

Interstellar Medium (ISM)

Week 3

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Thermal equilibrium

- In general, equilibrium means a state of balance.
 - ***Thermal equilibrium refers to steady states of temperature, which defines the average energy of material or photons.***
 - In a state of (complete) ***thermodynamic equilibrium (TE)***, no net flows of matter or of energy, no phase changes, and no unbalanced potentials (or driving forces), within the system. ***In TE, matter and radiation are in equilibrium at the same temperature T.***
 - If the material is (locally) in thermodynamic equilibrium at a well-defined temperature T , ***it is said to be in local thermodynamic equilibrium (LTE) even if it is not in equilibrium with the radiation field.***
- ***Note that thermal equilibrium differ from thermodynamic equilibrium.***

The state of LTE

- Macroscopically, LTE is characterized by the following three equilibrium distributions:
 - **Maxwellian velocity distribution** of particles, written here in terms of distribution for the absolute values of velocity,

$$f(v)dv = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) 4\pi v^2 dv$$

where m is the particle mass and k the Boltzmann constant.

- **Boltzmann excitation equation**,

$$\frac{n_i}{N_I} = \frac{g_i}{U_I} e^{-E_i/kT}$$

where n_i is the population of level i , g_i is its statistical weight, and E_i is the level energy, measured from the ground state; N_I and U_I are the total number density and the partition function of the ionization state I to which level i belongs, respectively.

- **Saha ionization equation**,

$$\frac{N_I}{N_{I+1}} = n_e \frac{U_I}{U_{I+1}} \left(\frac{h^2}{2\pi m_e kT}\right)^{3/2} e^{\chi_I/kT}$$

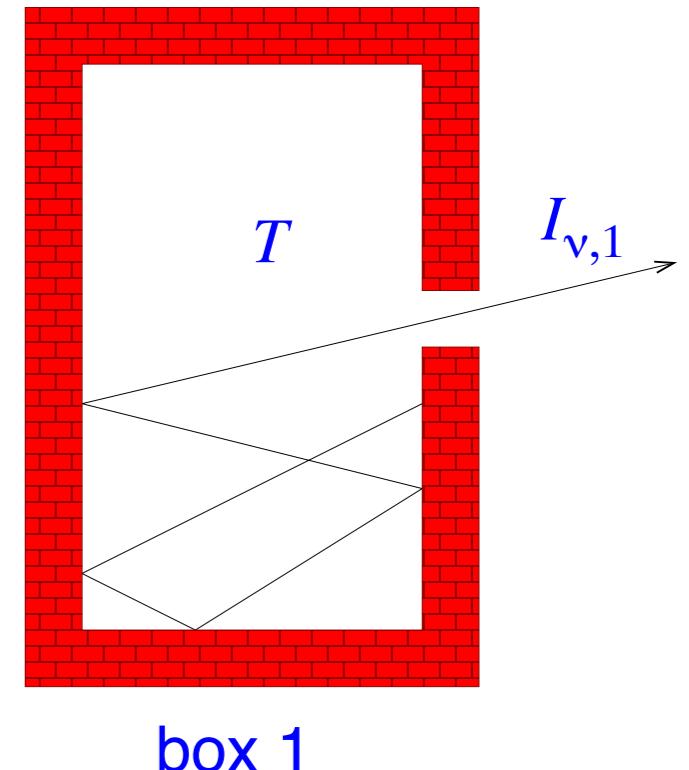
where χ_I is the ionization potential of ion I .

- Microscopically, LTE holds if all atomic processes are in detailed balance, i.e., if the number of processes $A \rightarrow B$ is exactly balanced by the number of inverse processes $B \rightarrow A$.

Blackbody

- Imagine a container bounded by opaque walls with a very small hole.

- ***Photons will be scattered and absorbed many times, (and eventually trapped and completely absorbed in the box).*** Under such conditions, the particles and photons continually share their kinetic energies. In perfect thermal equilibrium, ***the average particle kinetic energy will be equal to the average photon energy, and a unique temperature T can be defined.***

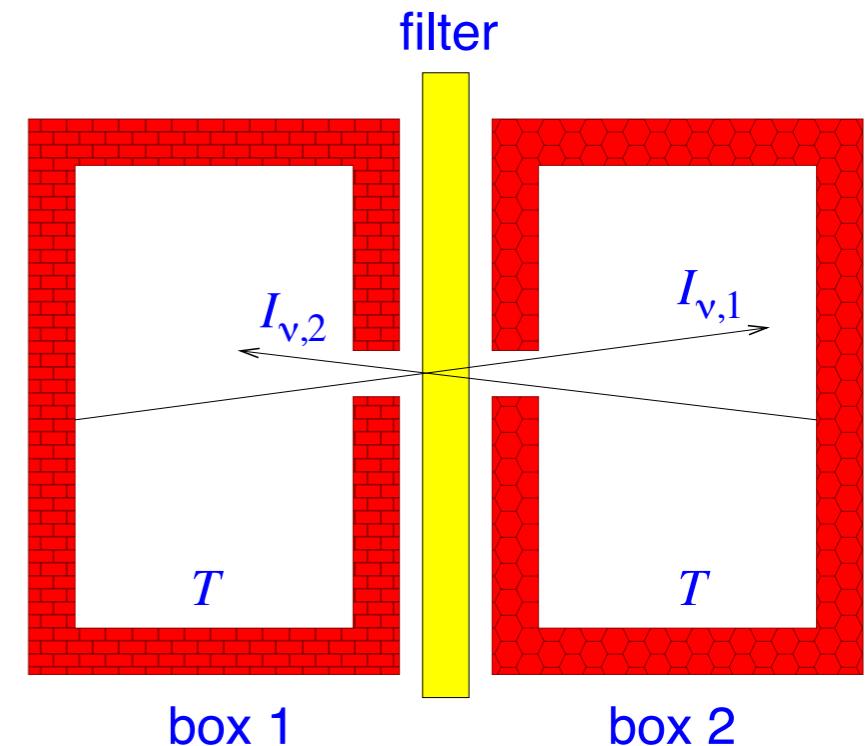


- A **blackbody** is an idealized physical body that absorbs all incident radiation regardless of frequency or angle of incidence (i.e., perfect absorber). The above cavity can be regarded to be a blackbody.
- Radiation from a blackbody in thermal equilibrium is called the **blackbody radiation**.

Blackbody radiation is the universal function.

- Now, consider another cavity (box 2), also at the same temperature, but made of different material or shape and connect two cavities with a filter transparent only in the narrow frequency range ν and $\nu + d\nu$.

- In equilibrium at T , radiation should transfer no net energy from one cavity to the other. Otherwise, one cavity will cool down and the other heats up; this violates the second law of thermodynamics.
- Therefore, the intensity or spectrum that passes through the holes should be a universal function of T and should be isotropic.
- The intensity and spectrum of the radiation emerging from the hole should be independent of the wall material (e.g., wood, copper, or concrete, etc) and any absorbing material that may be inside the cavity.



- The universal function is called the Planck function $B_\nu(T)$.
- This is the **blackbody radiation**.

Kirchhoff's Law in TE

- In (full) thermodynamic equilibrium at temperature T , by definition, we know that

$$\frac{dI_\nu}{ds} = 0 \quad \text{and} \quad I_\nu = B_\nu(T)$$

- We also note that

$$\frac{dI_\nu}{ds} = -\alpha_\nu I_\nu + j_\nu$$

- Then, we can obtain ***the Kirchhoff's law for a system in TE:***

$$\frac{j_\nu(T)}{\alpha_\nu(T)} = B_\nu(T)$$

- This is remarkable because it connects the properties $j_\nu(T)$ and $\alpha_\nu(T)$ of any kind of matter to the single universal spectrum $B_\nu(T)$.

Kirchhoff's Law in LTE

- Recall that Kirchhoff's law was derived for a system in thermodynamic equilibrium.
- ***Kirchhoff's law applies not only in TE but also in LTE:***
 - Recall that $B_\nu(T)$ is independent of the properties of the radiating /absorbing material.
 - In contrast, both $j_\nu(T)$ and $\alpha_\nu(T)$ depend only on the materials in the cavity and on the temperature of that material; they do not depend on the ambient radiation field or its spectrum.
 - Therefore, the Kirchhoff's law should be true even for the case of LTE.
 - ***In LTE, the ratio of the emission coefficient to the absorption coefficient is a function of temperature and frequency only.***
 - This generalized version of Kirchhoff's law is an exceptionally valuable tool for calculating the emission coefficient from the absorption coefficient or vice versa.

Implications of Kirchhoff's Law

- A good absorber is a good emitter, and a poor absorber is a poor emitter. (In other words, a good reflector must be a poor absorber, and thus a poor emitter.)

$$j_\nu = \alpha_\nu B_\nu(T) \rightarrow j_\nu \text{ increases as } \alpha_\nu \text{ increases}$$

- It is not possible to thermally radiate more energy than a blackbody, at equilibrium.

$$j_\nu < B_\nu(T) \text{ because } \alpha_\nu < 1$$

- The radiative transfer equation in LTE can be rewritten:

$$\boxed{\frac{dI_\nu}{d\tau_\nu} = -I_\nu + B_\nu(T)}$$

- ***Blackbody radiation vs. Thermal radiation***

- ***Blackbody radiation*** means $I_\nu = B_\nu(T)$. An object for which the intensity is the Planck function is emitting blackbody radiation.
- ***Thermal radiation is defined to be radiation emitted by “matter” in LTE***. Thermal radiation means $S_\nu = B_\nu(T)$. An object for which the source function is the Planck function is emitting thermal radiation.
- ***Thermal radiation becomes blackbody radiation only for optically thick media.***

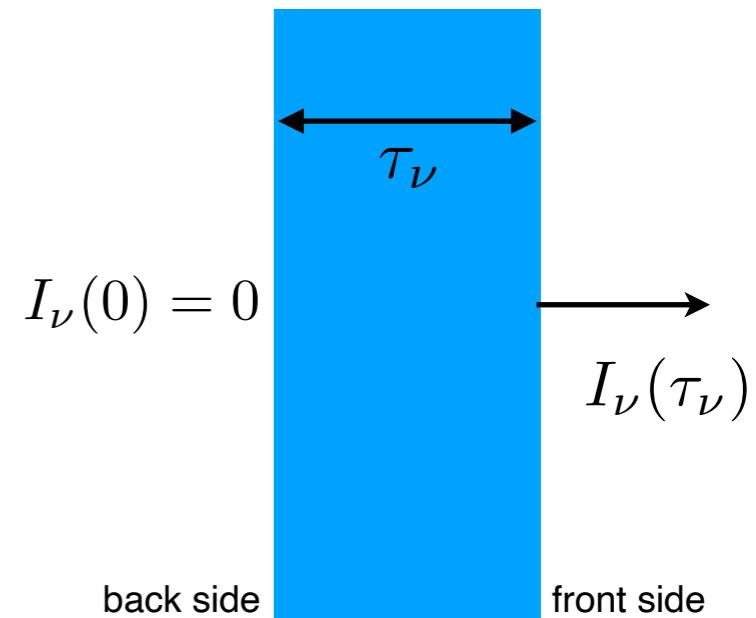
Blackbody Radiation vs. Thermal Radiation

- To see the difference between thermal and blackbody radiation,
 - Consider a slab of material with optical depth τ_ν that is producing thermal radiation.
 - If no light is falling on the back side of the slab, the intensity that is measured on the front side of the slab is

$$\begin{aligned} I_\nu(\tau_\nu) &= I_\nu(0)e^{-\tau_\nu} + S_\nu (1 - e^{-\tau_\nu}) \\ I_\nu(0) = 0 \quad \longrightarrow \quad S_\nu = B_\nu &= B_\nu (1 - e^{-\tau_\nu}) \end{aligned}$$

- If the slab is optical thick at frequency ν ($\tau_\nu \gg 1$), then

$$I_\nu = B_\nu \quad \text{as } \tau_\nu \rightarrow \infty$$



- If the slab is optically thin ($\tau_\nu \ll 1$), then

$$I_\nu \approx \tau_\nu B_\nu \ll B_\nu \quad \text{as } \tau_\nu \ll 1$$

This indicates that the radiation, although it is thermal, will not be blackbody radiation.

Thermal radiation becomes blackbody radiation only for optical thick media.

< Planck Spectrum (Spectrum of blackbody radiation) >

- There is no perfect blackbody.
 - However, the cosmic microwave background comes quite close; stars can sometimes be usefully approximated as blackbodies.
 - By the end of the 19th century, the blackbody spectrum was fairly well known empirically, from laboratory studies. In 1900, Max Planck, using his idea of quantized energies, derived the blackbody spectrum.

See Radiative Transfer (Rybicki & Lightman) for the derivation of the Planck function “Fundamentals of Statistical and Thermal Physics” (Federick Reif) or “Astrophysical Concepts” (Harwit) for more details.

Spectrum of blackbody radiation

- The frequency dependence of blackbody radiation is given by the ***Planck function***:

$$B_\nu d\nu = B_\lambda d\lambda$$

$$B_\nu(T) = \frac{2h\nu^3/c^2}{\exp(h\nu/k_B T) - 1} \quad \text{or} \quad B_\lambda(T) = \frac{2hc^2/\lambda^5}{\exp(hc/\lambda k_B T) - 1}$$

$h = 6.63 \times 10^{-27}$ erg s (Planck's constant)

$k_B = 1.38 \times 10^{-16}$ erg K⁻¹ (Boltzmann's constant)

- Energy density:***

$$u_\nu(T) = \frac{4\pi}{c} B_\nu(T) = \frac{8\pi h\nu^3/c^3}{\exp(h\nu/k_B T) - 1}$$

Note that the textbook Ryden's "Interstellar and Intergalactic Medium" use the symbol $\varepsilon_\nu(T)$ to denote the energy density.

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- Photon occupation number:
 - The photon occupation number is dimensionless, and is simply **the average number of photons per mode per polarization.**

$$n_\gamma(\nu) = \frac{1}{4\pi\rho_s} \frac{u_\nu}{h\nu} = \frac{\langle E \rangle}{h\nu}$$

$$\rho_s = \frac{2\nu^2}{c^3}$$

$$n_\gamma(\nu) = \frac{c^2}{2h\nu^3} I_\nu$$

- If the radiation field is a blackbody, the photon occupation number is given by

$$n_\gamma(\nu; T) = \frac{1}{\exp(h\nu/k_B T) - 1}$$

Bose-Einstein statistics

Stefan-Boltzmann Law

- Emergent flux is proportional to T^4 .

$$F = \pi \int_0^\infty B_\nu(T) d\nu = \pi B(T) \quad \leftarrow \quad B(T) = \int_0^\infty B_\nu(T) d\nu = \frac{ac}{4\pi} T^4 = \frac{\sigma_{\text{SB}}}{\pi} T^4$$

$$F = \sigma_{\text{SB}} T^4$$

Stephan – Boltzmann constant : $\sigma_{\text{SB}} = \frac{2\pi^5 k_{\text{B}}^4}{15c^2 h^3} = 5.67 \times 10^{-5} \text{ erg cm}^2 \text{ s}^{-1} \text{ K}^{-4} \text{ sr}^{-1}$

- Total energy density (*another form of the Stefan-Boltzmann law*)

$$u = \frac{4\pi}{c} \int_0^\infty B_\nu(T) d\nu = \frac{4\pi}{c} B(T) \quad u(T) = \left(\frac{T}{3400 \text{ K}} \right)^4 \text{ erg cm}^{-3}$$

$$u = aT^4$$

radiation constant : $a \equiv \frac{4\sigma_{\text{SB}}}{c} = 7.57 \times 10^{-15} \text{ erg cm}^{-3} \text{ K}^{-4}$

Rayleigh-Jeans Law & Wien Law

Rayleigh-Jeans Law (low-energy limit)

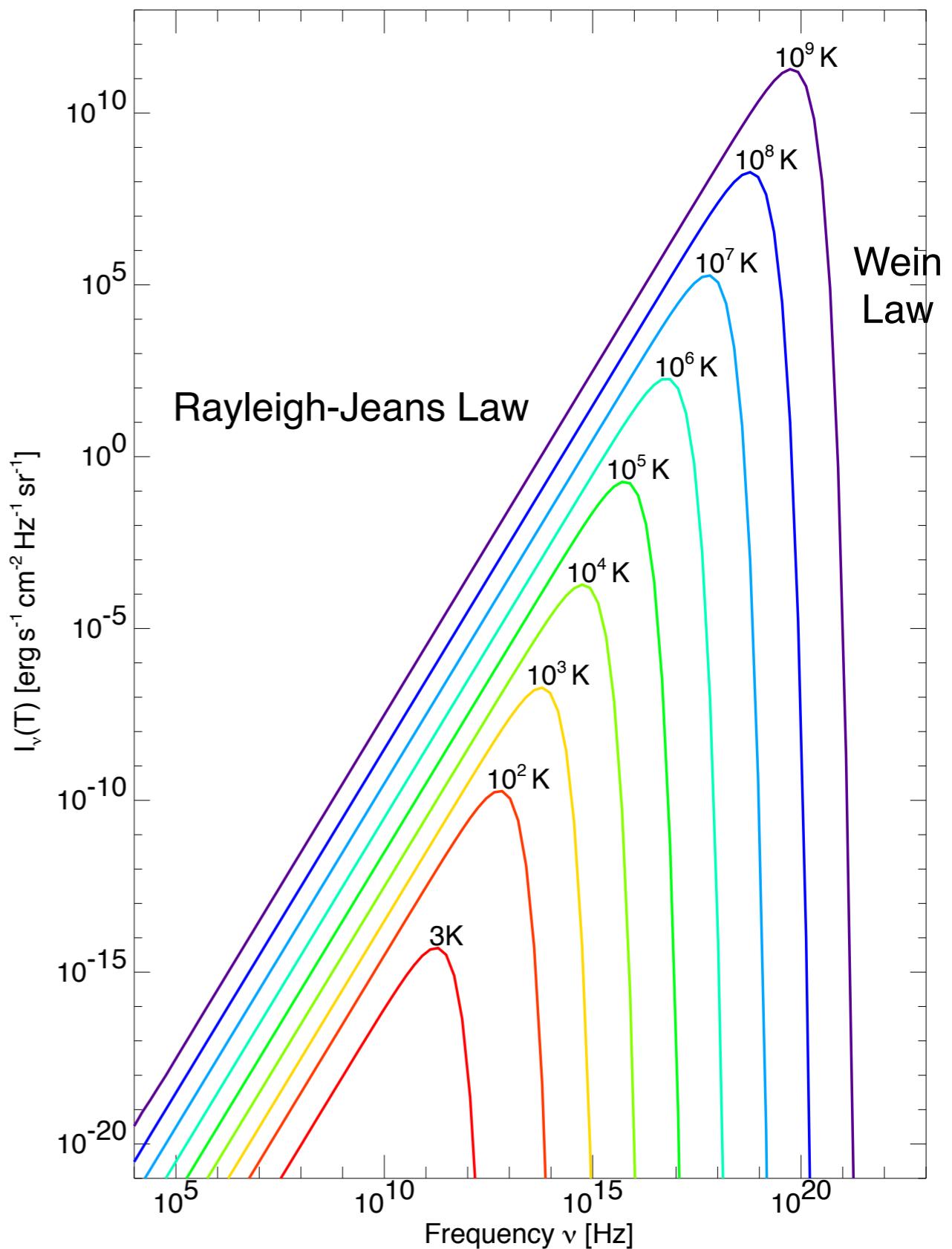
$$h\nu \ll k_B T \quad (\nu \ll 2 \times 10^{10} (T/1\text{ K}) \text{ Hz})$$

$$I_\nu^{RJ}(T) = \frac{2\nu^2}{c^2} k_B T$$

Wien Law (high-energy limit)

$$h\nu \gg k_B T$$

$$I_\nu^W(T) = \frac{2h\nu^3}{c^2} \exp\left(-\frac{h\nu}{k_B T}\right)$$



Characteristic Temperatures

- **Brightness Temperature:**

- The brightness temperature is defined to be the temperature such that a blackbody at that temperature would have specific intensity:

$$I_\nu = B_\nu(T_b) \rightarrow T_b(\nu) = \frac{h\nu/k_B}{\ln [1 + 2h\nu^3/(c^2 I_\nu)]}$$

- **Antenna Temperature:**

- Radio astronomers are used to working at very low frequencies. They define the antenna temperature as being the brightness temperature in the Rayleigh-Jeans tail.

$$I_\nu = \frac{2\nu^2}{c^2} k_B T_b \rightarrow T_A \equiv \frac{c^2}{2k_B \nu^2} I_\nu$$

- Radiative transfer equation in the RJ limit:

- ▶ If the matter has its energy levels populated according to an excitation temperature $T_{\text{exc}} \gg h\nu/k_B$, then the source function is given by $S_\nu(T_{\text{exc}}) = (2\nu^2/c^2) k_B T_{\text{exc}}$ from the generalized Kirchhoff's law.

$$\frac{dT_A}{d\tau_\nu} = -T_A + T_{\text{exc}} \quad \text{if } h\nu \ll k_B T_{\text{exc}}$$

$$\frac{dI_\nu}{d\tau_\nu} = -I_\nu + S_\nu$$

- ▶ Then, RT equation becomes

$$T_A = T_A(0)e^{-\tau_\nu} + T_{\text{exc}}(1 - e^{-\tau_\nu}) \quad \text{if } T_{\text{exc}} \text{ is constant.}$$

- **Color Temperature:**

- By fitting the spectrum to a blackbody curve without regarding to vertical scale (absolute intensity scale), a color temperature T_c is obtained.
- The color temperature correctly gives the temperature of a blackbody source of unknown absolute scale.

- **Effective Temperature:**

- The effective temperature of a source is obtained by equating the actual flux F to the flux of a blackbody at temperature T_{eff} .

$$F = \int \int I_\nu \cos \theta d\nu d\Omega = \sigma T_{\text{eff}}^4$$

Stefan-Boltzmann law

- **Excitation Temperature:**

- The excitation temperature of level u relative to level ℓ is defined by

Boltzmann distribution

$$\frac{n_u}{n_\ell} = \frac{g_u}{g_\ell} \exp\left(-\frac{E_{u\ell}}{k_B T_{\text{exc}}}\right) \rightarrow T_{\text{exc}} \equiv \frac{E_{u\ell}/k_B}{\ln\left(\frac{n_\ell/g_\ell}{n_u/g_u}\right)} \quad (E_{u\ell} \equiv E_u - E_\ell)$$

- Radio astronomers studying the 21 cm line sometimes use the term “**spin temperature**” T_{spin} for excitation temperature.

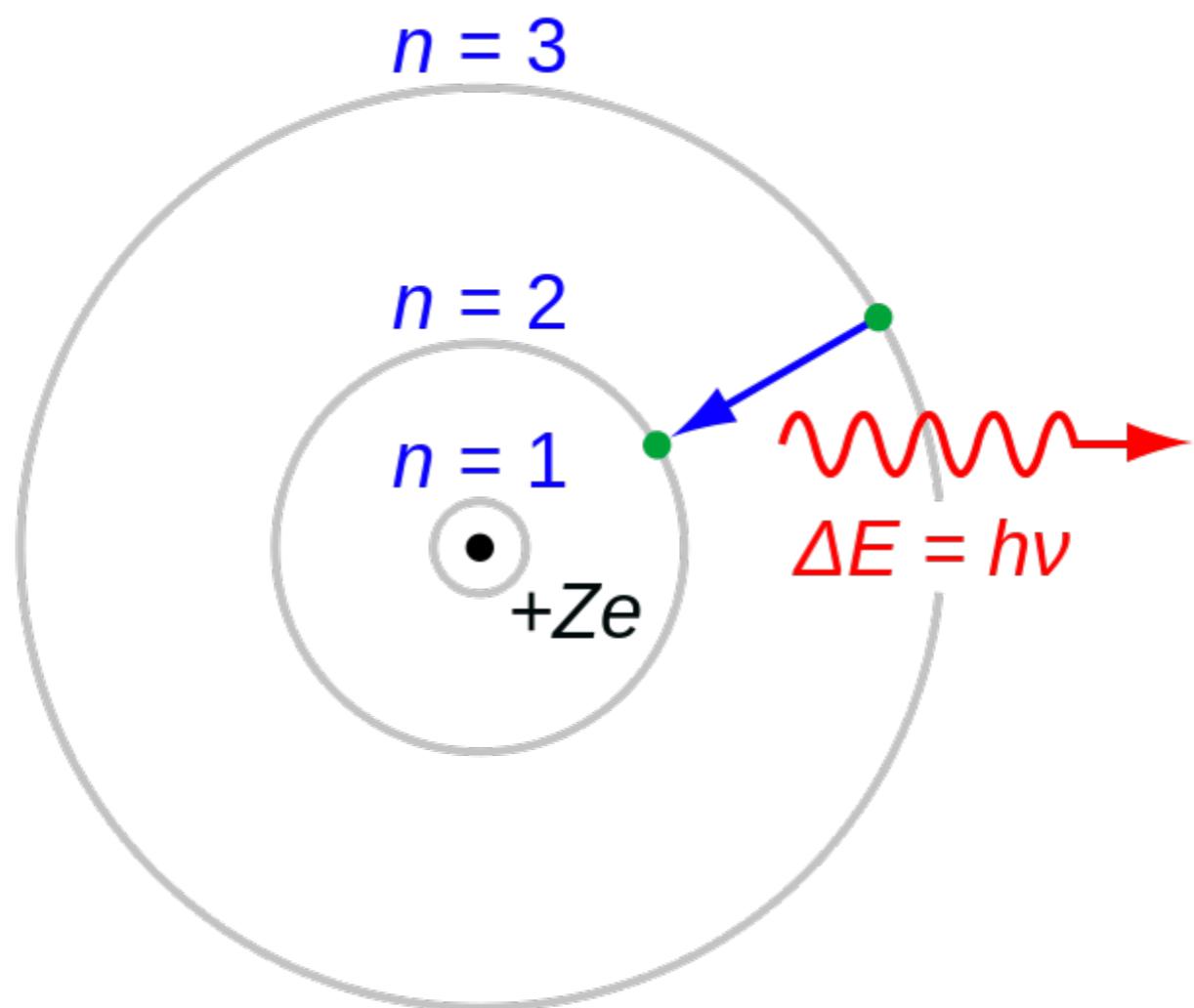
Atomic Structure, Spectroscopy

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]

Quantum Mechanics: Bohr model

- In atomic physics, the Bohr model, consists of a small, dense nucleus surrounded by orbiting electrons.
 - The negatively charged electron confined to an atomic shell encircles a small, positively charged atomic nucleus and where an electron jumps between orbits, is accompanied by an emitted or absorbed amount of electromagnetic energy.



Quantum Mechanics: Hydrogen Atom

- Each bound state of the hydrogen atom is characterized by a set of four quantum numbers (n, l, m, m_s)

- $n = 1, 2, 3, \dots$: principal quantum number
- $l = 0, 1, 2, \dots, n - 1$: orbital angular momentum quantum number
 - By convention, the values of l are usually designated by letters.

0	1	2	3	4	5	6	7	8	...
s	p	d	f	g	h	i	k	l	...

- $m = -l, -l + 1, \dots, 0, \dots, l - 1, l$: magnetic quantum number.
 - It determines the behavior of the energy levels in the presence of a magnetic field.
 - This is the projection of the electron orbital angular momentum along the z -axis of the system.

- 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.

- Degeneracy for a given n : $2 \times \sum_{l=0}^{n-1} (2l + 1) = 2n^2$

Schrödinger Equation

- 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*:

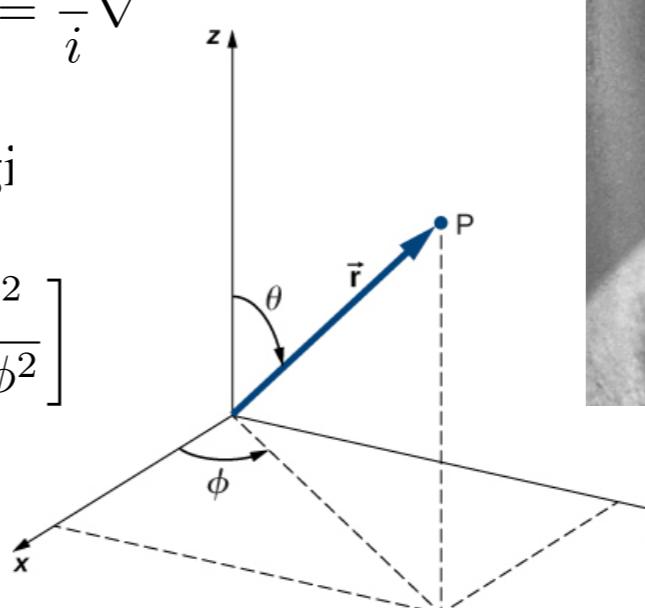
- The time-independent Schrödinger equation is obtained as follows:

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

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

momentum operator:

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



Erwin Schrödinger

Here, in the spherical coordinates, the Laplace operator is gi

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

Solution for 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:

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

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

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

spherical harmonics

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

$P_l^{|m|}$ = 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 : conjugate transpose)

- Wavefunctions for a hydrogen-like atom

Atomic Physics [Foot]

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

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

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

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

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

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

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

Here, $\rho \equiv \frac{Z}{na_0}r$

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

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

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

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

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

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

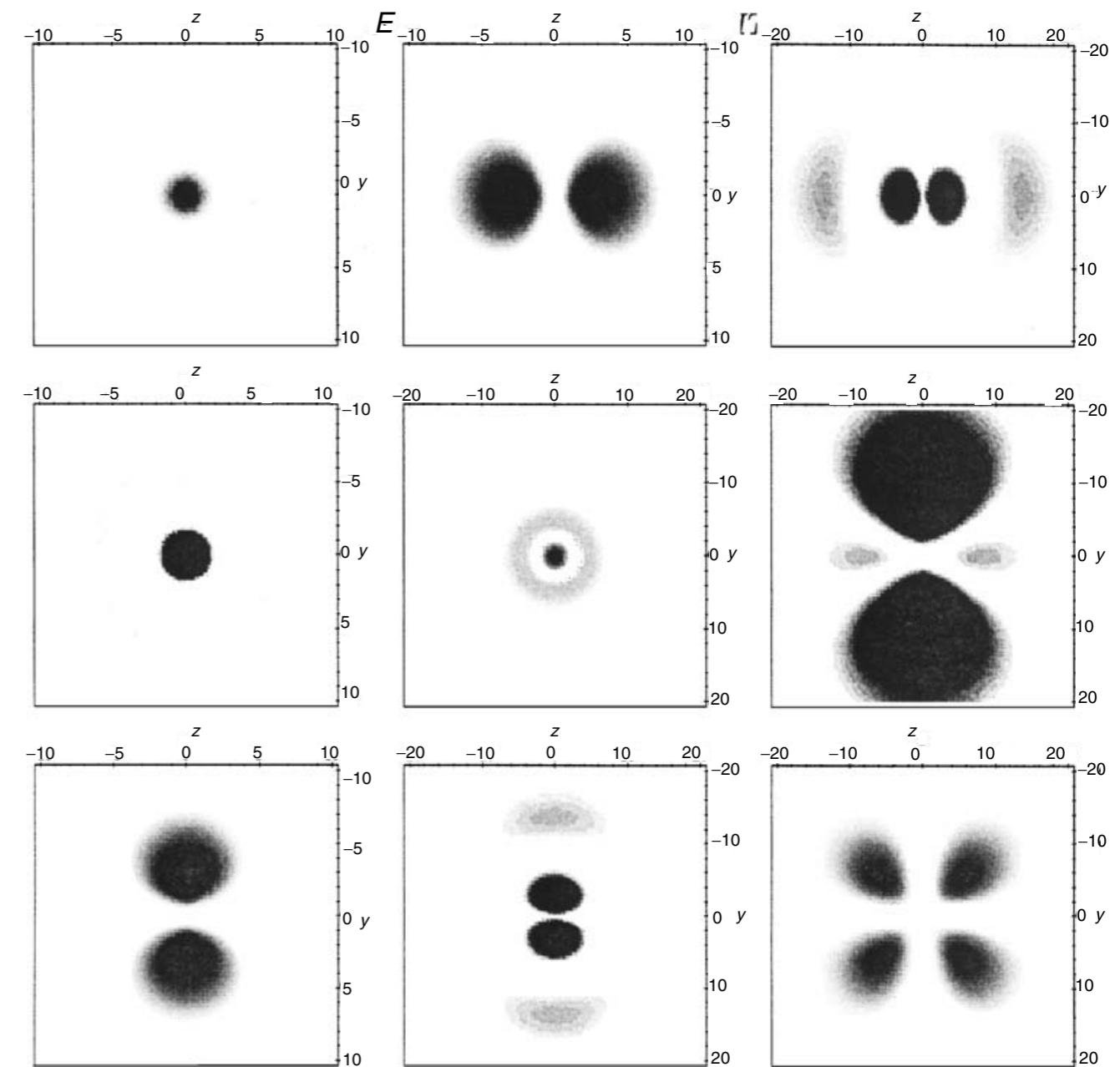
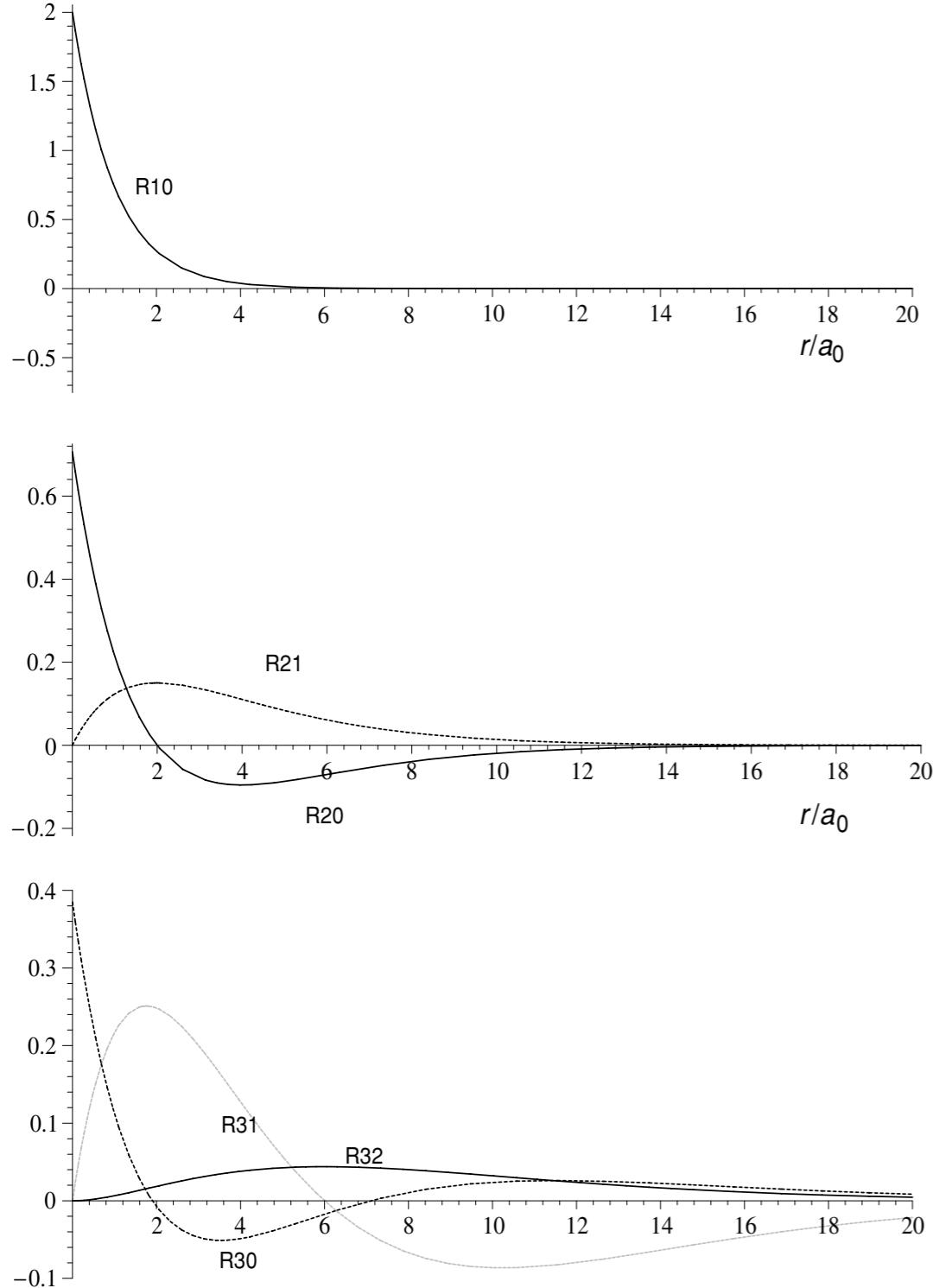
Normalisation: $\int_0^{2\pi} \int_0^\pi |Y_{l,m}|^2 \sin \theta d\theta d\phi = 1$

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

- 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.**



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

[Angular Momentum]

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

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

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

Here, the ℓ can have values $\ell = 0, 1, \dots, n - 1$.

The magnitude of the angular momenta are

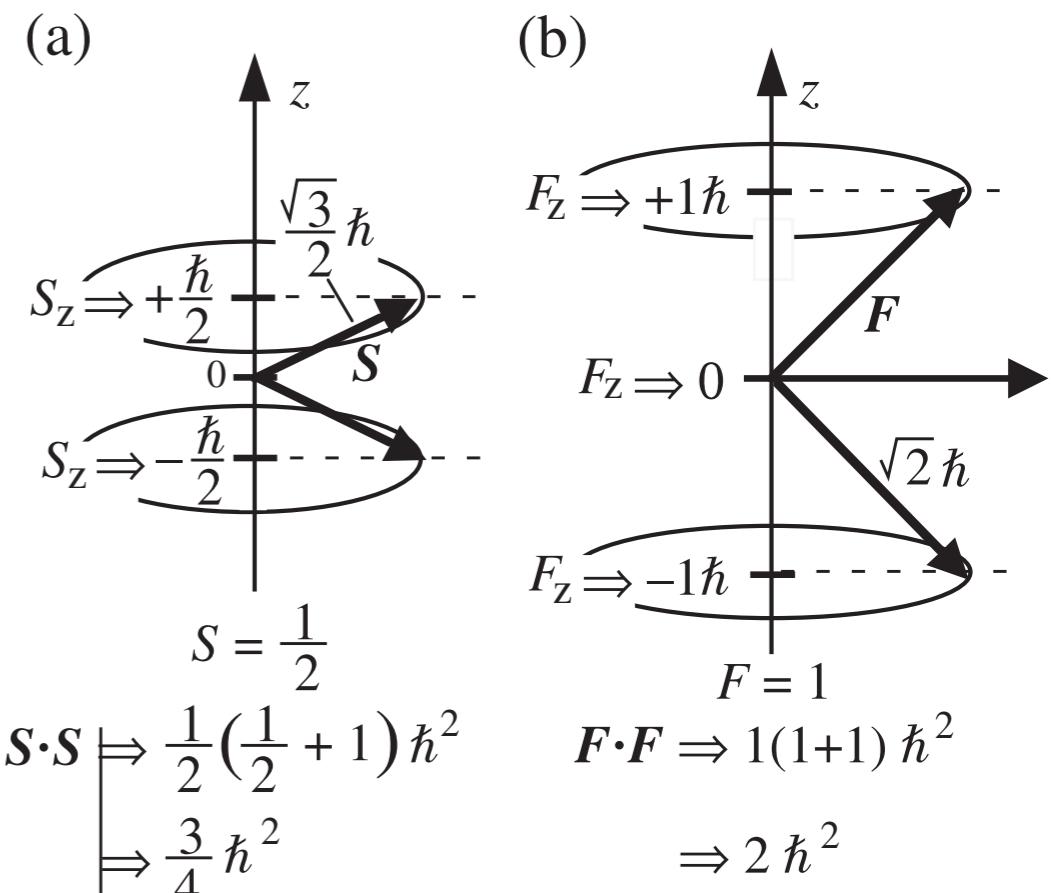
$$|\mathbf{L}| = \sqrt{\ell(\ell+1)}\hbar \quad \text{where } \ell = 0, 1, \dots, n - 1$$

The z -component have the following values.

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

- Electron has a spin of $s = \frac{1}{2}$ and it has two z -components:

$$s = \frac{1}{2}\hbar \rightarrow m_s = -\frac{1}{2}\hbar, \frac{1}{2}\hbar$$



Many electron systems : Schrödinger Equation

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

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

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 $N = 2$.

Many-Electron Systems - [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

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

- 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.

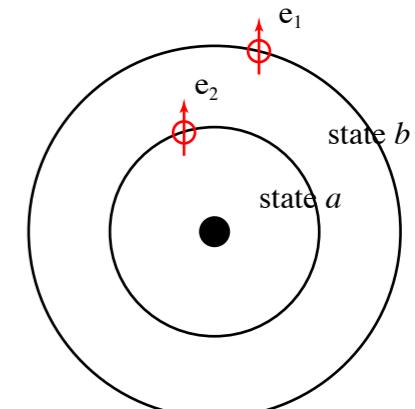
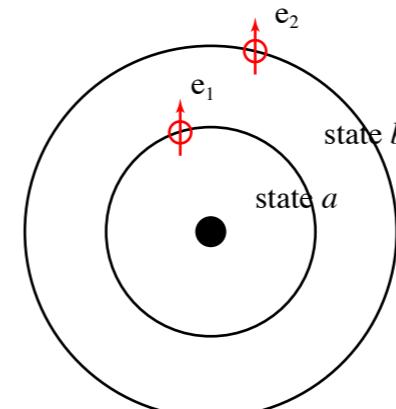
Central Field Approximation: Electron Configuration

- **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]

- 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 Exclusion Principle: *Wave functions are antisymmetric with respect to interchange of identical Fermions* (with a half-odd-integer spin). Within the central field approximation, a two-electron wave function which obeys the Pauli Principle can be written

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

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.



Wolfgang Ernst Pauli

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

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

[Electron Configuration - Orbitals]

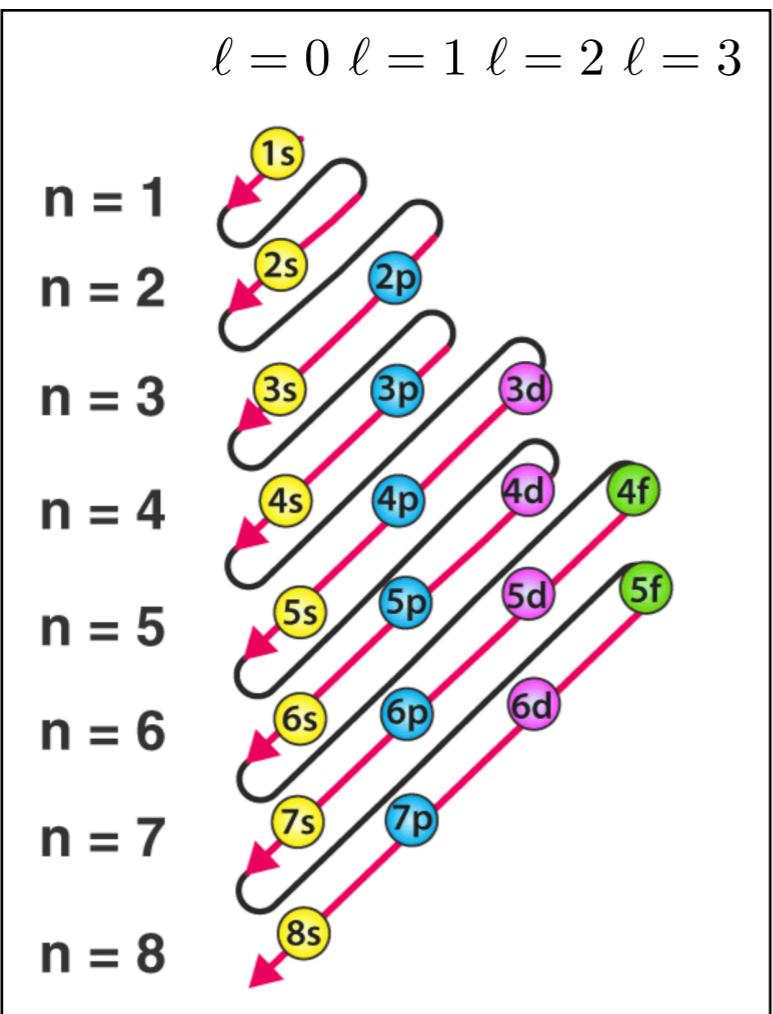
- $n = 1, 2, 3, \dots$: principal quantum number (주양자수)
- $l = 0, 1, 2, \dots, n-1$: orbital angular momentum (quantum number) for each electron (부양자수)

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

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

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

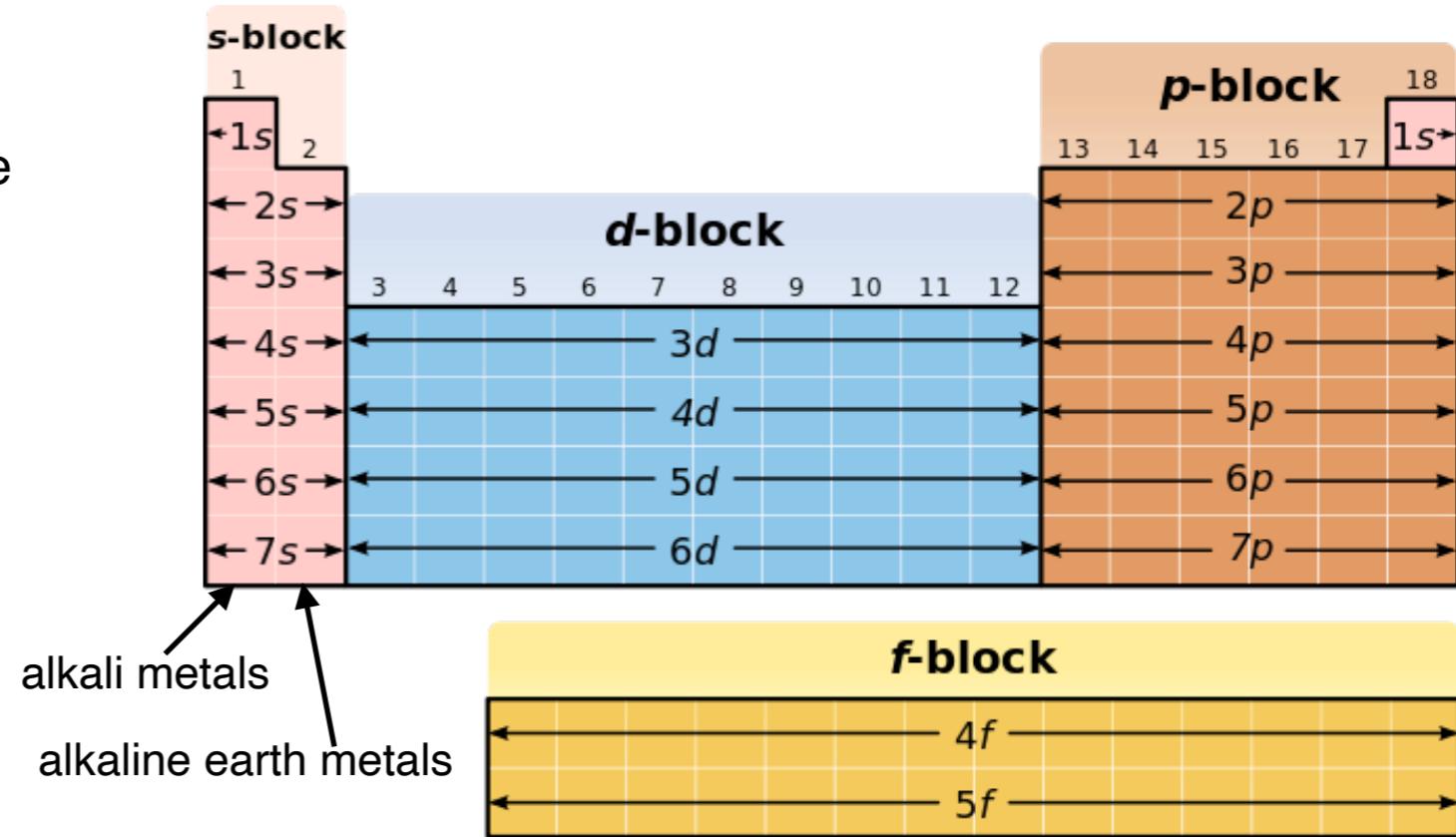
Energy ordering & Periodic Table

- 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.

The orbitals of complex atoms follow a revised energy ordering:

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



- 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 $3d$.

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

[LS Coupling]

- The configurations are split into “**terms**” according to the orbital angular momentum **L** and spin angular momentum **S**, and the “terms” are then split into “**levels**” further by the total angular momentum **J**.

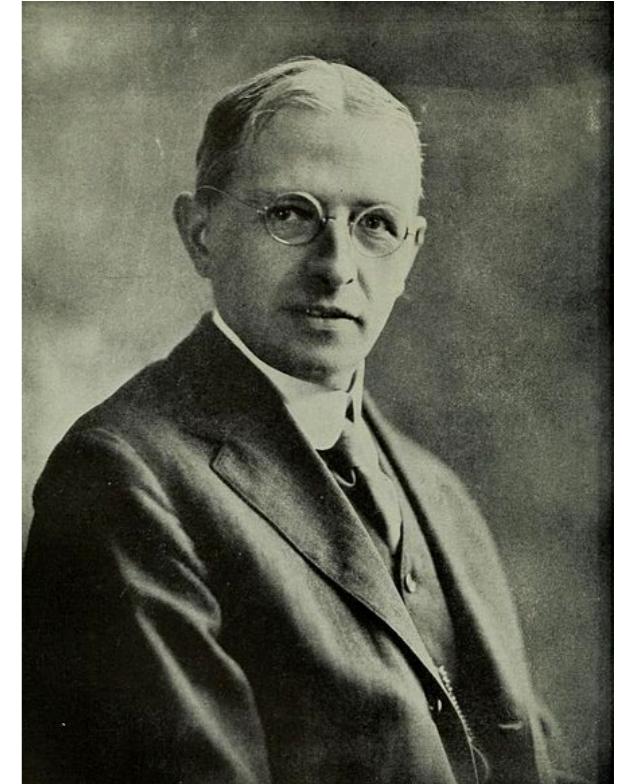
First, add all spin angular momenta for open shells:

$$\mathbf{S} = \sum_i \mathbf{s}_i = \mathbf{s}_1 + \mathbf{s}_2 + \dots$$

Second, add all orbital angular momenta for open shells:

$$\mathbf{L} = \sum_i \mathbf{l}_i = \mathbf{l}_1 + \mathbf{l}_2 + \dots$$

Finally, add the spin angular momentum and orbital angular momentum.



Henry Norris Russell

Hertzsprung-Russell diagram
Russell-Saunders coupling

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \rightarrow J = -|L - S|, -|L - S| + 1, \dots, |L + S| - 1, |L + S|$$

For instance, if $L = 1$ and $S = 1$, then $J = -1, 0, 1$.

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.

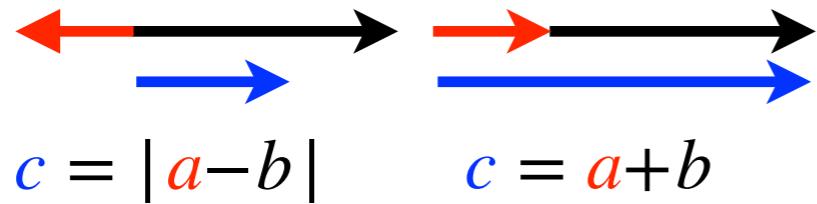
$$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i \quad \rightarrow \quad \mathbf{J} = \sum_i \mathbf{j}_i$$

- Why two coupling schemes?
 - They give the same results for 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.

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

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



- 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

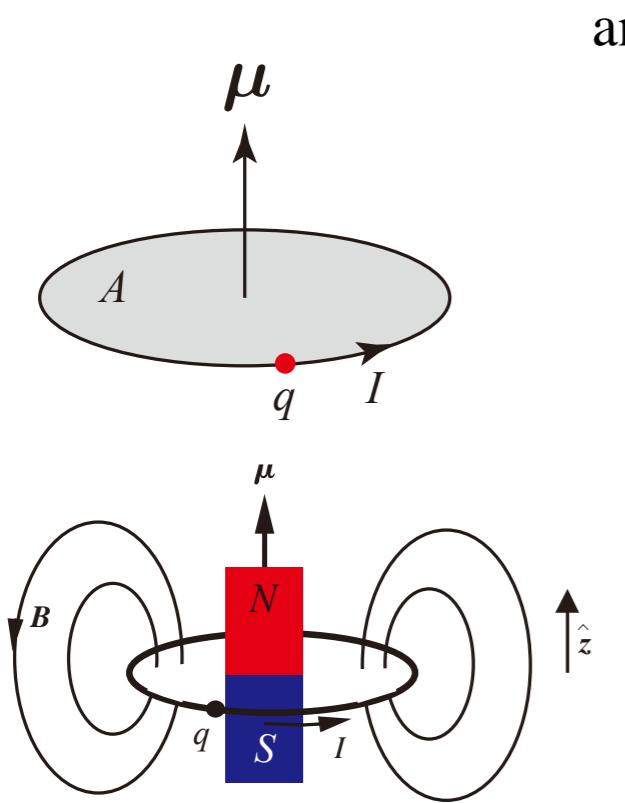
$$L = 1, 2, 3, 4, 5.$$

- 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

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

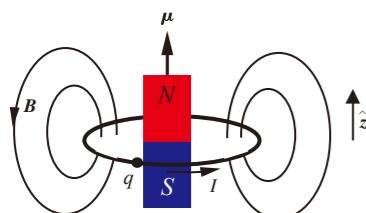
The magnetic moment of the electron is opposed to the direction of the spin \mathbf{S} , because of the negative charge.

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 **B** field.

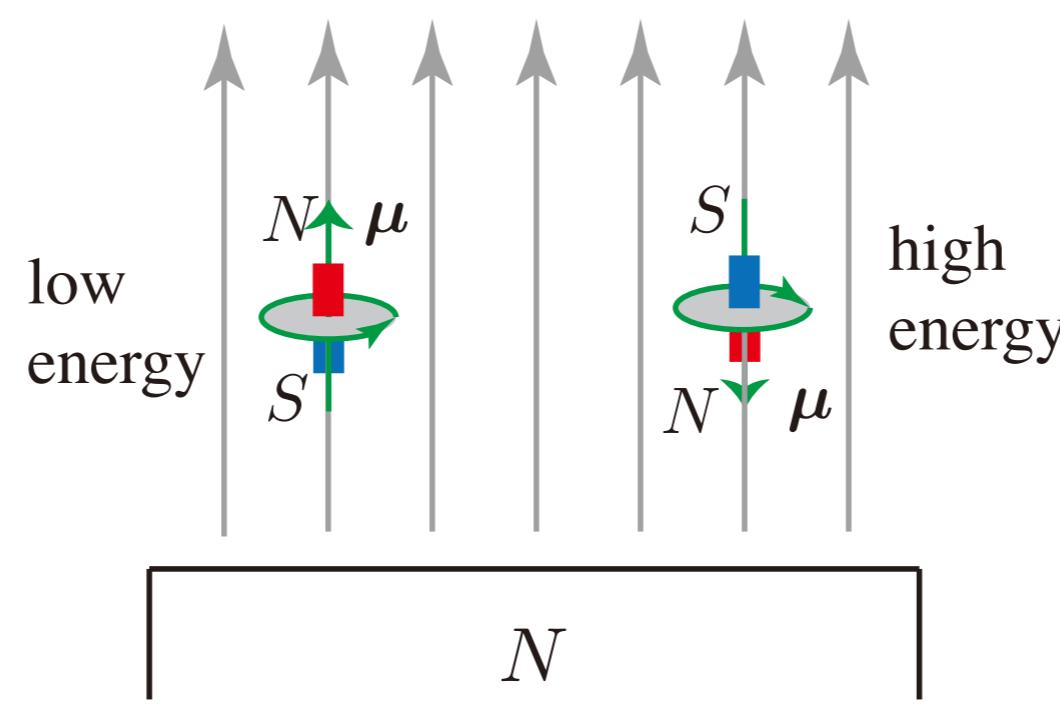
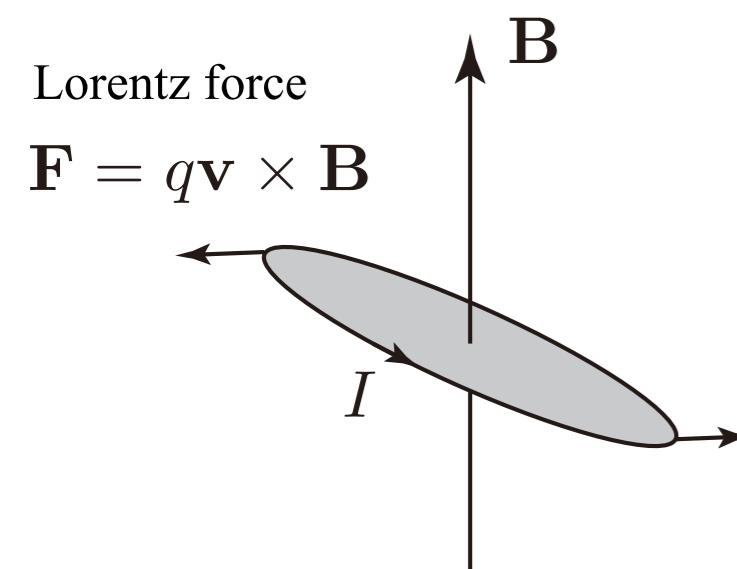
Integration of this torque over the appropriate angles yields a potential energy that is a function of the angle θ between the magnetic field \mathbf{B} and magnetic moment $\boldsymbol{\mu}$ vector. The lowest potential energy occurs when the two vectors are aligned. The potential energy E_{pot} turns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



$$E_{\text{pot}} = -\mu \cdot \mathbf{B} = -\mu B \cos \theta$$

$$E_{\text{pot}} < 0 \quad \text{if } \theta < \frac{\pi}{2}$$

$$E_{\text{pot}} > 0 \quad \text{if } \theta > \frac{\pi}{2}$$



torque $\tau = \mathbf{r} \times \mathbf{F}$

$$E_{\text{pot}} = -\mu \cdot \mathbf{B}$$

[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

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

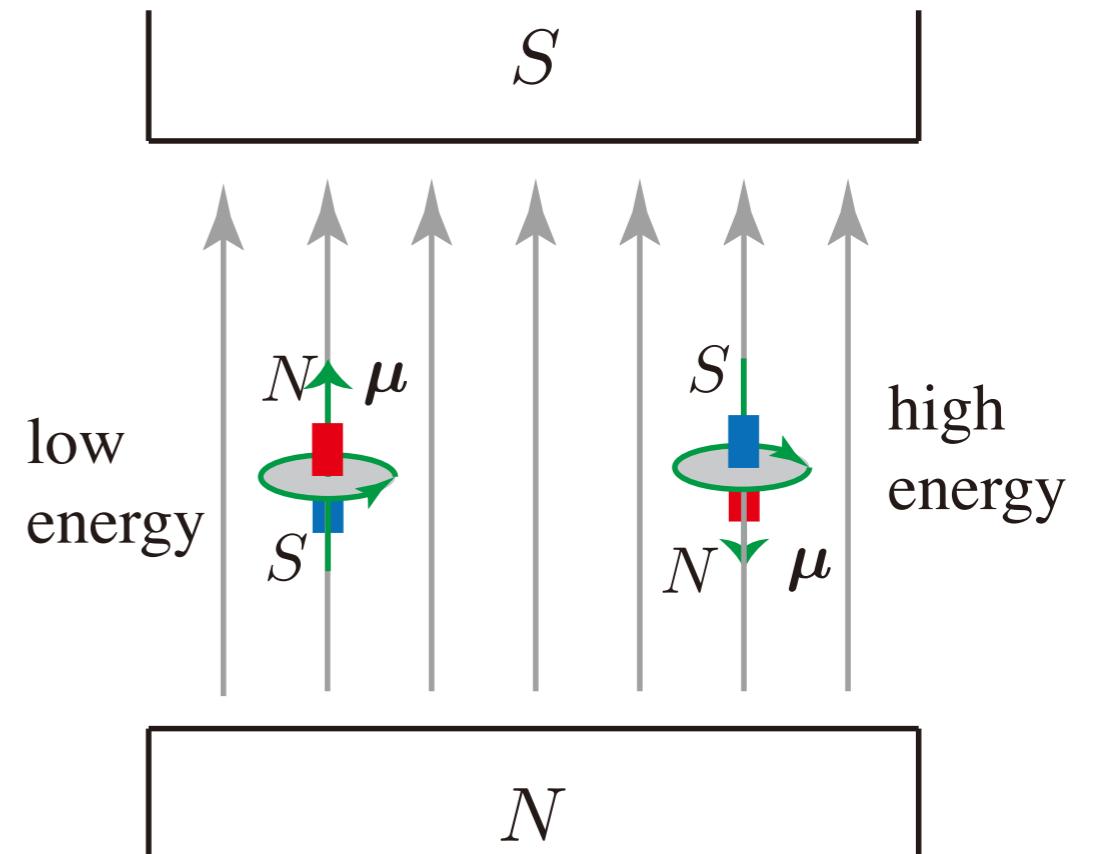
- For the sum of the interactions of all electrons will be

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

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

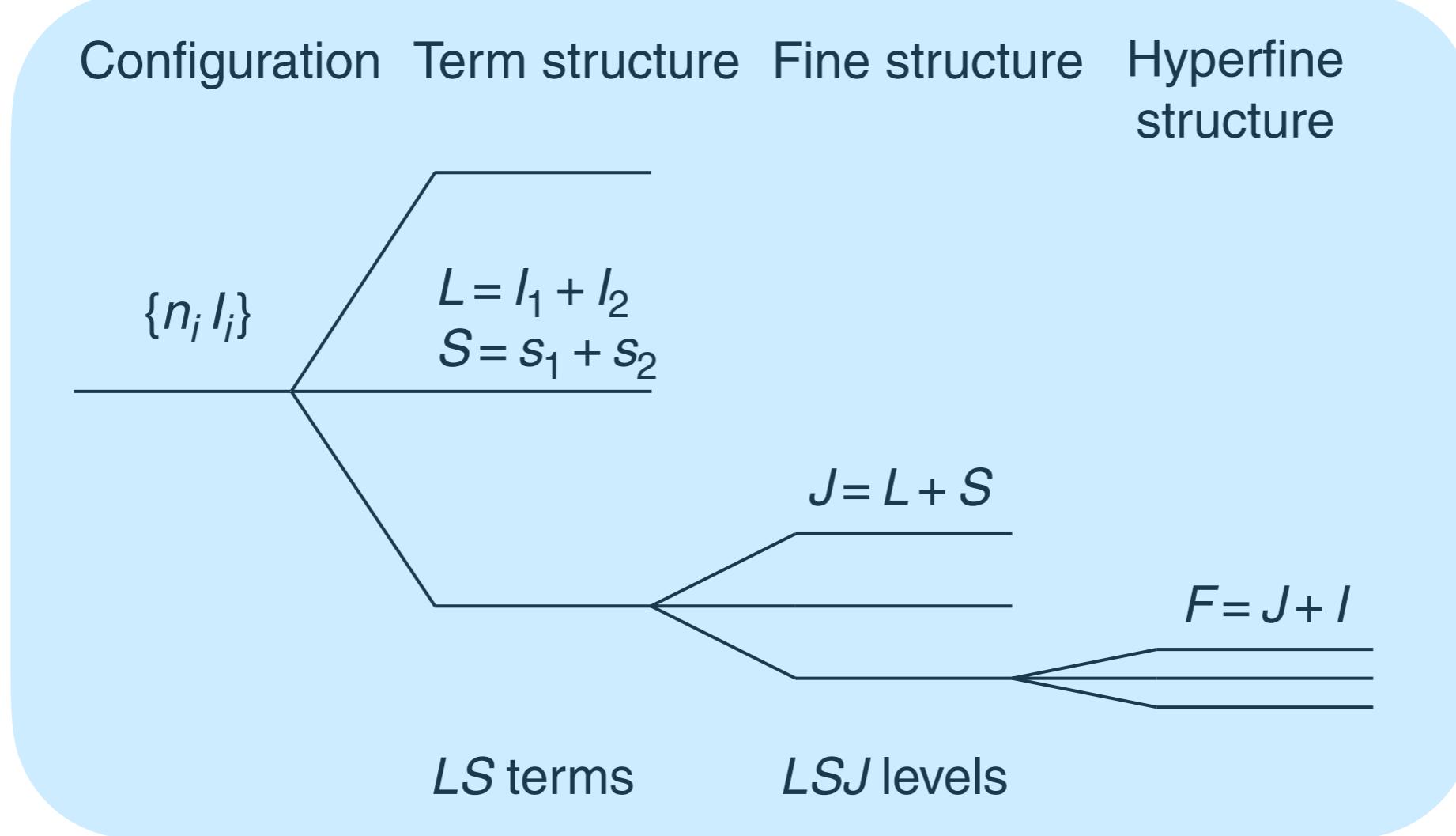
$$H_{\text{so}} = \frac{1}{2}\xi (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$



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

The states split into several J levels for a given S and L .

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

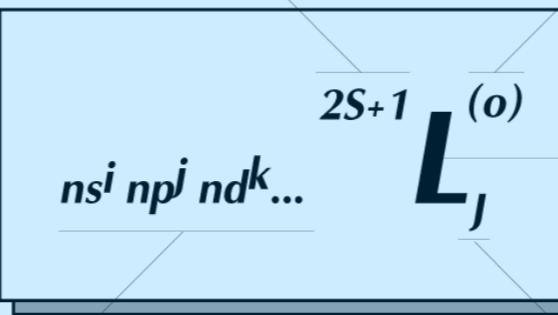


[Spectroscopic Notation]

- 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.

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 $L \geq 1$)

shells	$n = 1, 2, 3, 4, 5 \dots$
subshells	$\ell = 0, 1, 2, 3, 4 \dots \rightarrow s, p, d, f, g, \dots$
terms	$L = 0, 1, 2, 3, 4 \dots \rightarrow S, P, D, F, G, \dots$
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**

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.



- If the shell is exactly half-filled (e.g., p^3), the energy order does not obey a simple rule.
- 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

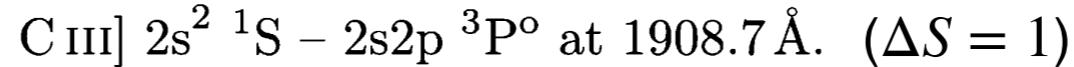
- **Selection Rules**

- (1) one electron jumps
 - (2) Δn any
 - (3) $\Delta l = \pm 1$
 - (4) parity change
 - (5) $\Delta S = 0$
 - (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 $F = 0 - 0$)
-
- selection rule for configuration
- intercombination** line if only this rule is violated.
- It is only rarely necessary to consider this.

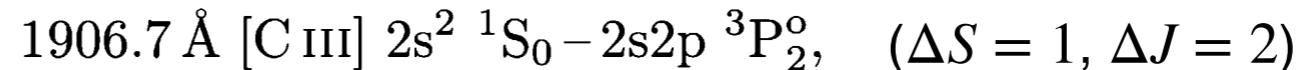
- **Allowed = Electric Dipole** : Transitions which satisfy all the above selection rules are referred to as **allowed transitions**. These transitions are strong and have a typical lifetime of $\sim 10^{-8}$ s. Allowed transitions are denoted without square brackets.

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.



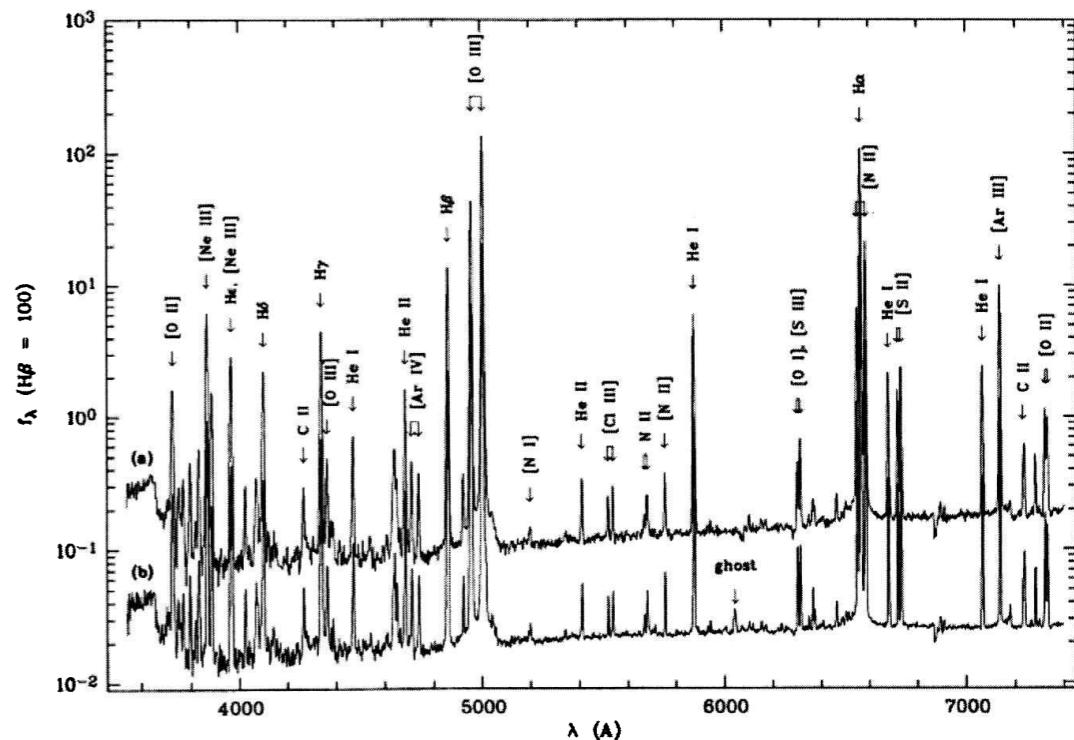
- **Resonance line** denotes the longest wavelength, dipole-allowed transition arising from the ground state of a particular atom or ion.

Forbidden Lines

- 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.***

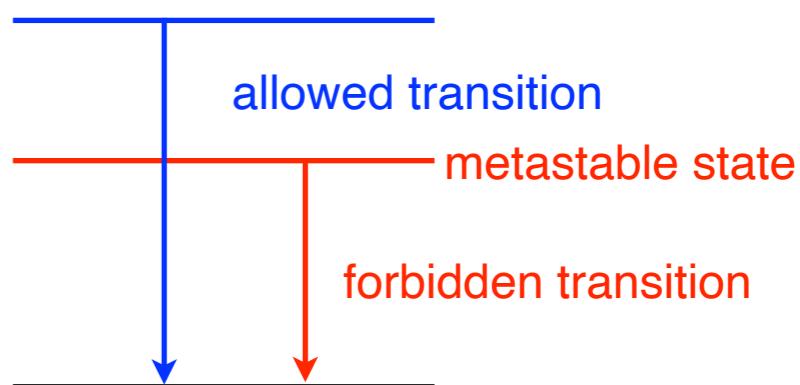
History: Nebulium?

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



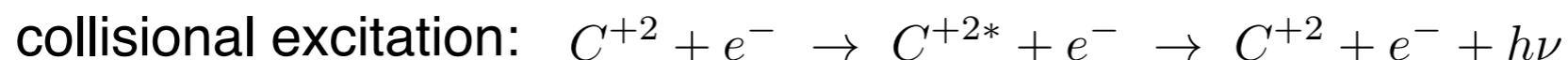
Optical spectra of NGC 6153, Liu et al. (2000, MNRAS)

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



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.



- 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

- The discussion on H-atom levels has assumed that all states with the same principal quantum number, n , have the same energy.
 - However, this is not correct: inclusion of relativistic (or magnetic) effects split these levels according to the total angular momentum quantum number J . ***The splitting is called fine structure.***
- For hydrogen, $S = \frac{1}{2} \rightarrow J = L \pm \frac{1}{2}$
- Spectroscopic notation: $(2S+1)L_J$

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	$1/2$	$5/2, 7/2$	$^2F^o$	$^2F_{5/2}^o, ^2F_{7/2}^o$

Note that the levels are called to be
 singlet if $2S+1 = 1$ $S = 0, J = L$
 doublet if $2S+1 = 2$ $S = 1/2, J = L \pm 1/2$
 triplet if $2S+1 = 3$ $S = 1, J = L - 1, L, L + 1$
 (when $L > 0$)

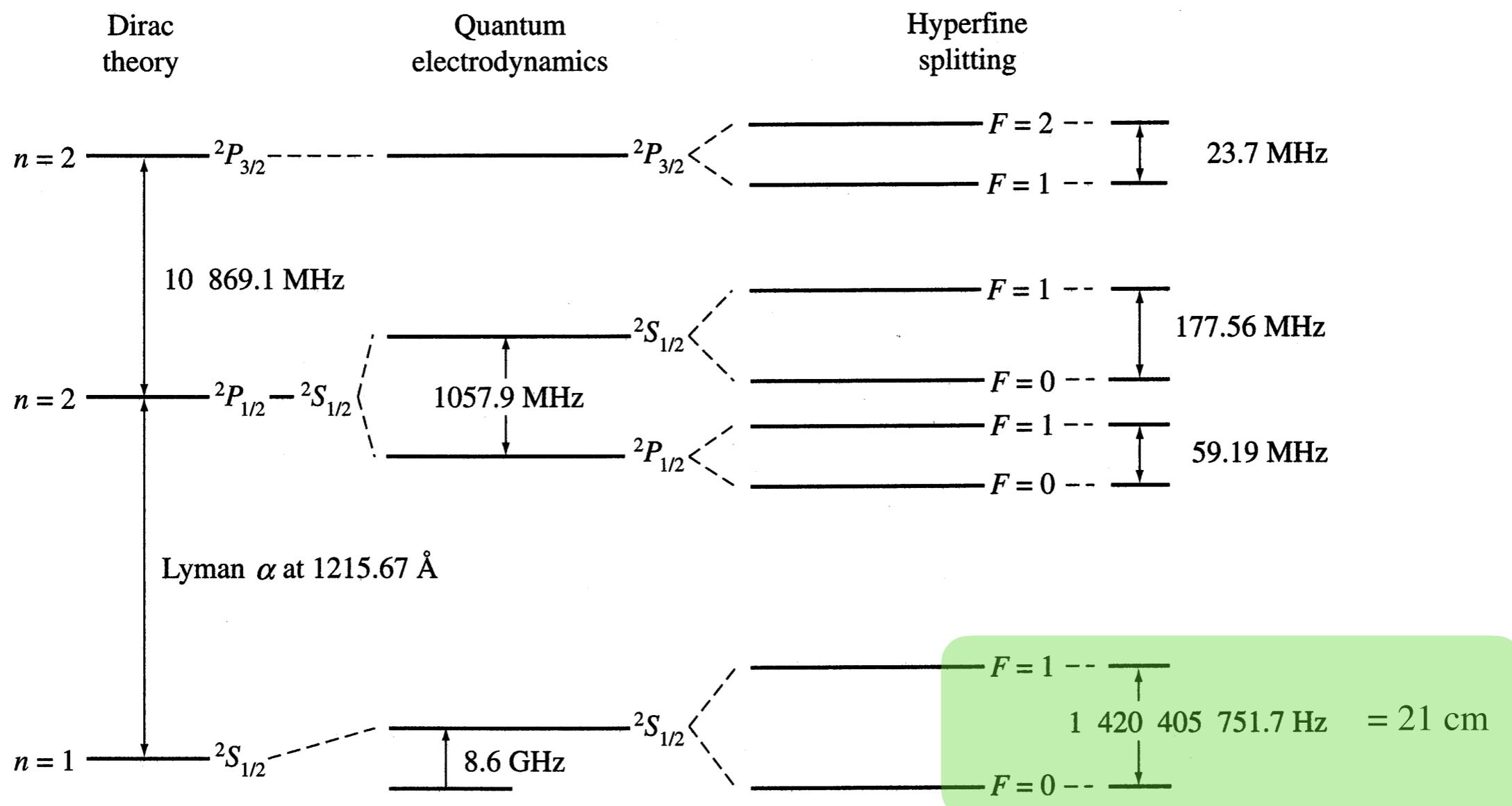
- The above table shows the fine structure levels of the H atom.
- Note that the states with principal quantum number $n = 2$ give rise to three fine-structure levels. In spectroscopic notation, these levels are $^2S_{1/2}$, $^2P_{1/2}^o$ and $^2P_{3/2}^o$.

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

$\Delta l = \pm 1$

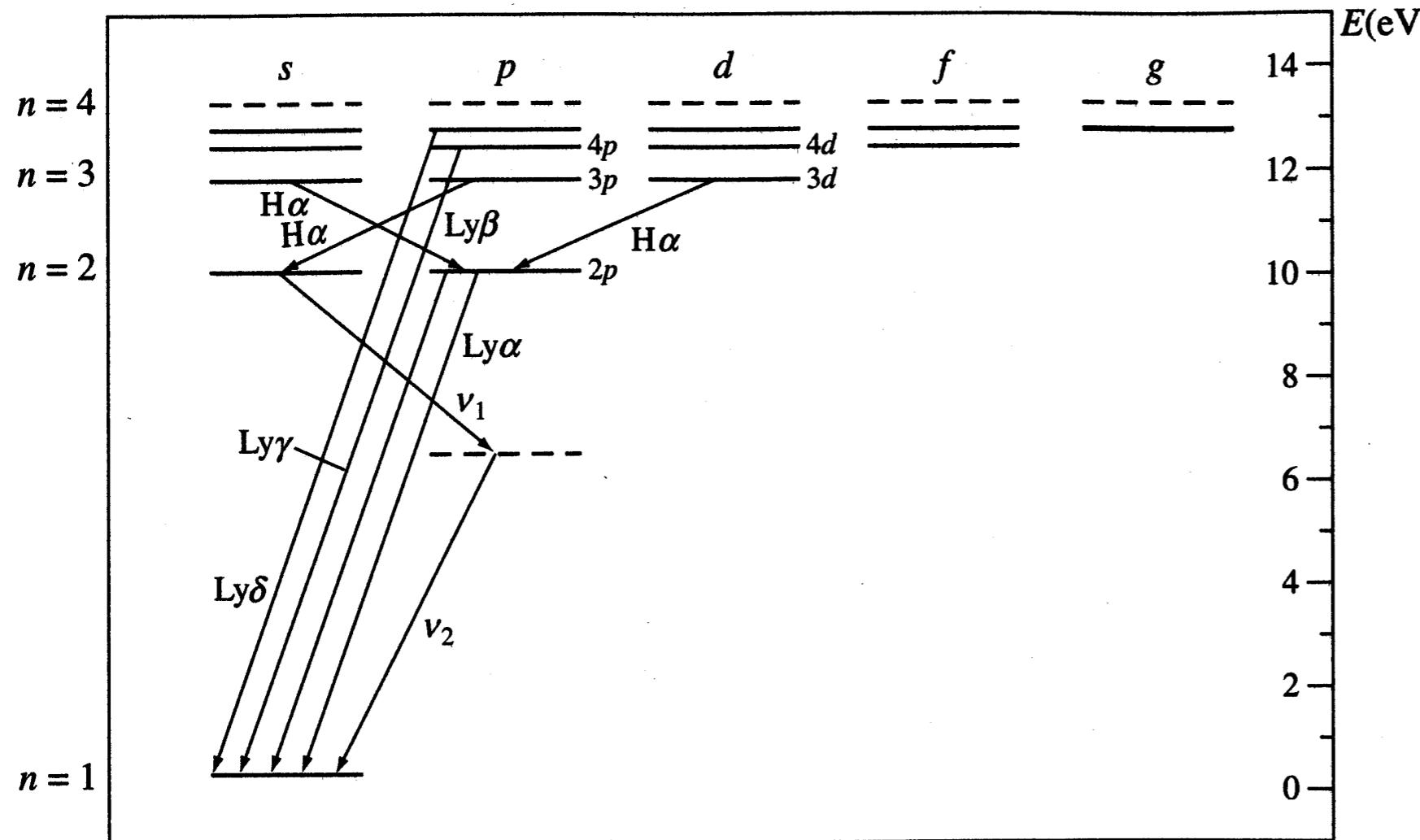
$\Delta S = 0$  For H atom, this is always satisfied as $S = 1/2$ for all states.

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

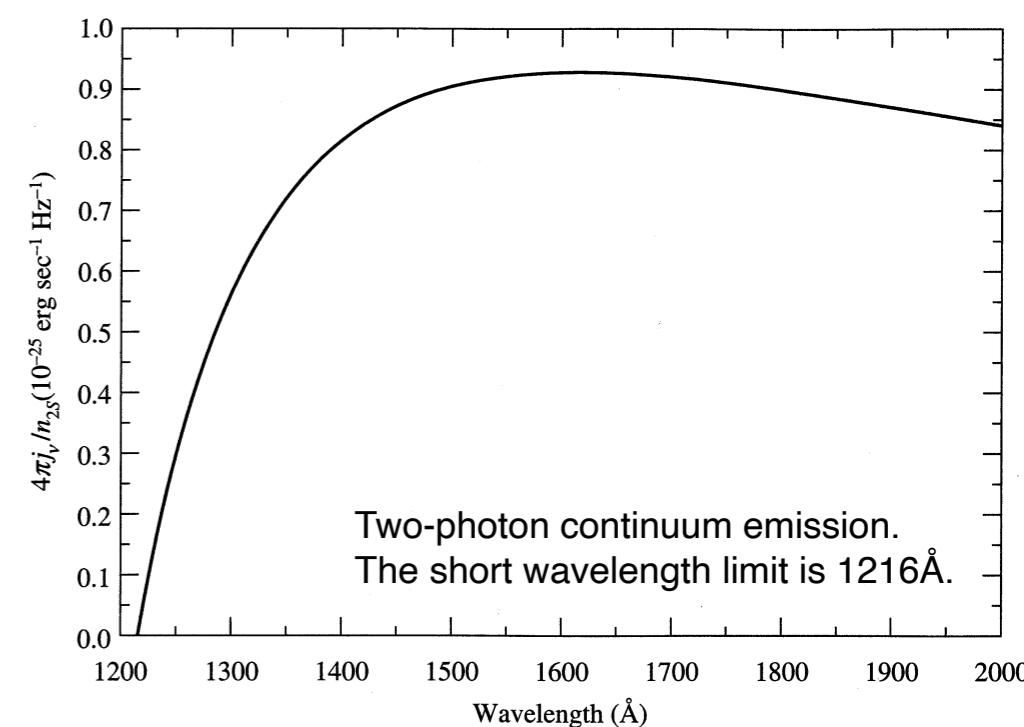
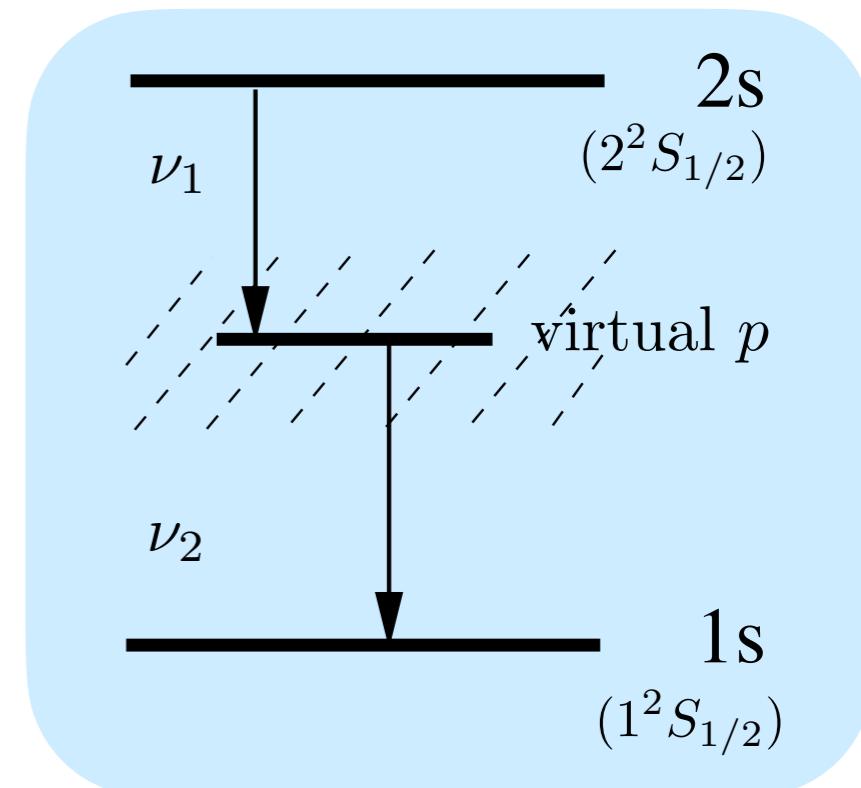
$$\tau_i = \left(\sum_j A_{ij} \right)^{-1} \quad \text{where } A_{ij} \text{ is the Einstein A coefficient}$$

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]

- (1) The ground state is $1s^2$.

This is a closed shell, with $L = 0$ and $S = 0$, hence it gives rise to a single, even parity term 1S , and level 1S_0 .

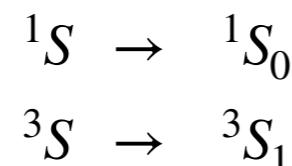
- (2) The first excited configuration is $1s2s$.

This has $l_1 = l_2 = 0$ and hence $L = 0$, but $s_1 = s_2 = \frac{1}{2}$ giving both $S = 0$ (singlet) or $S = 1$ (triplet) states.

S	L	J
0	0	0

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

S	L	J
0	0	0
1	0	1



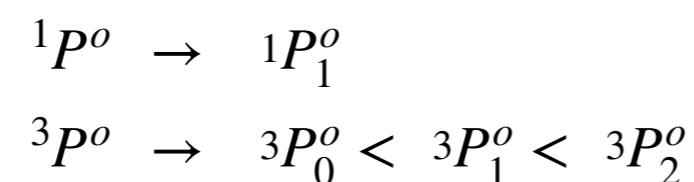
For a given configuration, the state with the maximum spin multiplicity is lowest in energy.

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.

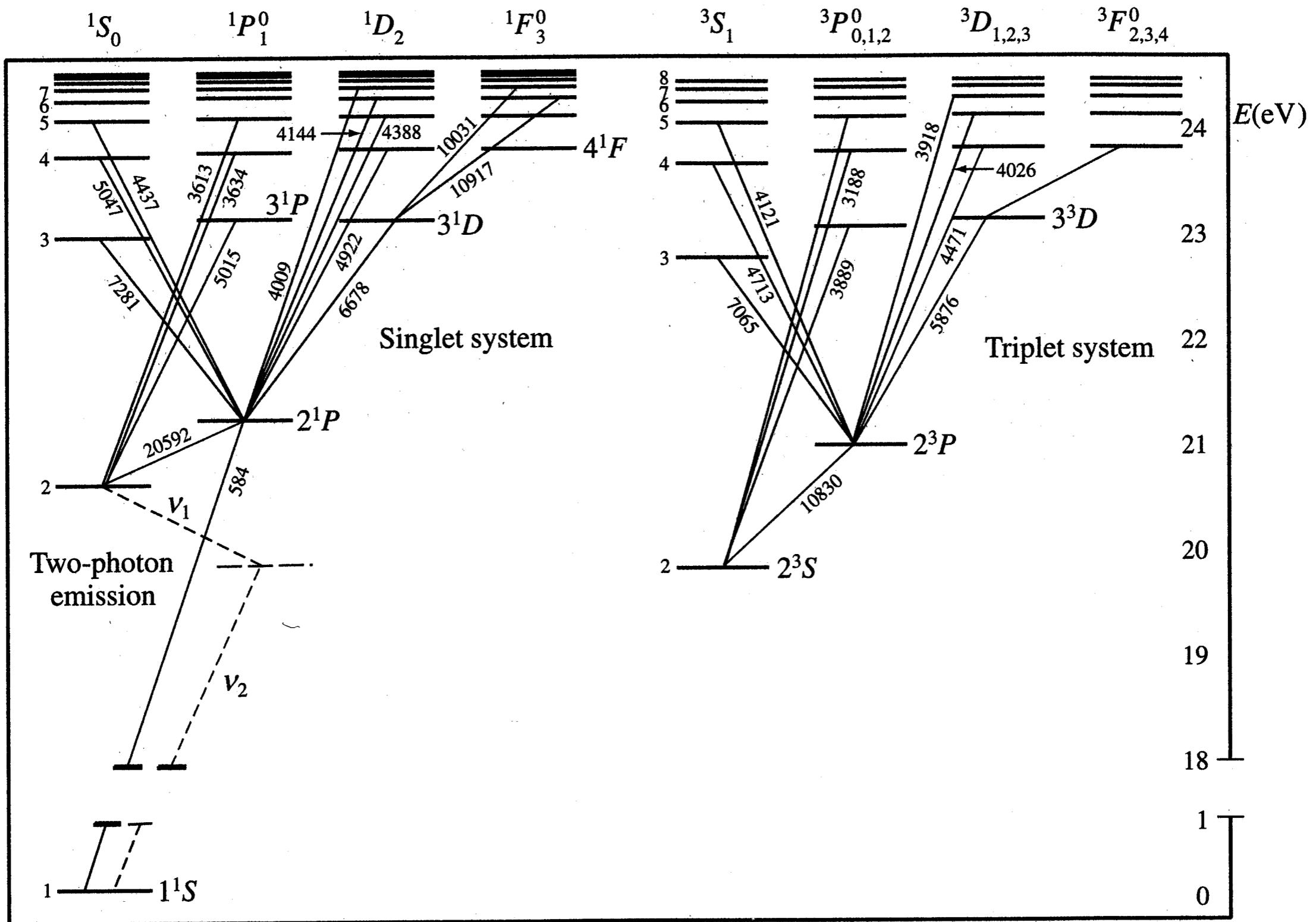
This has $l_1 = 0$ and $l_2 = 1$, giving $L = 1$; again $s_1 = s_2 = \frac{1}{2}$, giving both $S = 0$ and $S = 1$ terms.

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



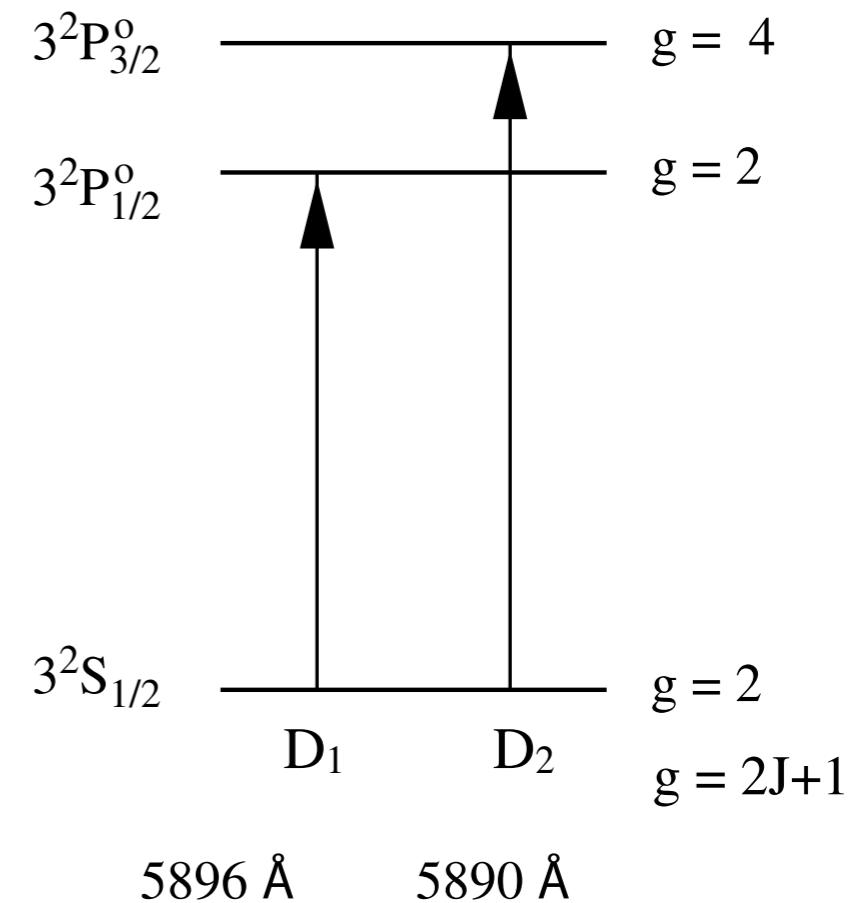
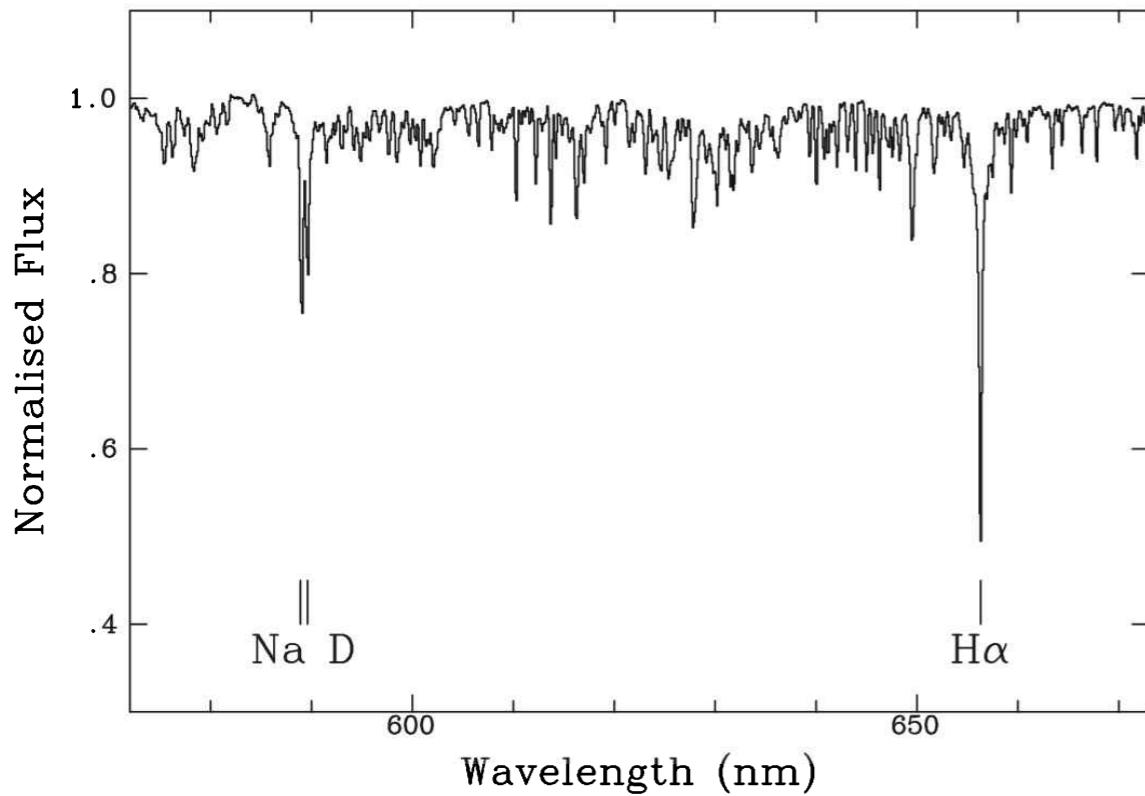
Following the rule above, the ${}^3P^o$ term is lower in energy than the ${}^1P^o$ term, in this case by 0.25 eV.

- Helium (Grotrian diagram)



LS coupling: 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 the ground state configuration of $1s^2 2s^2 2p^6 3s^1$ and the first excited state configuration of $1s^2 2s^2 2p^6 3p^1$.



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 : $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$
- 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 : $3\ ^2S_{1/2} - 4\ ^2P_{3/2}^o$

LS coupling: 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: 4p4d

4p4d electron configuration

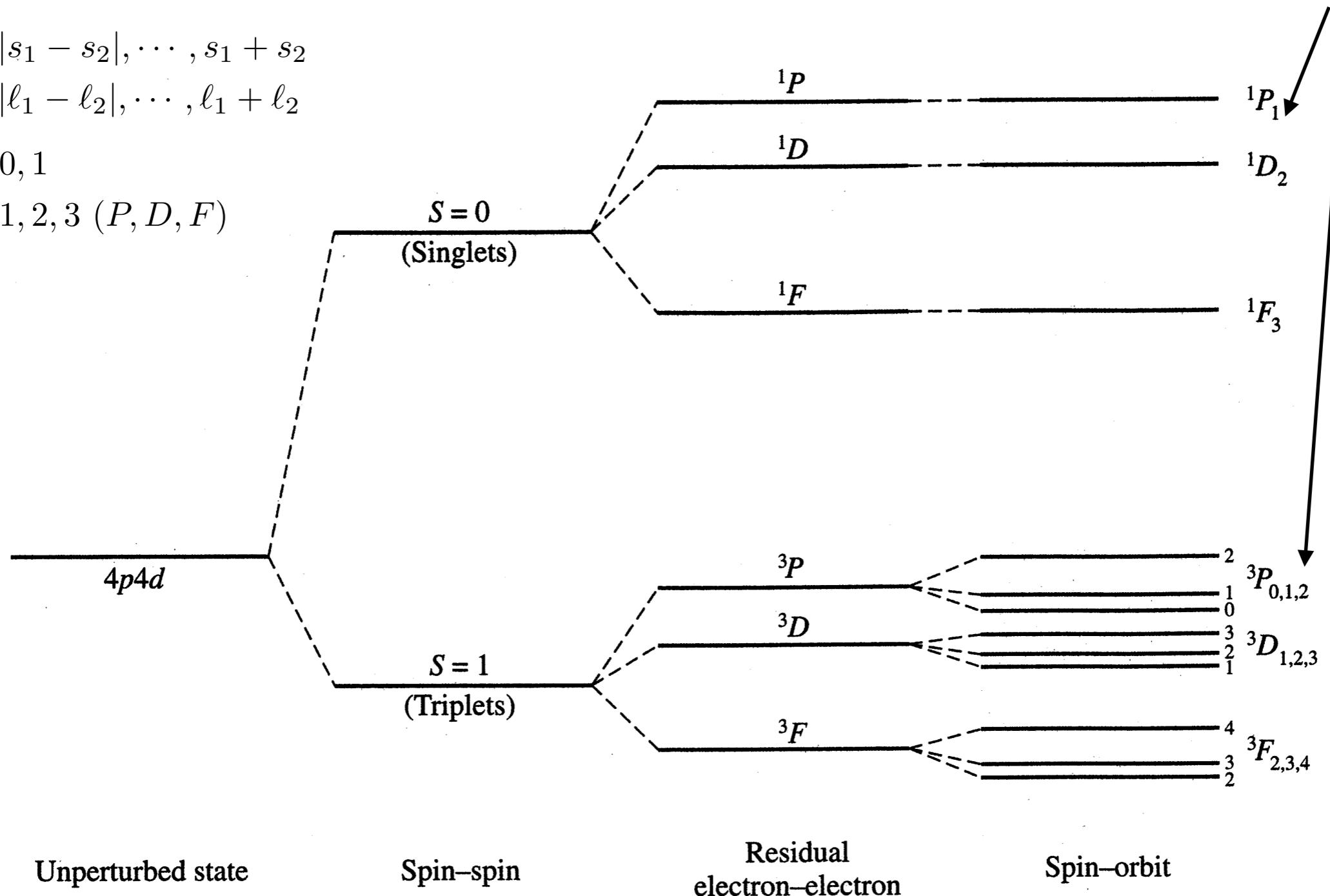
$$J = |L - S|, \dots, L + S$$

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

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

$$S = 0, 1$$

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



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. (The number of m_J is $2J+1$).

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.

Example: npn'p

npn'p electron configuration

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

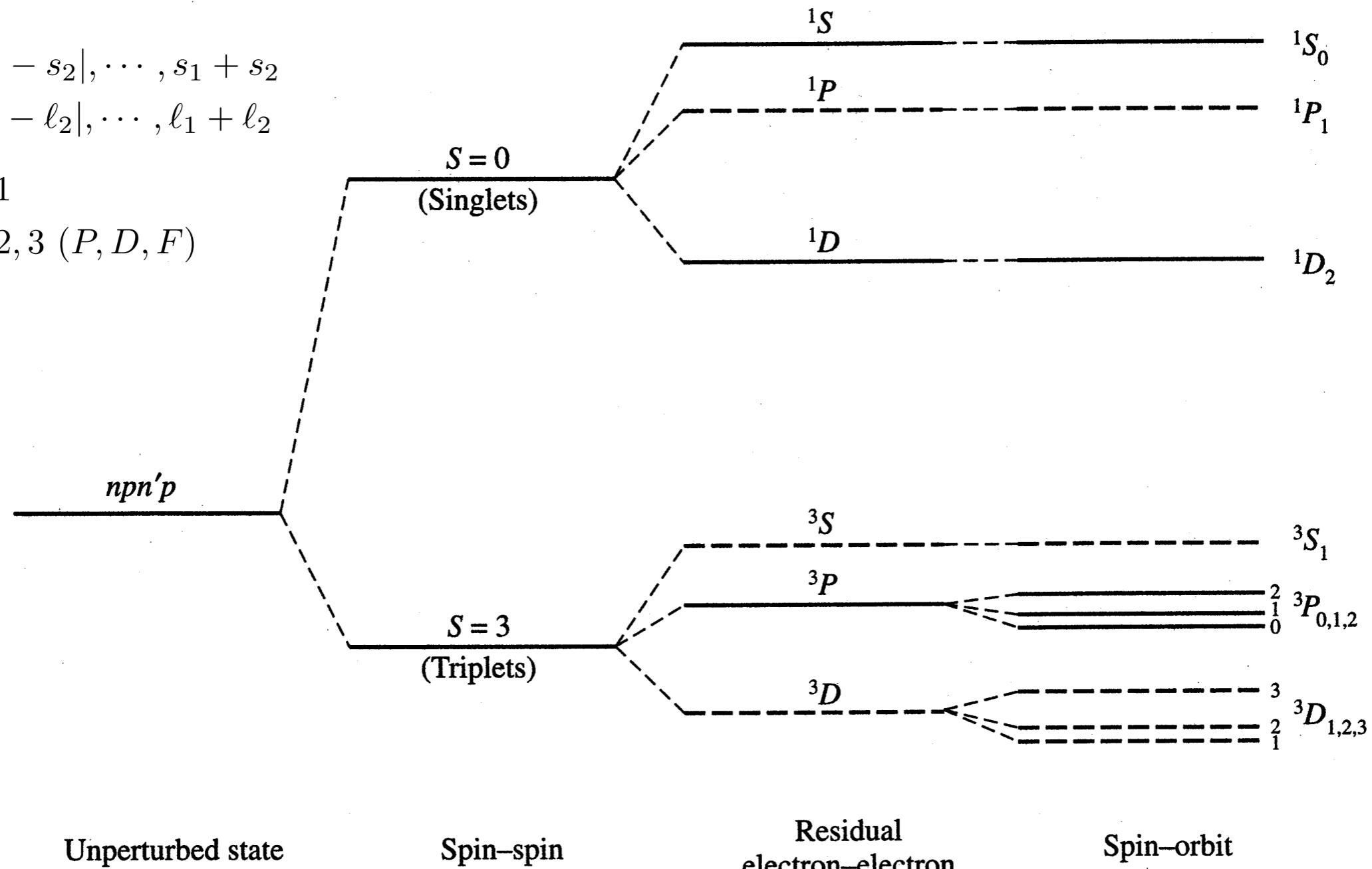
The levels for $n = n'$ will be explained in the next slides.

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

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

$$S = 0, 1$$

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



(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

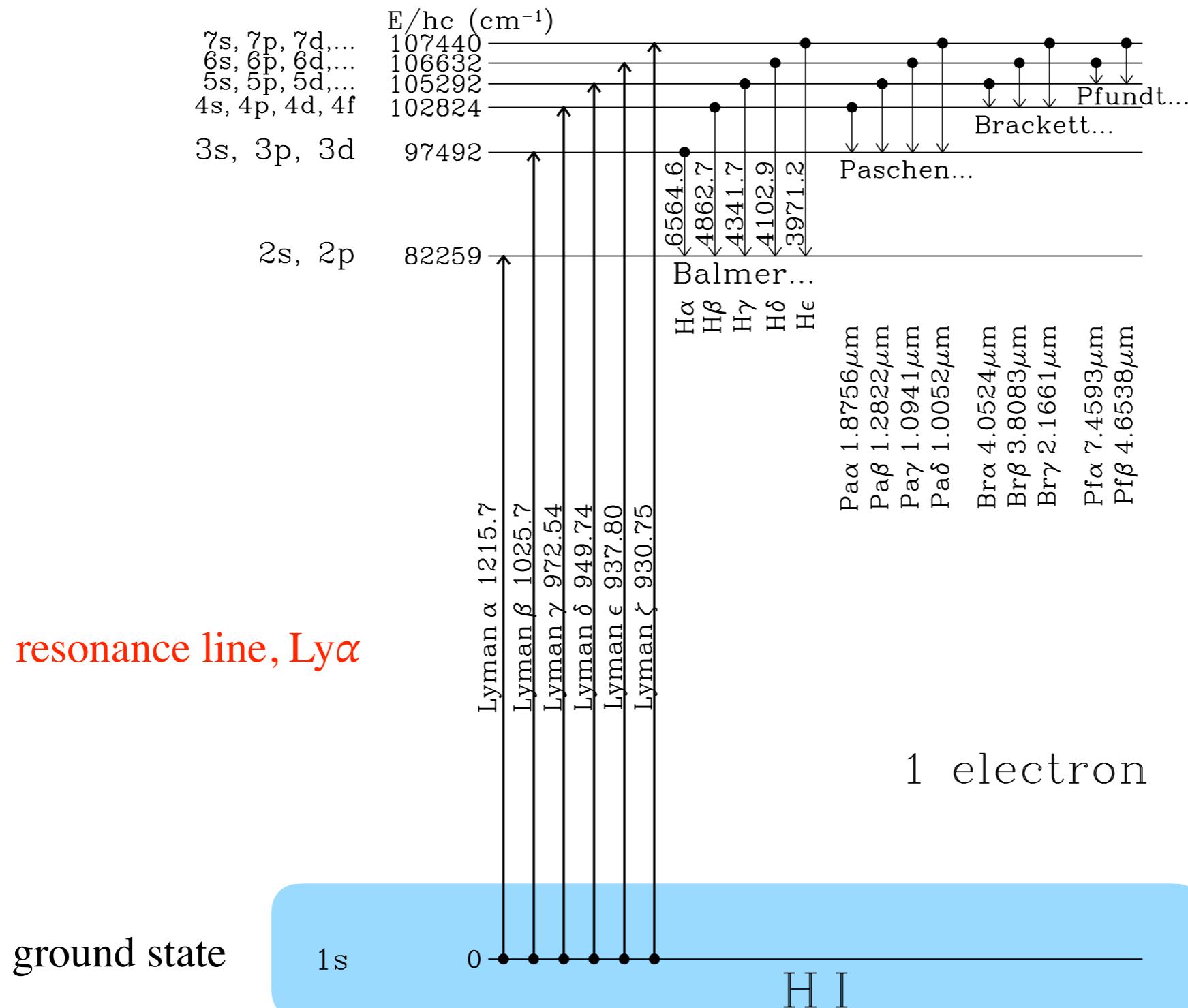
3D is also symmetric for both spin and orbital angular momenta

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. |

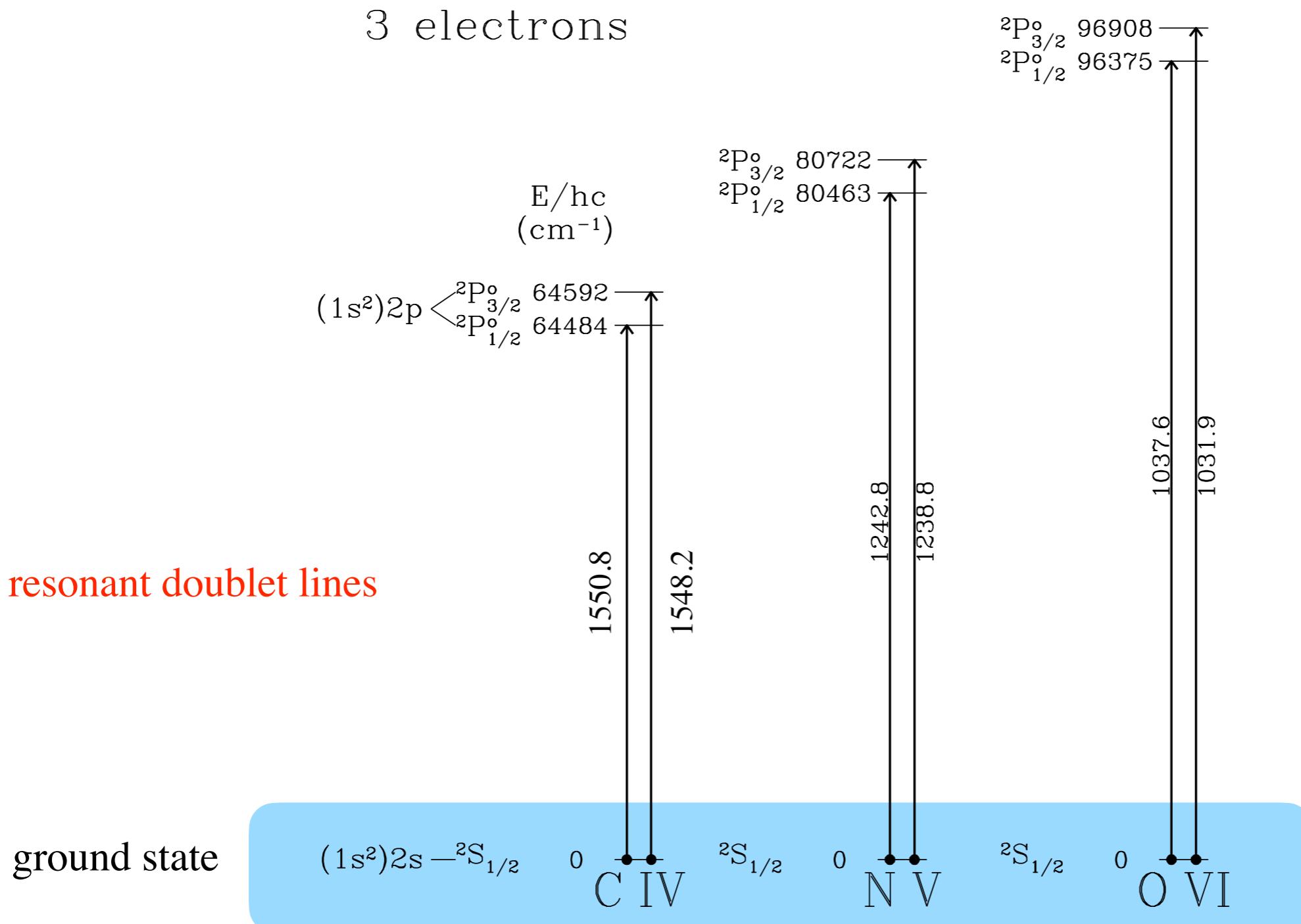
Energy Level Diagrams

- 1 electron



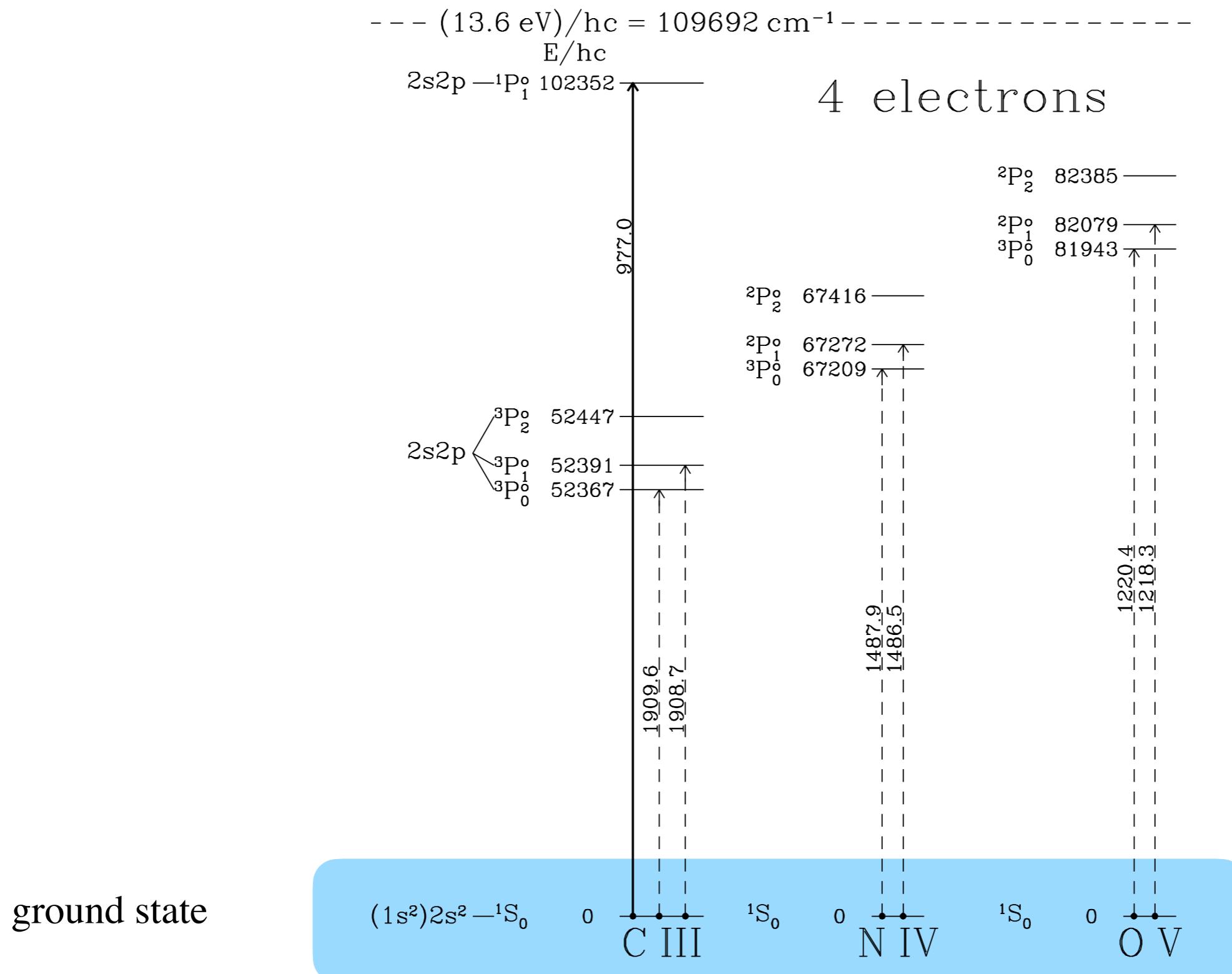
- 3 electrons (Lithium-like ions)

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



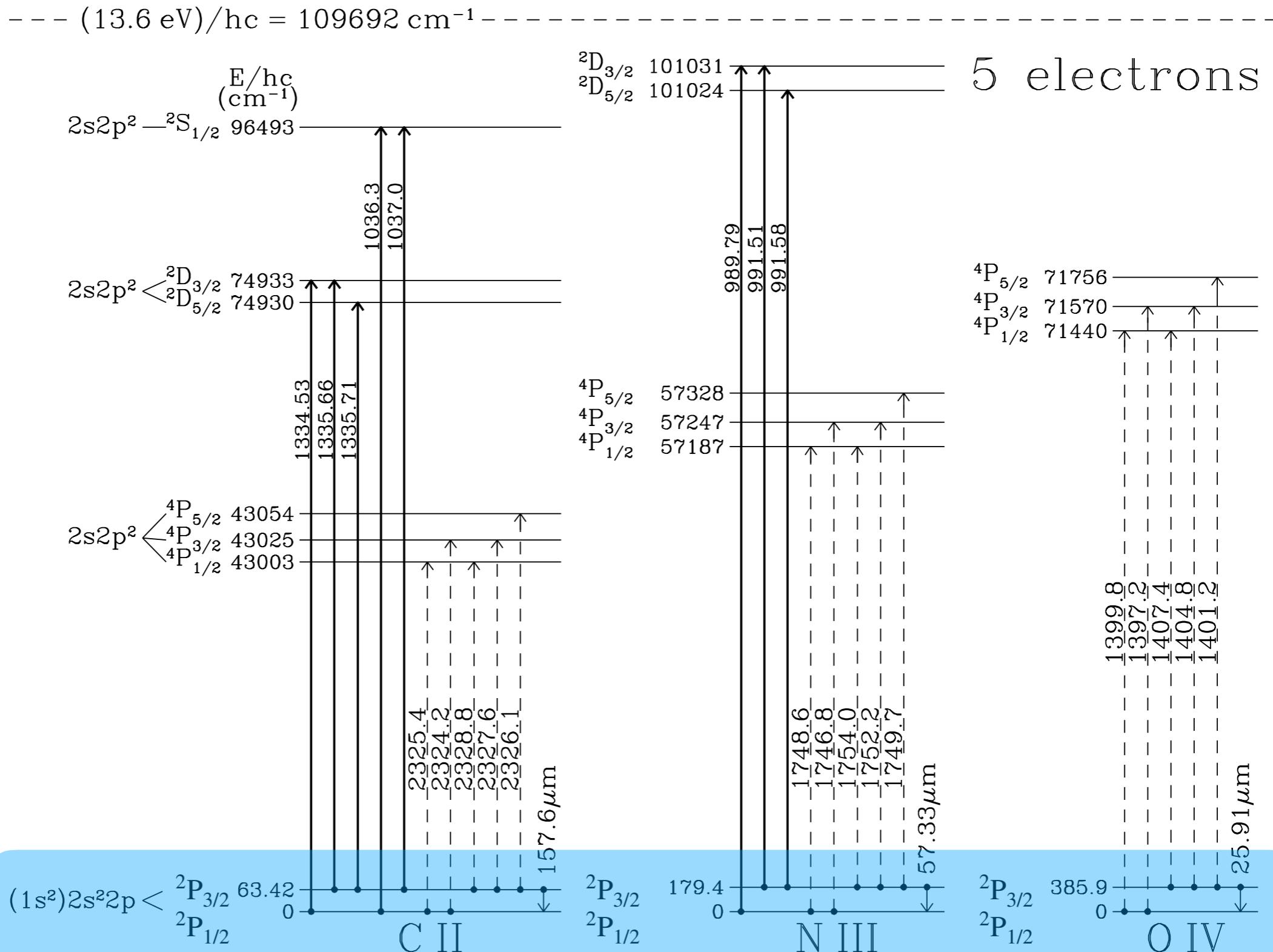
- 4 electrons

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



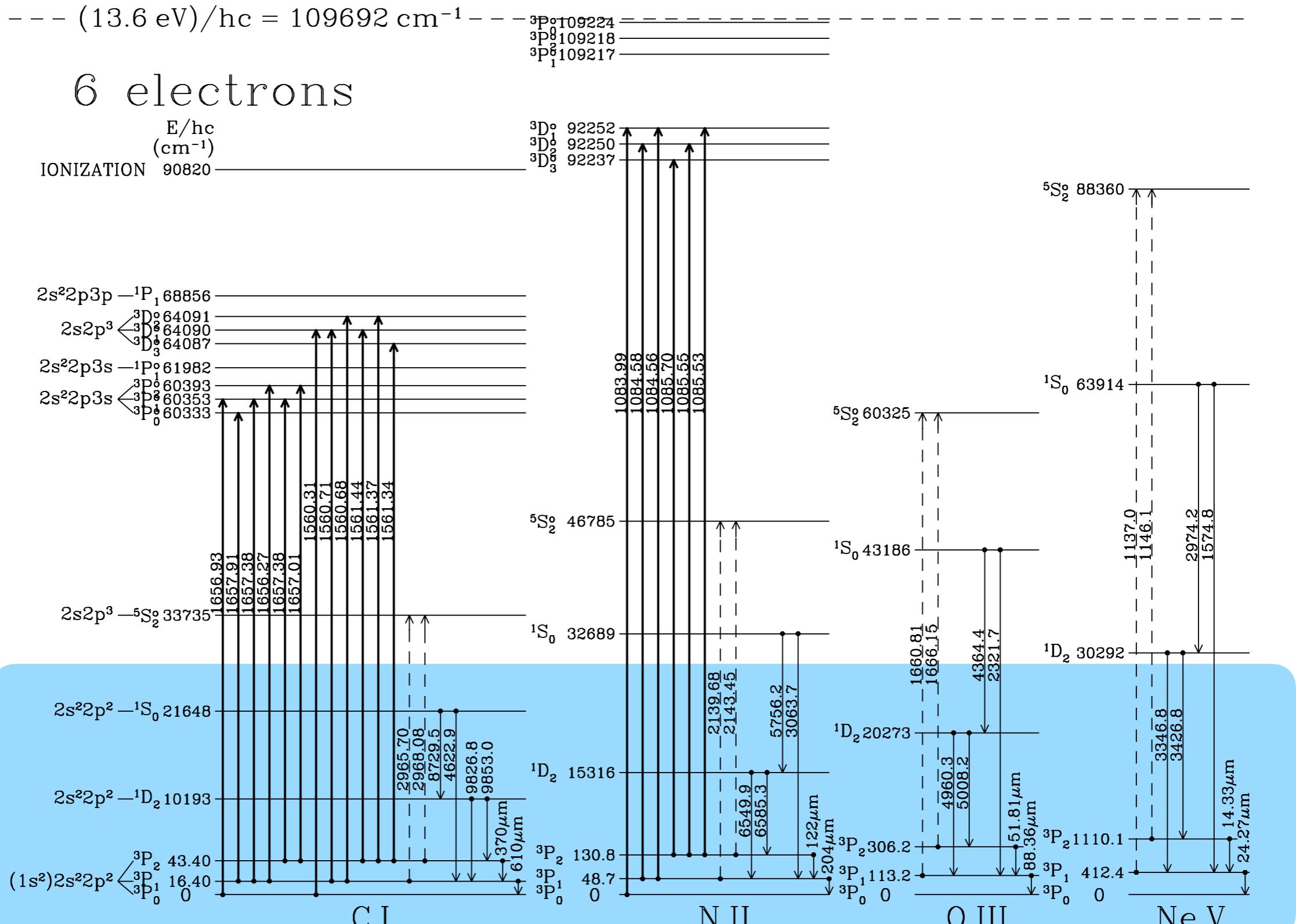
- 5 electrons

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



- 6 electrons

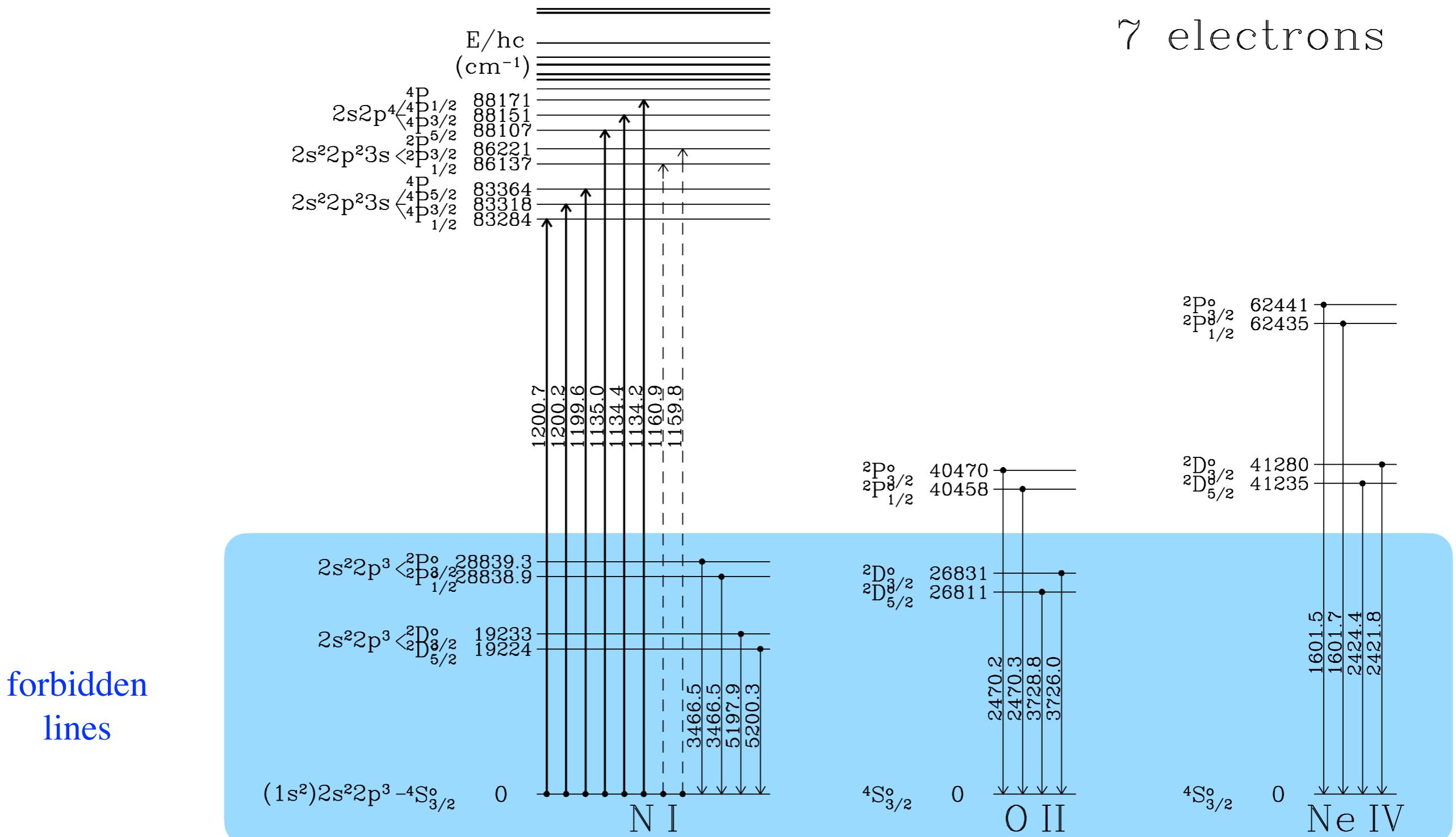
Upward heavy: resonance, Upward Dashed: intercombination
Downward solid: forbidden



- 7 electrons

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

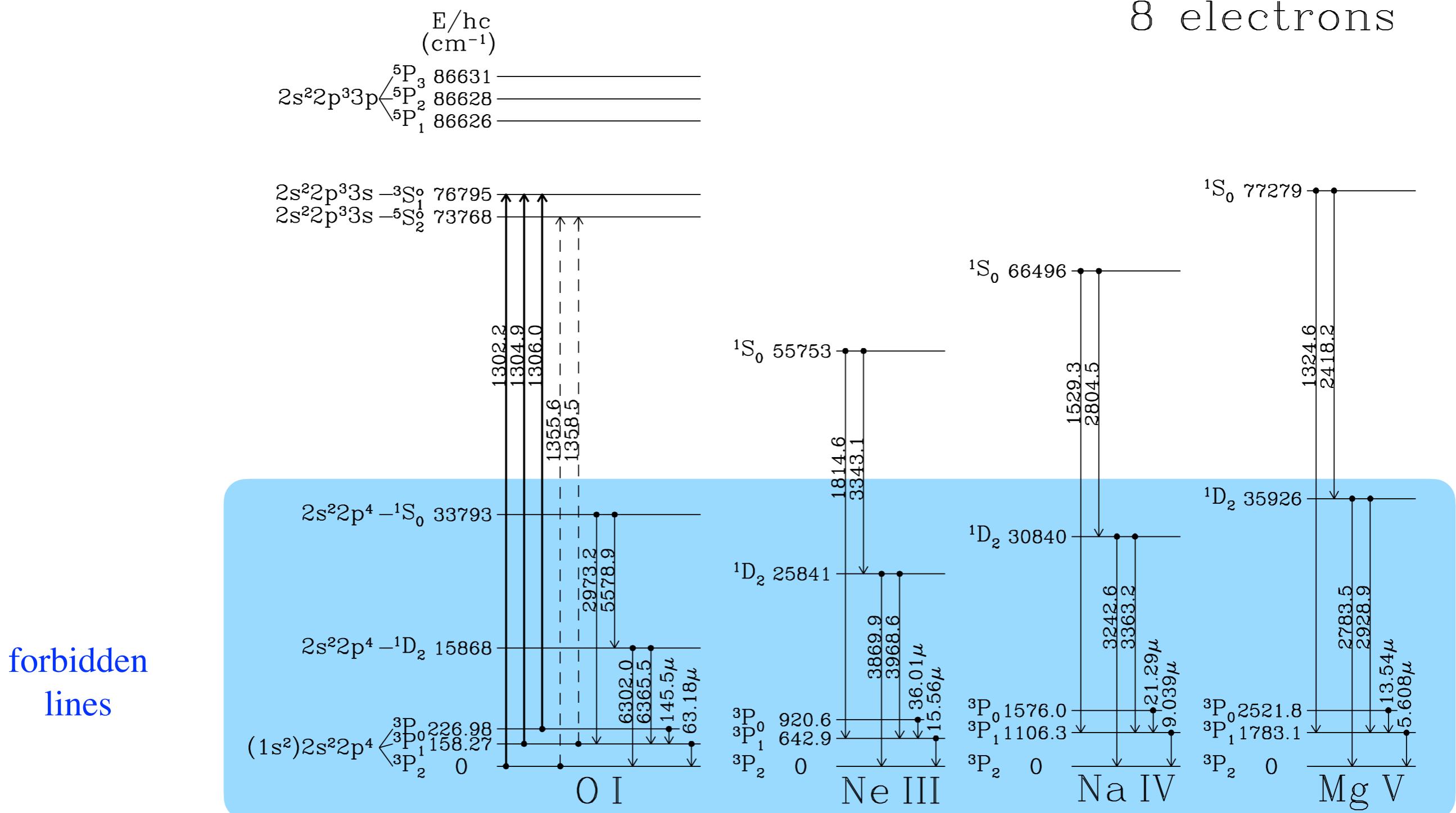
$$\text{---} (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{---} \text{---} \text{---}$$



- 8 electrons

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

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



forbidden
lines

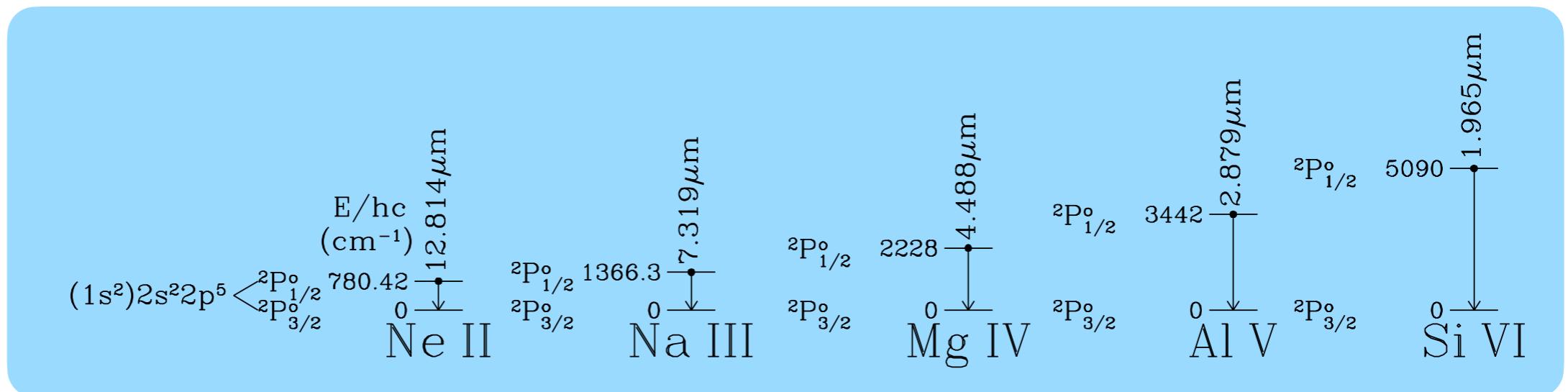
- 9 electrons

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

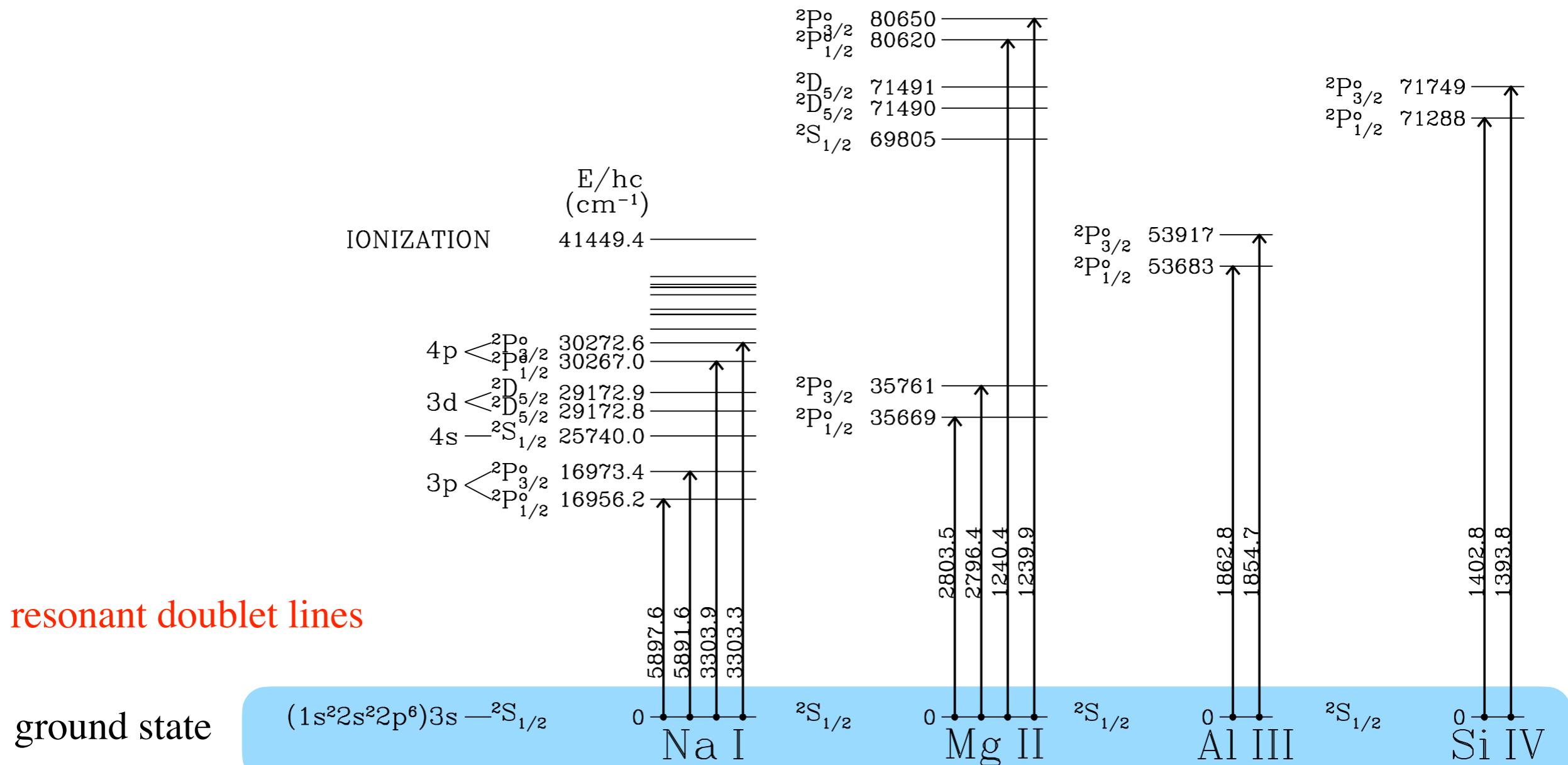


- 11 electrons

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

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

11 electrons

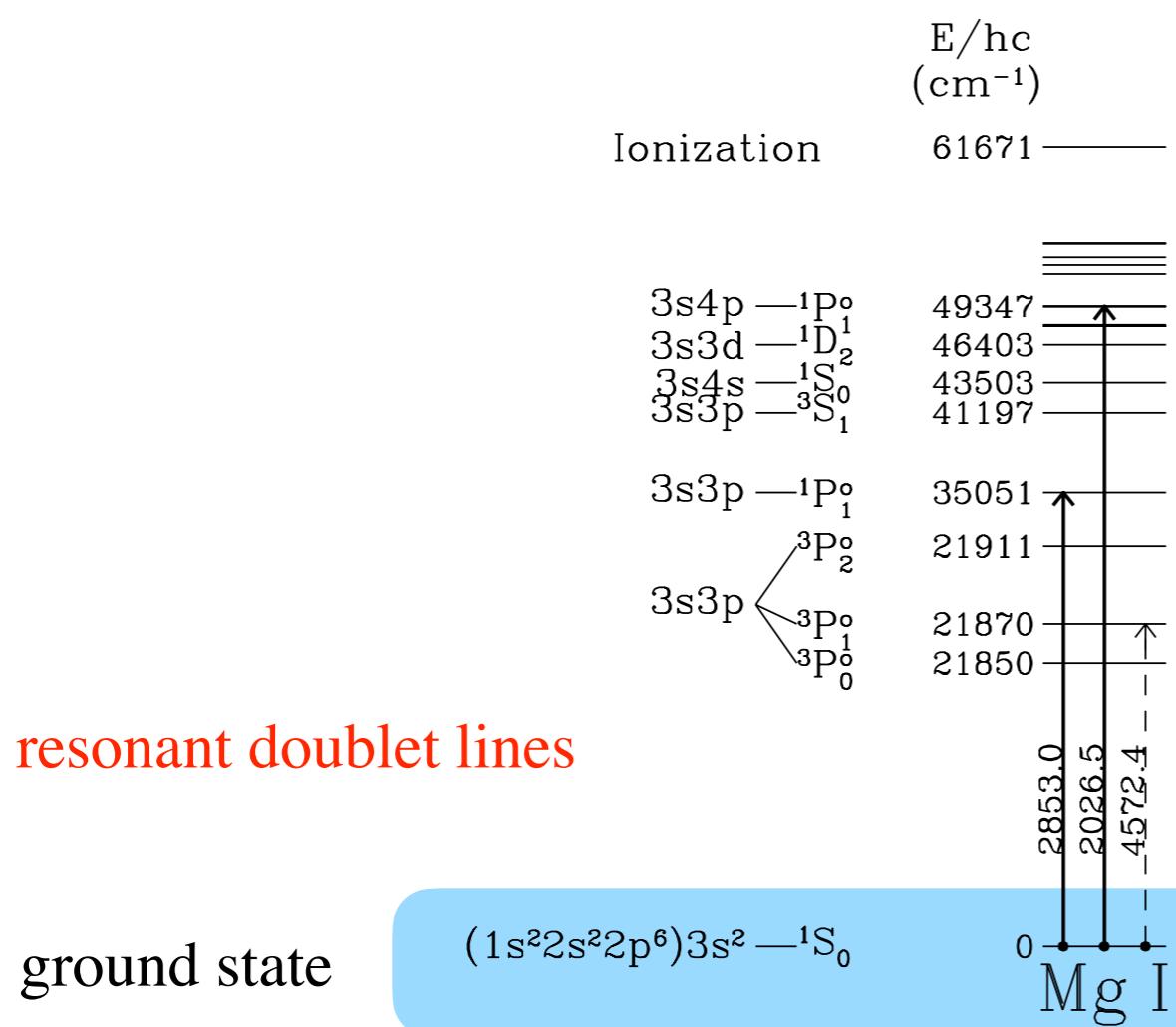


- 12 electrons

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

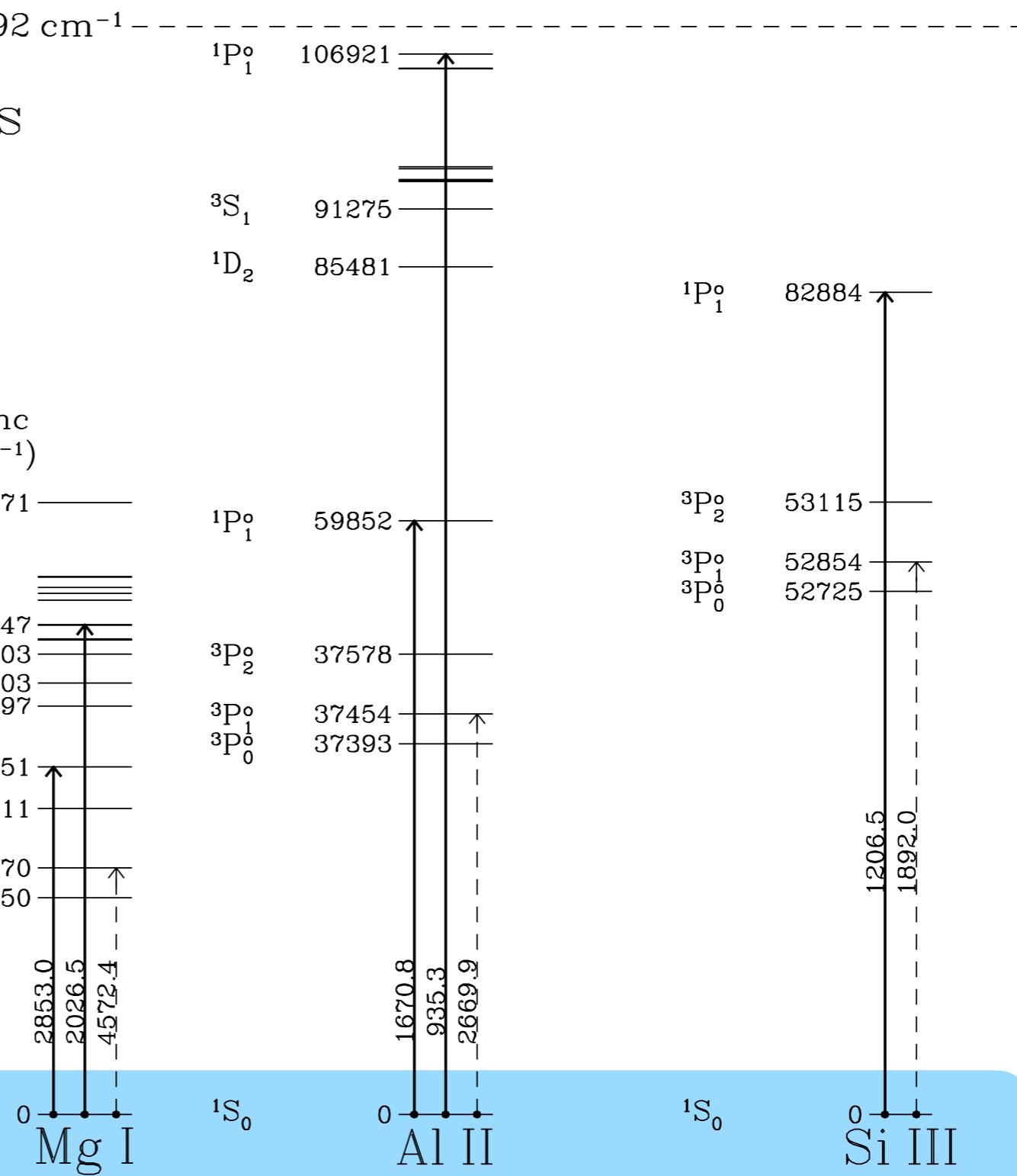
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1} \text{ ---}$$

12 electrons



resonant doublet lines

ground state

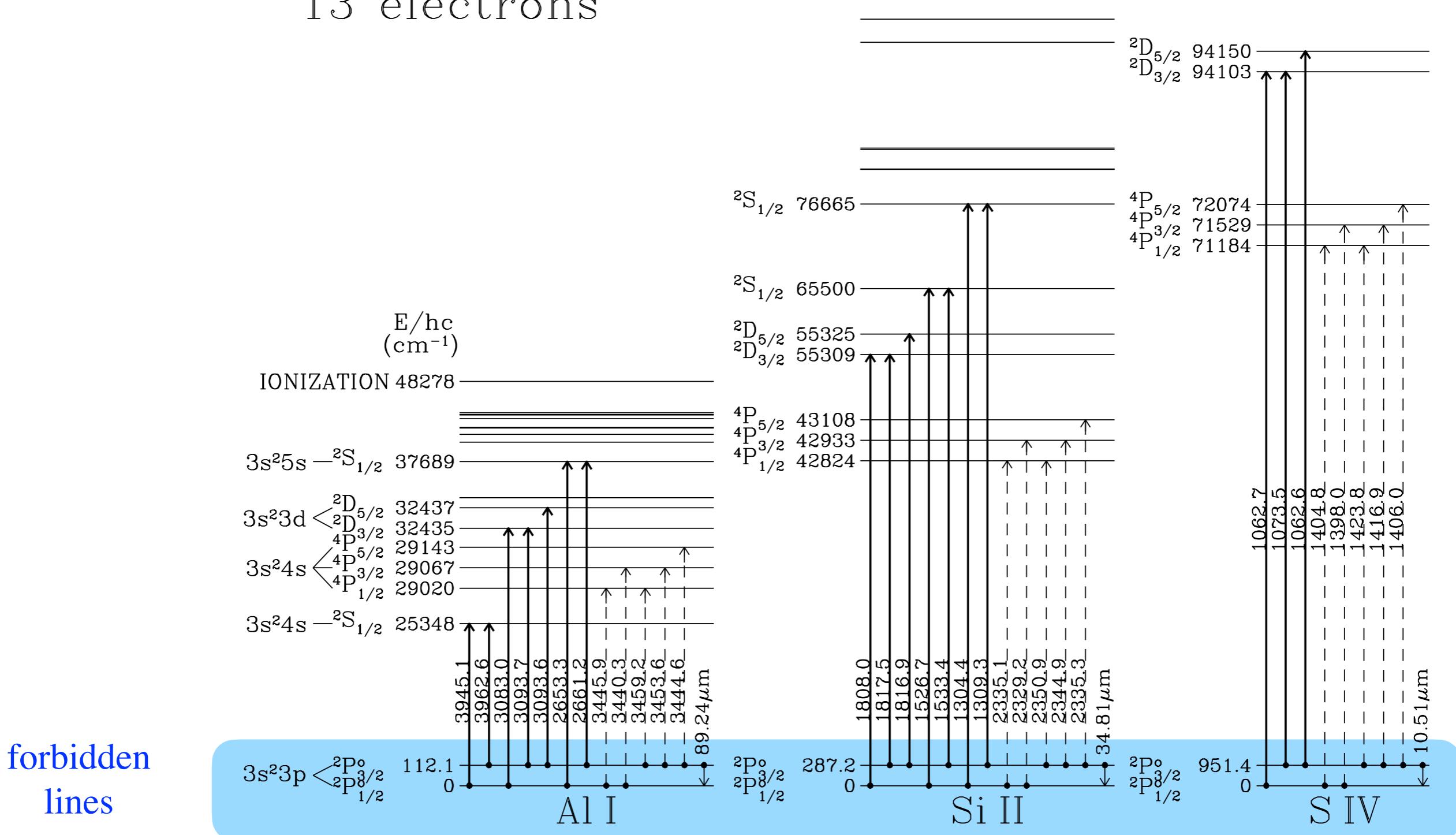


- 13 electrons

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

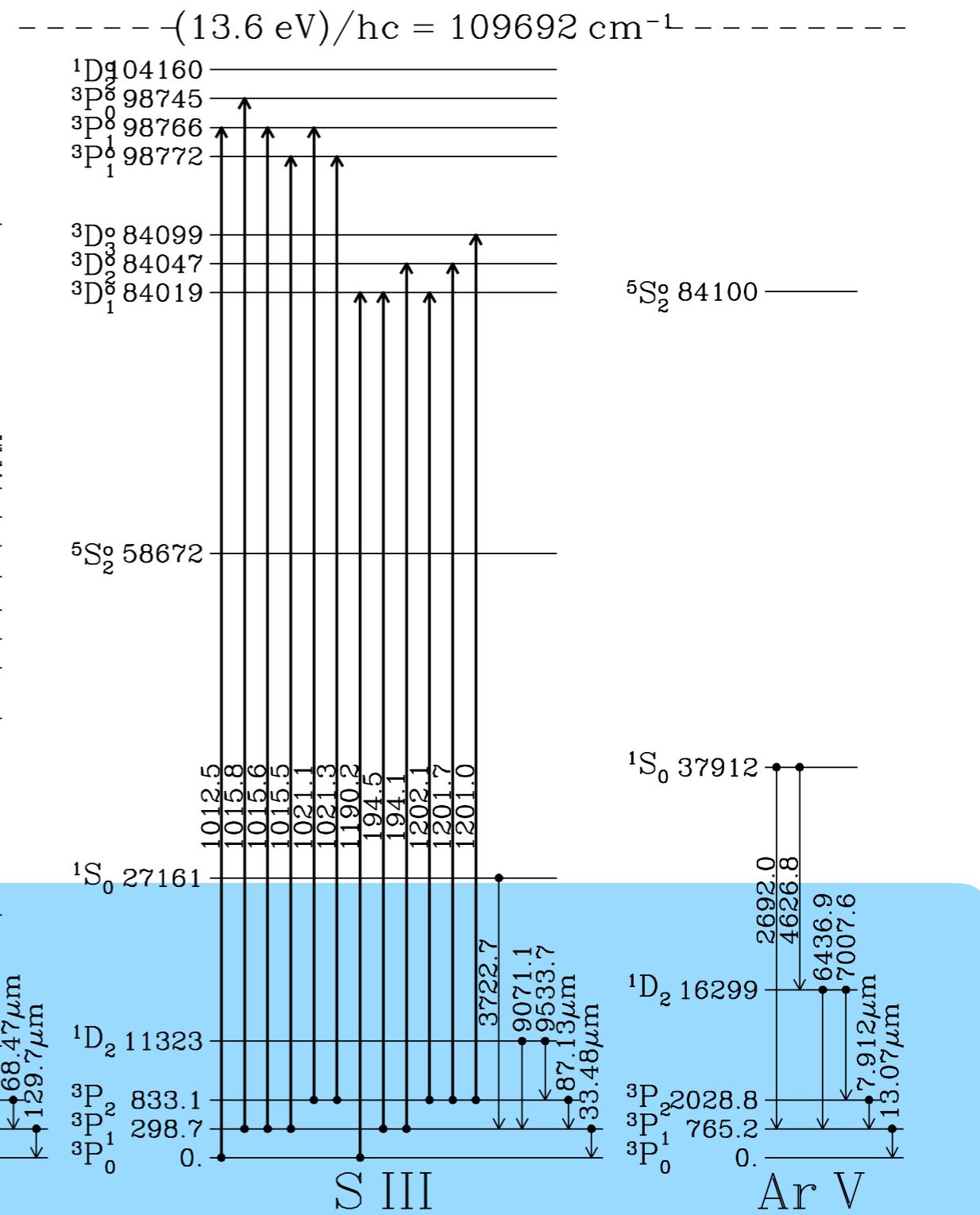
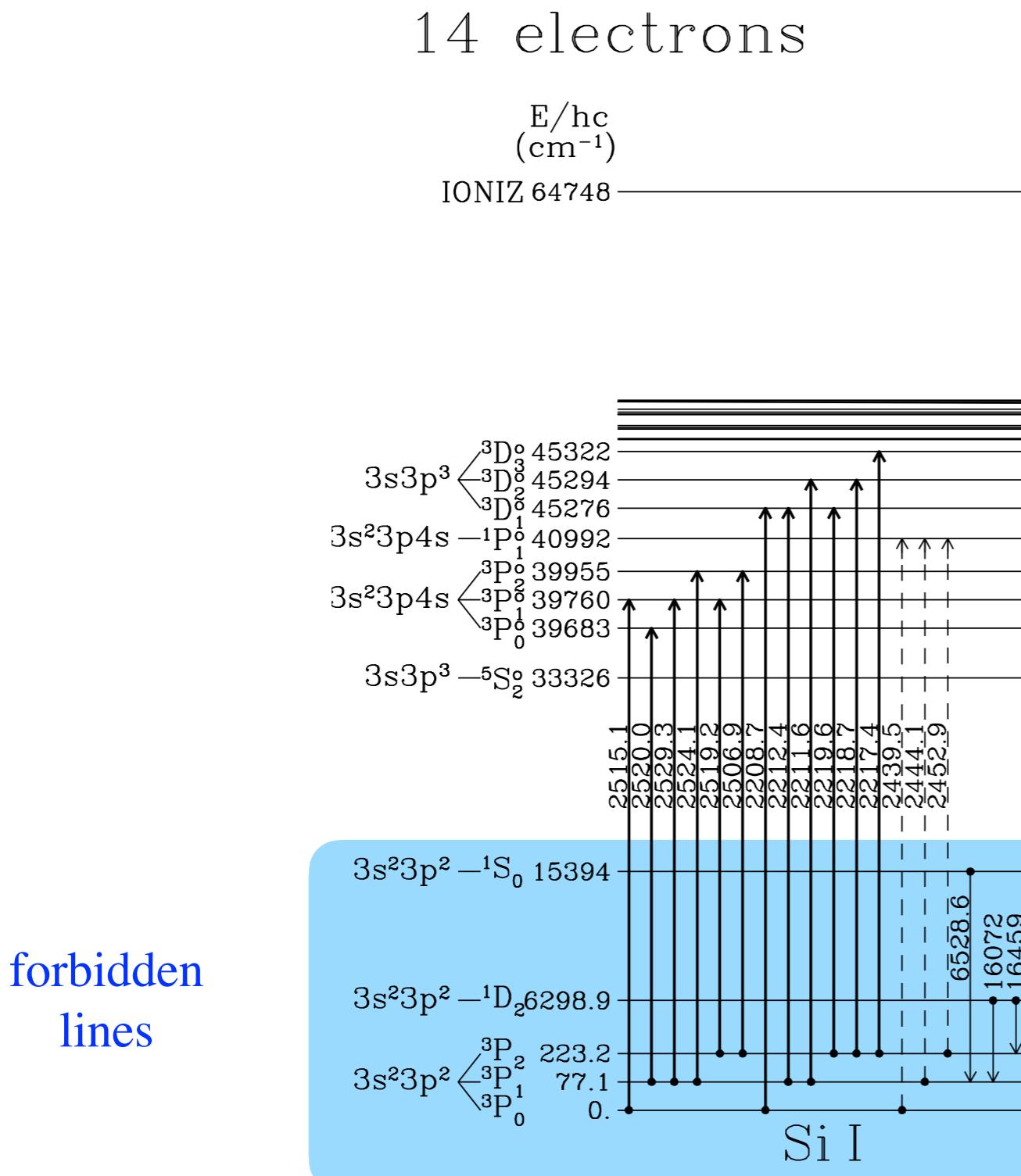
$$\text{--- } (13.6 \text{ eV})/\hbar c = 109692 \text{ cm}^{-1}$$

13 electrons



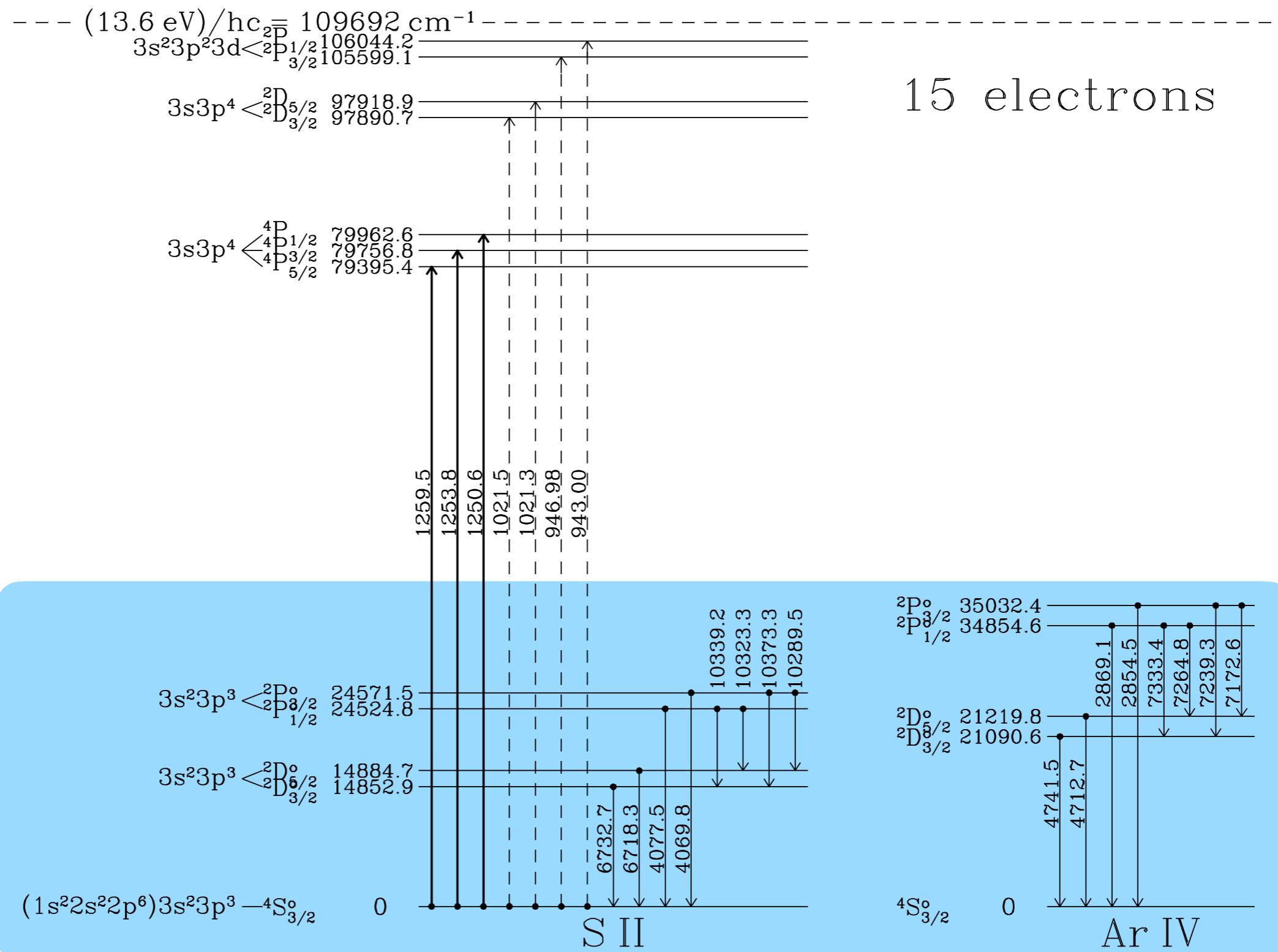
- 14 electrons

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



- 15 electrons

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



Homework (due date: 03/31)

[Q4] Atomic Spectroscopy

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) $3p4p$

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\AA line is an intercombination line and why 22.8\AA is a forbidden line.

