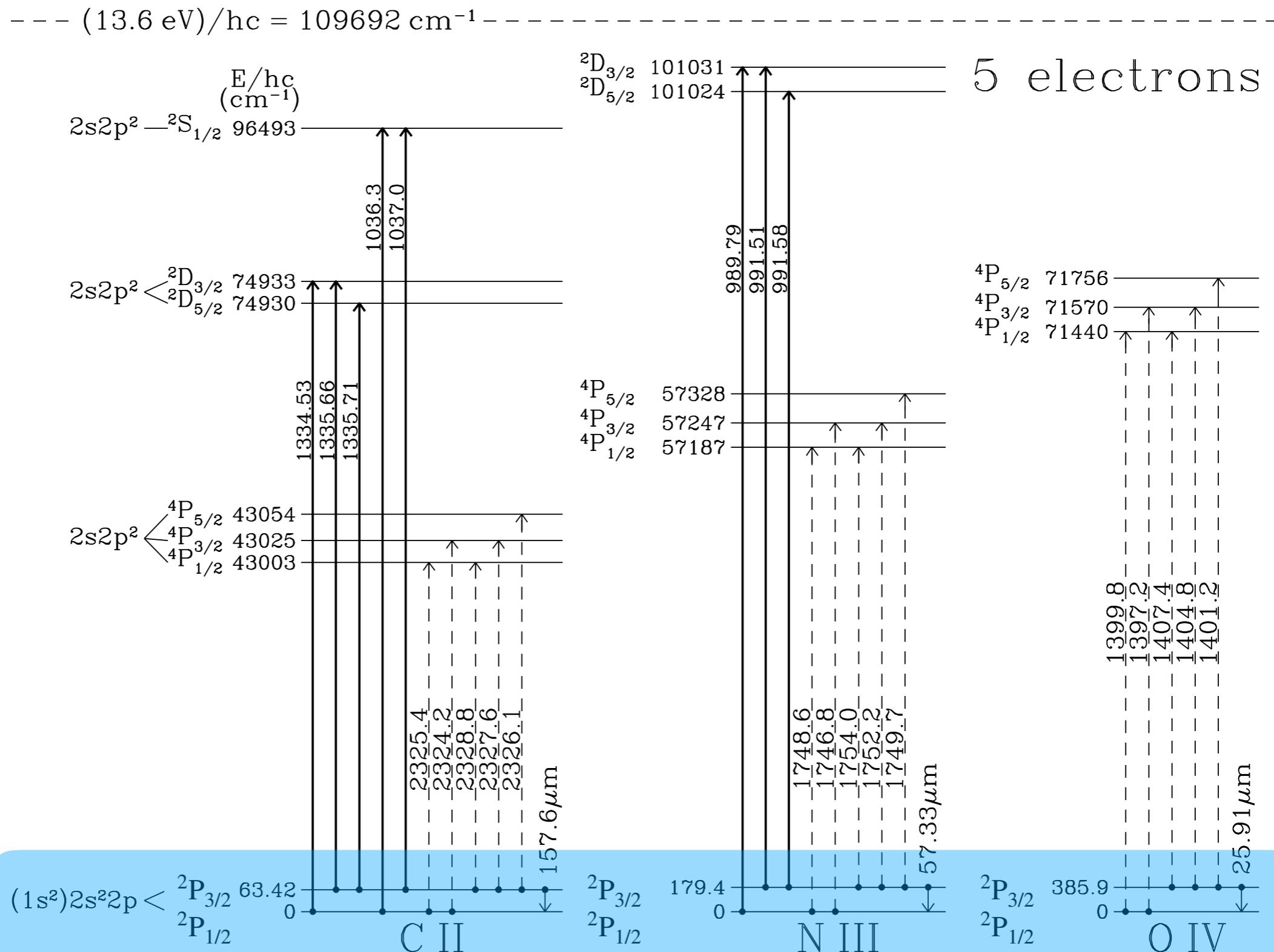
- 4 electrons

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



- 5 electrons

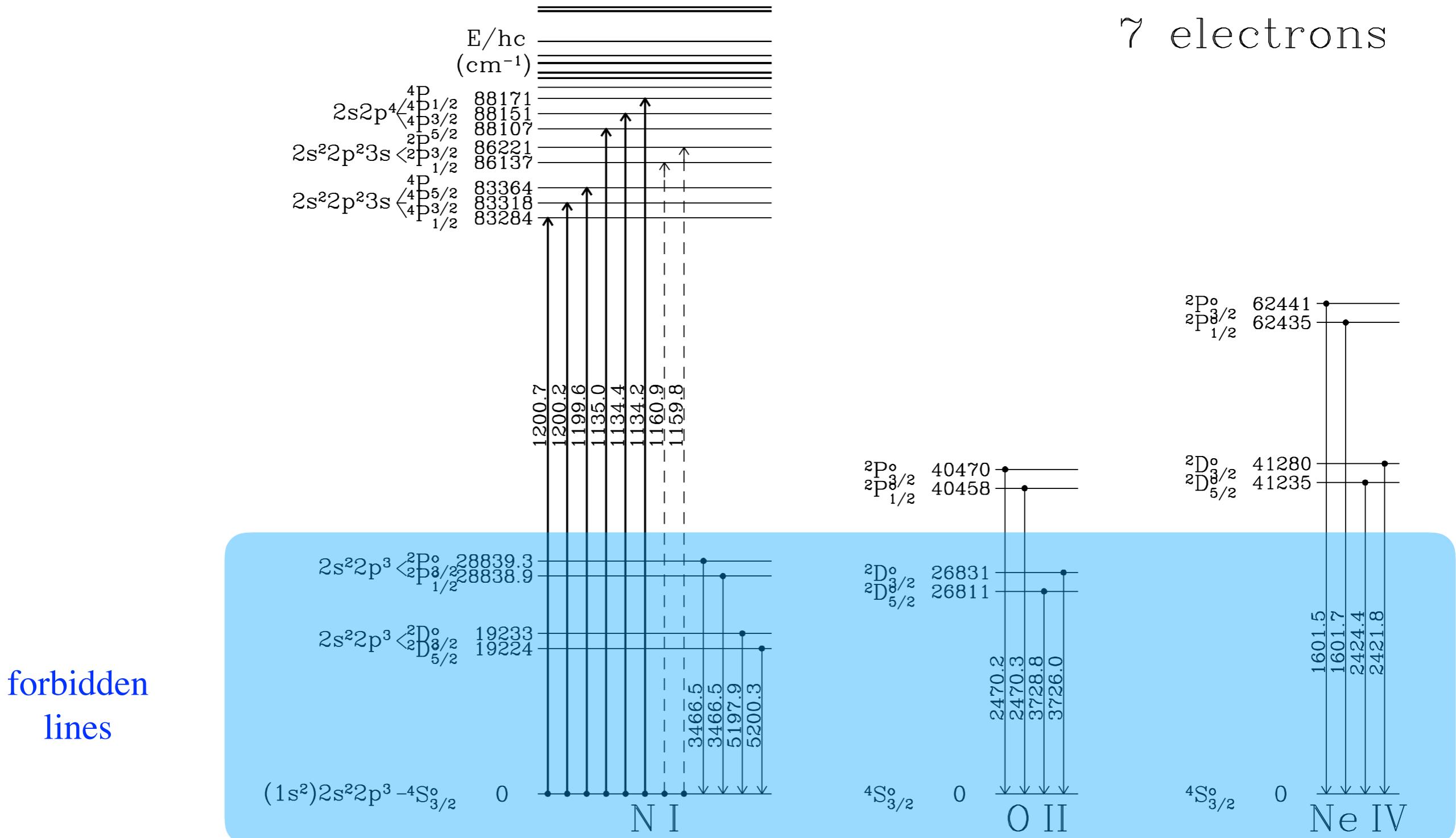
Upward heavy: resonance, Upward Dashed: intercombination
Downward solid: forbidden



- 7 electrons

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

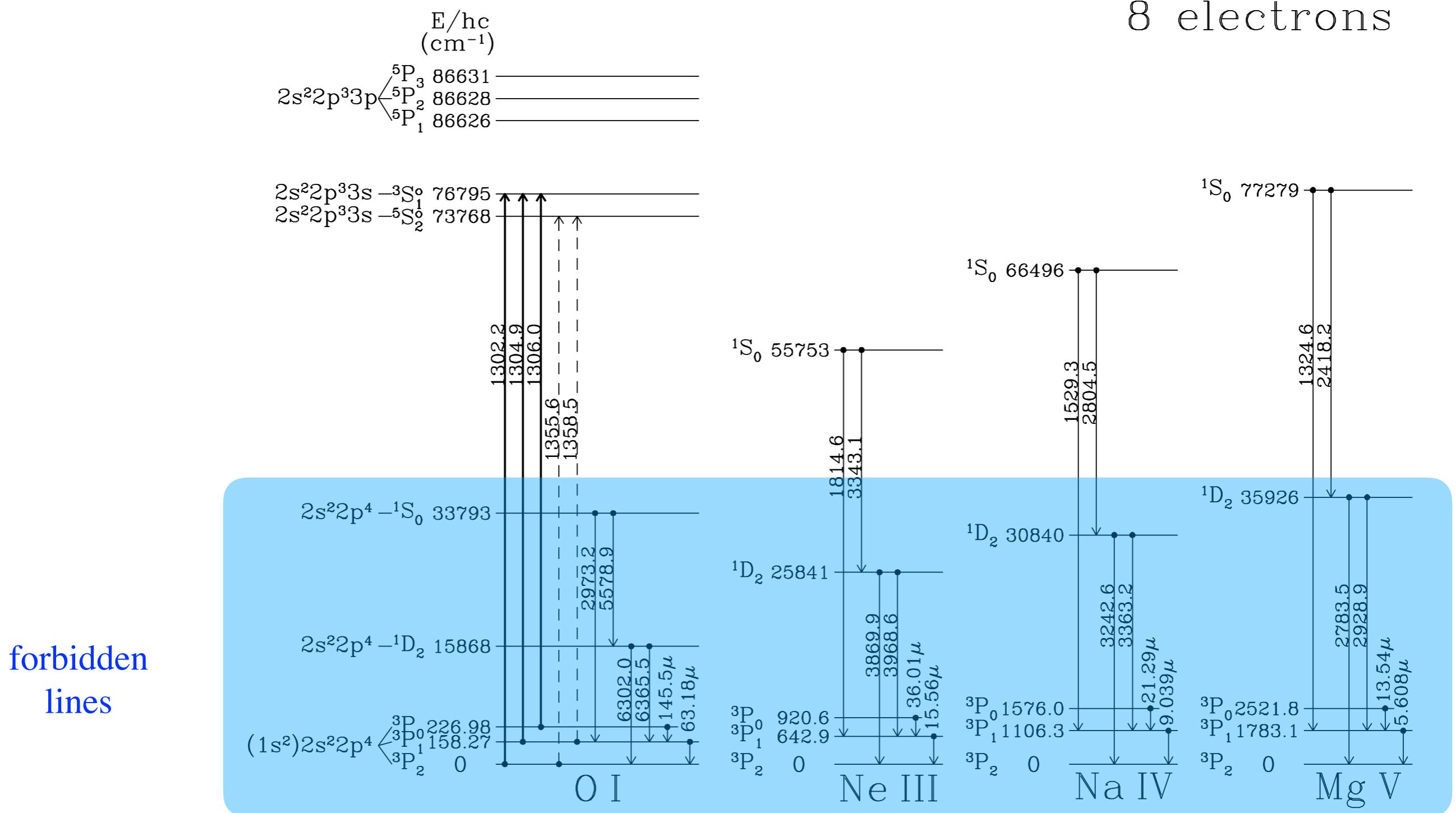
$$\text{---} (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{---}$$



- 8 electrons

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

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



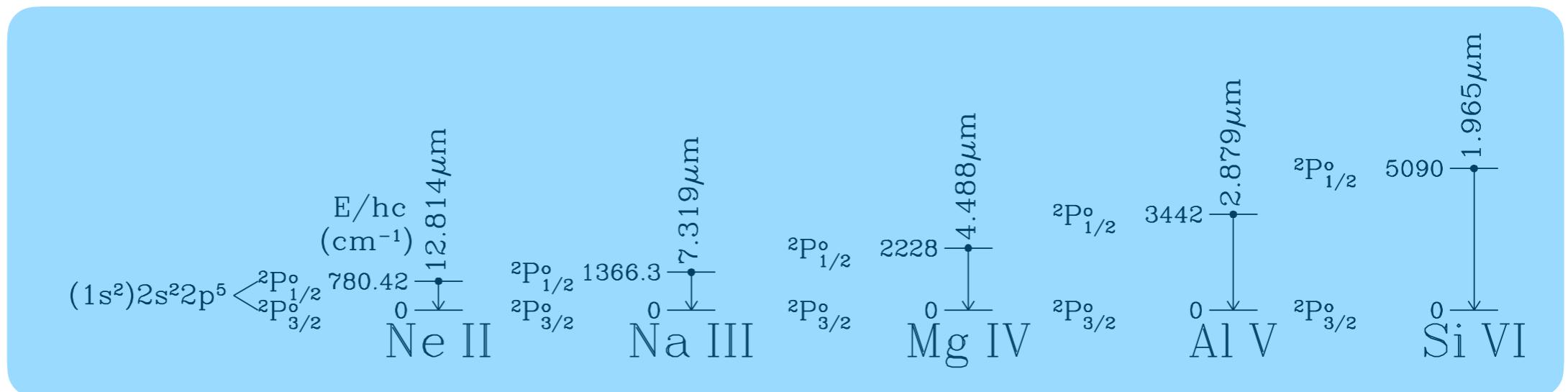
- 9 electrons

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

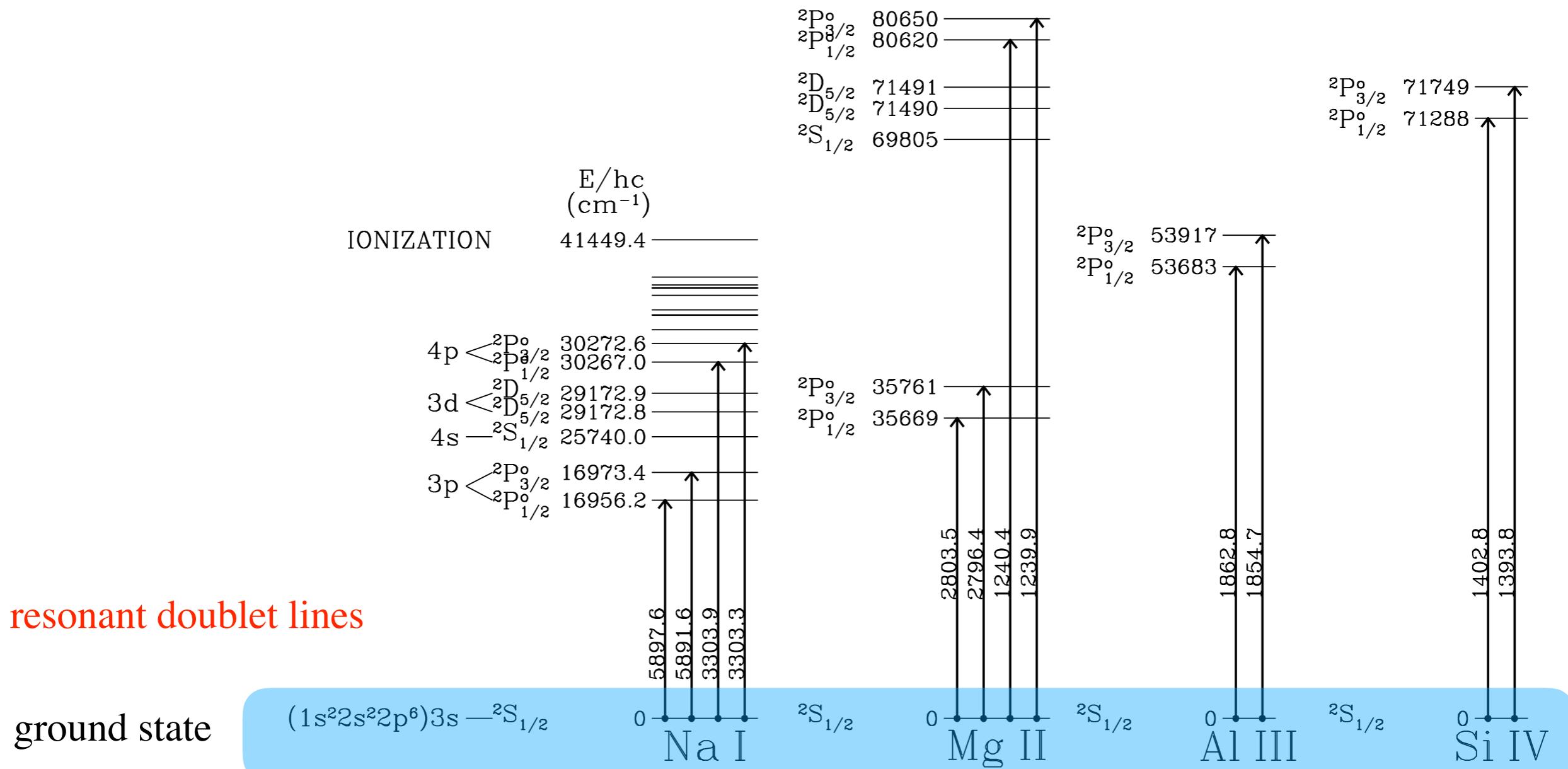


- 11 electrons

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

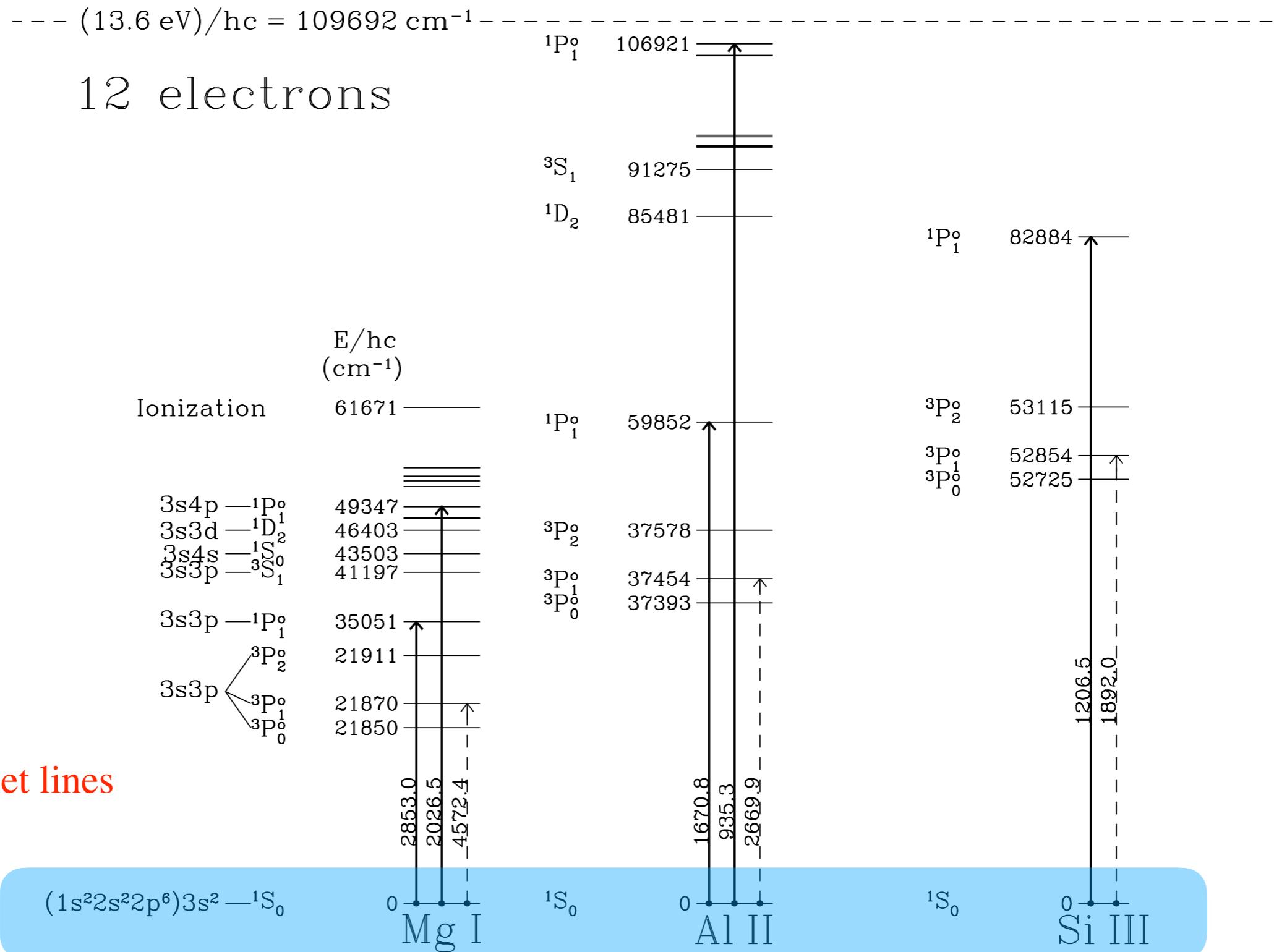
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{-----}$$

11 electrons



- 12 electrons

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



resonant doublet lines

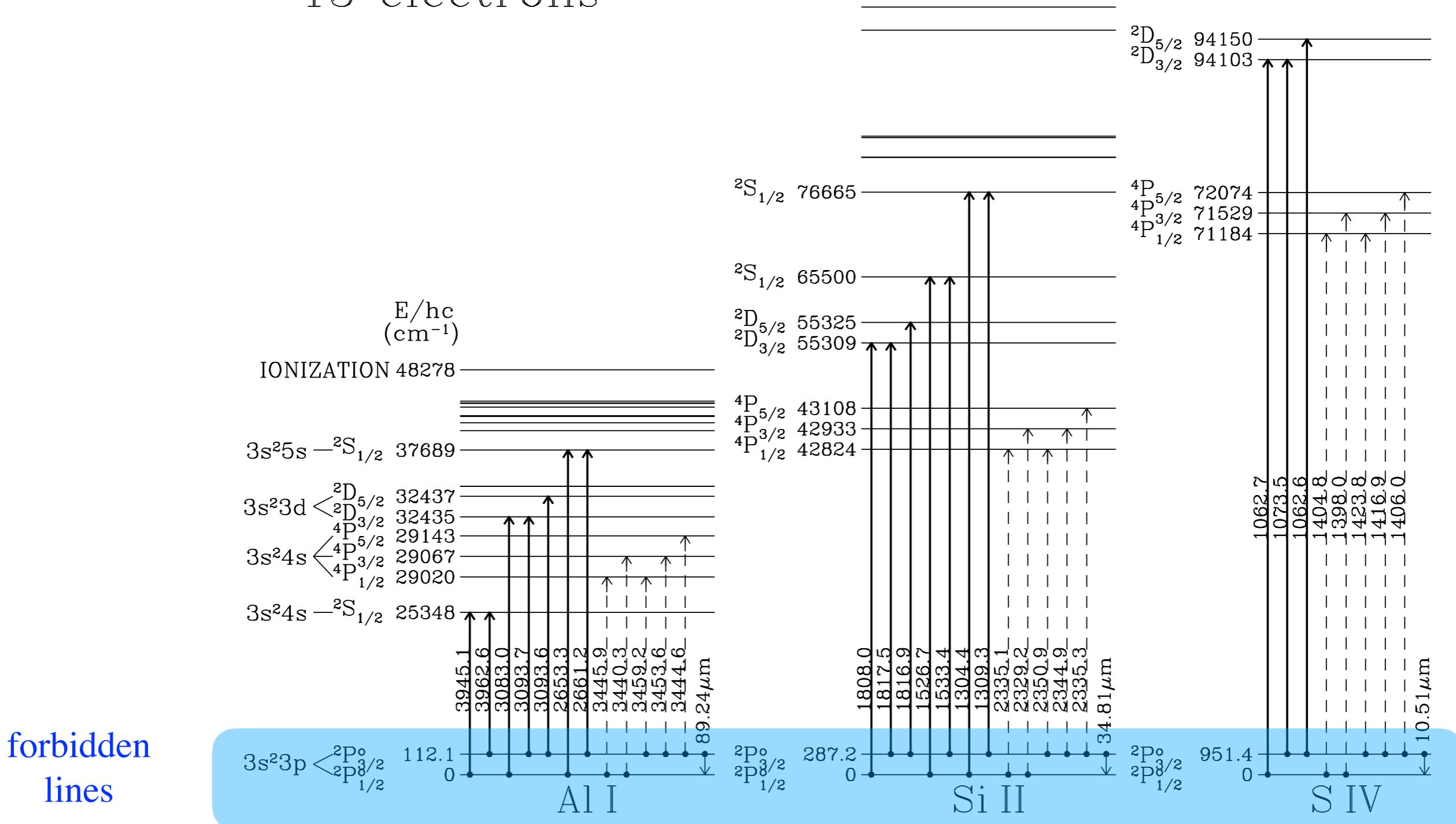
ground state

- 13 electrons

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

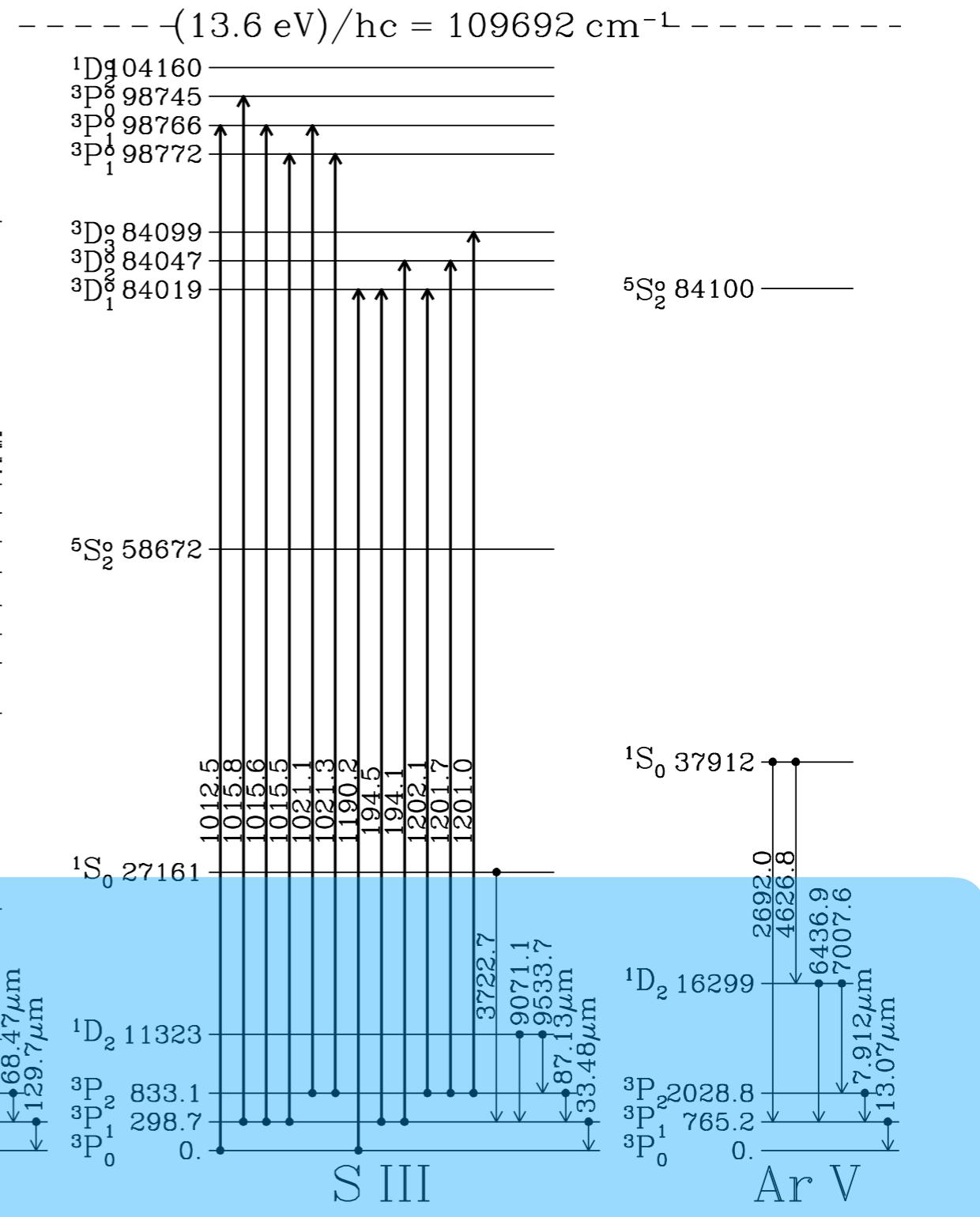
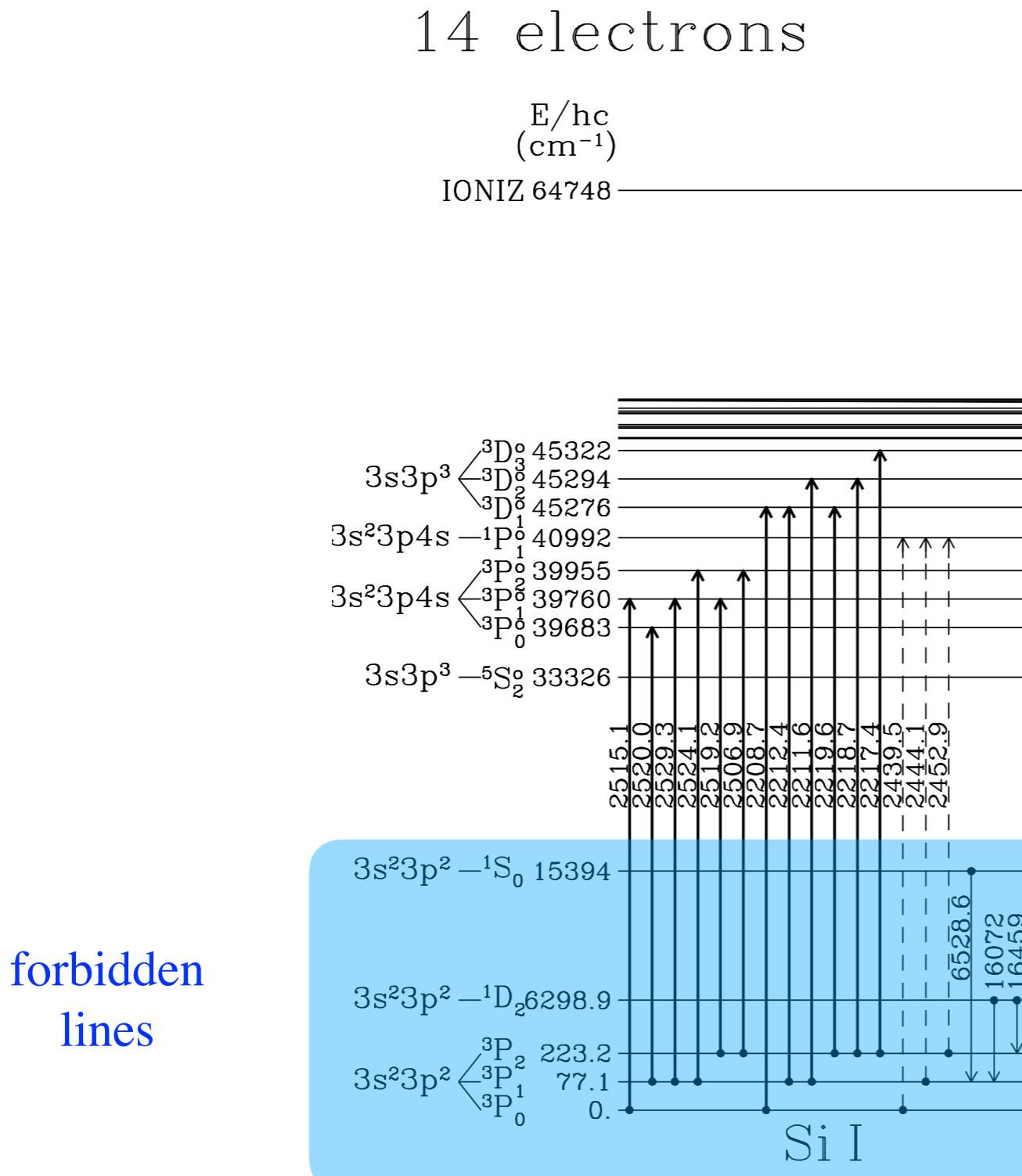
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1}$$

13 electrons



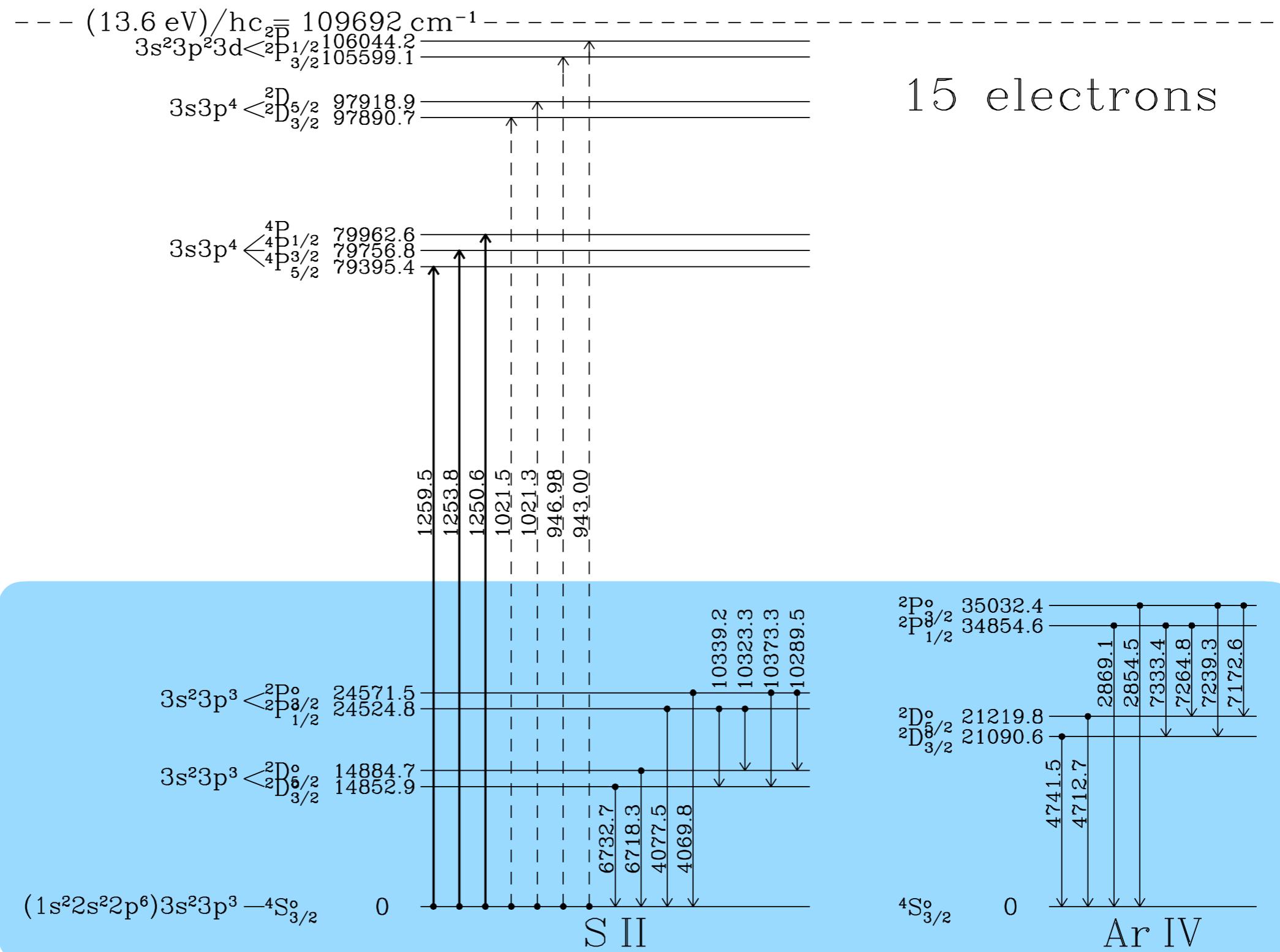
- 14 electrons

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



- 15 electrons

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



Homework

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
 1. $2s^2$
 2. $2p3s$
 3. $3p4p$
 4. $2p^43p$
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 figure shows the term diagram for helium-like oxygen, O VII, showing transitions from the $1s2l$ states. Explain why 22.1\AA line is an intercombination line and why 22.8\AA is a forbidden line.

