

Astrophysics

Lecture 13

November 30 (Wed.), 2022

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[Electron Configuration - Orbitals]

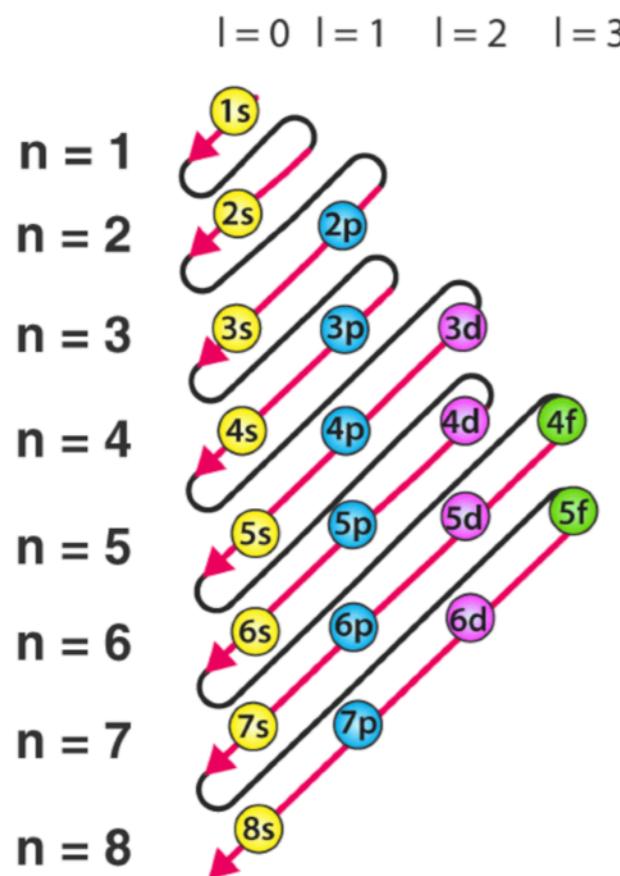
- $n = 1, 2, 3, \dots$: **principal quantum number**
- $l = 0, 1, 2, \dots, n-1$: **orbital angular momentum (quantum number) for each electron.**

$n = 1, 2, 3, 4, 5 \dots$

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

- The electron configuration represents how the electrons are filled in shells and subshells.

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \dots$



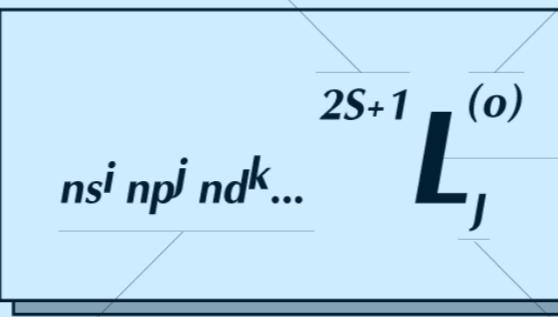
Shell (Principal Quantum Number Value)	Subshell (Angular Momentum Quantum Number)	Notation	Number of electrons
n=1	l=0	1s	2
n=2	l=0	2s	2
	l=1	2p	6
n=3	l=0	3s	2
	l=1	3p	6
	l=2	3d	10
n=4	l=0	4s	2
	l=1	4p	6
	l=2	4d	10
	l=3	4f	14

[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,...

[Angular Momentum]

- The orbital angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and its z-component have the following eigenvalues.

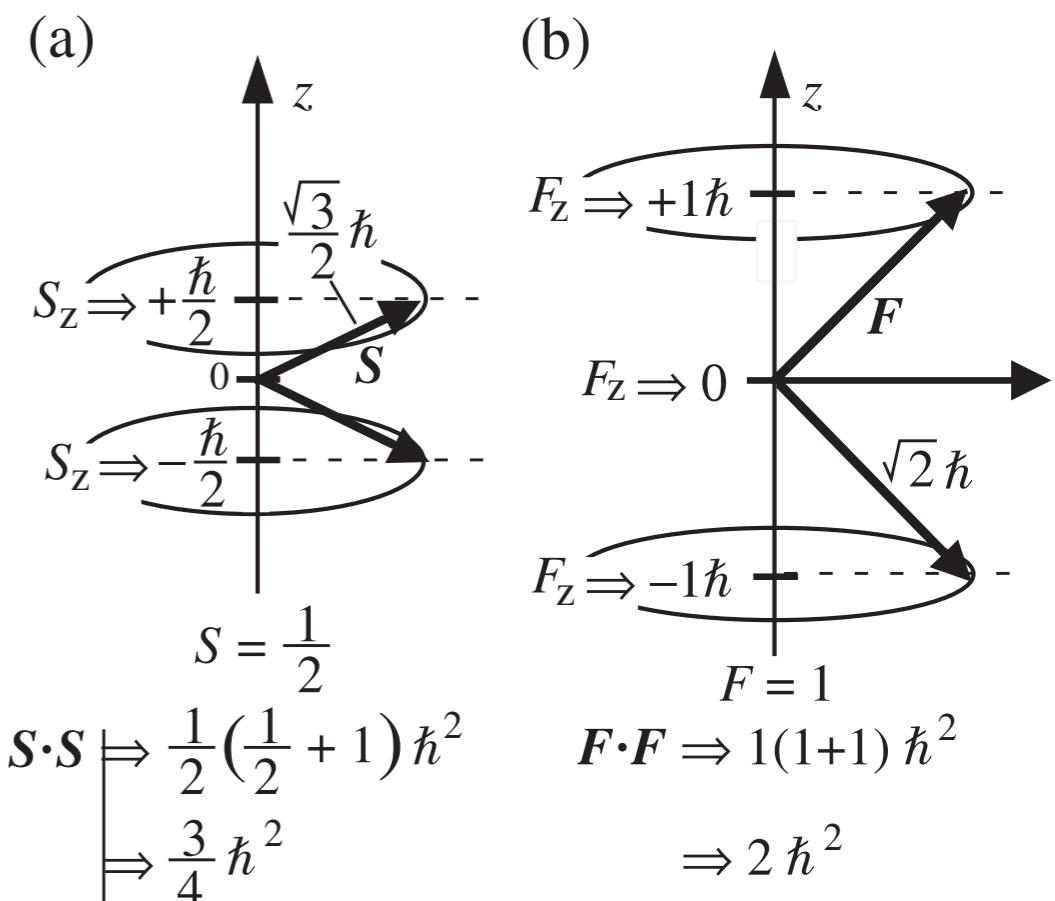
$$\mathbf{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, \quad L_z Y_{lm} = m\hbar Y_{lm}$$

The sizes of the angular moment and z-component are

$$|\mathbf{L}| = \sqrt{\ell(\ell+1)}\hbar \quad \text{where } \ell = 0, 1, \dots, n-1$$

The z-component is

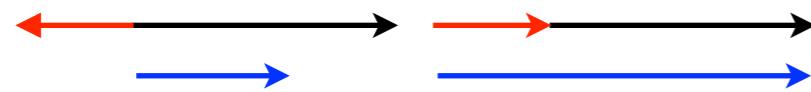
$$L_z = m\hbar \quad \text{where } m = -\ell, -\ell+1, \dots, \ell-1, \ell$$



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

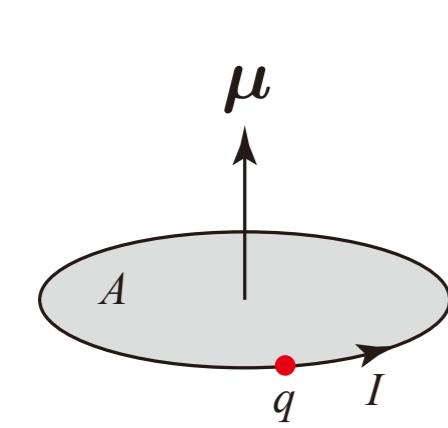
$$L = 1, 2, 3, 4, 5.$$

- Each angular momentum has z -components of. $m = -L, -L + 1, \dots, L, L + 1$.

[Magnetic moments]

- Relation between the magnetic moment and angular momentum

Consider a charge q with mass m that orbits in a circle at radius r about the z -axis with angular velocity ω .



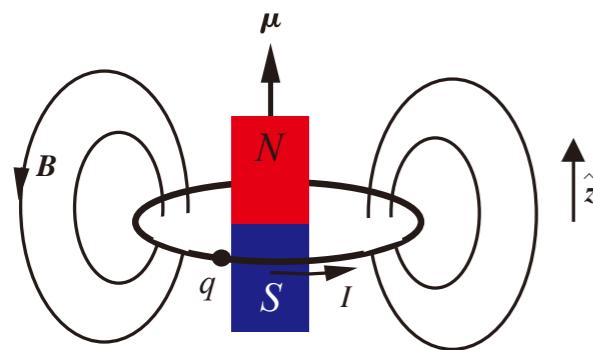
angular momentum

$$\begin{aligned}\mathbf{J} &= \mathbf{r} \times \mathbf{p} \\ &= r \times (mv)\hat{\mathbf{z}} \\ &= mr^2\omega\hat{\mathbf{z}}\end{aligned}$$

magnetic momentum

$$\begin{aligned}\mu &= IA\hat{\mathbf{z}} \\ \text{current } I &= \frac{dq}{dt} = \frac{q}{P} = \frac{q\omega}{2\pi} \\ \text{area } A &= \pi r^2 \\ \mu &= \frac{1}{2}q\omega r^2\hat{\mathbf{z}}\end{aligned}$$

↑
period $P = \omega/2\pi$



Consequently, the classical relation between magnetic moment and angular momentum for an orbiting charge is

$$\mu = \frac{q}{2m}\mathbf{J}$$

Now consider a spinning sphere with uniform mass and charge distributions. It consists of many orbiting charge and mass elements, each obeying the above equation. Thus, the equation is also valid for the entire sphere.

In quantum mechanics, **the magnetic moment of the electron**, which is a point charge with zero radius, is given by

$$\boldsymbol{\mu}_e = -g_e \frac{e}{2m_e} \mathbf{S} \quad (\text{where } g_e = 2.0 \text{ in Dirac equation})$$

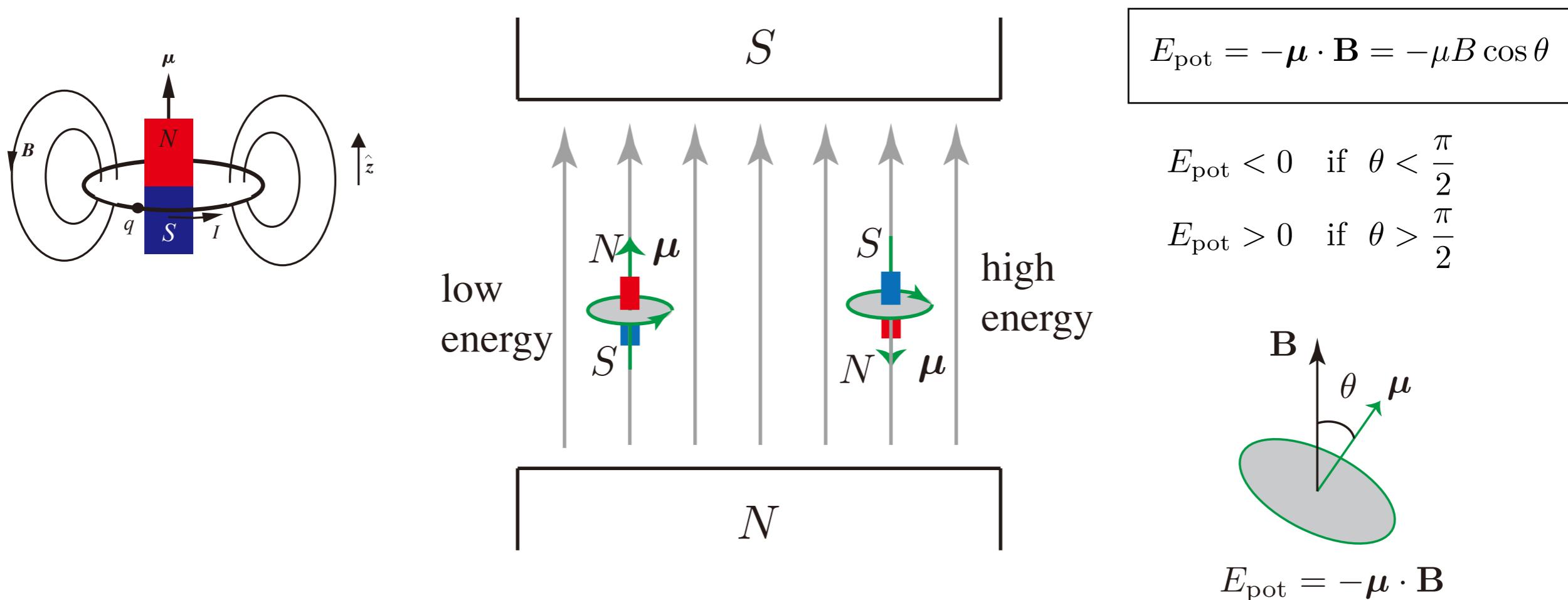
The magnetic moment of the electron is opposed to the direction of the spin \mathbf{S} , because of the negative charge.

Magnetic dipole in a magnetic field

- A magnetic dipole will tend to align with an external magnetic field just as a compass needle aligns itself with the magnetic field of the earth.

One can visualize the external field acting on a magnet. This magnet experiences a torque tending to align it with the \mathbf{B} field.

Integration of this torque over the appropriate angles yields a potential energy that is a function of the angle θ between the magnetic field \mathbf{B} and magnetic moment μ vector. The lowest potential energy occurs when the two vectors are aligned. The potential energy E_{pot} turns out to be the negative dot product of the vectors μ and \mathbf{B} :



[Spin-Orbit Coupling]

- The fact that the remaining spin-orbit splitting is much smaller makes the LS coupling scheme a very useful one.
- **Fine-structure splitting:** Relativistic effects couple electron orbital angular momentum and electron spin to give the so-called fine structure in the energy levels. Inclusion of relativistic effects splits the **terms** into **levels** according to their J value.
- When the electron will move around the nucleus with a non relativistic velocity \mathbf{v} , the electric field exerting on the electron will be $\mathbf{E} = Ze\frac{\mathbf{r}}{r^3}$. (Note that the nucleus has a positive charge Ze .)

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

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

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

$$= \frac{Ze}{m_e c r^3} \mathbf{L} \quad (\mathbf{L} = \mathbf{r} \times \mathbf{p})$$

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

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

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

$$\boldsymbol{\mu}_e = -\frac{e}{m_e} \mathbf{S}$$

- Then, the interaction energy is

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

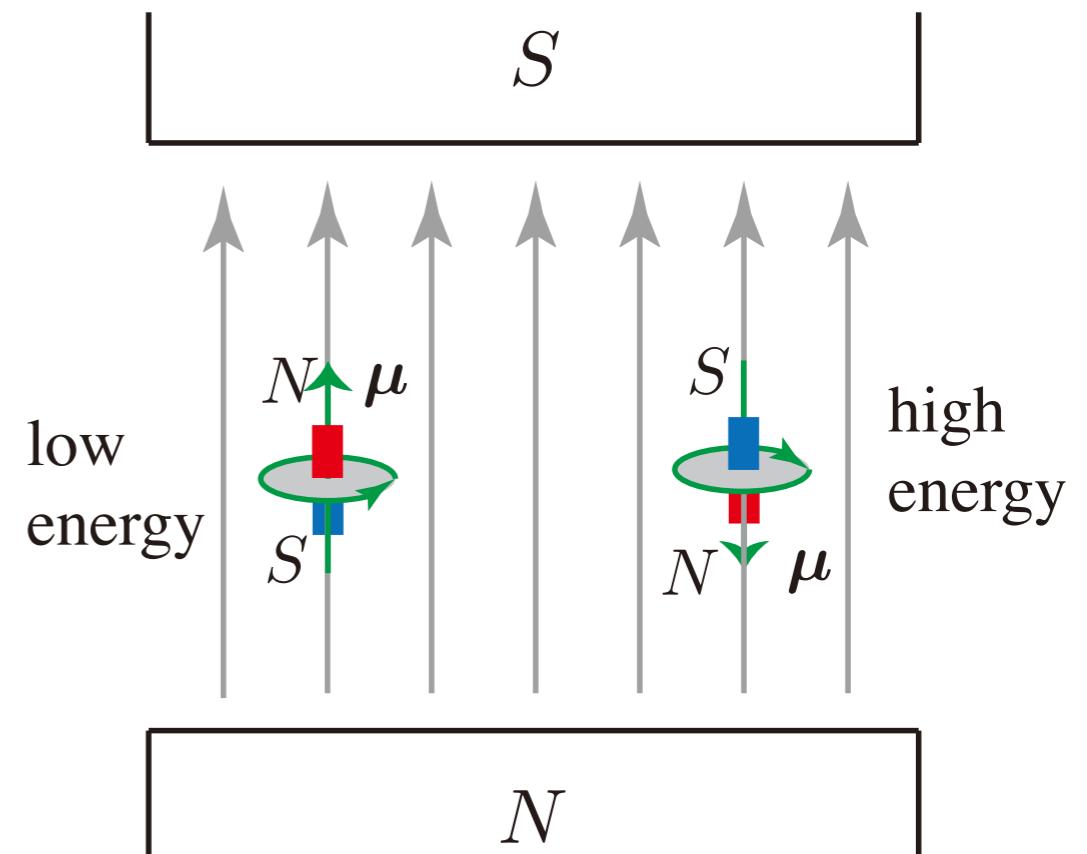
- For the sum of the interactions of all electrons will be

$$H_{\text{so}} = \xi (\mathbf{S} \cdot \mathbf{L})$$

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

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

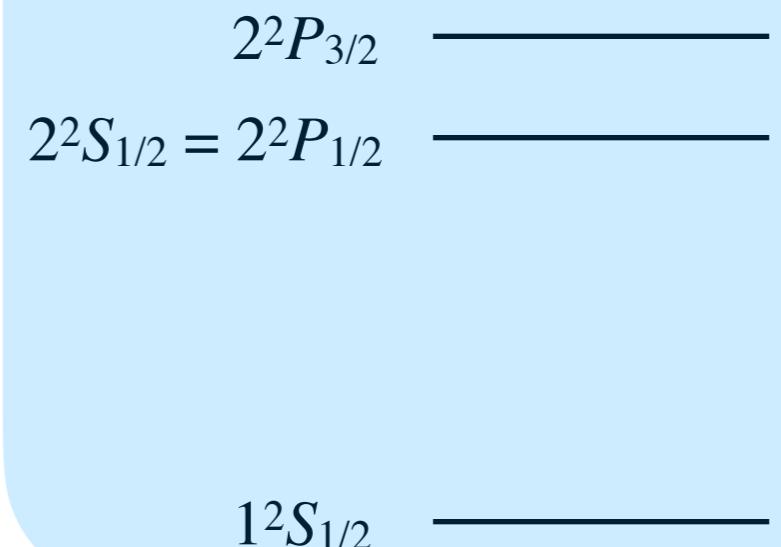


[Hydrogen Atom] : Fine Structure

- Fine structure of the hydrogen atom

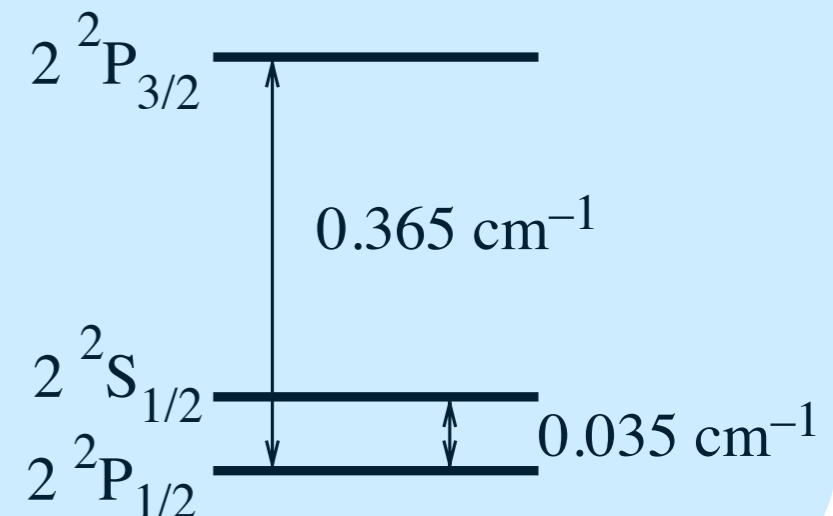
configuration	L	S	J	term	level
ns	0	$1/2$	$1/2$	2S	$^2S_{1/2}$
np	1	$1/2$	$1/2, 3/2$	$^2P^o$	$^2P_{1/2}^o, ^2P_{3/2}^o$
nd	2	$1/2$	$3/2, 5/2$	2D	$^2D_{3/2}, ^2D_{5/2}$
nf	3	$1/2$	$5/2, 7/2$	$^2F^o$	$^2F_{5/2}^o, ^2D_{7/2}^o$

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

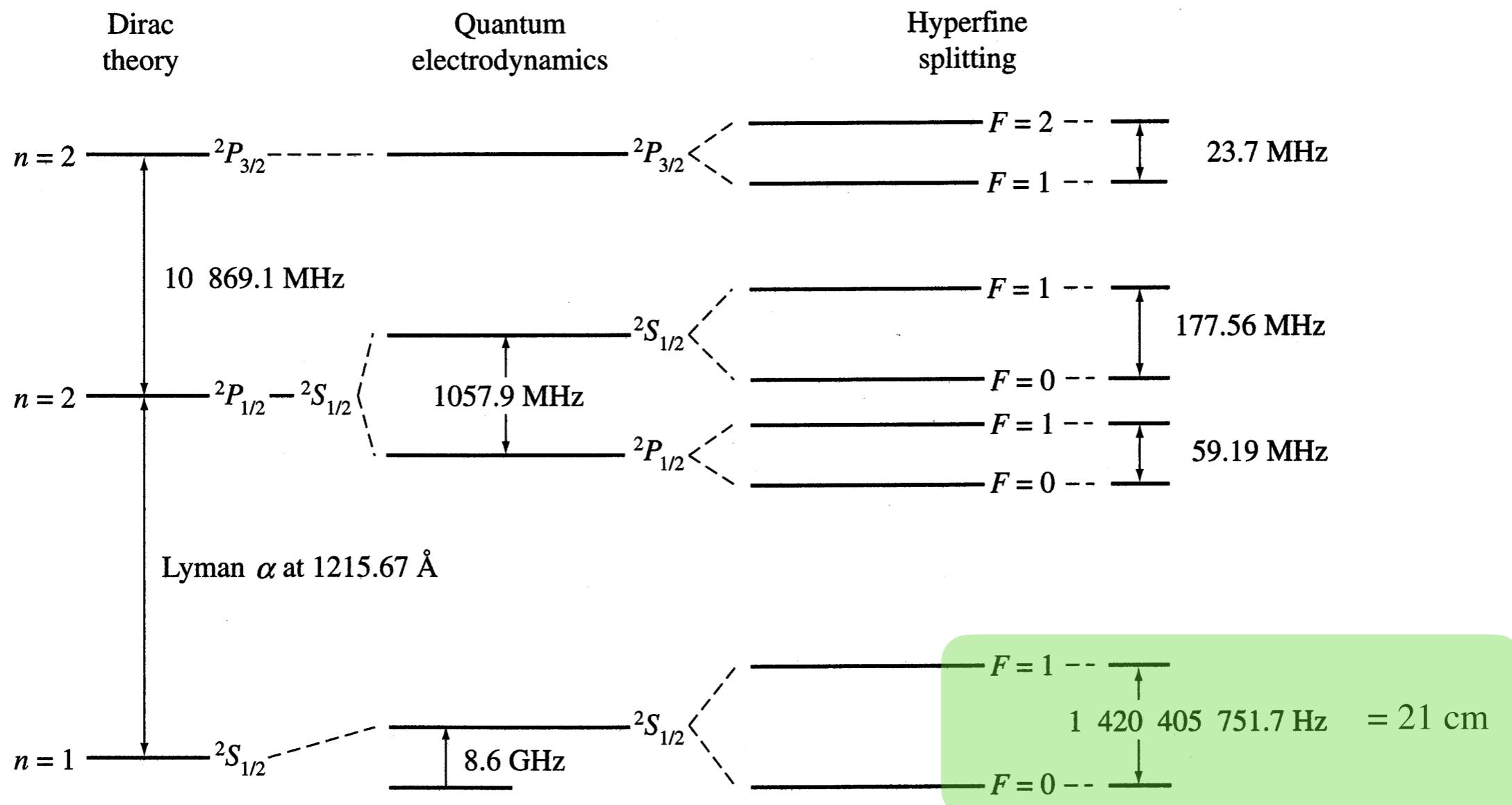


Hydrogen Atom : Hyperfine Structure

- 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.

Δn any  selection rule for configuration

$\Delta l = \pm 1$

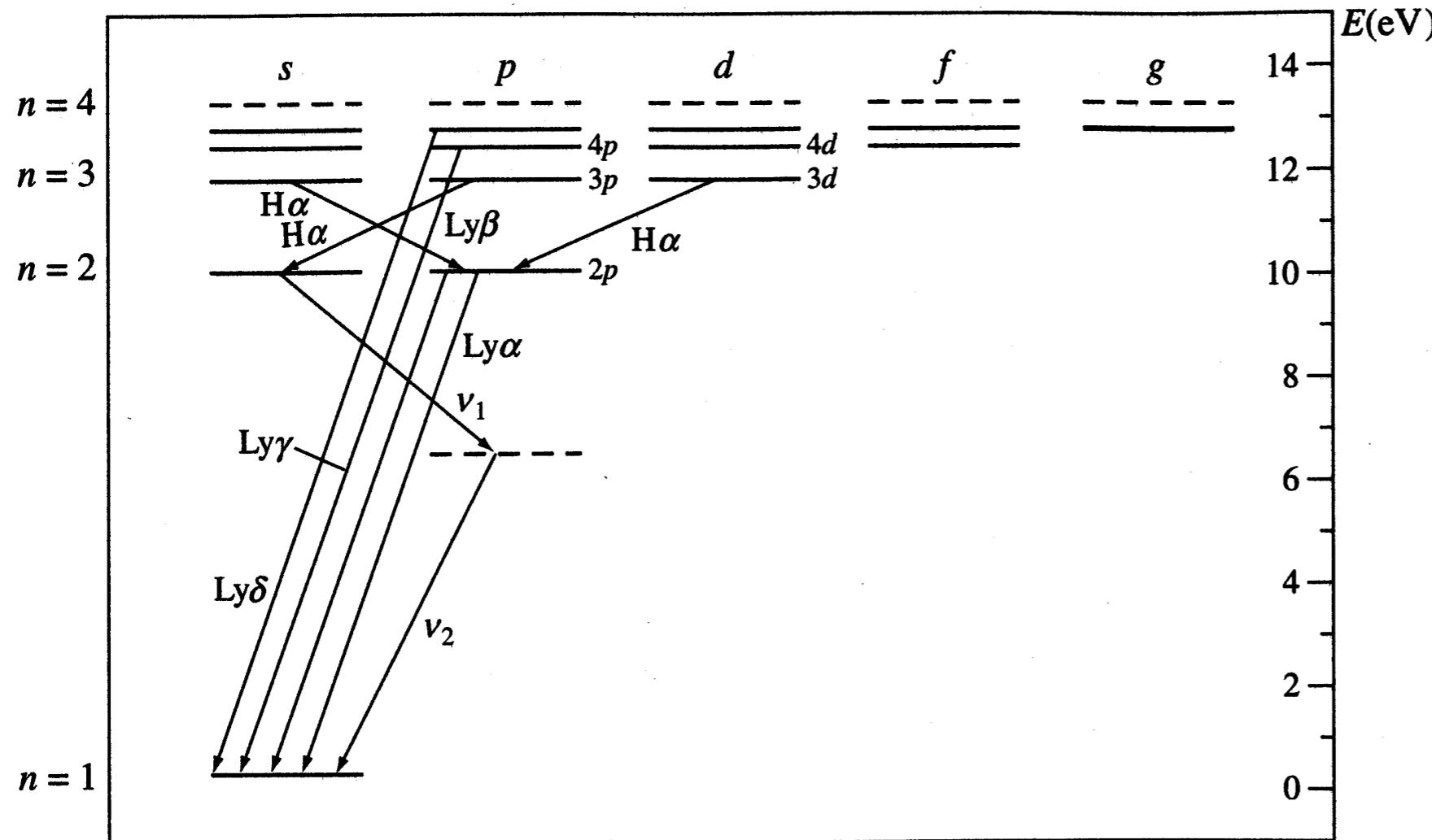
$\Delta S = 0$  For H atom, this is always satisfied as $S = 1/2$ for all states.

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

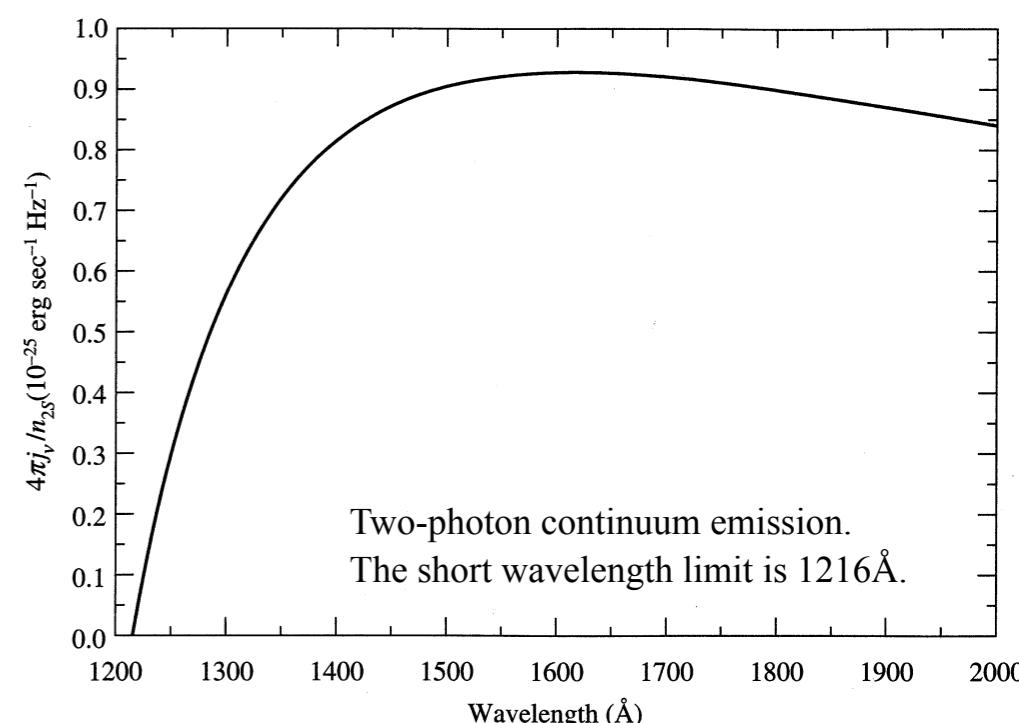
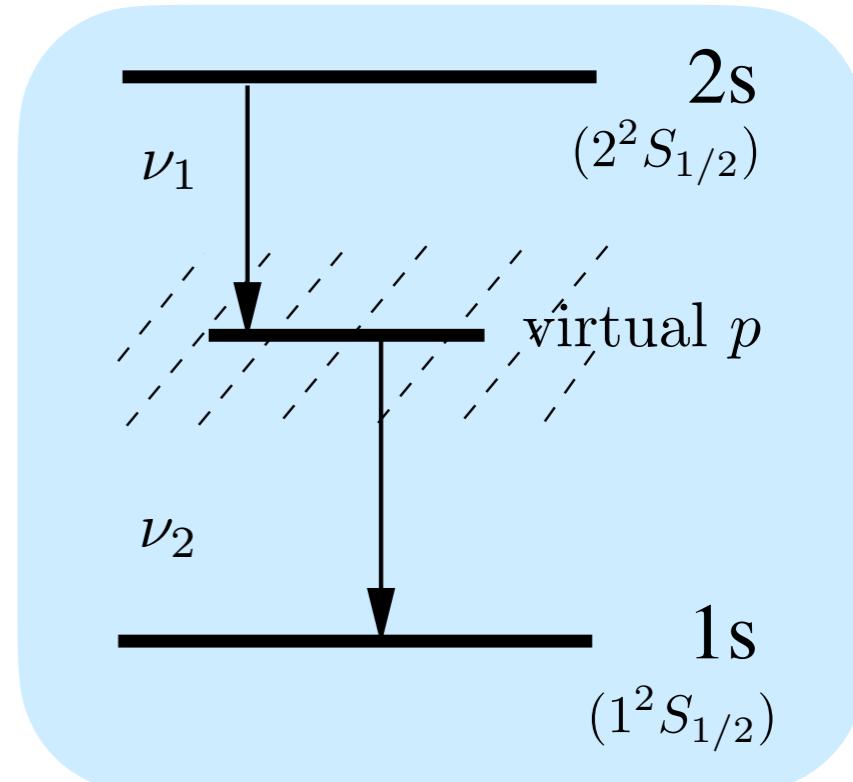
$$\tau_i = \left(\sum_j A_{ij} \right)^{-1} \quad \text{where } A_{ij} \text{ is the Einstein A coefficient}$$

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 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 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]

- (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.

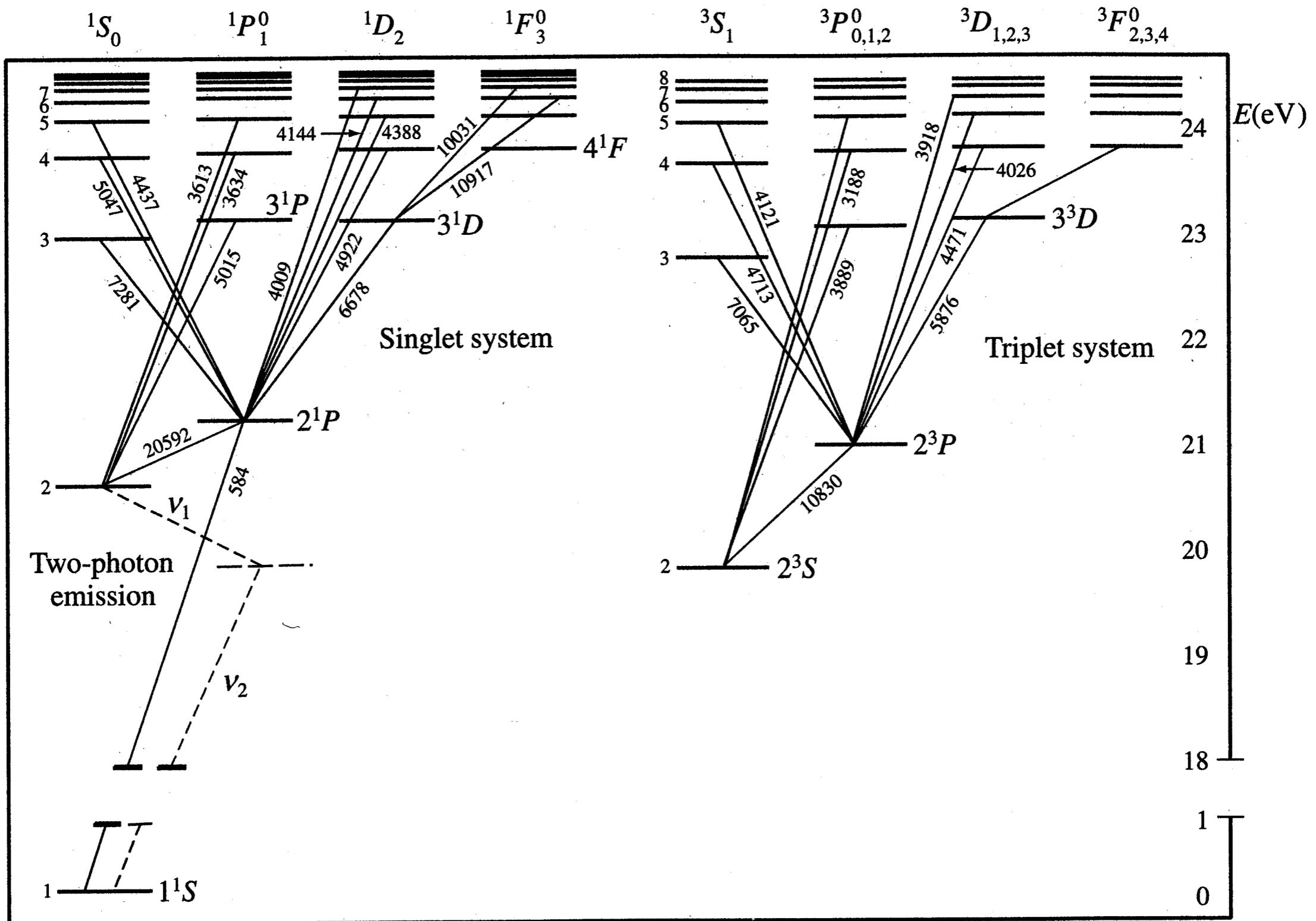
This has $l_1 = 0$ and $l_2 = 1$, giving $L = 1$; again $s_1 = s_2 = \frac{1}{2}$, giving both $S = 0$ and $S = 1$ terms.

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

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

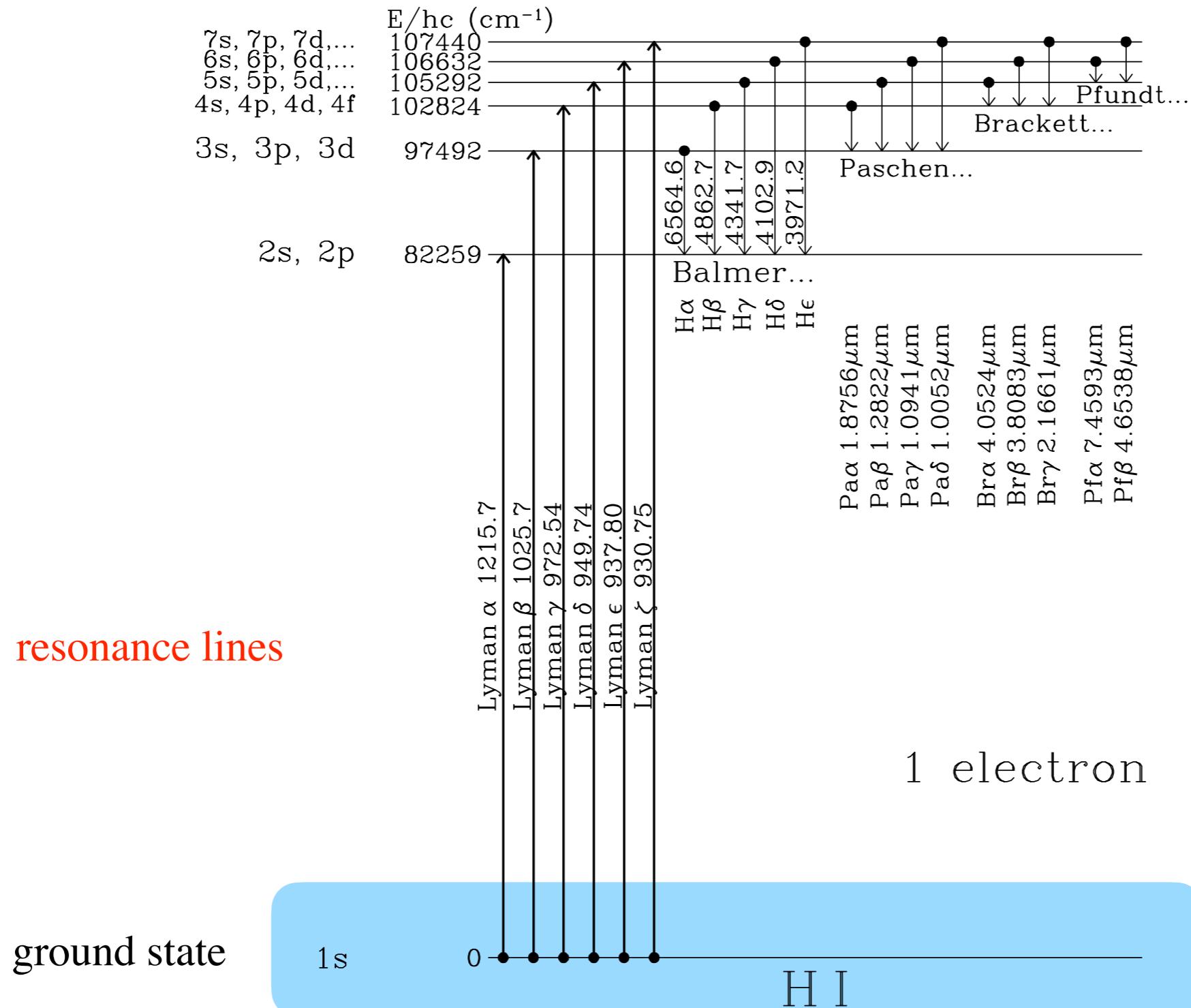
Following the rule above, the ${}^3P^o$ term is lower in energy than the ${}^1P^o$ term, in this case by 0.25 eV.

- Helium (Grotrian diagram)



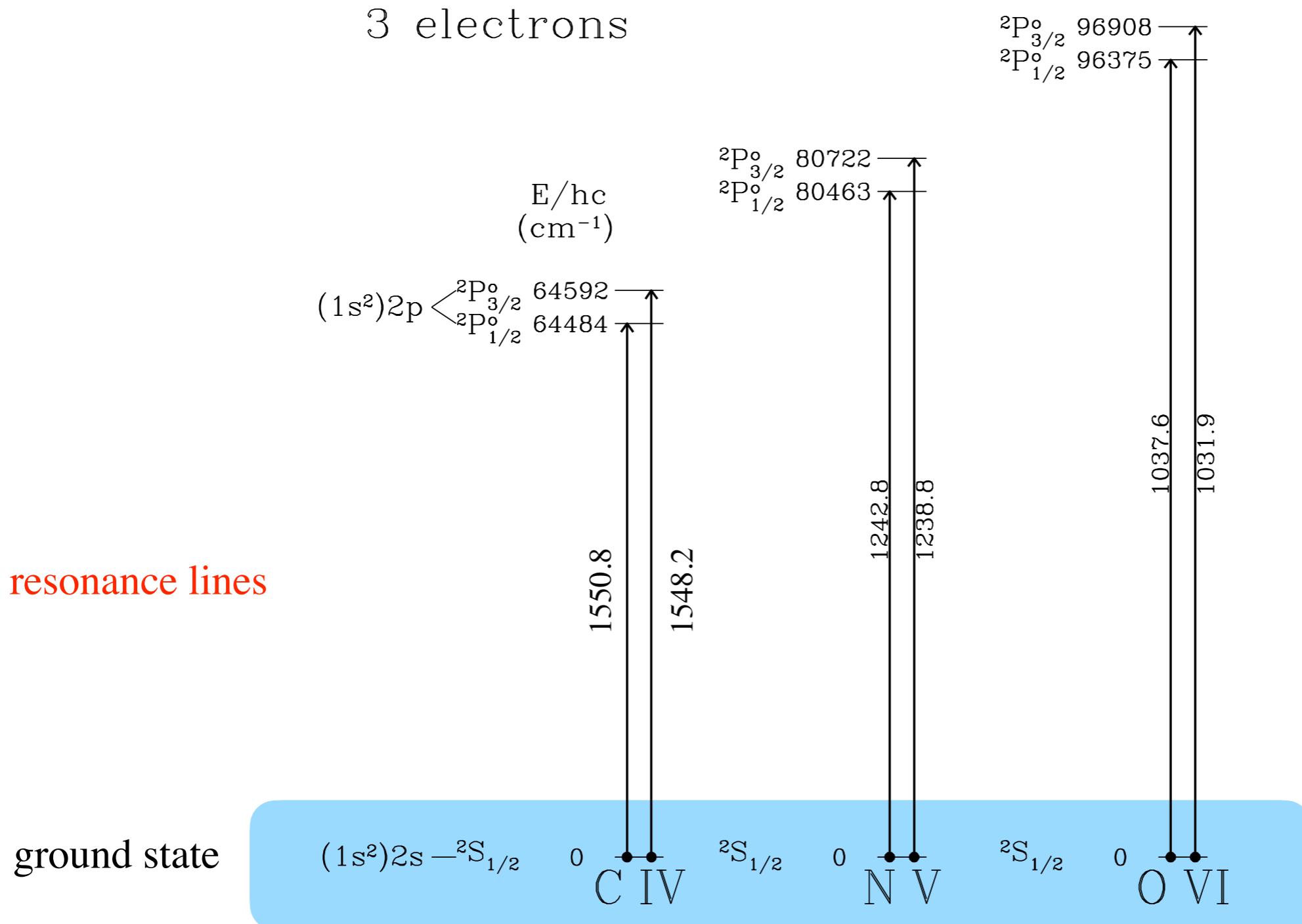
[Energy Level Diagrams]

- 1 electron



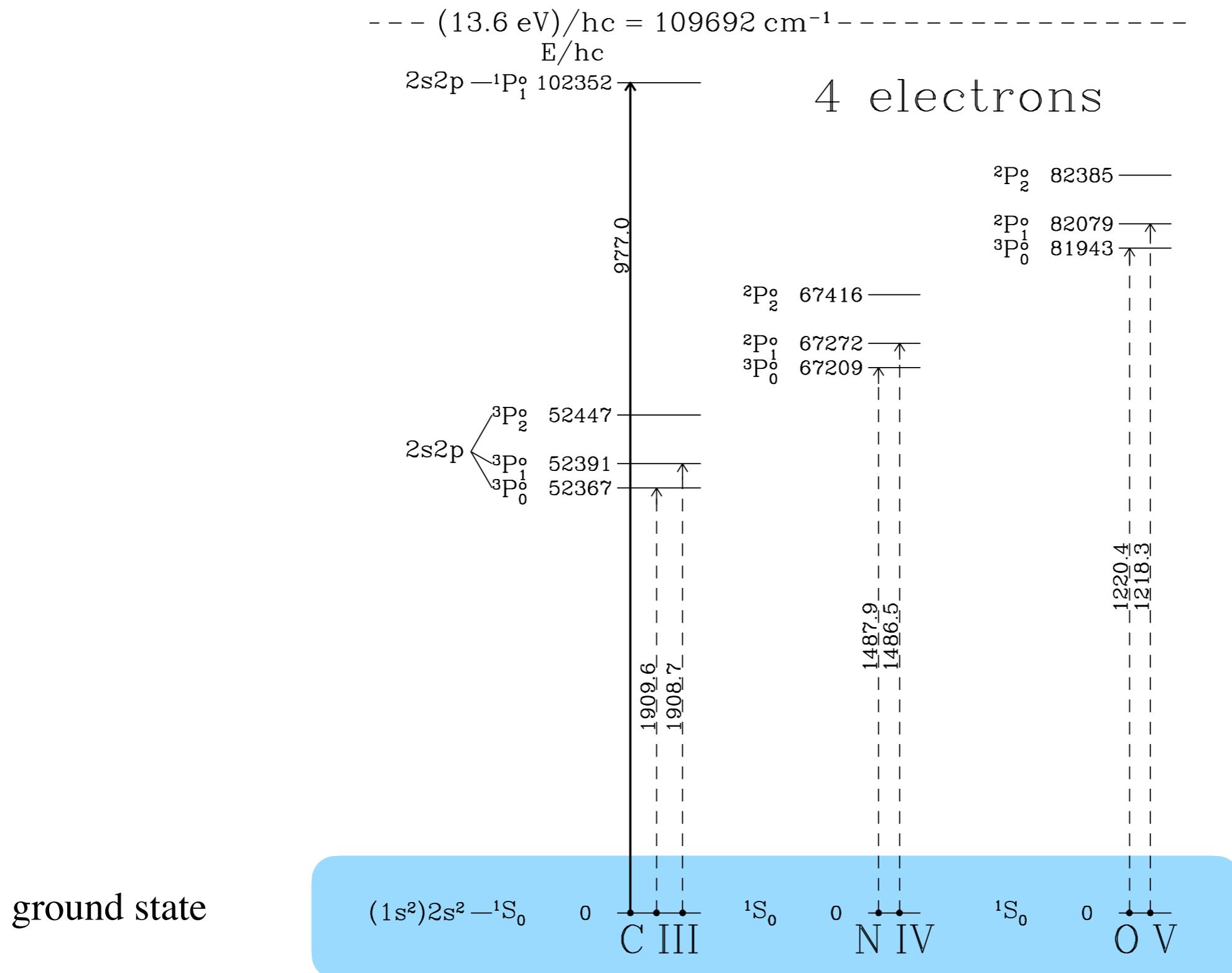
- 3 electrons (Lithium-like ions)

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



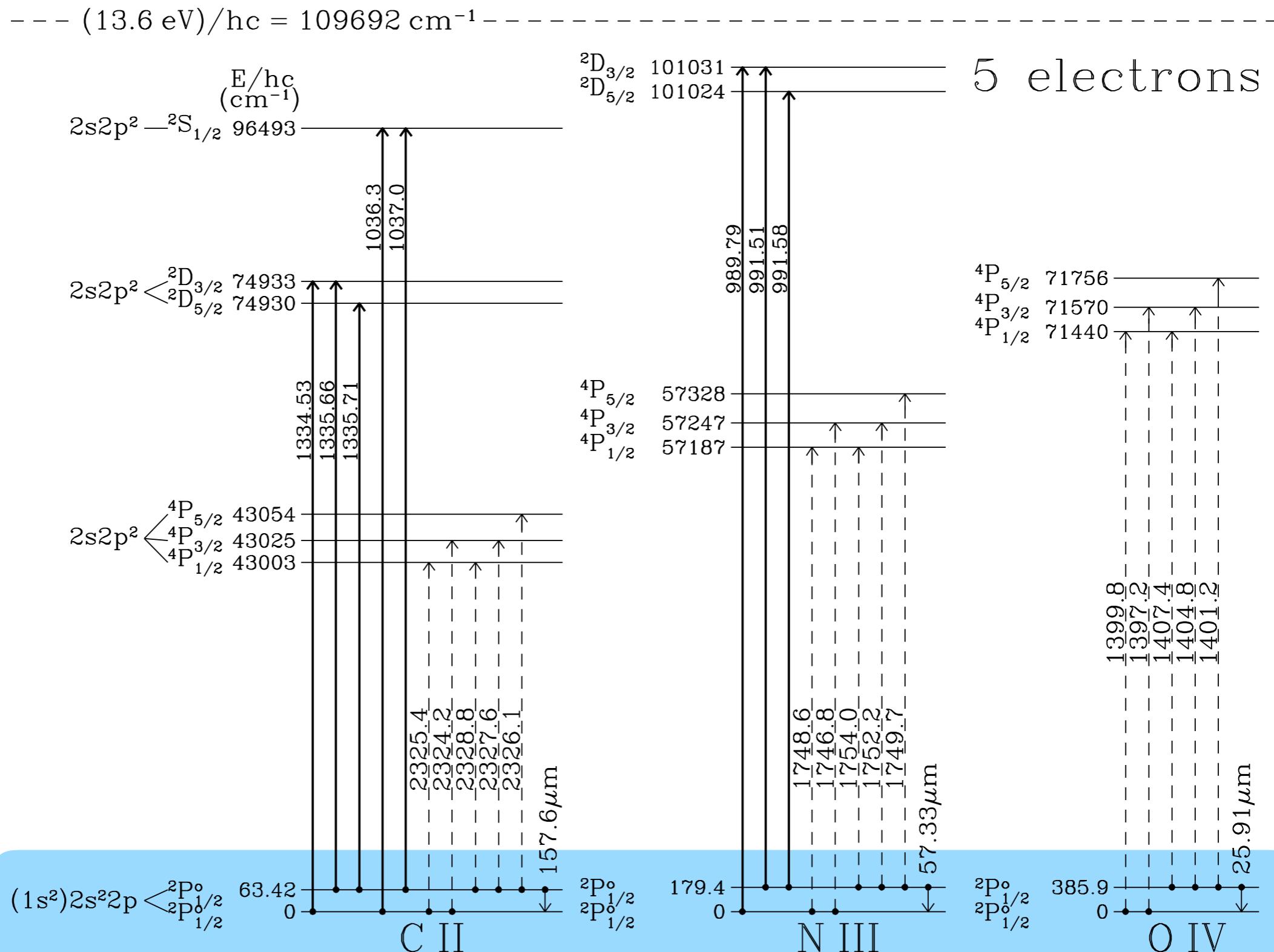
- 4 electrons

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



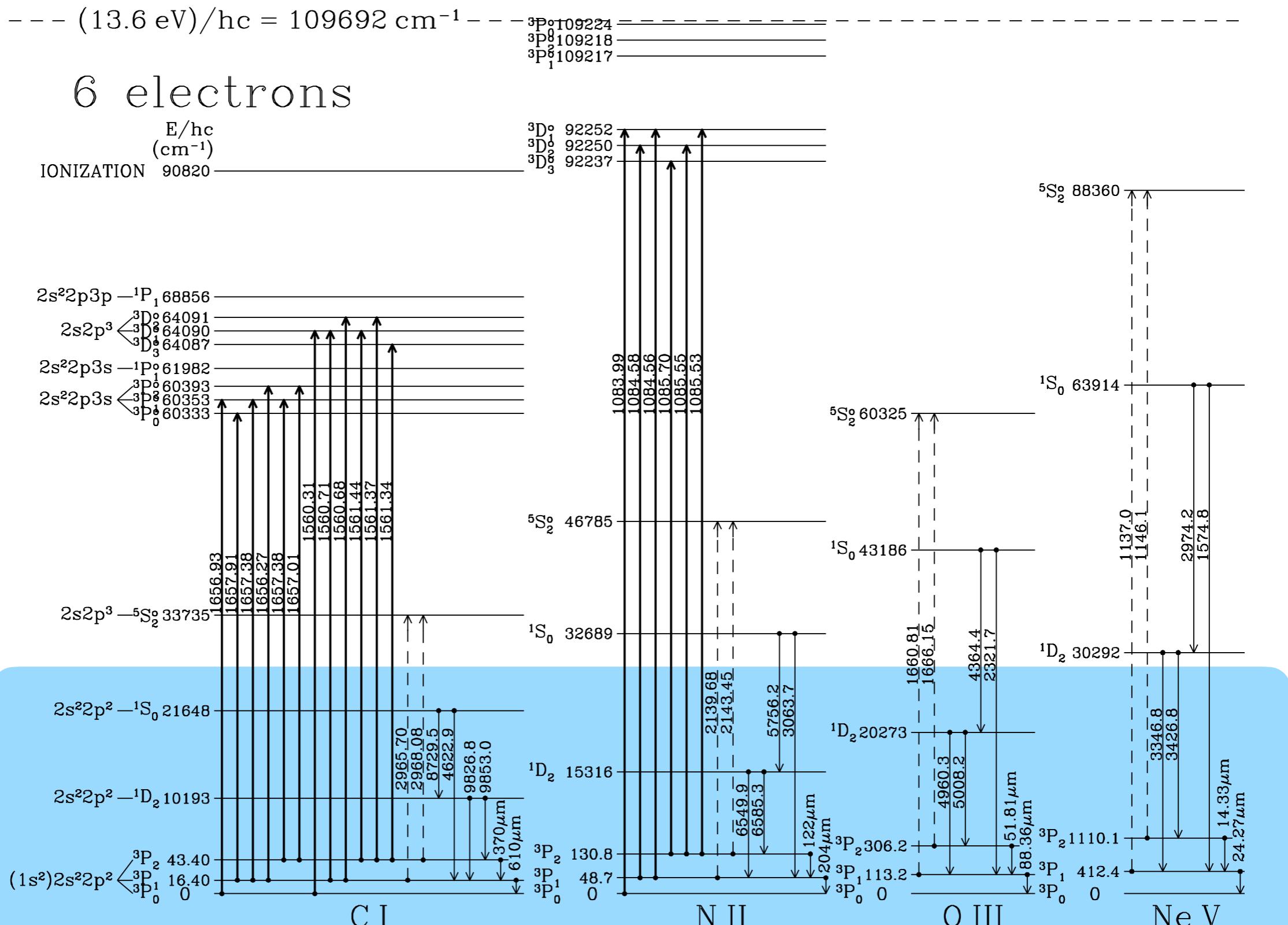
- 5 electrons

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



- 6 electrons

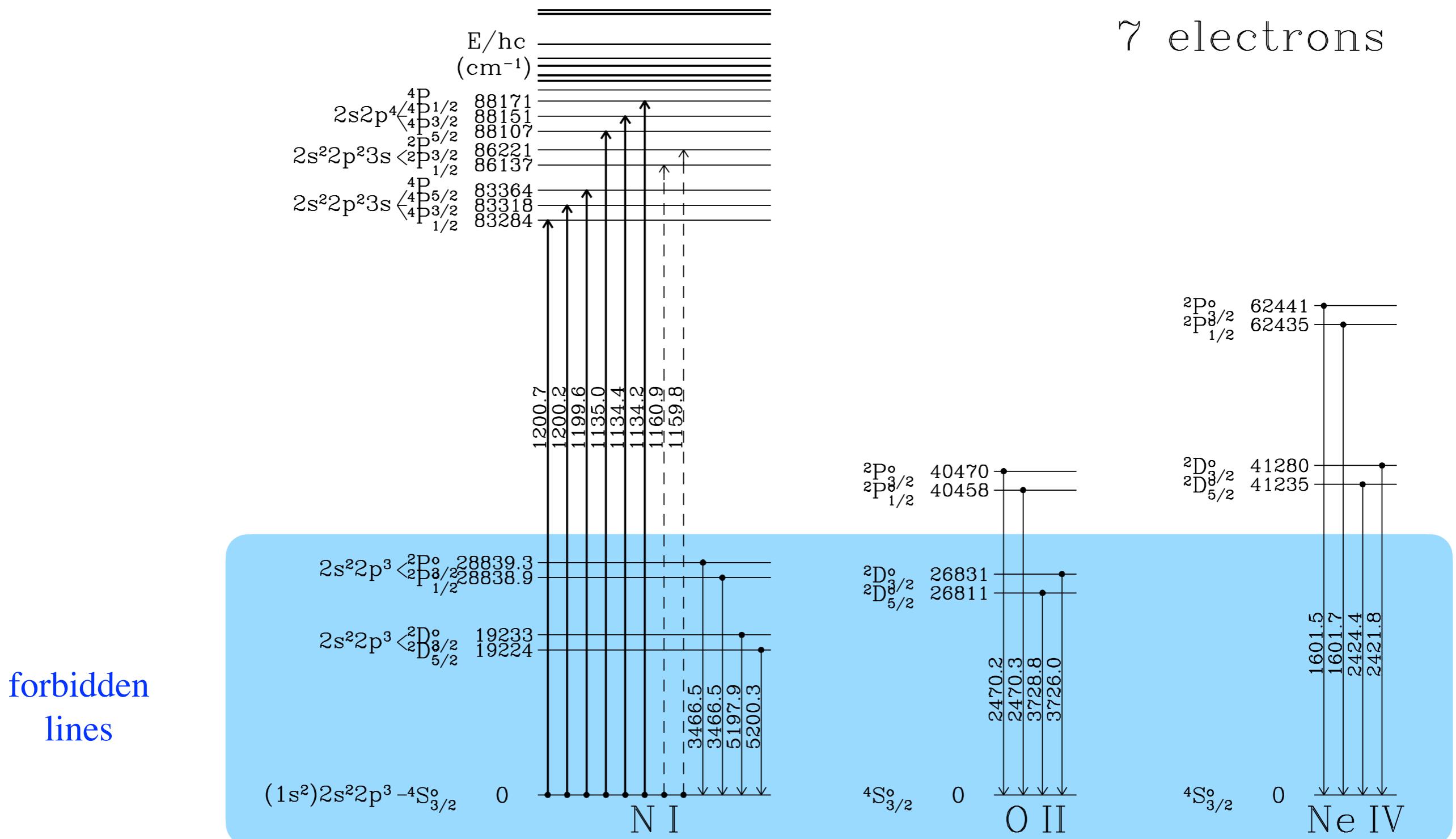
Upward heavy: resonance, Upward Dashed: intercombination
Downward solid: forbidden



- 7 electrons

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

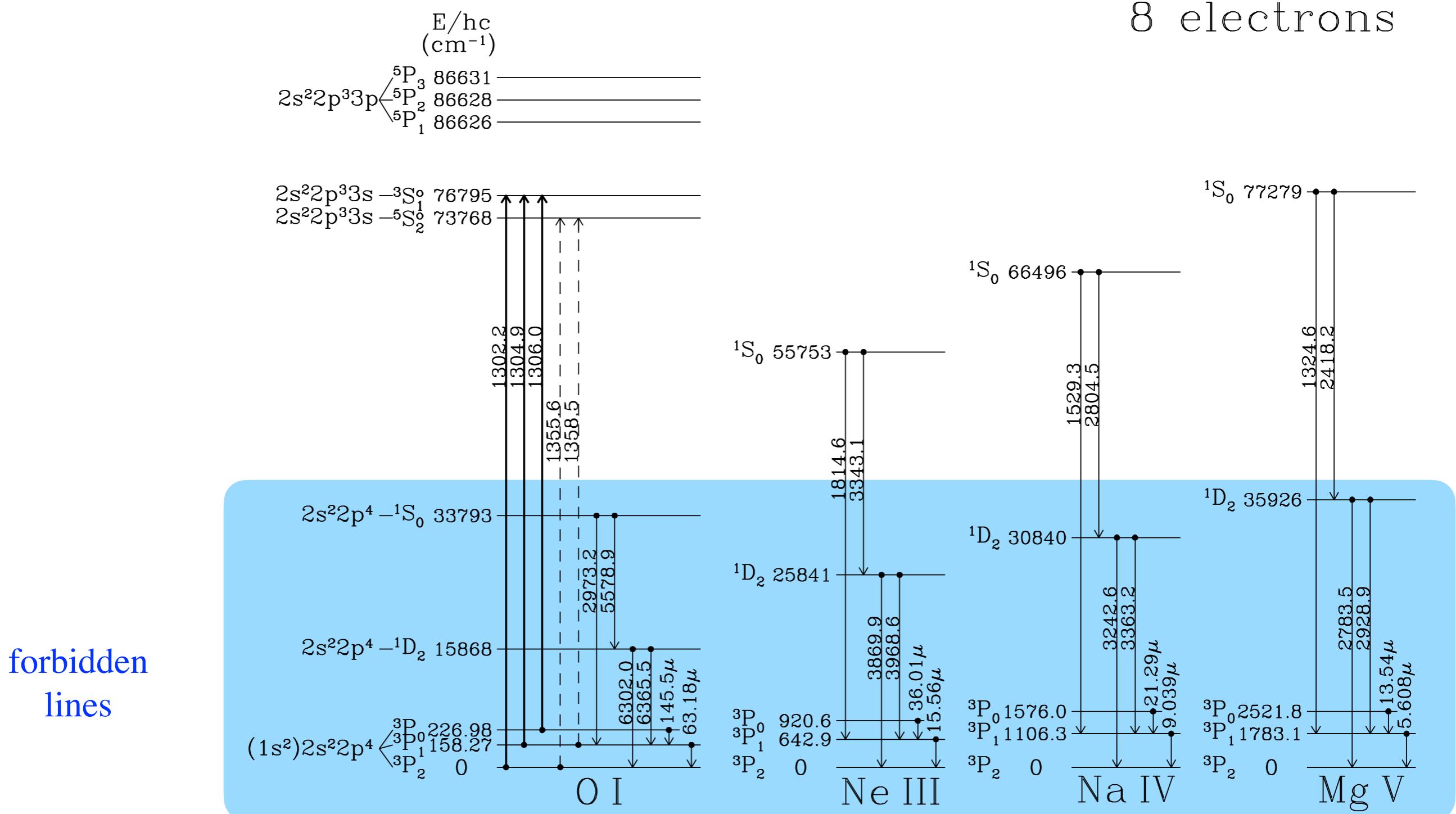
$$\text{---} (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{---} \text{---} \text{---}$$



- 8 electrons

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

--- (13.6 eV)/hc = 109692 cm⁻¹ -----



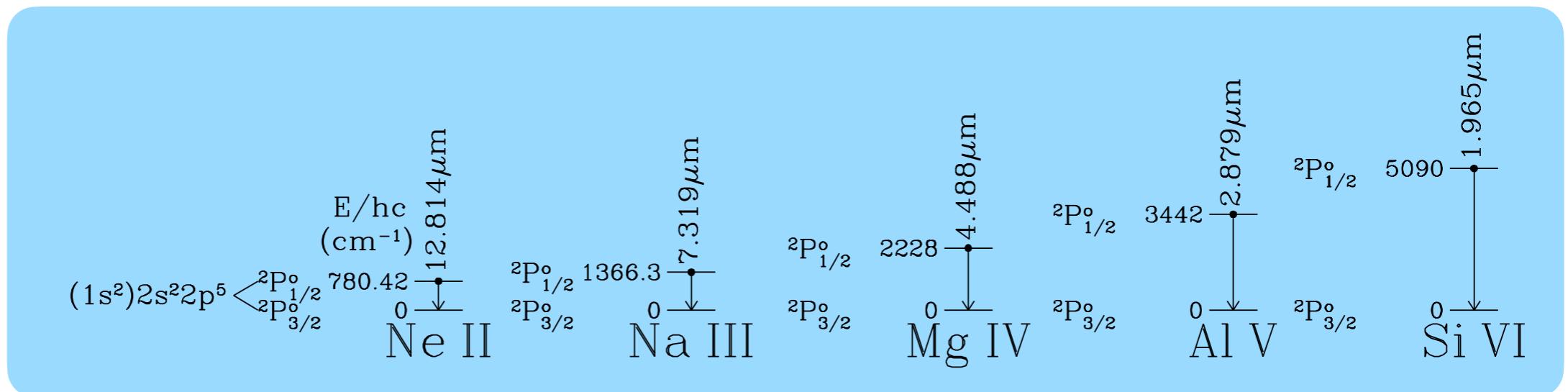
- 9 electrons

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

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

9 electrons

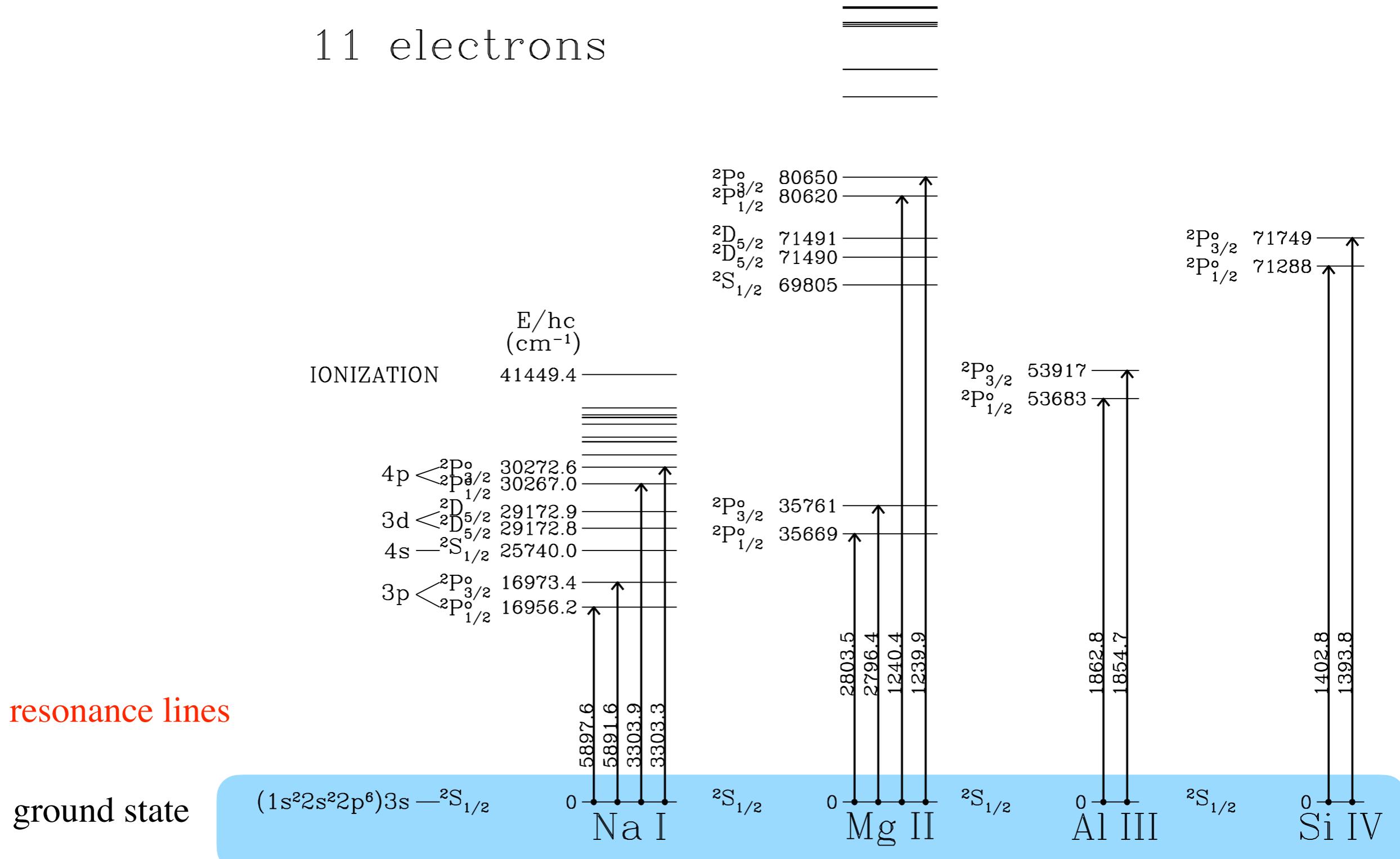
forbidden
lines



- 11 electrons

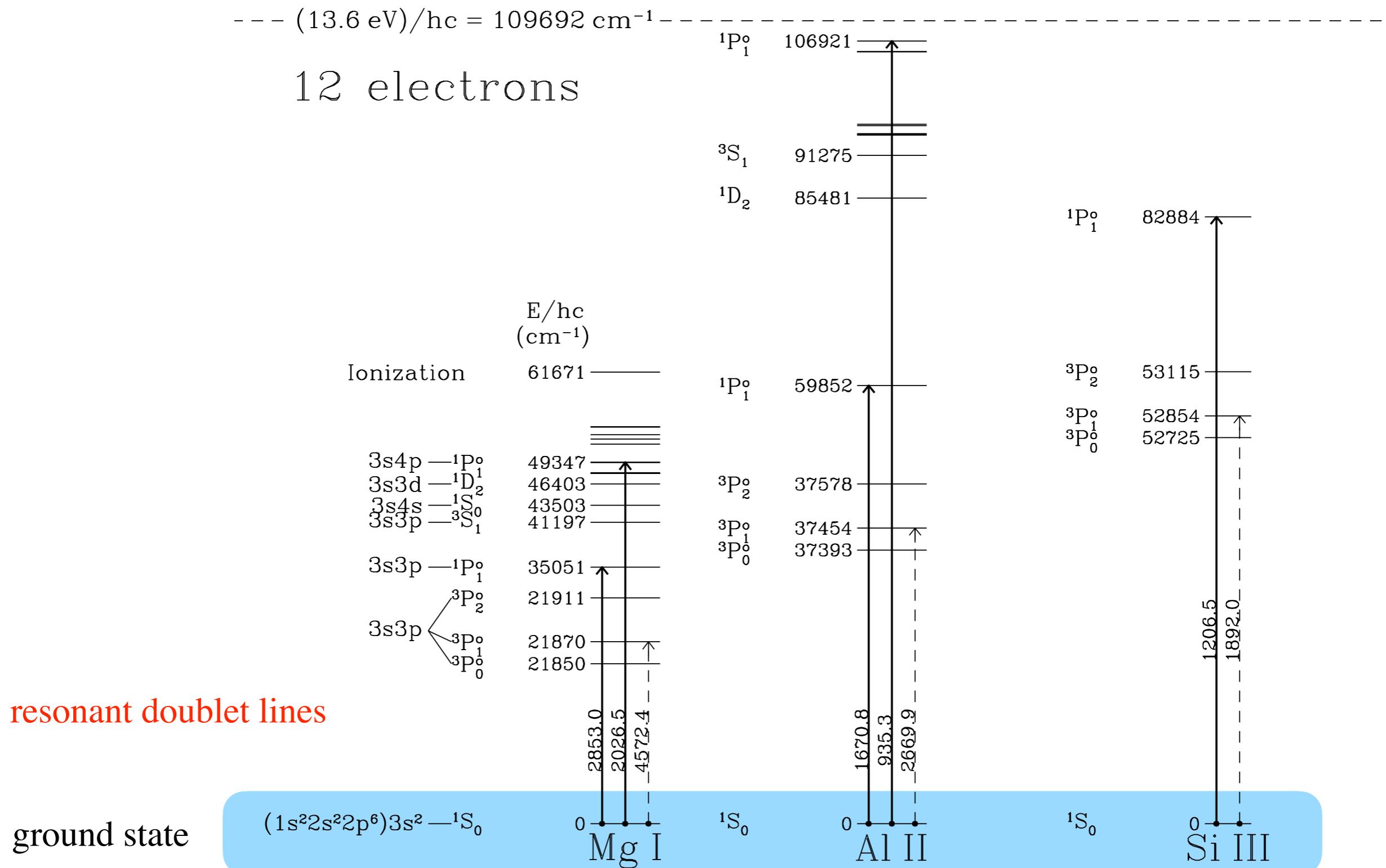
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{ --- }$$

11 electrons



- 12 electrons

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

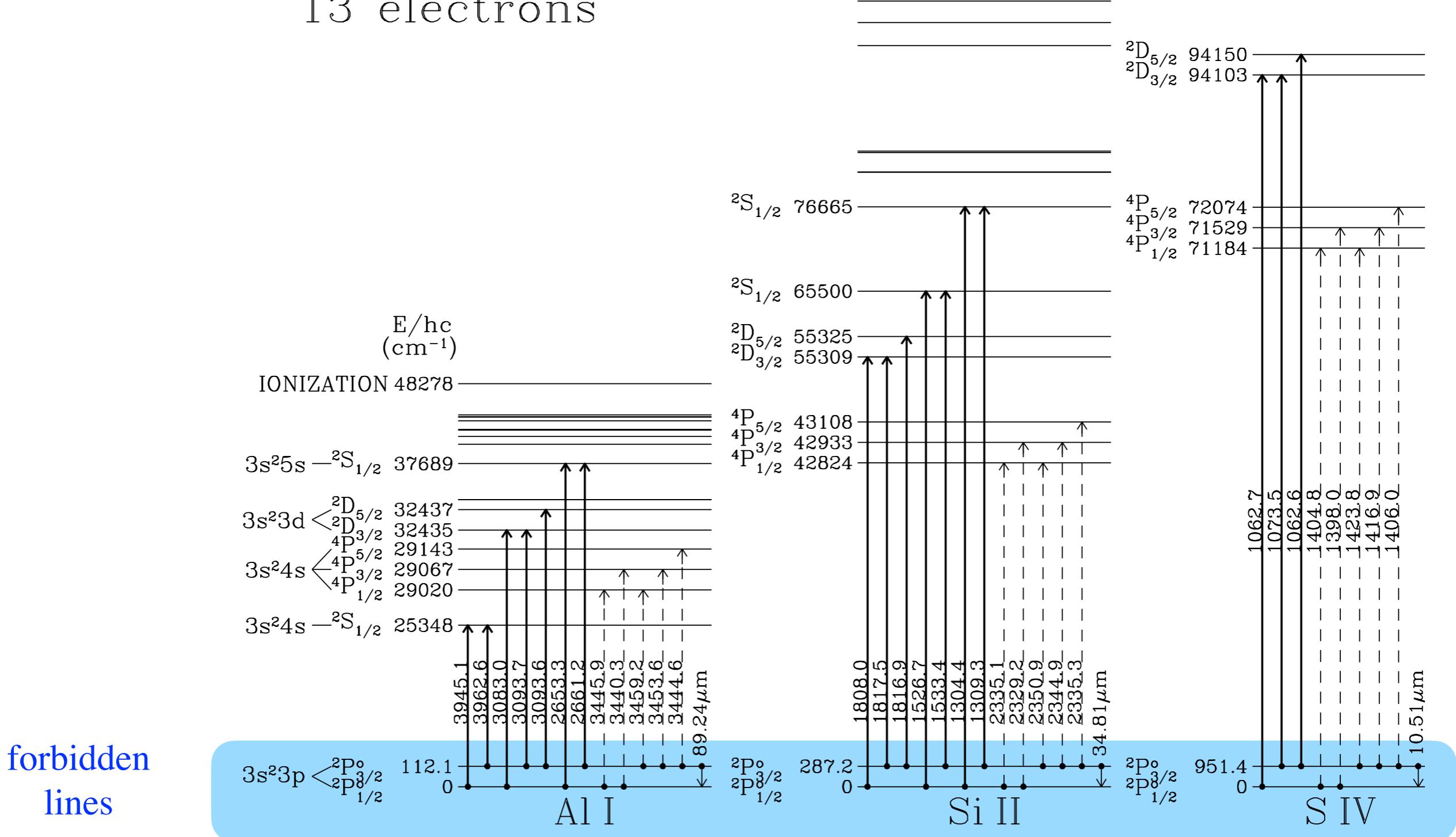


- 13 electrons

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

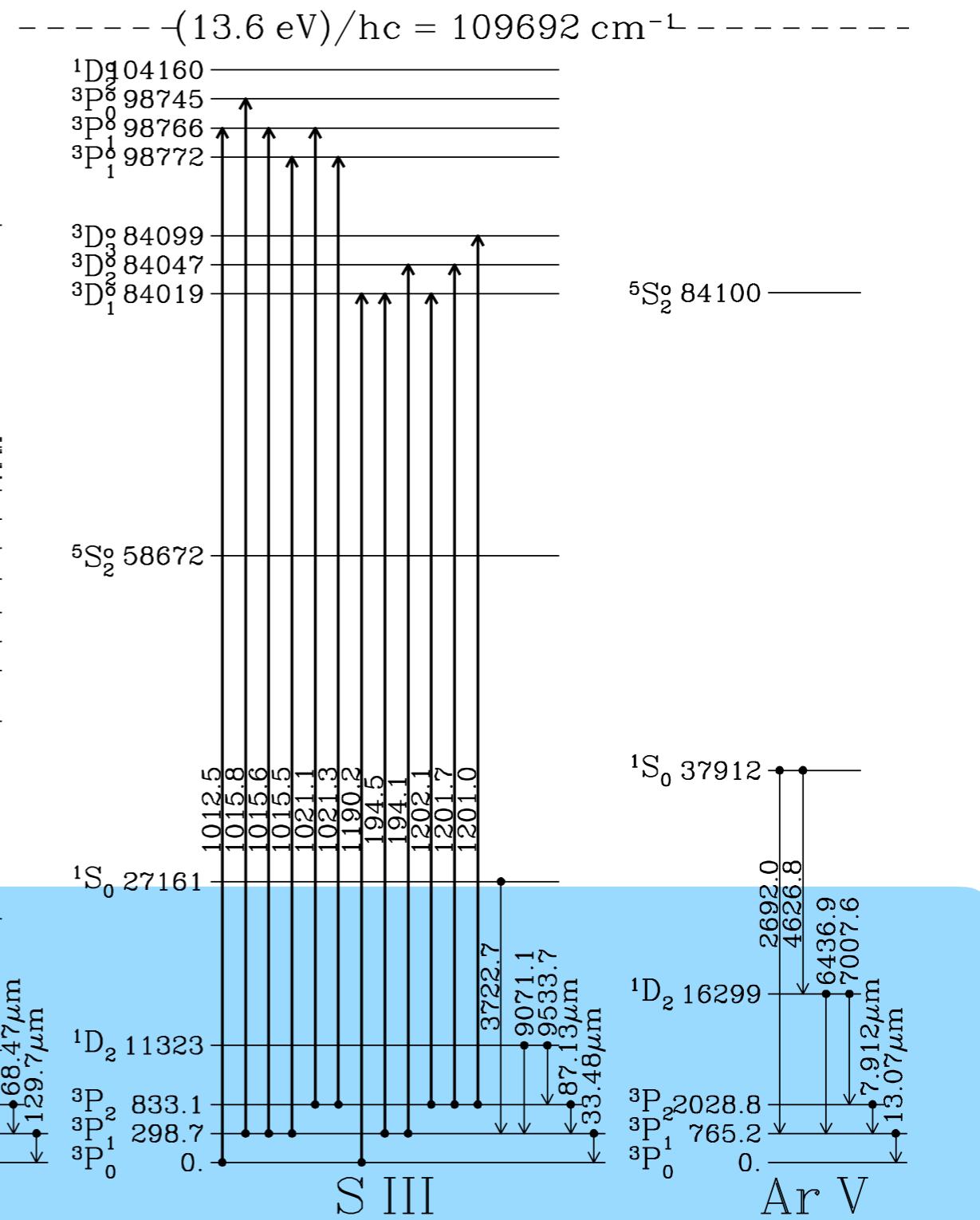
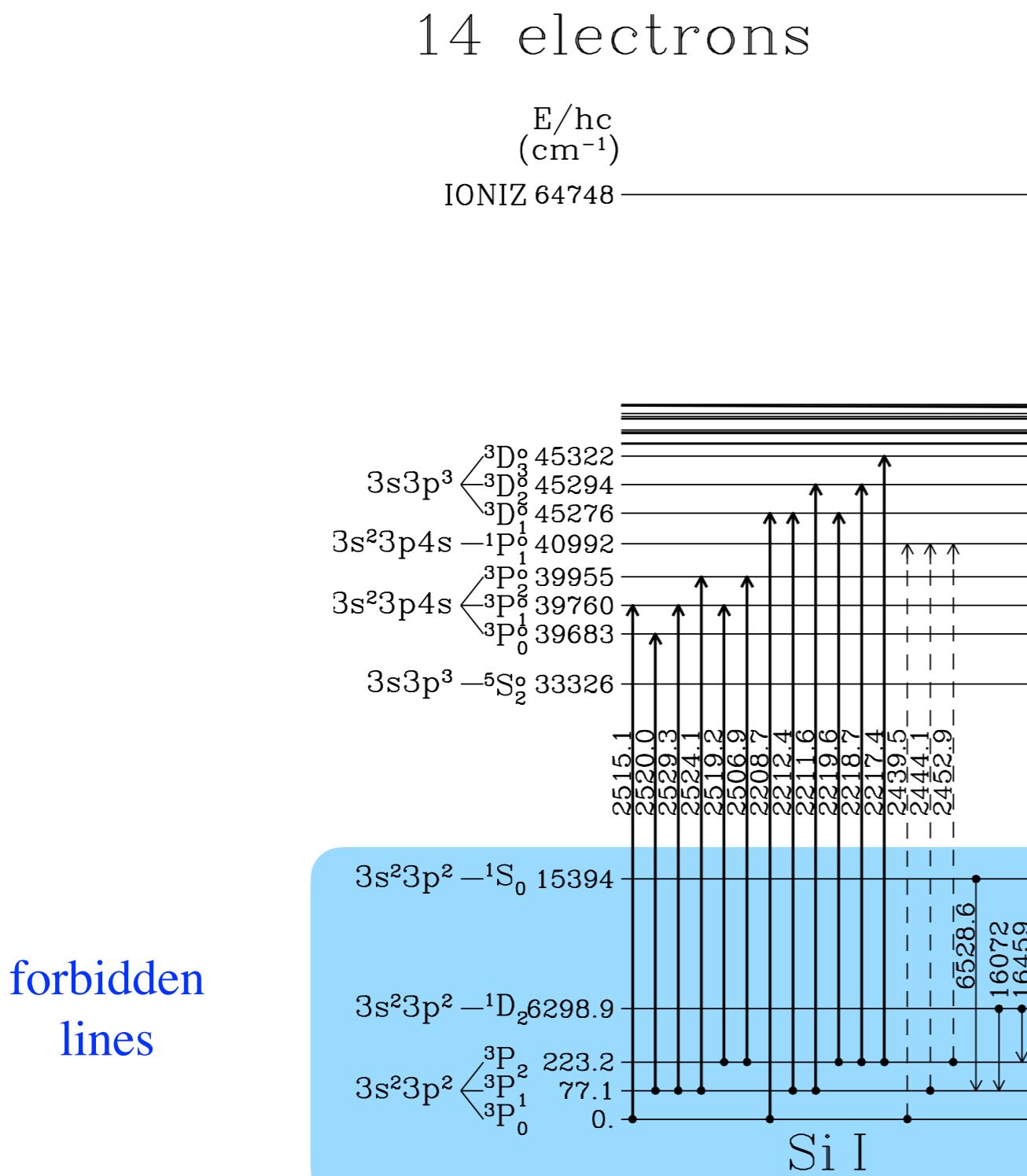
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1}$$

13 electrons



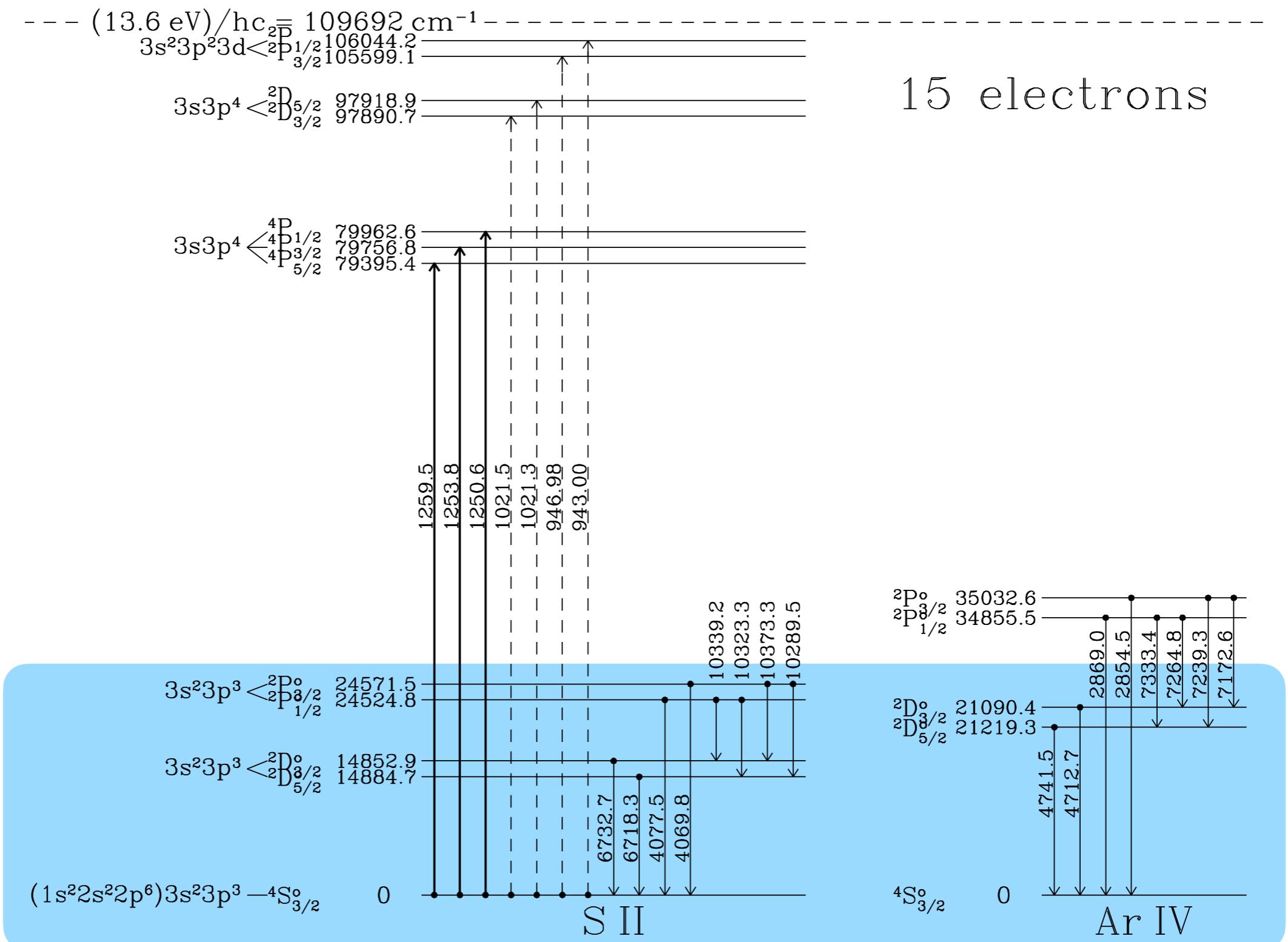
- 14 electrons

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



- 15 electrons

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



forbidden
lines

[Zeeman Effect]

- **Zeeman effect**

the splitting of atomic energy levels in the presence of an external magnetic field.

- **Zeeman effect at 1420MHz**

The upper level of the 1420 MHz hyperfine transition of hydrogen is the $F = 1$ state. Its angular momentum has three possible projections onto a given axis. The three states are

$$F_z = m_F \hbar \quad (m_F = -1, 0, +1)$$

The three states have the same energy (i.e., they are degenerate), but if the atoms are immersed in an external magnetic field, the three states take on different energies. This is a consequence of the interaction of the magnetic moment of the hydrogen atom with the external field.

$$\begin{aligned} E_{\text{pot}} &= -\boldsymbol{\mu} \cdot \mathbf{B} \simeq g_e \frac{e}{2m_e} \mathbf{F} \cdot \mathbf{B} \\ &= g_2 \frac{e\hbar}{2m_e} m_F B \end{aligned}$$

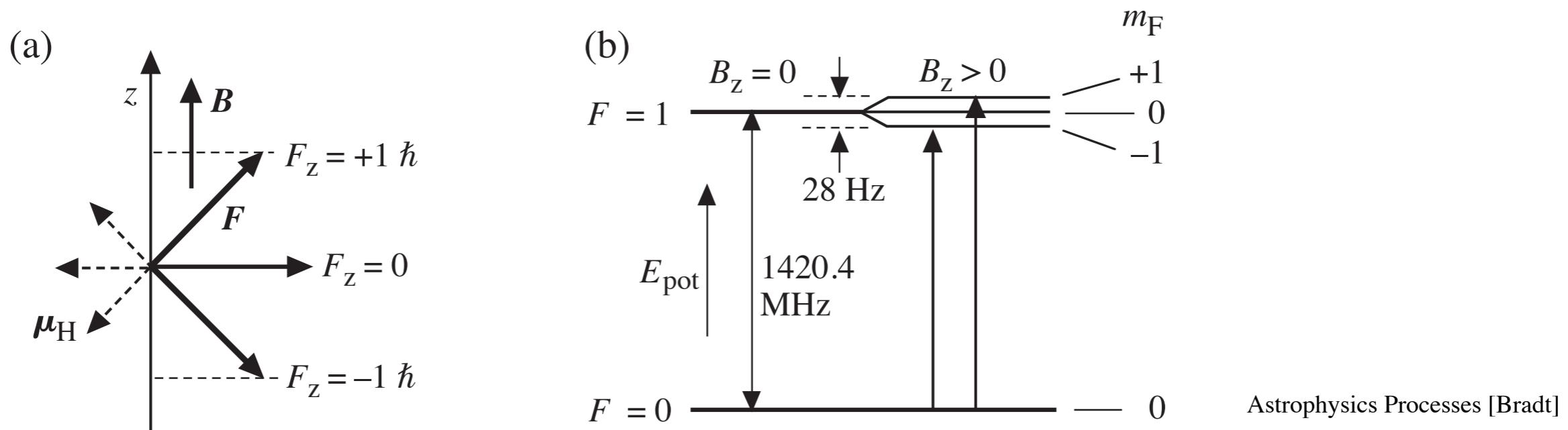
$\mu \simeq \mu_e$ because μ arises almost totally from the electron.

The separation between the +1 and -1 levels is

$$\Delta E_{\text{pot}} = E_{\text{pot}}(m_F = +1) - E_{\text{pot}}(m_F = -1) = g_e \frac{e\hbar}{m_e} B$$

In the $F = 0$ ground state, the total angular momentum is zero. Therefore, the magnetic moment is zero and no Zeeman splitting occurs in the ground state.

Photons carry one unit of angular momentum \mathbf{J} . The allowed transitions are from the $F = 0$ ($m_F = 0$) to the $F = 1$ ($m_F = +1$) or $F = 1$ ($m_F = -1$).

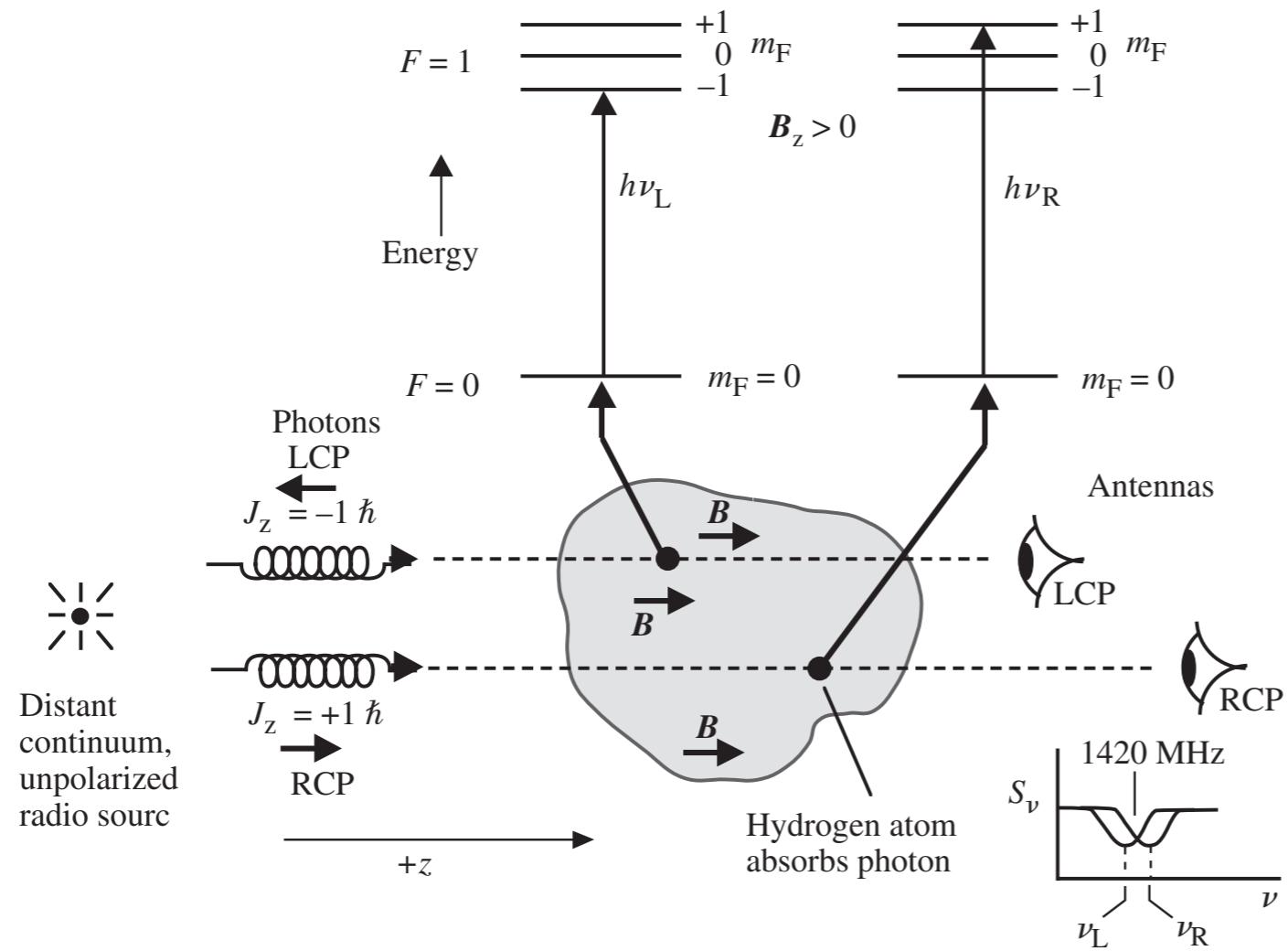


Energy levels for Zeeman absorption by hydrogen atom in an external magnetic field \mathbf{B} . The z-axis is taken to be in the direction of \mathbf{B} .

- (a) The three allowed projections ($m_F = +1, 0, -1$) of the angular momentum for the $F = 1$ state. The atomic magnetic moment μ_H , which is directed opposite to the angular momentum, interacts with the magnetic field to perturb the energy state.
- (b) Energy levels showing (left) the 1420-MHz transition for $B = 0$ and (right) the Zeeman splitting of the upper energy level into the three sublevels for $B_z > 0$. The two allowed transitions to the upper states are shown; they differ in frequency by 28 Hz for $B_z = 1$ nT.

In quantum theory, a single photon is always circularly polarized with $S = \pm \hbar$ (no state with $S = 0$). Linearly polarized photon state is a superposition of a pair of circularly polarized photons.

A magnetic field of order $10 \mu\text{G}$ shifts the frequency by about one part in 10^8 of the hyperfine splitting. This shift is much smaller than the frequency shift $v/c \sim 10^{-5}$ due to a radial velocity of a few km s^{-1} , and it would be nearly impossible to detect, except that it leads to a shift in frequency between two circular polarization modes. The Zeeman effect in H I 21 cm can therefore be detected by taking the difference of the two circular polarization signals. This technique has been used to measure the magnetic field strength in a number of H I regions.



$$\nu_R - \nu_L = \frac{eB_z}{2\pi m_e} = 28.0 \left(\frac{B_z}{1.0 \text{nT}} \right) \text{ Hz}$$

Left circularly polarized (LCP) photons are absorbed at a slightly lower frequency.

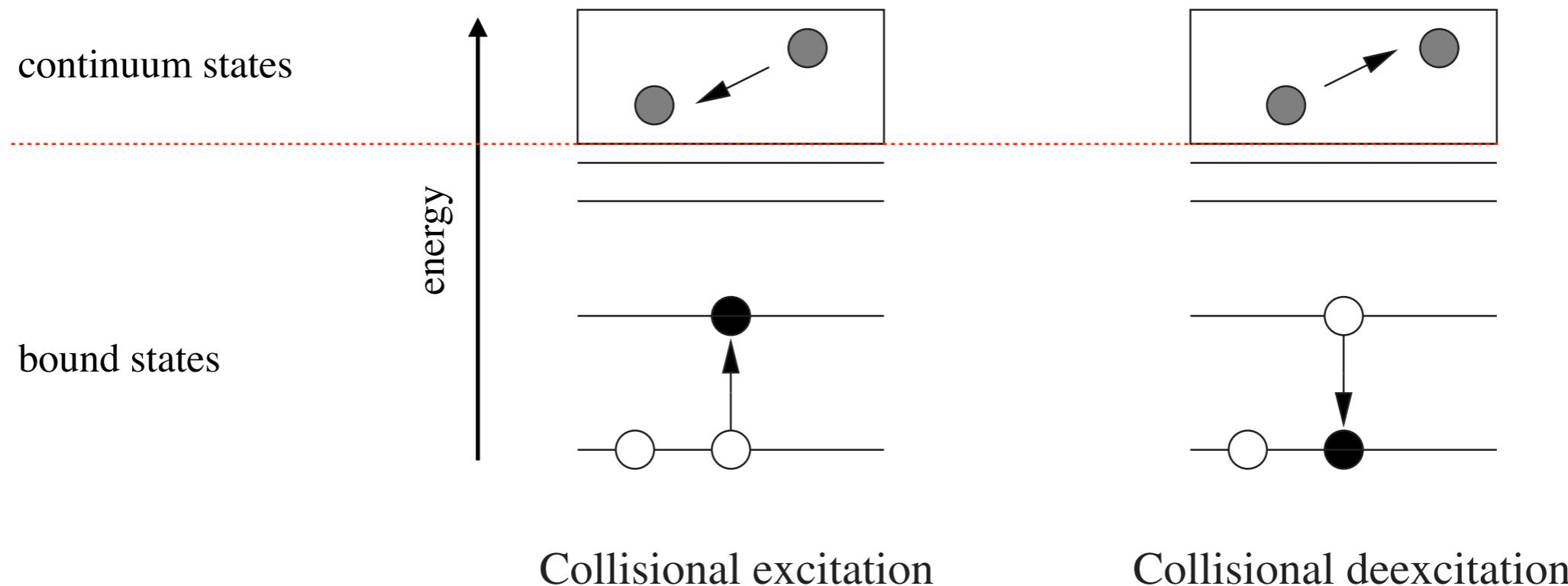
Right circularly polarized (RCP) photons are absorbed at a slightly higher frequency.

[Electron-Ion Collisional Processes]

- To predict the emergent spectra of astrophysical plasmas, we need to understand the details of how excited atomic levels are populated. For the most part, it involves the study of electron-ion collisional processes in gas.
- Each electron-ion collisional process is accompanied by a quantum mechanical inverse, which can be viewed as the same process time-reversed.
- There are essentially four (+1) key electron-ion collisional processes.
 - Collisional Excitation / Deexcitation
 - Collisional Ionization / 3-Body Recombination
 - Radiative Recombination / Photoionization
 - Dielectronic Capture / Autoionization
- + Charge Exchange

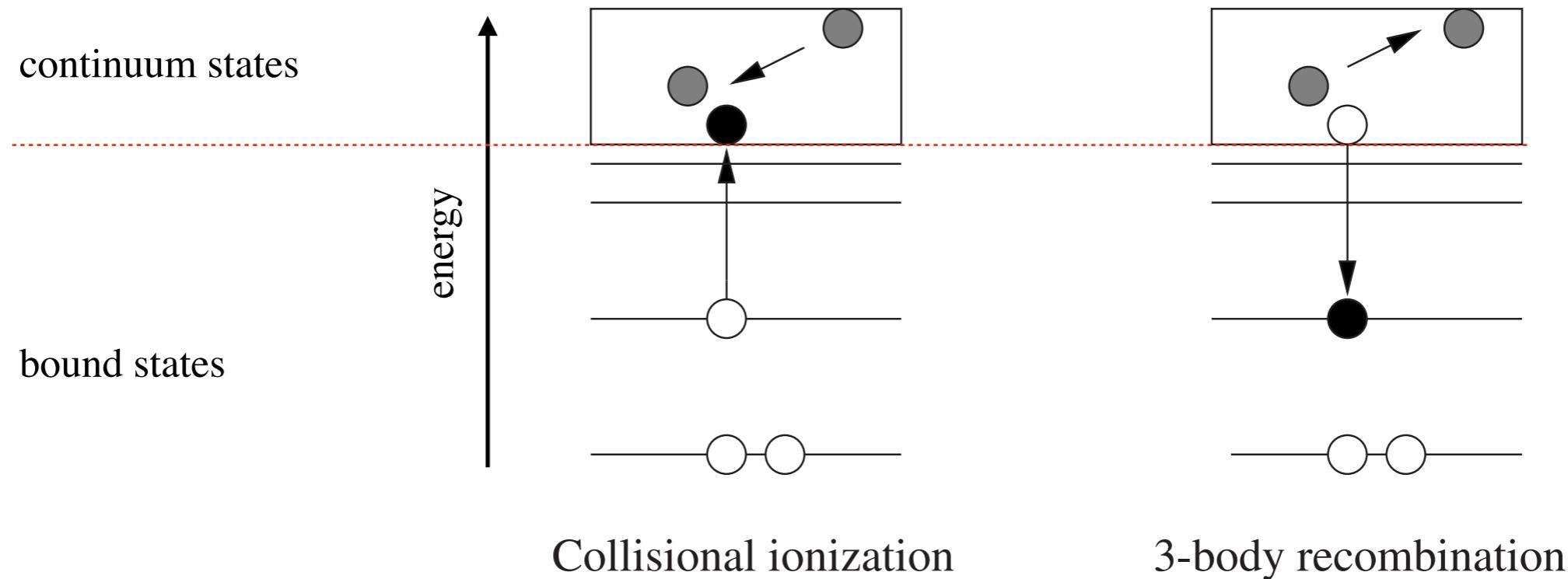
(1) Collisional Excitation / Deexcitation

- In collisional excitation, the interaction between a passing electron in a continuum state and a bound electron in a discrete state result in the excitation of the bound electron to a higher energy discrete level.
- To conserve energy, the colliding electron gives up a fraction of its energy and thus “falls” into a lower continuum state.
- The inverse process is collisional deexcitation, where a passing electron interacting with an excited atom actually gains energy as a result of the collisions.



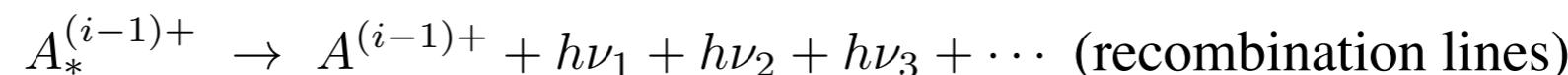
(2) Collisional ionization / 3-body recombination

- Collisional ionization is similar to collisional excitation, except that in this case, the final state of the initially bound electron is also a continuum state.
- The inverse process if 3-body recombination. Here, two initially free electrons interact with the ion in the same collision. One of the two gets captured into a bound discrete level, while the other carries off the excess energy in a higher continuum state.

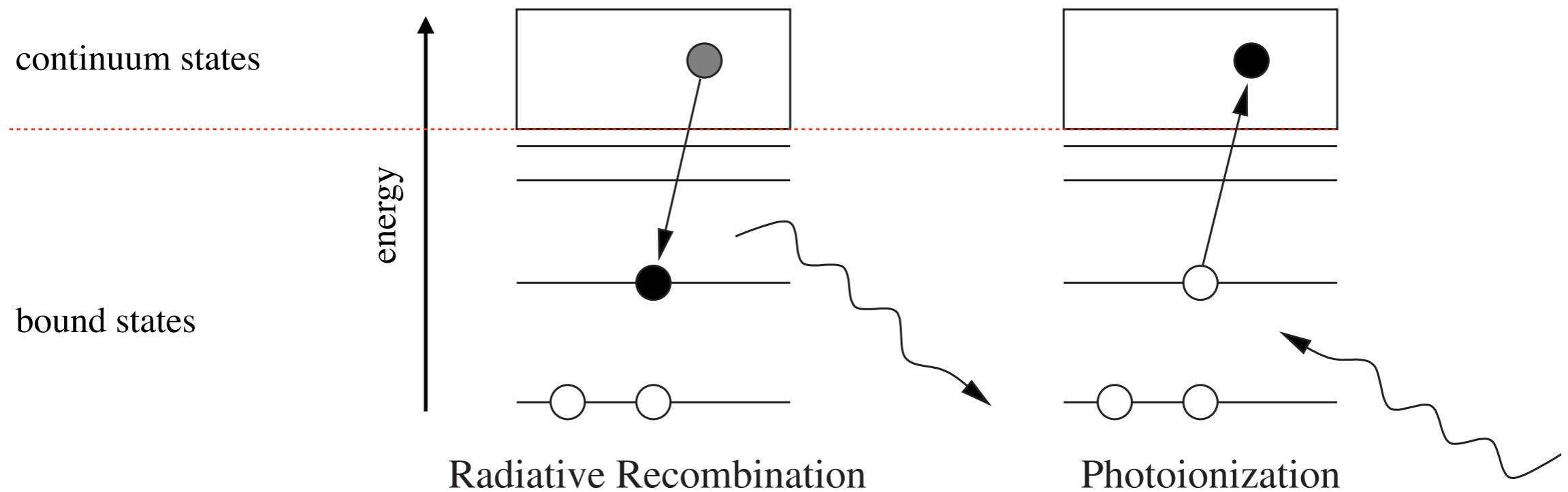


(3) Radiative Recombination / Photoionization

- In radiative recombination a free electron in a continuum state decays into a bound discrete state through the emission of a photon. This is actually a form of a spontaneous emission, similar to the radiative decay between two bound levels.

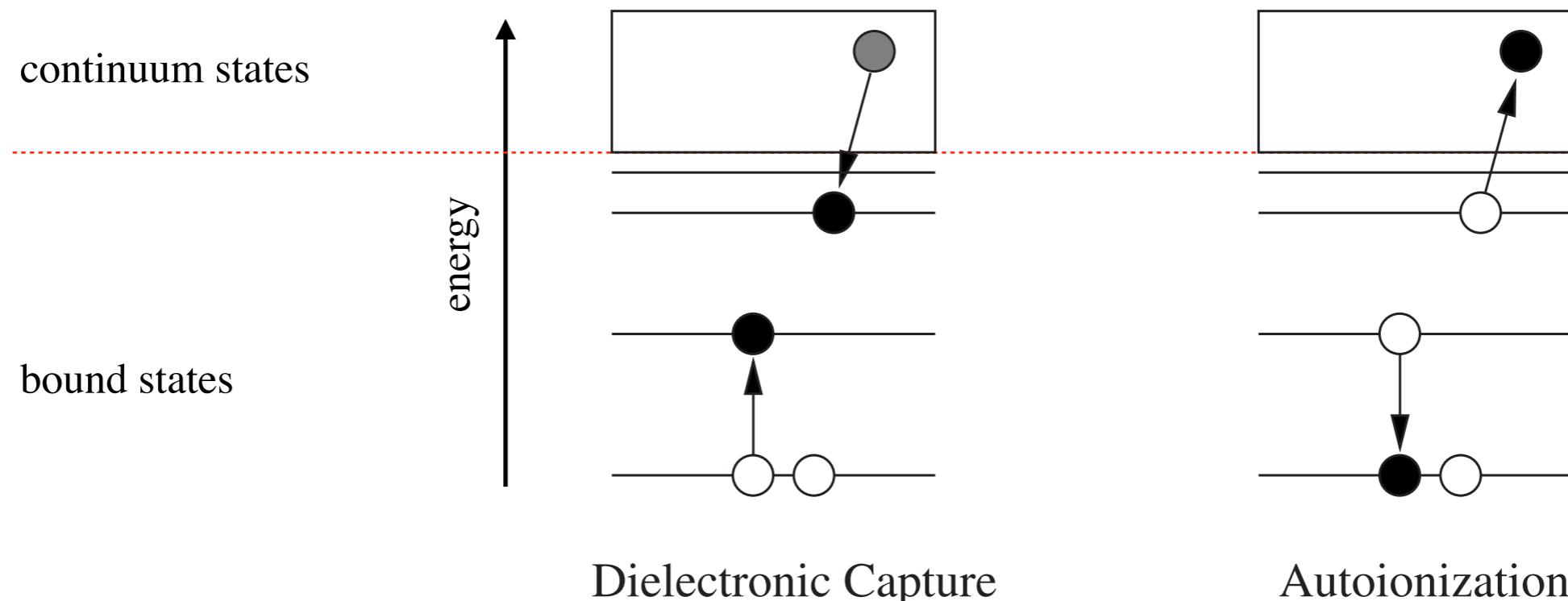


- The inverse process is photoionization or bound-free absorption.
 - Interstellar medium (ISM) is transparent to $h\nu < 13.6 \text{ eV}$ photons, but is very opaque to ionizing photons. In fact, the ISM does not become transparent until $h\nu \sim 1 \text{ keV}$. Sources of ionizing photons include massive, hot young stars, hot white dwarfs, and supernova remnant shocks.



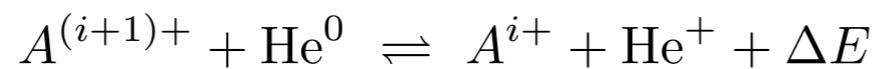
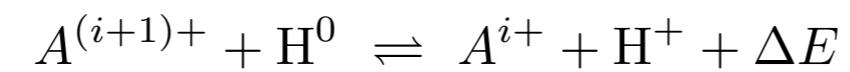
(4) Dielectronic Capture / Autoionization

- Dielectronic capture (recombination) is a resonant radiationless process in which the decay of an electron from a continuum state to a bound state is accompanied by the elevation of a core electron into an excited state. The resulting atom is doubly excited, and it has a total energy above the ionization potential of the initial ion.
- The inverse process is autoionization, where a doubly excited atom decays via the emission of a weakly bound outer electron. If the core excitation is associated with a “hole”, in one of the orbitals of an inner shell, this process is usually called Auger decay.



(5) Charge Exchange

- During the collision of two ionic species, the charge clouds surrounding each interact, and it is possible that an electron is exchanged between them.
- Since, in virtually all diffuse astrophysical plasmas, hydrogen and helium are overwhelmingly the most abundant species, the charge-exchange reactions which are significant to the ionization balance of the plasma are



[Ionization Equilibrium]

- **Collisional Ionization Equilibrium (CIE) or coronal equilibrium**
 - dynamic balance at a given temperature between collisional ionization from the ground states of the various atoms and ions, and the process of recombination from the higher ionization stages.
 - In this equilibrium, effectively, all ions are in their ground state.
 - Software: **Chianti** (<https://www.chiantidatabase.org/>)

- **Photoionization Equilibrium**
 - dynamic balance between photo-ionization and the process of recombination.
 - Software: **Cloudy** (<https://trac.nublado.org/>), **MAPPINGS** (<https://mappings.anu.edu.au/>), **MOCASSIN** (<https://github.com/mocassin>, <https://mocassin.nebulosresearch.org/>)

- **Ionization balance under conditions of Local Thermodynamic Equilibrium (LTE)**
 - The ionization equilibrium in LTE is described by the Saha equation.

$$\frac{n_{r+1}n_e}{n_r} = \frac{G_{r+1}g_e}{G_r} \frac{(2\pi m_e kT)^{3/2}}{h^3} \exp\left(-\frac{\chi_r}{kT}\right)$$

n_{r+1} : density of atoms in ionization state $r + 1$

n_r : density of atoms in ionization state r

n_e : density of electrons

G_{r+1} : partition function of ionization state $r + 1$

G_r : partition function of ionization state r

g_e : statistical weight of the electron, $g_e = 2$

χ_r : ionization potential of state r (to reach state $r + 1$)

$$G_r = \sum_j g_{r,k} \exp\left(-\frac{E_{r+1,j}}{kT}\right)$$