

# Astrophysics [Part I]

Lecture 5  
April 5 (Fri), 2019

(updated on April 4)

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## Books

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- Astronomical Spectroscopy, Jonathan Tennyson
- Physics of the Interstellar and Intergalactic Medium, Bruce T. Draine
- Physics and Chemistry of the Interstellar Medium, Sun Kwok
- Astrophysics of the Diffuse Universe, Michael A. Dopita & Ralph S. Sutherland

# Atomic Structure, Radiative Transitions

# Schrödinger Equation

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

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

The time and space parts of the wave function can be separated:  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{iEt/\hbar}$

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

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

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

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

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

The first term contains a kinetic energy operator for the motion of each electron and the Coulomb attraction between that electron and the nucleus.

The second term contains the electron-electron Coulomb repulsion term.

The Coulomb repulsion between pairs of electrons means the above equation is not analytically solvable, even for the simplest case, the helium atom for which  $N = 2$ .

# Reviews of QM

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

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

- Wavefunction for a hydrogen-like atom:

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

radial function:

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

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

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

spherical harmonics

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

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

- Wavefunctions for a hydrogen-like atom

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- Probability:

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

- Properties of the spherical harmonics:

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

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

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

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- Degeneracy for a given  $n$ .

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

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

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

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

- Spin

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

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

# Many-Electron Systems - [Central Field Approximation]

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

**Self-consistent field approximation:** We assume that each electron moves in the potential of the nucleus plus the averaged potential due to the other  $N - 1$  electrons.

**Central field approximation (or orbital approximation):** In addition, when this averaged potential is assumed to be spherically symmetric, the force acting on each electron only depends on its distance from the nucleus at the center. It provides a useful classification of atomic states and also a starting point.

Let us assume that each electron moves in its own (angle-independent) central potential given by  $V_i(r_i)$ . This gives a simplified Schrödinger equation for the motion of each electron:

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

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

**Orbitals:** The solutions of the above equation are known as orbitals.

Using this approximation, the total energy and the total wave function of the system are given by the sum of single electron energies and the product of single electron wave functions, respectively.

$$E = \sum_i E_i$$

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

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

## [Indistinguishable Particles]

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

$$|\Psi(1, 2)|^2 = |\Psi(2, 1)|^2$$

The equation has two possible solutions:

- symmetric solution       $\Psi(1, 2) = \Psi(2, 1)$
- antisymmetric solution     $\Psi(1, 2) = -\Psi(2, 1)$

**Pauli Principle:** Wave functions are **antisymmetric** with respect to interchange of identical Fermions.

Within the central field approximation, a two-electron wave function which obeys the Pauli Principle can be written

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

**Pauli exclusion principle:** If the two spin-orbitals are the same ( $\phi_a = \phi_b$ ), then the total wave function is zero, i.e.,  $\Psi(1, 2) = 0$ , and no physical (normalizable) state exists. The Pauli exclusion principle is summarized as “**No two electrons can occupy the same spin-orbital.**”

This exclusion provides the degeneracy pressure which holds up the gravitational collapse of white dwarfs and neutron stars.

# [Electron Configuration]

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- **The electron configuration** is the distribution of electrons of an atom (or molecule) in atomic (or molecular) **orbitals**. Electronic configurations describe electrons as each moving independently in an orbital, in an average field created by all other orbitals.

The configuration of an atomic system is defined by specifying the  $nl$  values of all the electron orbitals:  $nl^x$  means  $x$  electrons in the orbital defined by  $n$  and  $l$ . Following the Pauli exclusion principle, each orbital labelled  $nl$  actually consists of orbitals with  $2l+1$  different  $m$  values, each with two possible values of  $s_z$ . Thus the  $nl$  orbital can hold a maximum  $2(2l+1)$  electrons.

- **shells, subshells:**

Shells correspond with the principal quantum numbers (1, 2, 3, ...). They are labeled alphabetically with letters used in the X-ray notation (K, L, M, ...).

Each shell is composed of one or more subshells. The first (K) shell has one subshell, called “1s”; The second (L) shell has two subshells, called “2s” and “2p”.

The valence shell is the outermost shell of an atom. A valence electron is an electron that can participate in the formation of a chemical bond.

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- **open shell configuration, closed shell configuration:**

the ground state configuration of carbon, which has six electrons:  $1s^2 2s^2 2p^2$

the ground state configuration of neon atom, which has ten electrons:  $1s^2 2s^2 2p^6$

A closed shell or sub-shell makes no contribution to the total orbital or spin angular momentum ( $L$  or  $S$ ).

- Atomic ions which have the same number of electrons form what are called **isoelectronic series**.

- Electronically-excited states of atoms usually arise when one of the outermost electrons jumps to a higher orbital.

States with two electrons simultaneously excited are possible but are less important. For many systems, all of these states are unstable. They have sufficient energy to autoionize by spontaneously ejecting an electron.

# [Electron Configuration]

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- **Energy ordering:**

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

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

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

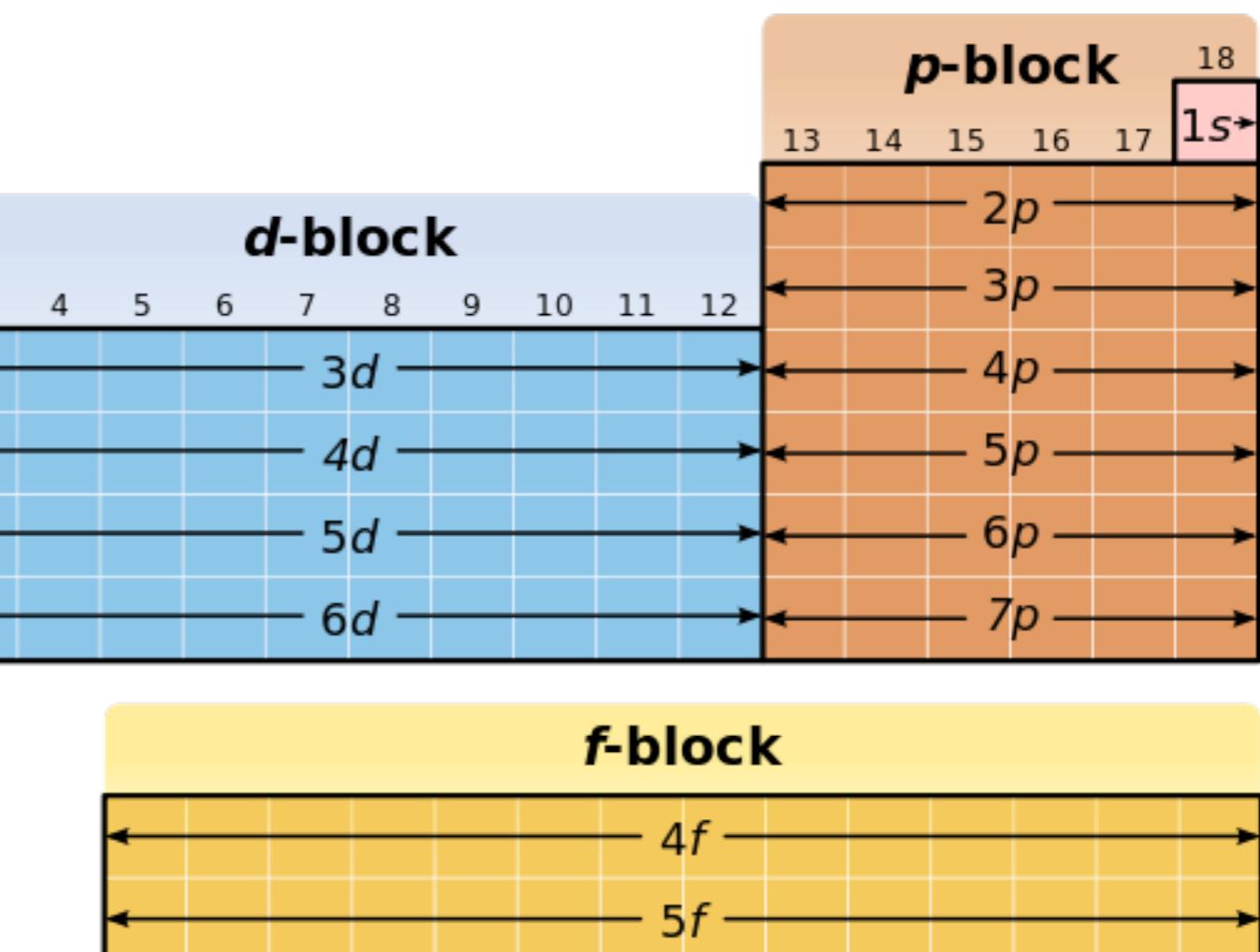
The lowest energy or ground state configuration involves filling the atomic orbitals in energy order from the lowest energy orbitals upwards.

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

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

The subshell structure of elements up to argon ( $Z = 18$ ) is filled up in a naturally straightforward manner, first according to  $n$  and then according to  $l$ .

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



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- Negative ions:

Not all atoms can bind an extra electron to form a stable negative ion. H, C and O can bind an electron while He and N cannot.

Most negative ions have only one stable level, and so possess no line ('bound-bound') spectrum. The only possible transitions are continuous bound-free absorption (photoionization).

Negative ions are much less astronomically important than positive ones.

# [The Electrostatic Interaction, LS coupling, Terms]

- **The Electrostatic Interaction**

The specification of the electron configuration (the  $n, l$  values of all electrons) leaves a great deal of unspecified information, since we are not given the values of  $m_l$  and  $m_s$ . In the central field approximation all of these states are degenerate.

The Hamiltonian is

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

where

$H_0 \equiv$  central field approximation

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

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

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

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

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

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

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- 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 **v**, the electric field exerting on the electron will be  $E = Ze \frac{\mathbf{r}}{r^3}$ . (Note that the nucleus has a positive charge  $Ze$ .)

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

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

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

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

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

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

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

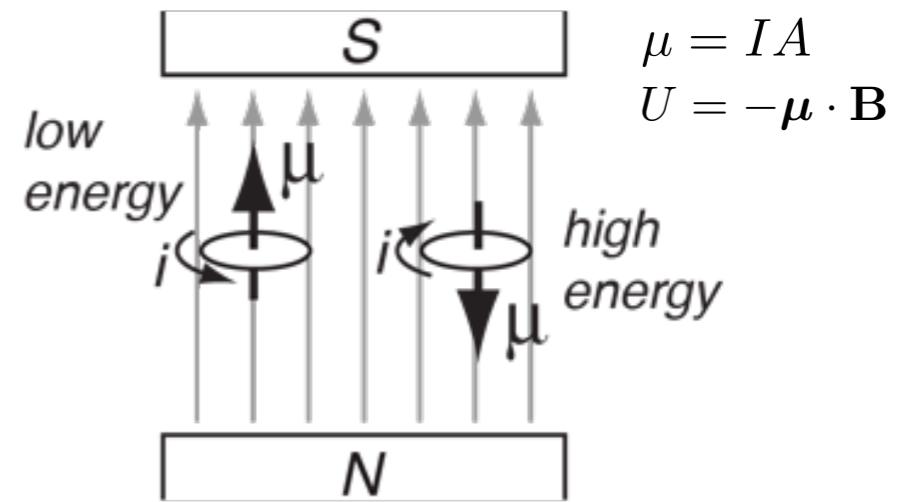
$$\boldsymbol{\mu} = -\frac{e}{m_e c} \mathbf{s}$$

- Then, the interaction energy is

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

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

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



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

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

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

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

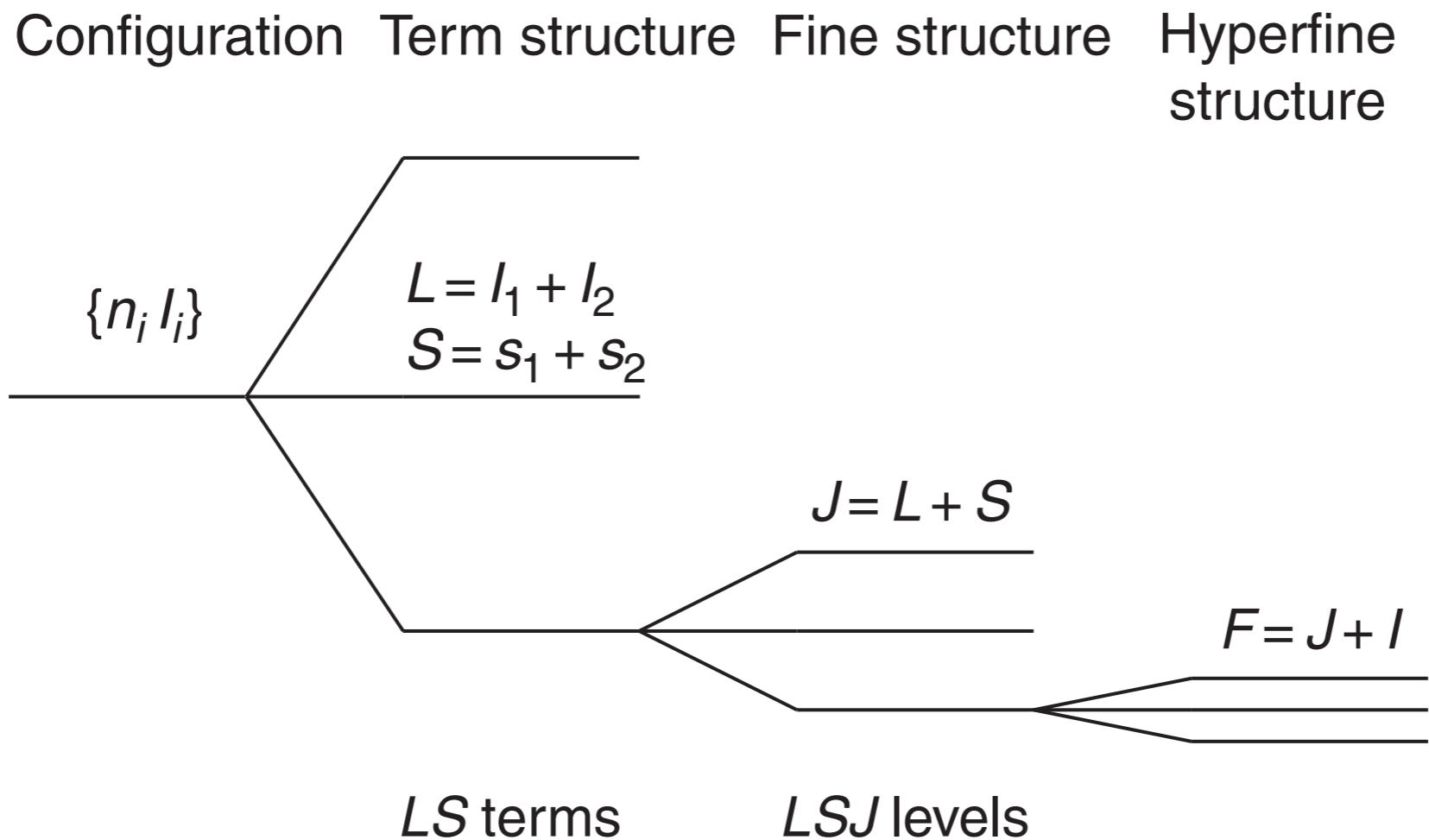
The eigen energy of the operator is given by  $E_{\text{so}} = \frac{1}{2} C [J(J+1) - L(L+1) - S(S+1)]$ .

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

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

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

- Electronic configuration and energy level splitting



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- **Active electrons:** As a result of the Pauli Principle, closed shells and sub-shells have both  $L = 0$  and  $S = 0$ . This means that it is only necessary to consider ‘active’ electrons, those in open or partially-filled shells.
  - **Parity of the wave function**

The parity of the wave function is determined by how the wave function behaves upon inversion. The square of the wave function, i.e., the probability distribution of the electrons, must be unchanged by the inversion operation.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \pm \Psi(-\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_N)$$

Even parity states are given by + sign and odd parity states are given by - sign.

The parity arising from a particular configuration can be determined simply by summing the orbital angular momentum quantum numbers for each of the electrons.

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

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

# [Spectroscopic Notation]

- Spectroscopic Notation

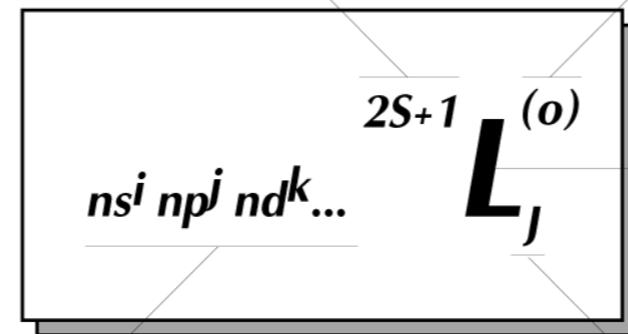
**Total Term Spin Multiplicity:**

$S$  is vector sum of electron spins ( $\pm 1/2$  each)

Inner full shells sum to 0

**Term Parity:**

$o$  for odd, nothing for even



**Total Term Orbital Angular Momentum:**

Vector sum of contributing electron orbitals.

Inner full shells sum to 0.

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

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

A state with  $S = 0$  is a ‘singlet’ as  $2S+1 = 1$ .

A state with  $S = 1/2$  is a ‘doublet’ as  $2S+1 = 2$

One with  $S = 1$  is a ‘triplet’ as  $2S+1 = 3$

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

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

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

sharp, principal, diffuse, fundamental,...

# [LS combinations]

- **Equivalent and Nonequivalent Electrons**

Nonequivalent electrons are those differing in either  $n$  or  $l$  values, whereas equivalent electrons have the same  $n$  and  $l$  values.

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

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

We can find there are 15 distinguishable states allowed.

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

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

$m_l_1$	$m_l_2$	$m_s_1$	$m_s_2$	Label	$m_l_1$	$m_l_2$	$m_s_1$	$m_s_2$	Label
+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	OUT	0	-1	+	+	11
		+	-	1			+	-	12
		-	+	1			-	+	13
		-	-	OUT			-	-	14
+1	0	+	+	2	-1	+1	+	+	6
		+	-	3			+	-	8
		-	+	4			-	+	7
		-	-	5			-	-	9
+1	-1	+	+	6	-1	0	+	+	11
		+	-	7			+	-	13
		-	+	8			-	+	12
		-	-	9			-	-	14
0	+1	+	+	2	-1	-1	+	+	OUT
		+	-	4			+	-	15
		-	+	3			-	+	15
		-	-	5			-	-	OUT
0	0	+	+	OUT					
		+	-	10					
		-	+	10					
		-	-	OUT					

OUT : Pauli excluded states.

Only distinguishable states are labelled.

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

Label	$M_L$	$M_s$	$M_J$	Label	$M_L$	$M_s$	$M_J$
1	+2	0	+2	9	0	-1	-1
2	+1	+1	+2	10	0	0	0
3	+1	0	+1	11	-1	+1	0
4	+1	0	+1	12	-1	0	-1
5	+1	-1	0	13	-1	0	-1
6	0	+1	+1	14	-1	-1	-2
7	0	0	0	15	-2	0	-2
8	0	0	0				

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

(Example 1)  $4p4d$  electron configuration

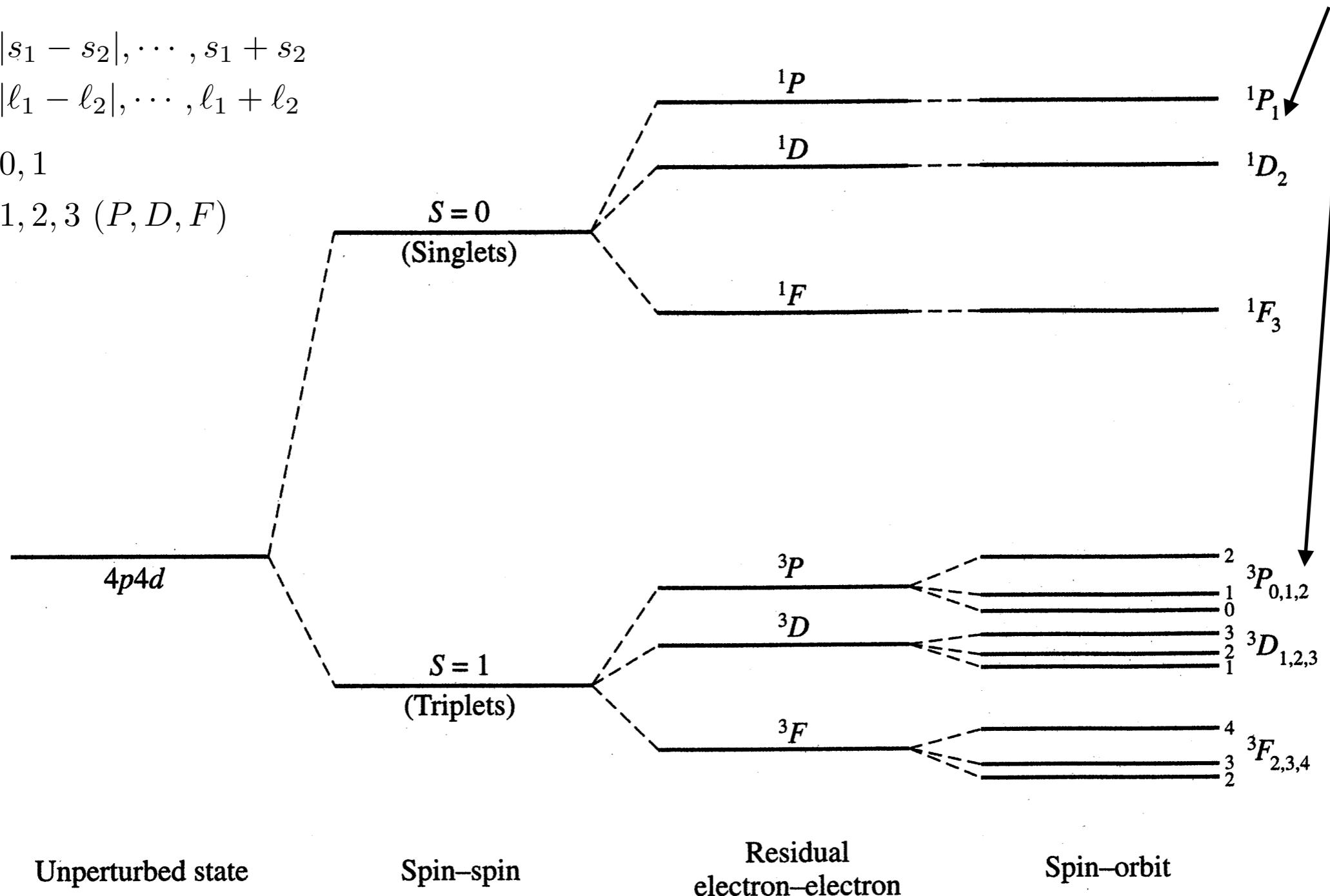
$$J = |L - S|, \dots, L + S$$

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

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

$$S = 0, 1$$

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



(Example 2)  $nnp'p$  electron configuration

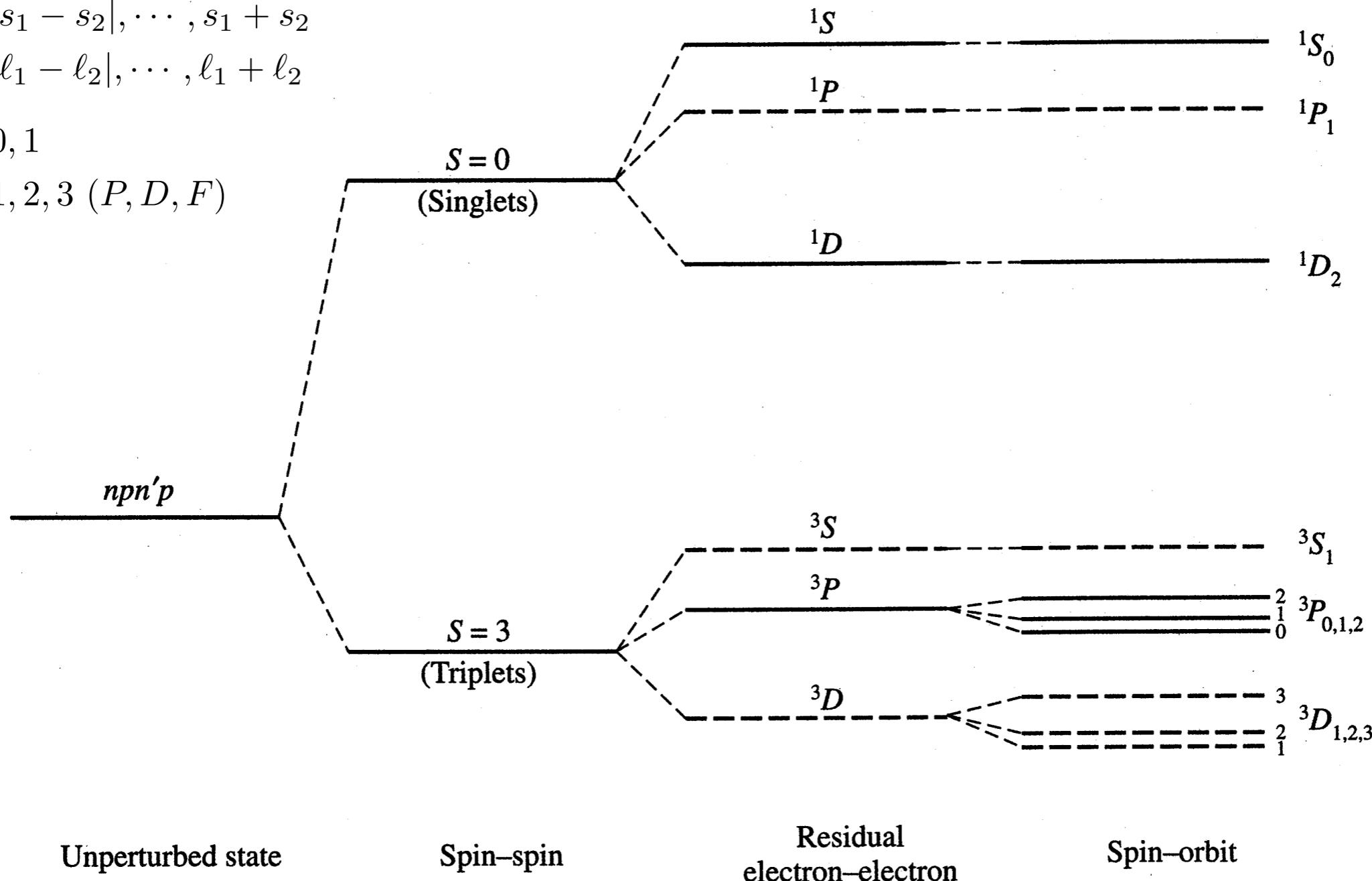
The dashed levels are missing if the two electrons are equivalent ( $n = n'$ )

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

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

$$S = 0, 1$$

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



[Kowk, Physics and Chemistry of the ISM]

Atomic terms arising from  $p^n$  and  $d^n$  configurations

Electron configuration	Terms
$p^1, p^5$	$^2P$
$p^2, p^4$	$^1S, ^1D, ^3P$
$p^3$	$^2P, ^2D, ^4S$
$d^1, d^9$	$^2D$
$d^2, d^8$	$^1S, ^1D, ^1G, ^3P, ^3F$
$d^3, d^7$	$^2P, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$
$d^4, d^6$	$^1S, ^1D, ^1F, ^1G, ^1I, ^3P, ^3D, ^3F, ^3G, ^3H, ^5D$
$d^5$	$^2S, ^2P, ^2D, ^2F, ^2G, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

Source: Bernath 1995, *Spectra of Atoms and Molecules*, Table 5.6.

[Draine, Physics of the ISM and IGM]

**Table 4.1** Terms for  $ns$  and  $np$  Subshells

Ground configuration	Terms (in order of increasing energy)	Examples
$\dots ns^1$	$^2S_{1/2}$	HI, He II, C IV, N V, O VI
$\dots ns^2$	$^1S_0$	He I, C III, N IV, O V
$\dots np^1$	$^2P_{1/2,3/2}^o$	C II, N III, O IV
$\dots np^2$	$^3P_{0,1,2}, ^1D_2, ^1S_0$	CI, N II, O III, Ne V, S III
$\dots np^3$	$^4S_{3/2}^o, ^2D_{3/2,5/2}^o, ^2P_{1/2,3/2}^o$	NI, O II, Ne IV, S II, Ar IV
$\dots np^4$	$^3P_{2,1,0}, ^1D_2, ^1S_0$	O I, Ne III, Mg V, Ar III
$\dots np^5$	$^2P_{3/2,1/2}^o$	Ne II, Na III, Mg IV, Ar IV
$\dots np^6$	$^1S_0$	Ne I, Na II, Mg III, Ar III

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

Blue: No fine structure in the ground state.

# [Hund's rules]

---

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

- (1) **S-rule:** For a given configuration, the state with the maximum spin multiplicity is lowest in energy.

The electrons repel each other, and therefore their mutual electrostatic energy is positive. The farther away the electrons get, the lower will be the contribution of the electrostatic energy to the total energy.

- (2) **L-rule:** For a given configuration and spin multiplicity, the state with the maximum orbital angular momentum is the lowest in energy.

- (3) **J-rule:** The lowest energy is obtained for lowest value of  $J$  in the normal case and for highest  $J$  value in the inverted case.

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



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

---

- Helium atom

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

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

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

This has  $l_1 = l_2 = 0$  and hence  $L = 0$ ,  
but  $s_1 = s_2 = \frac{1}{2}$  giving both  $S = 0$  (singlet) or  $S = 1$  (triplet) states. The energy ordering of atomic states is given by Hund's rules. Hund's first rule governs ordering of terms with different spin multiplicities:

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

So the  ${}^3S$  term ( ${}^3S_1$  level) is lower in energy than the  ${}^1S$  term ( ${}^1S_0$  level). In practice the splitting between these terms is 0.80 eV.

- (3) The next excited configuration is  $1s2p$ , which has odd parity.

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

Following the rule above, the  ${}^3P^o$  term is lower than the  ${}^1P^o$  term,  
in this case by 0.25 eV. The  ${}^3P^o$  is also split into three levels:  ${}^3P_0^o$ ,  ${}^3P_1^o$   
and  ${}^3P_2^o$ .

- O III

Consider O III with the configuration:  $1s^2 2s^2 2p3d$ .

$1s^2$  and  $2s^2$  are closed, so contribute no angular momentum.

For the  $2p$  electron  $l_1 = 1$  and  $s_1 = \frac{1}{2}$ ;

for the  $3d$  electron  $l_2 = 2$  and  $s_2 = \frac{1}{2}$ .

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

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

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

$J = \underline{L} + \underline{S} \Rightarrow$	$L$	$S$	$J$	Level
	1	0	1	${}^1P_1^o$
	1	1	0, 1, 2	${}^3P_0^o, {}^3P_1^o, {}^3P_2^o$
	2	0	2	${}^1D_2^o$
	2	1	1, 2, 3	${}^3D_1^o, {}^3D_2^o, {}^3D_3^o$
	3	0	3	${}^1F_3^o$
	3	1	2, 3, 4	${}^3F_2^o, {}^3F_3^o, {}^3F_4^o$

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

=> 6 terms and 12 levels

# [Selection Rules]

---

- **Selection Rules**

Laporte rule: All electric dipole transitions connect states of opposite parity.

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

- (1) For electric dipole transitions, Rules 1, 2 and 3 must always be obeyed. e.g., C IV 1548, 1550 Å
- (2) Intercombination lines violate rule 4. e.g., C III] 1908.7 Å
- (3) Forbidden lines violate rule 5 and/or 6. Electric quadrupole and magnetic dipole transitions are also described as forbidden. e.g., [N II] 6585 Å, [S II] 6716 Å, [C II] 157 μm

Electric dipole	Electric quadrupole	Magnetic dipole
1. $\Delta J = 0, \pm 1$ Not $J = 0 - 0$	$\Delta J = 0, \pm 1, \pm 2$ Not $J = 0 - 0, \frac{1}{2} - \frac{1}{2}, 0 - 1$	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$
2. $\Delta M_J = 0, \pm 1$	$\Delta M_J = 0, \pm 1, \pm 2$	$\Delta M_J = 0, \pm 1$
3. Parity changes	Parity unchanged	Parity unchanged
4. $\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
5. One electron jumps $\Delta n$ any $\Delta l = \pm 1$	One or no electron jumps $\Delta n$ any $\Delta l = 0, \pm 2$	No electron jumps $\Delta n = 0$ $\Delta l = 0$
6. $\Delta L = 0, \pm 1$ Not $L = 0 - 0$	$\Delta L = 0, \pm 1, \pm 2$ Not $L = 0 - 0, 0 - 1$	$\Delta L = 0$

# [Alkali Atoms]

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

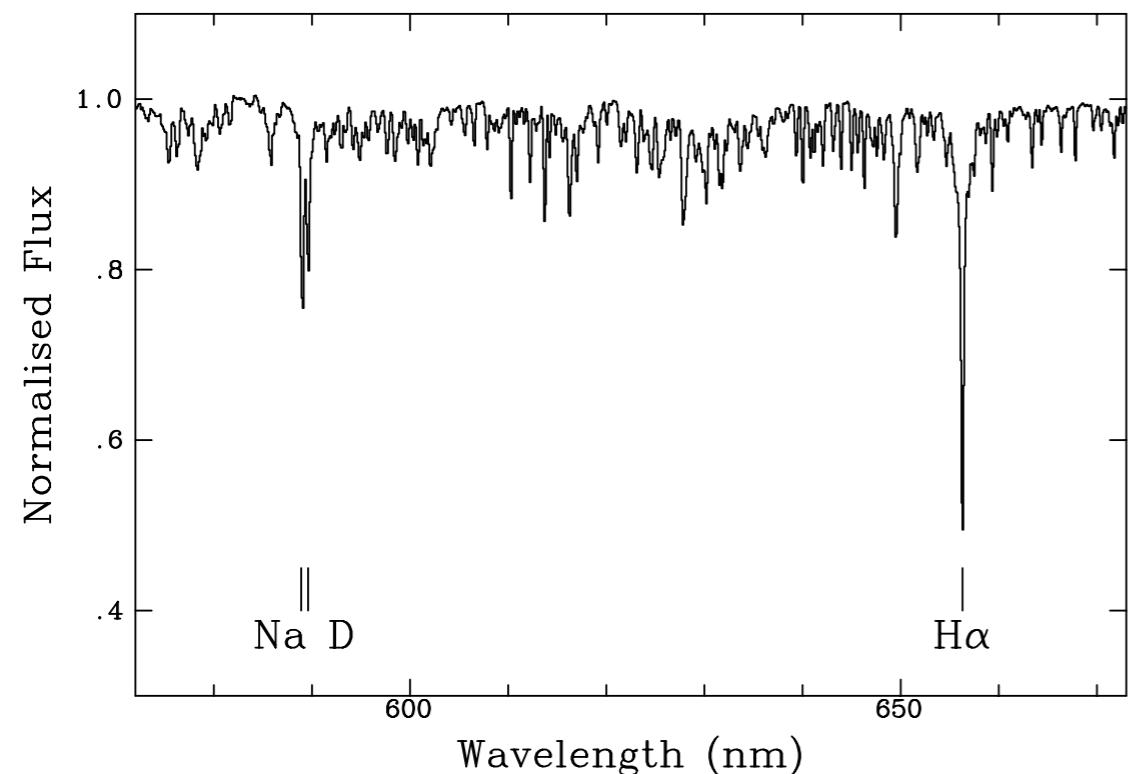
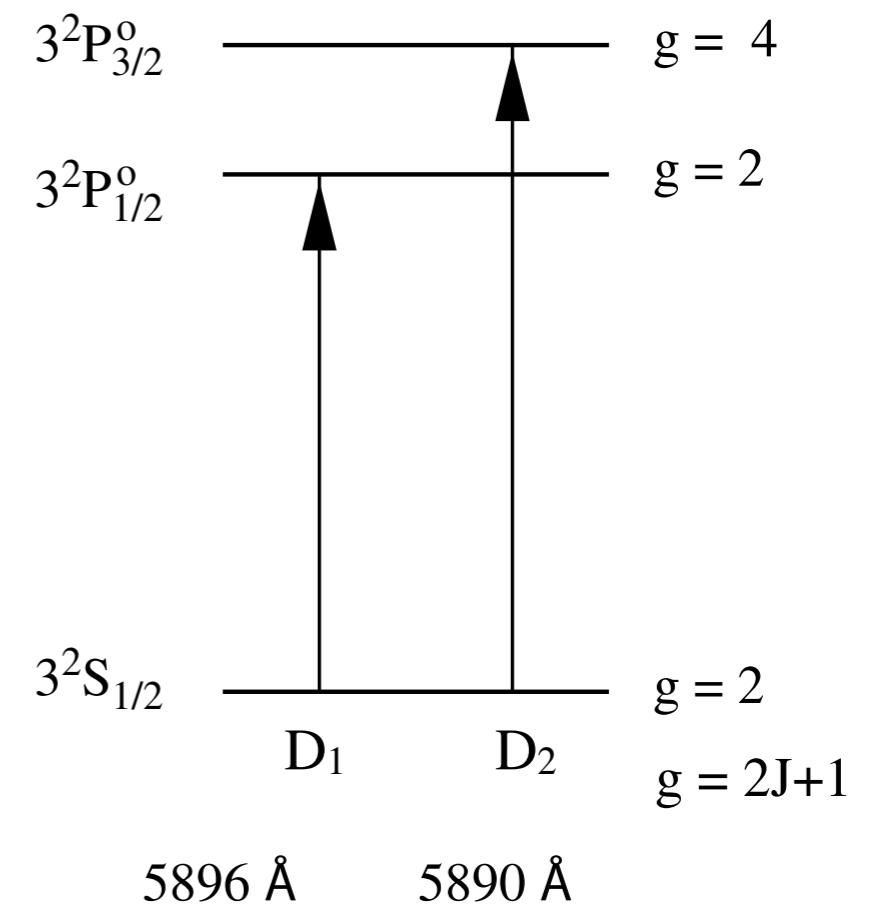


Fig. 6.6. A solar spectrum reflected from the Moon just before a lunar eclipse taken at the University of London Observatory. (S.J. Boyle, private communication.)



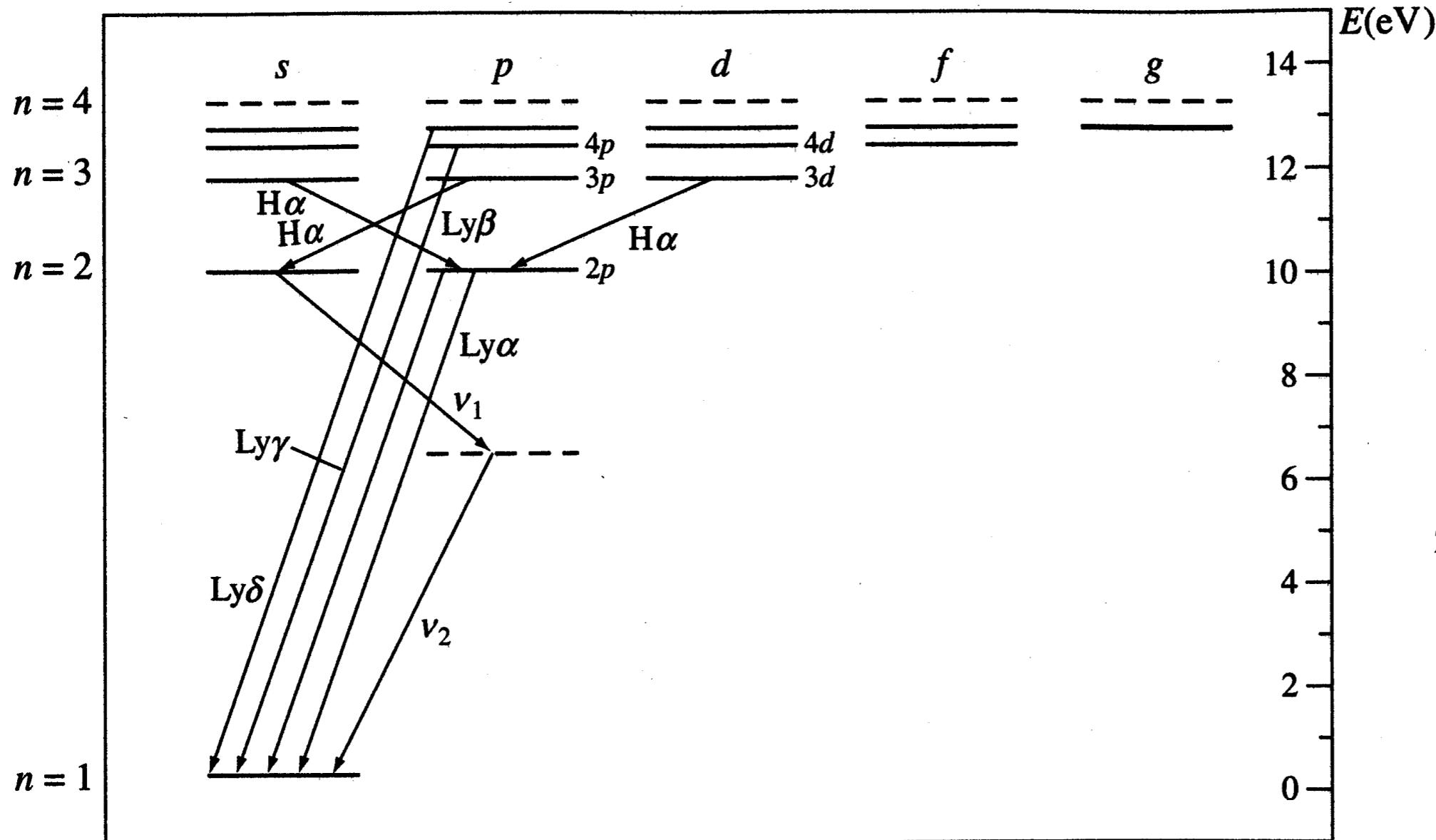
Na D lines:

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

- 
- Ca II (potassium-like calcium)
    - H 3968.47 Å line :  $4\ ^2S_{1/2} - 4\ ^2P_{1/2}^o$
    - K 3933.66 Å line :  $4\ ^2S_{1/2} - 4\ ^2P_{3/2}^o$
  - Mg II (sodium-like magnesium)
    - 2802.7 Å line :  $3\ ^2S_{1/2} - 3\ ^2P_{1/2}^o$
    - 2795.5 Å line :  $3\ ^2S_{1/2} - 3\ ^2P_{3/2}^o$
  - C IV (lithium-like carbon)
    - 1550.8 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{1/2}^o$
    - 1548.2 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$
  - N V (lithium-like nitrogen)
    - 1242.8 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{1/2}^o$
    - 1238.8 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$
  - O VI (lithium-like oxygen)
    - 1037.6 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{1/2}^o$
    - 1031.9 Å line :  $2\ ^2S_{1/2} - 2\ ^2P_{3/2}^o$

# [Hydrogen]

- Hydrogen



Lyman series:

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

Balmer series:

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

Paschen series:

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

Brackett series:

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

Pfund series:

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

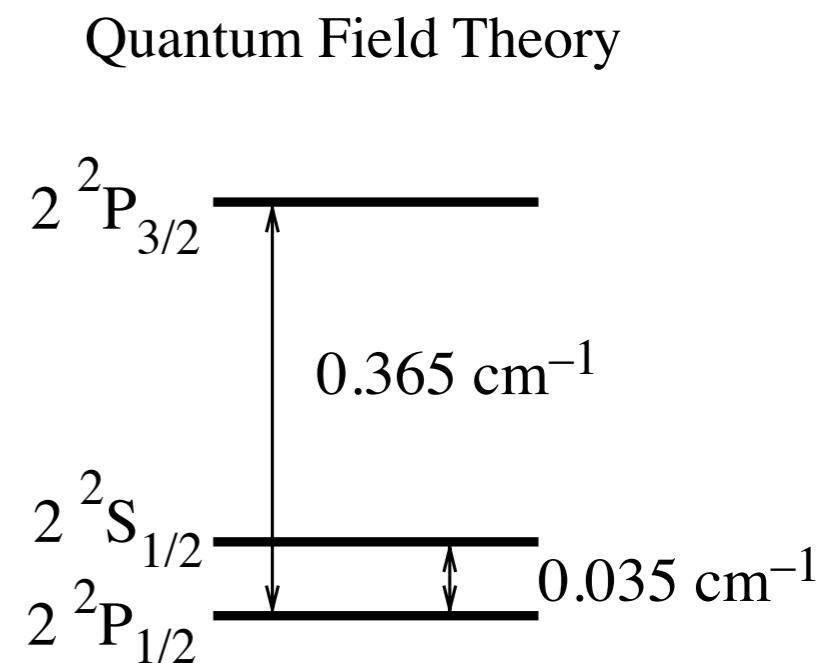
Humphreys series:

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

- Fine structure of the hydrogen atom

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

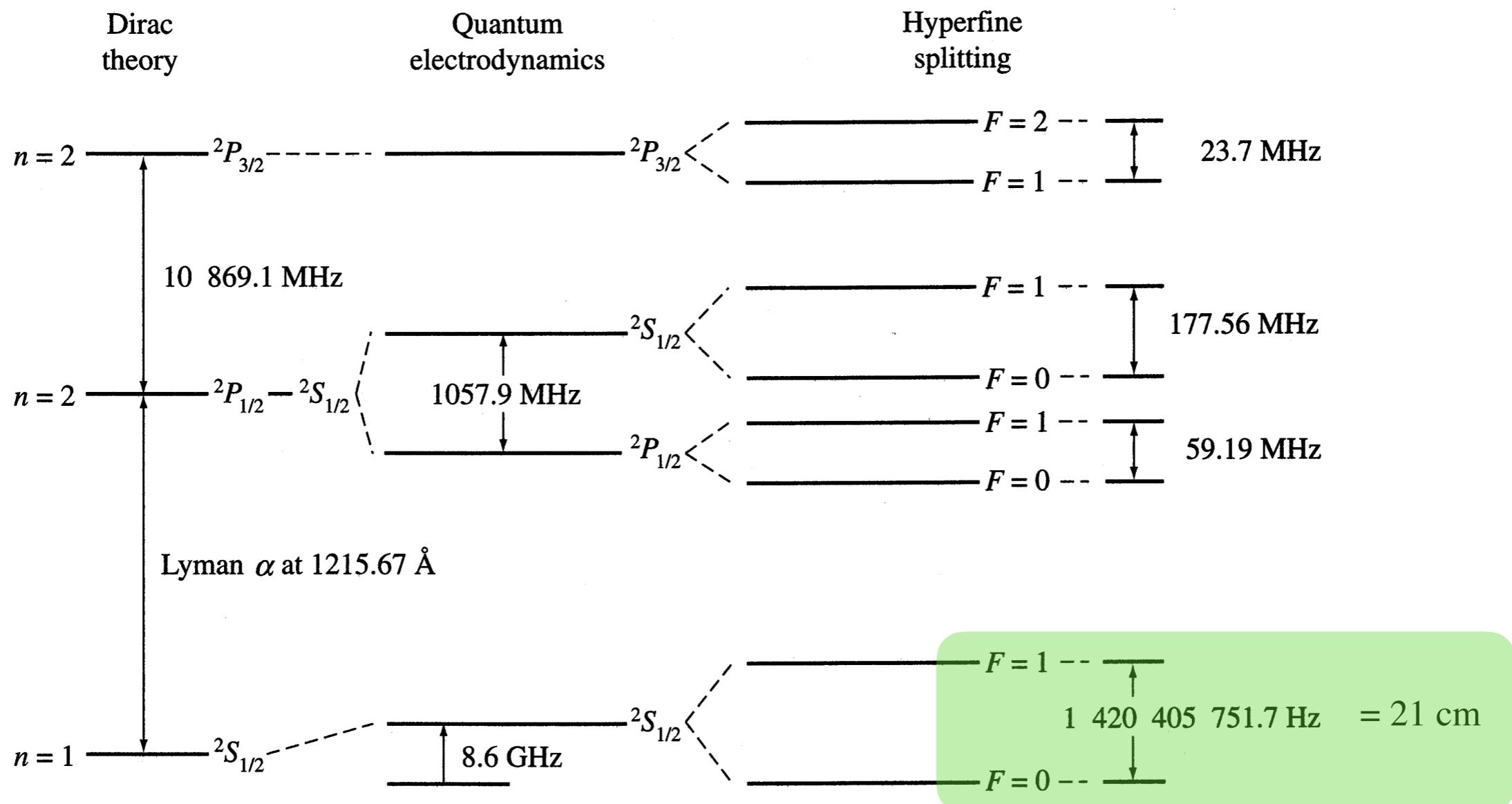
- Splitting in the  $n = 2$  levels of atomic hydrogen. The larger splitting is the fine structure and the smaller one the Lamb shift.  
According to the Dirac equation, the  $^2S_{1/2}$  and  $^2P_{1/2}$  orbitals should have the same energies. However, the interaction between the electron and the vacuum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



- Hyperfine Structure in the H atom

Coupling the nuclear spin  $I$  to the total electron angular momentum  $J$  gives the final angular momentum  $F$ . For hydrogen this means

$$F = J + I = J \pm \frac{1}{2}$$



- Hydrogen: lifetime of excited states

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

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

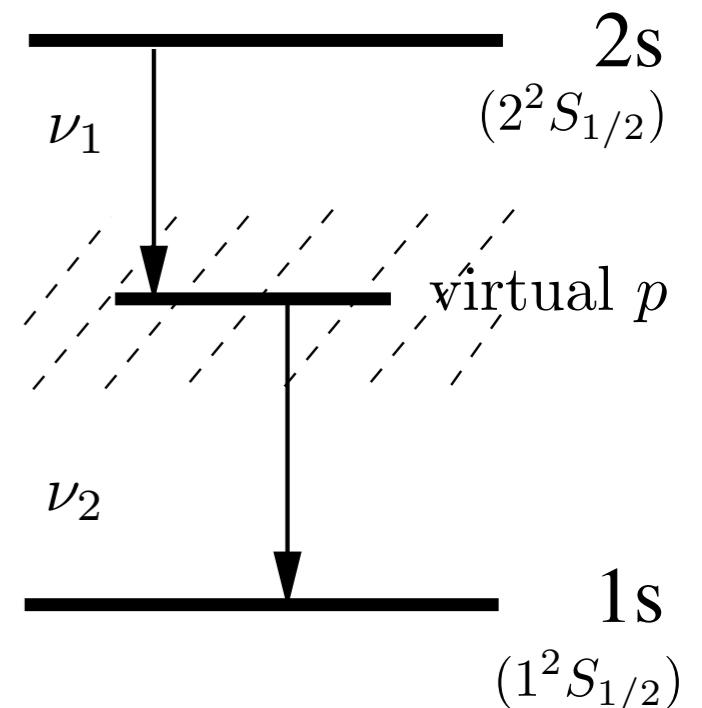
Lifetimes for allowed transitions are shown, a few times  $10^{-9}$  s.

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

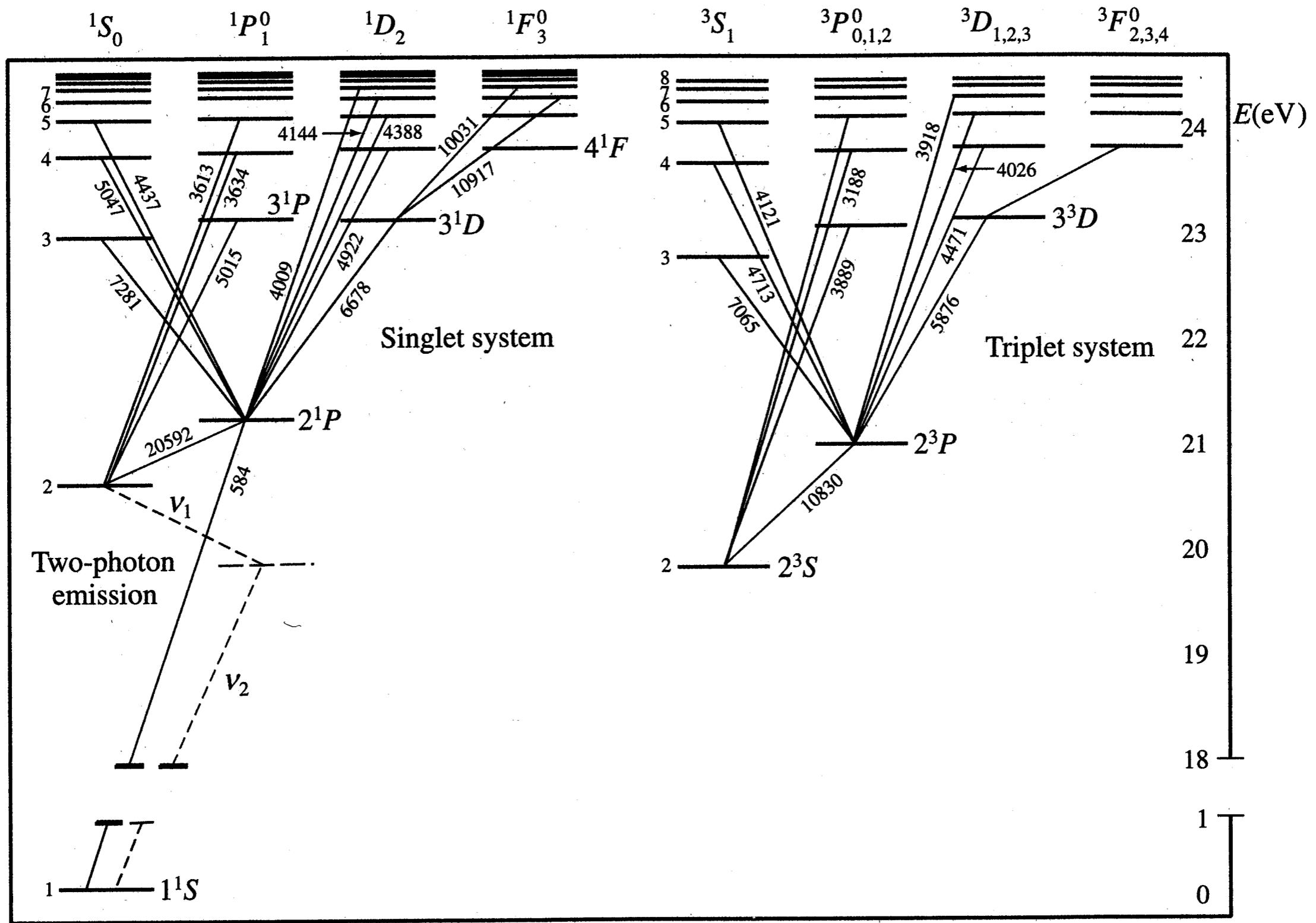
- Two-photon radiation

In low-density environments, an electron in the  $2^2S_{1/2}$  level can jump to a virtual  $p$  state, which lies between  $n = 1$  and  $n = 2$  levels. The electron then jumps from this virtual state to the ground state, in the process emitting two photons with total frequency  $\nu_1 + \nu_2 = \nu_{\text{Ly}\alpha}$ .

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



- Helium (Grotrian diagram)



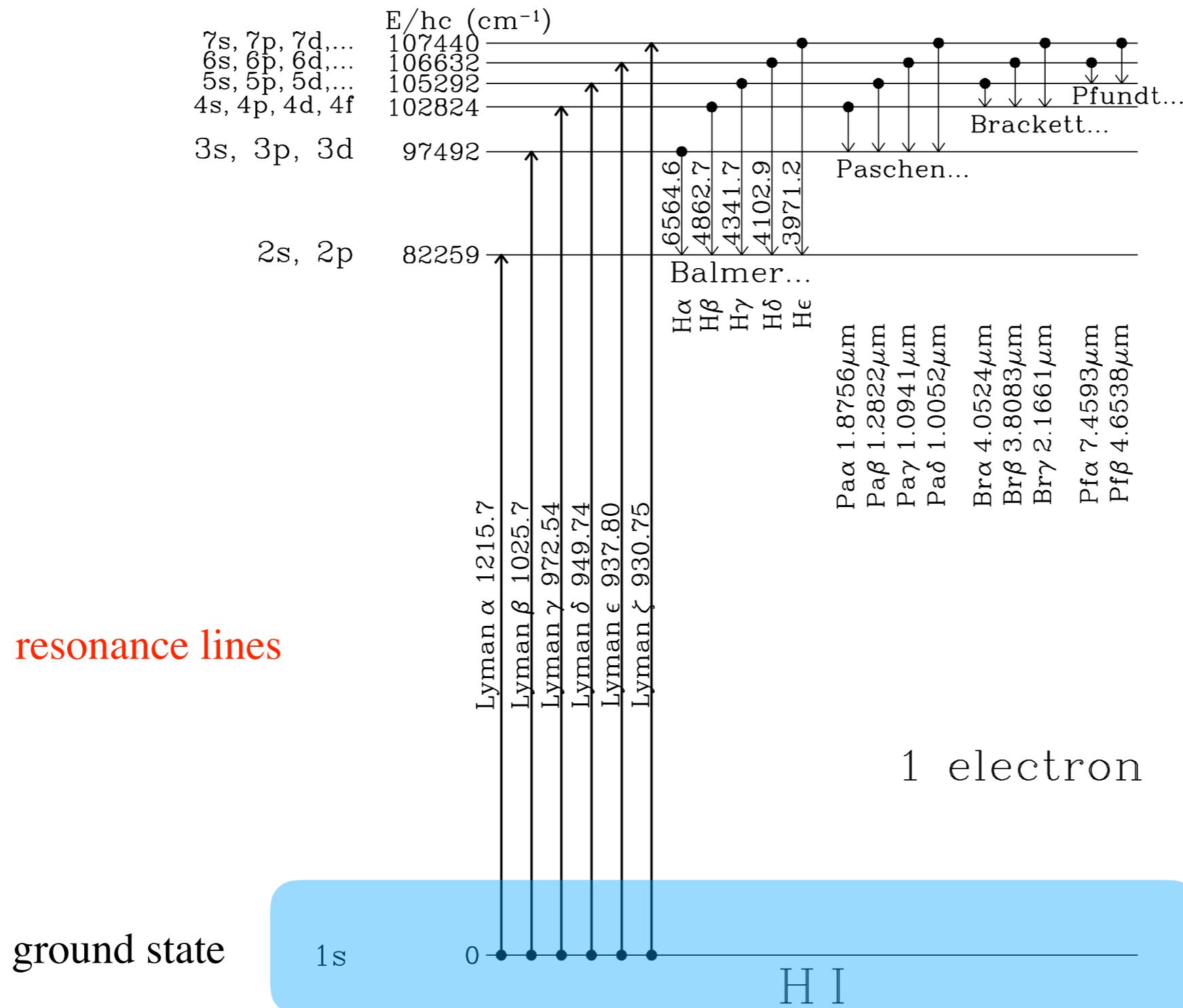
# [Notations]

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- Notations for Spectral Emission Lines and for Ions
  - There is a considerable confusion about the difference between these two ways of referring to a spectrum or ion, for example, C III or C<sup>+2</sup>. These have very definite different physical meanings and cannot be used interchangeably.
  - C<sup>+2</sup> is a baryon and C III is a set of photons.
  - C<sup>+2</sup> refers to carbon with two electrons removed, so that is doubly ionized, with a net charge of +2.
  - C III is the spectrum produced by carbon with two electrons removed. The C III spectrum will be produced by impact excitation of C<sup>+2</sup> ( $C^{+2} + e^- \rightarrow C^{+2*} + e^- \rightarrow C^{+2} + e^- + h\nu$ ) or by recombination of C<sup>+3</sup> ( $C^{+3} + e^- \rightarrow C^{+2} + h\nu$ ). So, depending on how the spectrum is formed. C III may be emitted by C<sup>+2</sup> or C<sup>+3</sup>.
  - There is no ambiguity in absorption line studies - only C<sup>+2</sup> can produce a C III absorption line. This had caused many people to think that C III refers to the matter rather than the spectrum. But this notation is ambiguous in the case of emission lines.

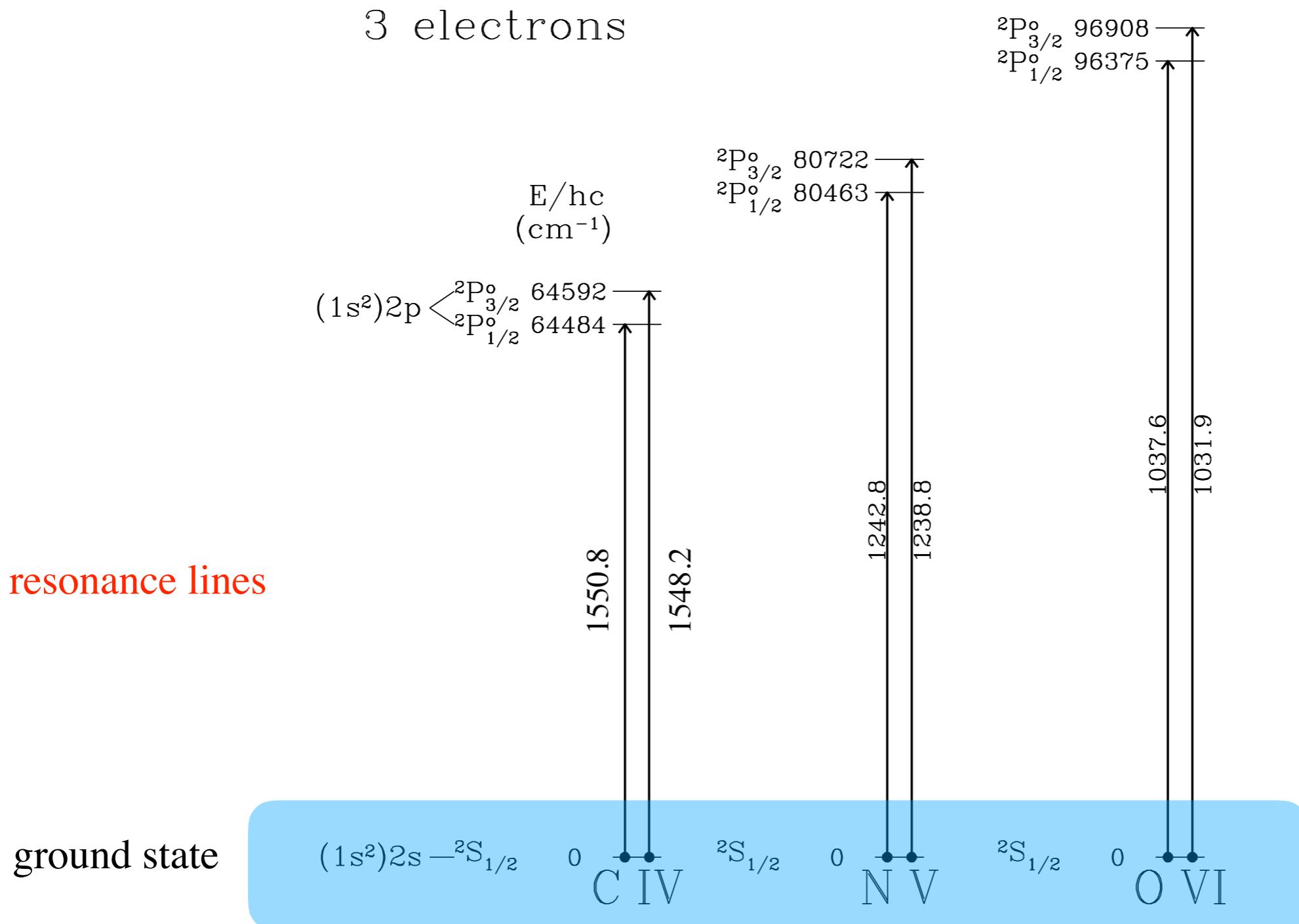
# [Energy Level Diagrams]

- 1 electron



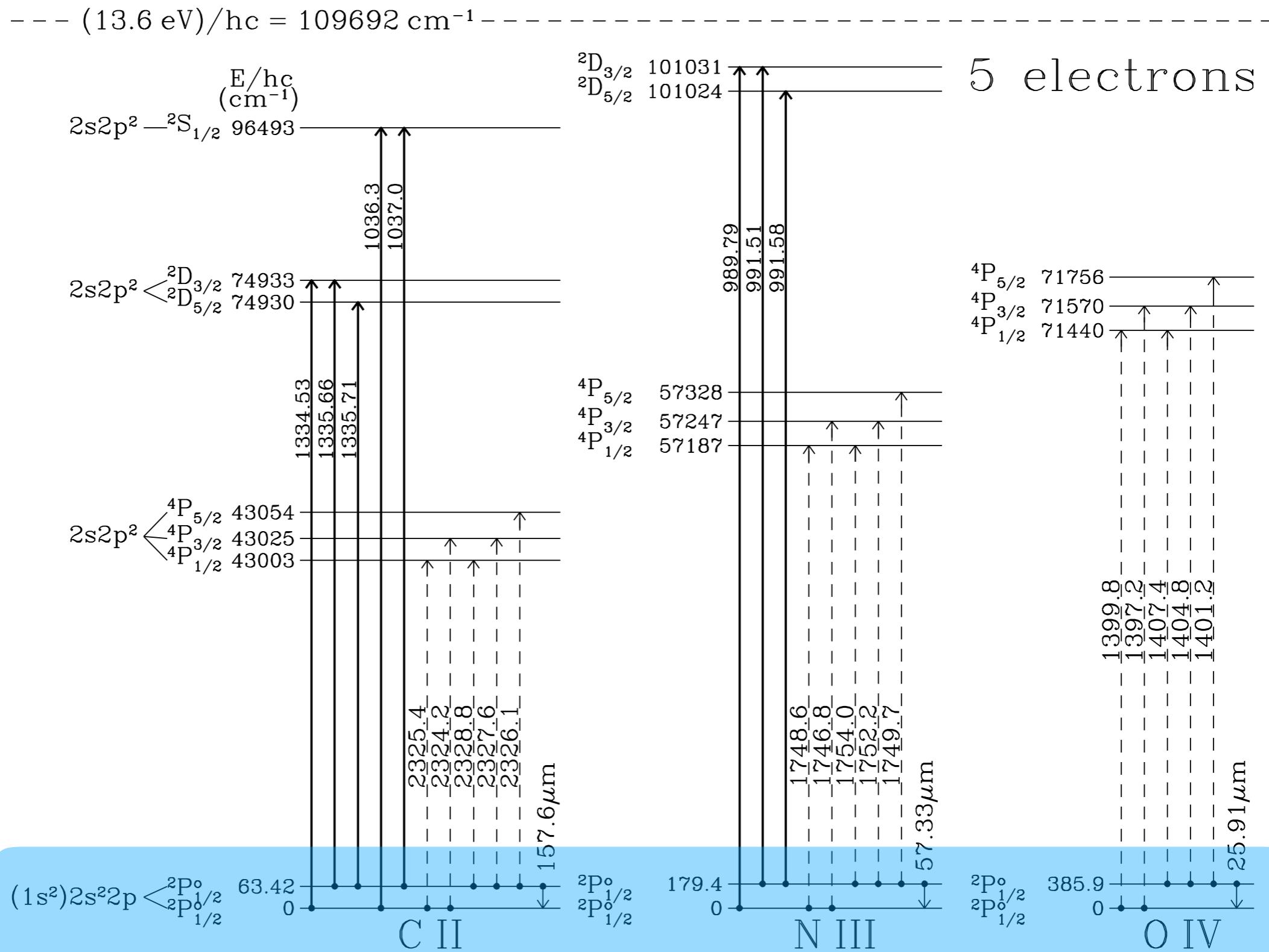
- 3 electrons (Lithium-like ions)

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



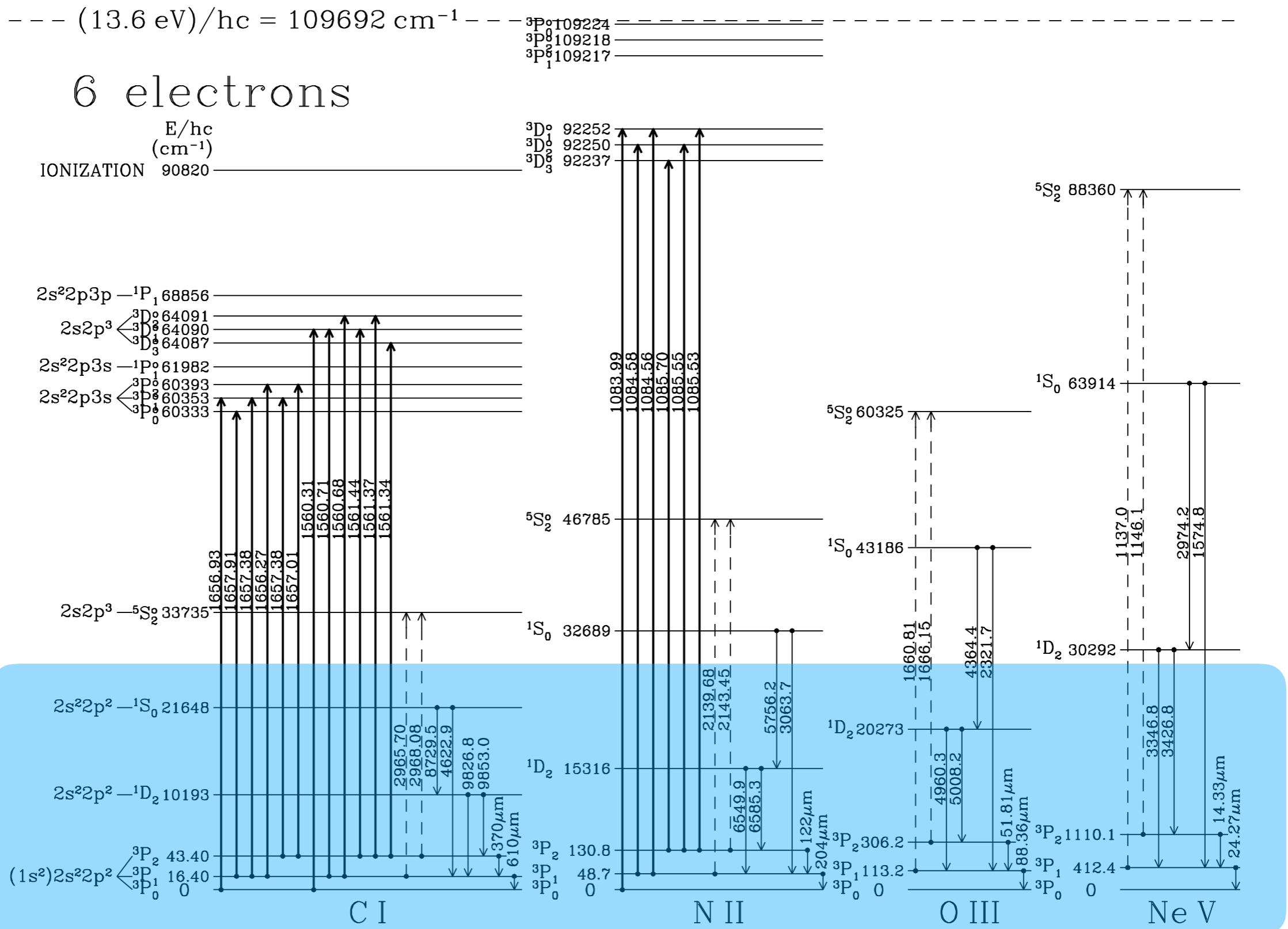
- 5 electrons

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



- 6 electrons

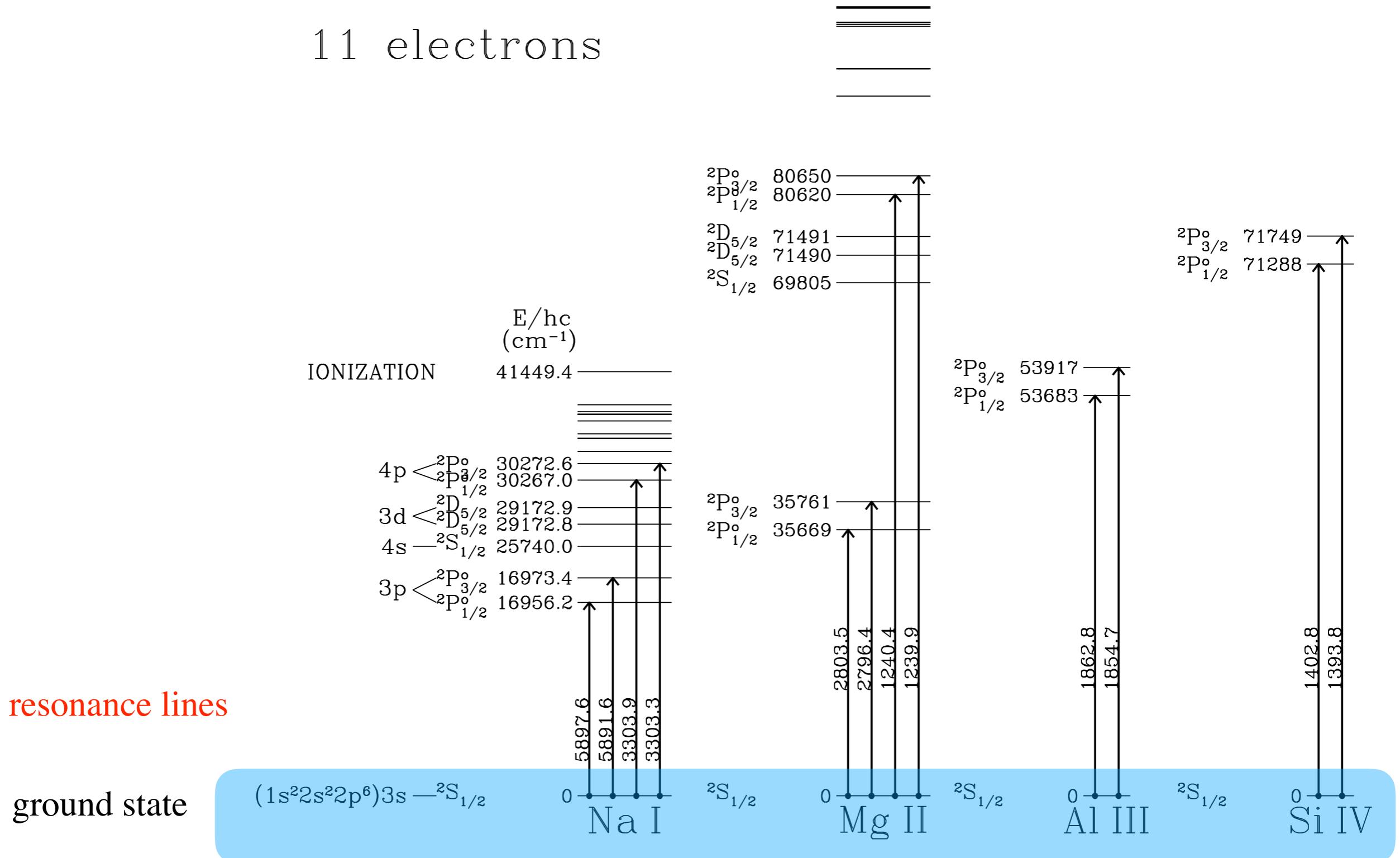
Upward heavy: resonance, Upward Dashed: intercombination  
Downward solid: forbidden



- 11 electrons

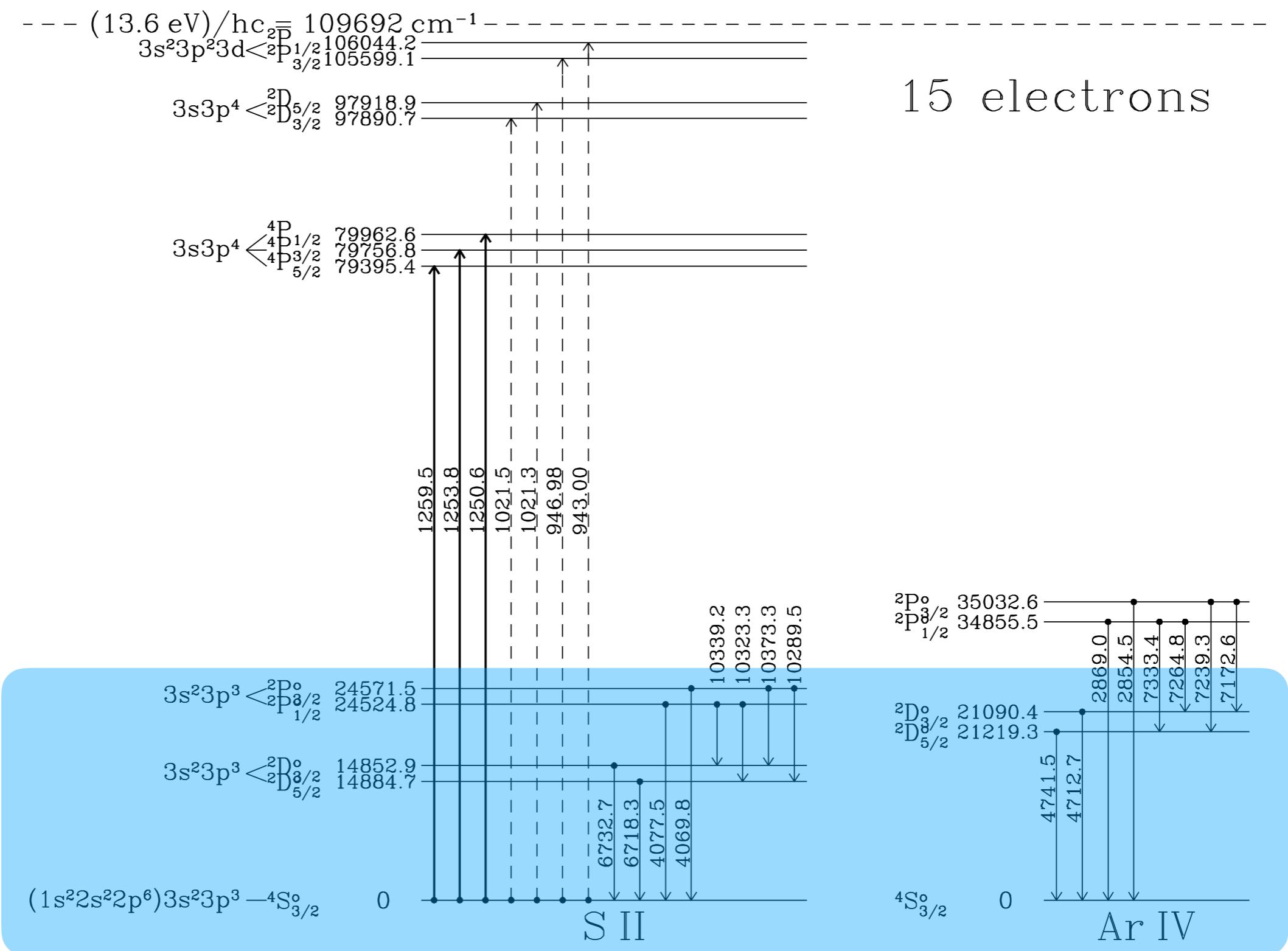
$$--- \frac{(13.6 \text{ eV})}{\hbar c} = 109692 \text{ cm}^{-1} ---$$

11 electrons



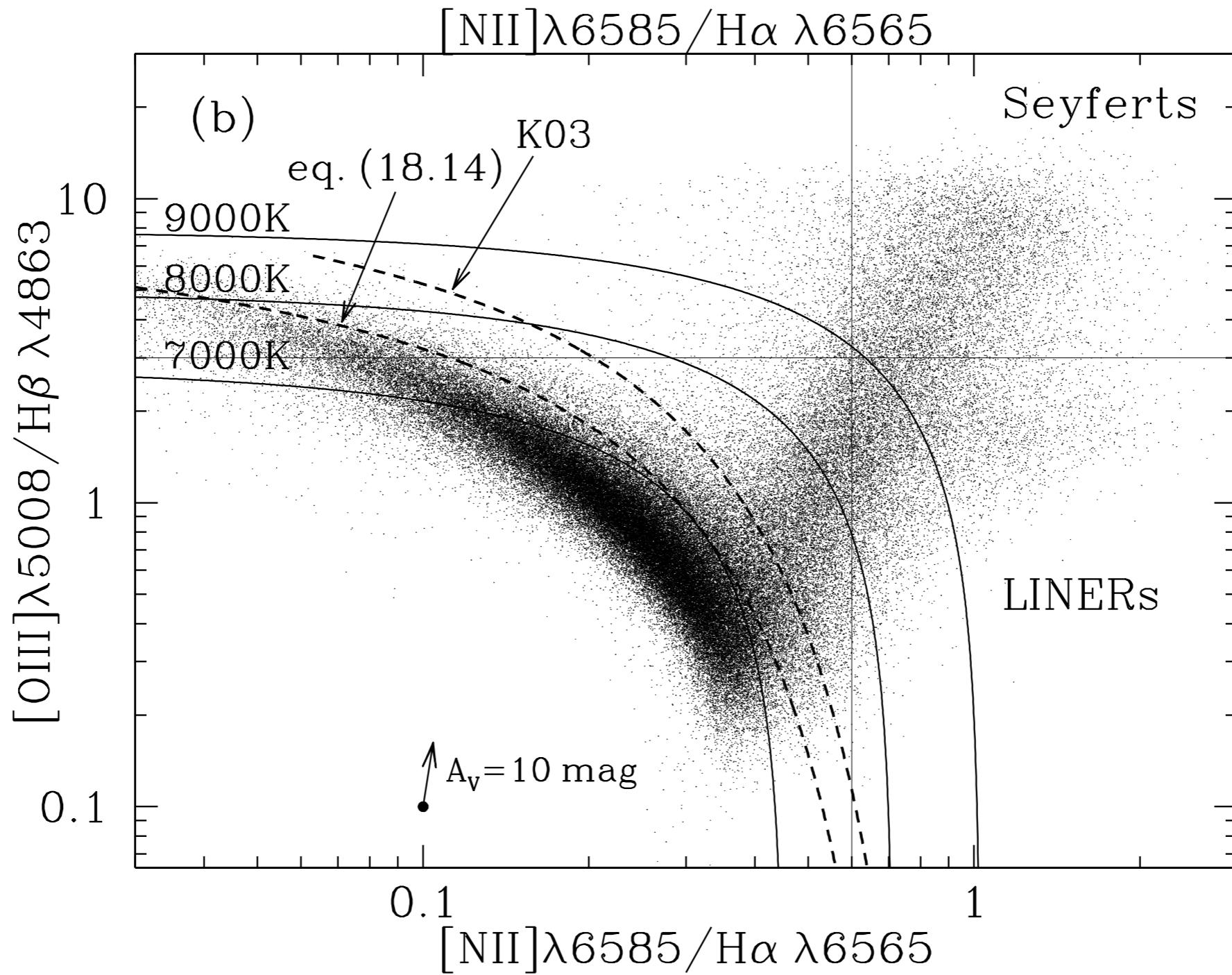
- 15 electrons

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



- BPT diagram

Baldwin, Phillips & Terlevich (1981, PASP, 93, 5)



- 
- Configurations

## Terms

Fine Structure (Spin-Orbit Interaction)

Hyperfine Structure (Interaction with Nuclear Spin)

- Zeeman Effect:

When a static magnetic field  $\mathbf{B}_0$  is applied, each of the fine-structure levels  $\mathcal{L}_J$  splits into  $2J+1$  energy levels, with energies depending on the value of  $\mathbf{J} \cdot \mathbf{B}_0$ . The energy splittings are small, of order  $\mu_B B_0 \approx 5.78 \times 10^{-15} (B_0 / \mu\text{G}) \text{ eV}$ , where  $\mu_B \equiv e\hbar/2m_e c$  is the **Bohr magneton**. Interstellar magnetic field strengths are of order  $1 - 100 \mu\text{G}$ , and therefore the Zeeman shifts are too small to be measured for transitions in the sub-mm or shortward ( $h\nu \gtrsim 10^{-4} \text{ eV}$ ).

However, in the case of atomic hydrogen, the hyperfine splitting gives rise to the 21-cm transition, with an energy  $h\nu = 5.9 \times 10^{-6} \text{ eV}$ , and, therefore, an applied field of order  $10 \mu\text{G}$  shifts the frequency by about one part in  $10^8$ . This shift is much smaller than the frequency shift  $v/c \sim 10^{-5}$  due to a radial velocity of a few  $\text{km s}^{-1}$ , and it would be nearly impossible to detect, except that it leads to a shift in frequency between the two circular polarization modes. The Zeeman effect in HI 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 HI regions.

# [Atomic Processes]

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- **Ionization**
  - Photoionization and Auger-ionization
  - Collisional Ionization (Direct ionization and Excitation-autoionization)
- **Recombination**
  - Radiative recombination  $\Leftrightarrow$  Photoionization
  - Dielectronic Recombination (not dielectric!)
  - Three-body recombination  $\Leftrightarrow$  Direct collisional ionization
- **Charge exchange**
- **Excitation and de-excitation**
  - Collisional excitation
  - Collisional de-excitation
  - Radiative de-excitation (spontaneous emission)

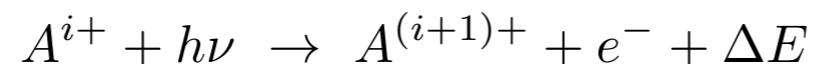
# [Photoionization]

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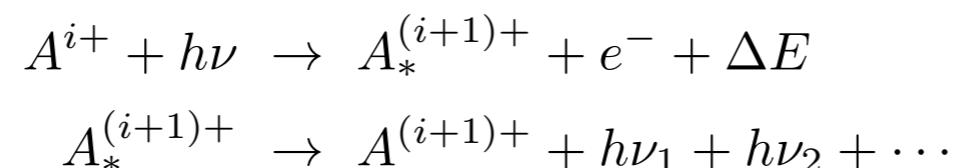
- Interstellar medium (ISM) is transparent to  $h\nu < 13.6$  eV photons, but is very opaque to ionizing photons. In fact, the ISM does not become transparent until  $h\nu \sim 1$  keV.

Sources of ionizing photons include massive, hot young stars, hot white dwarfs, and supernova remnant shocks.

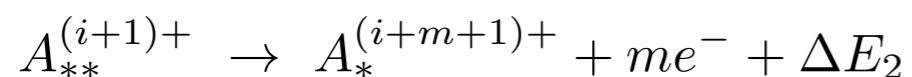
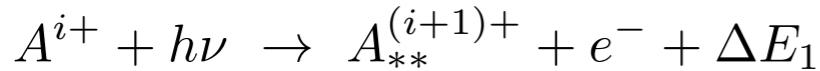
- From the Outer Shells
  - Photoionization is the inverse process to radiative recombination.



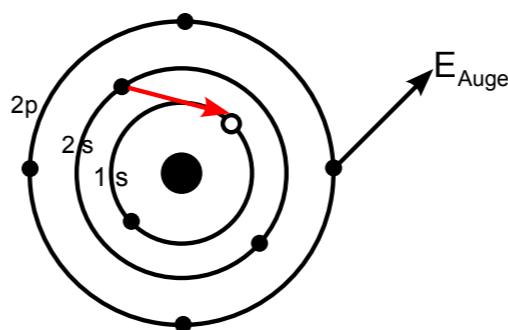
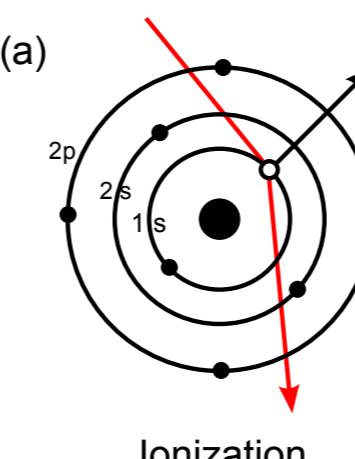
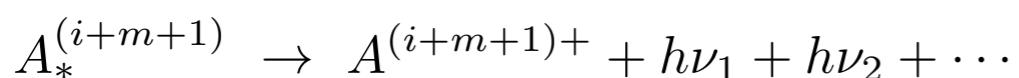
- If the incoming photon has sufficient energy, it may leave the ionized species in an excited state.



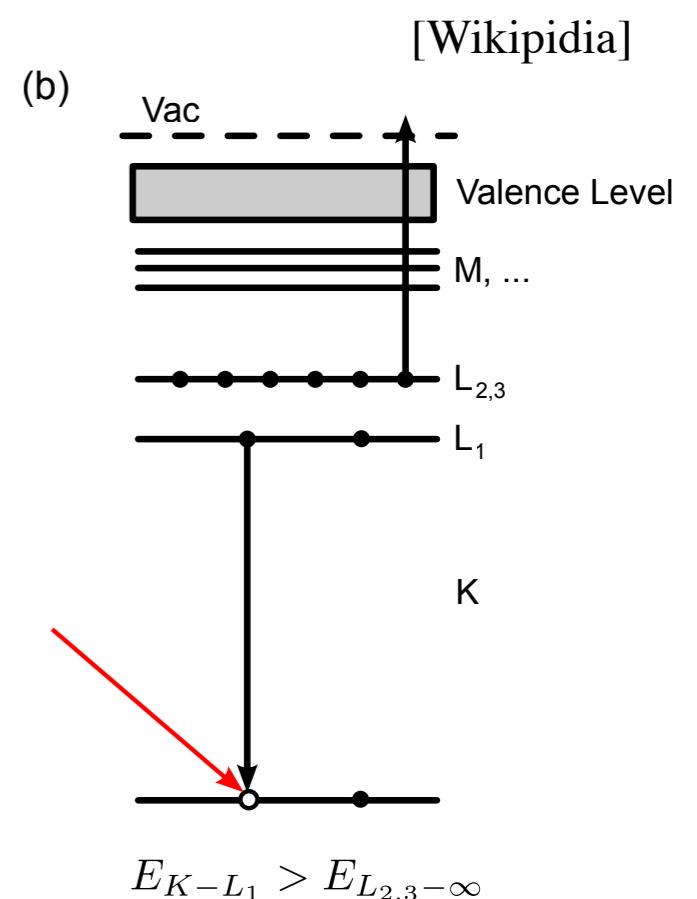
- Inner Shell Photoionization
  - If the energy of the incoming photon still higher, it becomes possible to remove one of the inner shell electrons which also results in a change in the electron configuration in the excited species. This may be followed by a radiative readjustment back to the ground state.
  - However, in this case, **Auger ionization** becomes more probable. High frequency photons may eject an inner shell electron from an ion or atom, and the resulting ion may then fill the gap in its inner shell with an outer electron, ejecting another outer electron to remove the energy in a radiationless transition called an Auger transition. Such a process will produce very energetic electrons which will lose their energy in heating up the gas.



(radiationless autoionization,  $m \geq 1$ )

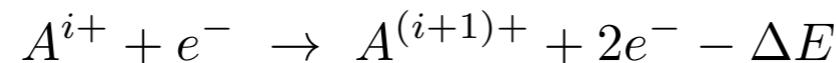


Auger electron emission

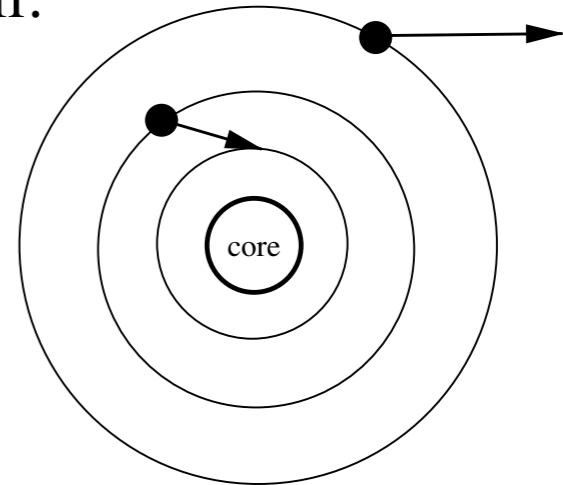
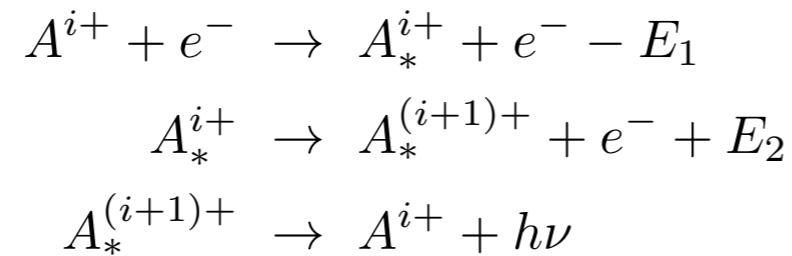


# [Collisional ionization]

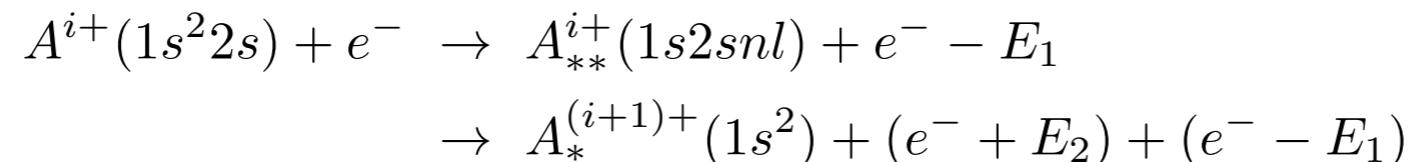
- Direct collisional ionization: The process whereby an electron strikes an ion  $A$  (with charge  $i+$ ), with sufficient energy to strip out a bound electron:



- Excitation-autoionization: At sufficiently high electron impact energies, more than one electron of the target nucleus may be excited, leaving the atom in an unstable state, which is stabilized by the radiationless ejection of an electron, possibly followed by a radiative decay of the ionized atom back to its ground state. This process is favored in heavy elements which have a large number of inner shell electrons and only one or two electrons in the outer shell.



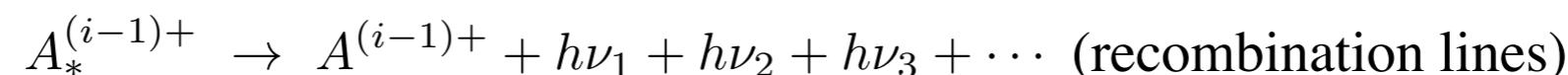
- For example, in collisions of Li-like ions, excitation and autoionization can occur via excitation of the 1s-electron into states with principal quantum numbers  $n \geq 2$ . After the decay of a doubly excited state, one has an additional electron in the final channel.



# [Recombination]

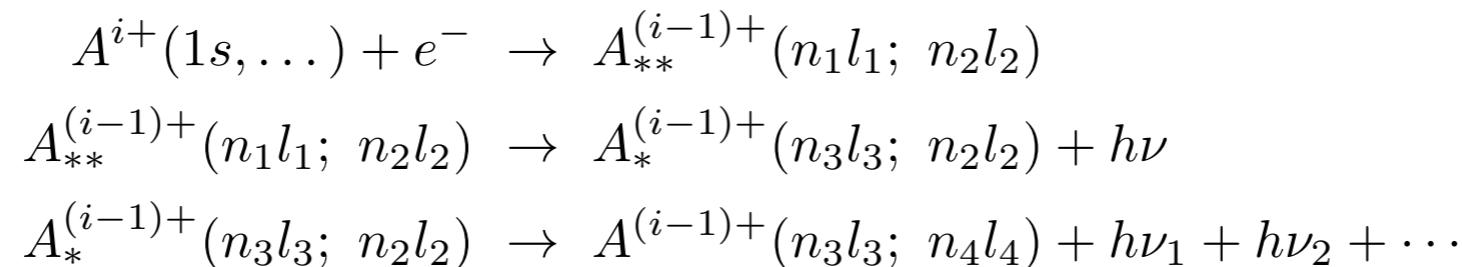
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- Radiative recombination
  - Radiative recombination is the process of capture of an electron by an ion where the excess energy is radiated away in a photon.
  - The electron is captured into an excited state. The recombined but still excited ion radiates several photons in a radiative cascade, as it returns to the ground state:



- The photon in the first line represents a **recombination continuum** ( $h\nu$ ) photon. However, photons ( $h\nu_1, h\nu_2, h\nu_3$ ) represent quantized transitions and are therefore termed **recombination lines**.
- The total effective recombination rate can be written as the sum of the recombination rate to each state.

- 
- Dielectronic recombination
    - Dielectronic recombination (DR) is a resonant two-step process in which a few electron is captured by the incident ion into an autoionizing state followed by a stabilizing radiation decay of the resulting ion in the second step. The DR is often more important than radiative recombination.

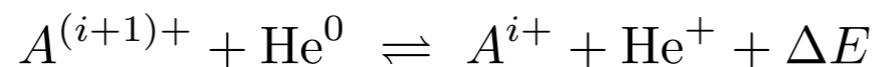
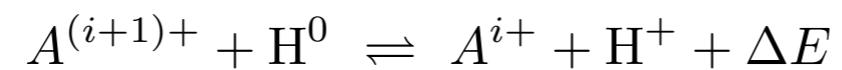


- The first step is a double-electron process, often called dielectronic capture, through which one free electron is captured and another core electron is simultaneously excited forming a doubly excited state. One of the electron is in an autoionizing state,  $n_1 l_1$ , and the other is in an excited state,  $n_2 l_2$ . In the second step, the ion in a doubly excited state emits a photon and decays into a stable state below the ionization limit.
- There is a competitive process for the decay of the doubly excited ion. - the autoionization or Auger decay associated not with the radiative transition but with a change in ion charge.

## [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]

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- 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.
- Photoionization Equilibrium:
  - dynamic balance between photo-ionization and the process of recombination.
- Ionization balance under conditions of local thermodynamic equilibrium (LTE)
  - The ionization equilibrium in LTE is described by the Saha equation.
  - In LTE, the excited states are all populated according to Boltzmann's law.

# [Collisional Excitation]

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- Under the conditions of very low density and weak radiation fields,
  - The vast majority of the atoms reside in the ground state.  
collisional excitation timescale  $\gg$  radiative decay time scale  
This condition will remain true even if the excited state has a radiative lifetime of several second, which is frequently the case for the forbidden transitions observed in ionized astrophysical plasmas.
  - flux of an emission line  $\propto$  flux number of collisions  $\propto$  product of the number densities of the two colliding species by the probability that a collision will produce a collisional excitation.
  - If the energy gap between the ground state and the excited state  $E_{12}$  is much larger than the mean energy of the colliding species ( $\sim T$ ), then, because there are few very energetic collisions, relatively few collisional excitations can occur. Therefore, the resulting emission line will be very much weaker than when  $E_{12} < kT$ .  
This gives us the possibility of measuring temperature from the relative strengths of lines coming from excited levels at different energies above the ground state.

- 
- At high enough densities,
    - The collisional timescales are short.
    - The population in any upper level is set by the balance between collisional excitation, and the collisional de-excitation out of these levels, and are governed by the Boltzmann equilibrium.
  - At intermediate densities,
    - The collisional rates and the radiative decay rates are compatible.
    - The intensity of an emission line is determined by both the temperature and the density.
    - If the temperature is known, the density can be determined from the intensity ratio of two such lines.

# [Collisional Rate]

---

- **Collisional Rate (Two Level Atom)**

- The collisional cross section is in general varying approximately inversely as the impact energy (because of the focusing effect of the Coulomb force).

$$\begin{aligned}\sigma_{12}(v) &= (\pi a_0^2) \left( \frac{hR}{\frac{1}{2}m_e^2 v^2} \right) \frac{\Omega_{12}}{g_1} \text{ cm}^2 \quad \text{for } \frac{1}{2}m_e^2 v^2 > E_{12} \\ &= \frac{\pi \hbar^2}{m_e^2 v^2} \frac{\Omega_{12}}{g_1}\end{aligned}$$

$$\text{or } \sigma_{12}(E) = \frac{h}{8\pi m_e E} \frac{\Omega_{12}}{g_1}$$

where,  $a_0 = \frac{h^2}{m_e c^2} = 5.12 \times 10^{13}$  cm, Bohr radius

$$R = \frac{m_e e^4}{4\pi \hbar^3} = 109,737 \text{ cm}^{-1}, \text{ Rydberg constant}$$

- The collision strength  $\Omega_{12}$  is a function of electron velocity (or energy) but is often approximately constant near the threshold.  $g_1$  is the statistical weight of the lower level.

- 
- Advantage of using the collision strength
    - ◆ It removes the primary energy dependence for most atomic transitions.
    - ◆ The symmetry between the upper and the lower states.

Using the principle of detailed balance, which states that in thermodynamic equilibrium each microscopic process is balanced by its inverse.

$$n_e n_1 v_1 \sigma_{12}(v_1) f(v_1) dv_1 = n_e n_2 v_2 \sigma_{21}(v_2) f(v_2) dv_2$$

where  $v_1$  and  $v_2$  are related by  $\frac{1}{2}m_e v_1^2 = \frac{1}{2}m_e v_2^2 + E_{12}$ , and using the Boltzmann equation of thermodynamic equilibrium,

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{kT}\right)$$

we derive the following relation

$$g_1 v_1^2 \sigma_{12}(v_1) = g_2 v_2^2 \sigma_{21}(v_2)$$

and the symmetry of the collision strength between levels.

$$\Omega_{12} = \Omega_{21}$$

- 
- Collisional excitation and de-excitation rates

If  $\Omega_{21}$  is a constant, the total collisional de-excitation rate per unit volume per unit time is

$$\begin{aligned}
 R_{21} &= n_e n_2 q_{21} \\
 &= n_e n_2 \int_0^\infty v \sigma_{21}(v) f(v) dv \\
 &= n_e n_2 \left( \frac{2\pi\hbar^4}{km_e^2} \right)^{1/2} T^{-1/2} \frac{\Omega_{21}}{g_2} \\
 &= n_e n_2 \frac{8.62942 \times 10^{-6}}{T^{1/2}} \frac{\Omega_{21}}{g_2} \text{ cm}^{-3} \text{ s}^{-1},
 \end{aligned}$$

and the collisional excitation rate per unit volume per unit time is  $R_{12} = n_2 n_1 q_{12}$ , where

$$\begin{aligned}
 q_{12} &= \int_0^\infty v \sigma_{12}(v) f(v) dv \\
 &= \left( \frac{2\pi\hbar^4}{km_e^2} \right)^{1/2} T^{-1/2} \frac{\Omega_{12}}{g_1} \exp\left(-\frac{E_{12}}{kT}\right) \\
 &= \frac{g_2}{g_1} q_{21} \exp\left(-\frac{E_{12}}{kT}\right)
 \end{aligned}$$

- 
- Quantum mechanical sum rule for collision strengths for the case where one term consists of a single level and the second consists of a multiplet, if either  $S = 0$  or  $L = 0$ ,

$$\Omega_{(SLJ, S'L'J')} = \frac{(2J' + 1)}{(2S' + 1)(2L' + 1)} \Omega_{(SL, S'L')}$$

Here,  $(2J'+1)$  is the statistical weight of an individual level in the multiplet, and  $(2S'+1)(2L'+1)$  is the statistical weight of the multiplet. We can regard the collision strength as “shared” amongst these levels in proportion to the statistical weights of the individual levels ( $g_J = 2J+1$ ).

- ♦ C-like ions ( $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s^2 2p^2$ ) forbidden or inter combination transitions.

ground states (triplet) -  ${}^3P_0 : {}^3P_1 : {}^3P_2 = 1 : 3 : 5$

excited states (singlets) -  ${}^1D_2, {}^1S_1$

- ♦ Li-like ions ( $1s^2 2s^1 \rightarrow 1s^2 2p^1$ ) resonance transitions

ground state (singlet) -  ${}^2S_{1/2}$

excited states (doublet) -  ${}^2P_{3/2} : {}^2P_{1/2} = 2 : 1$

- 
- Limiting Cases
    - ♦ In the low density limit, the collisional rate between atoms and electrons is much slower than the radiative de-excitation rate of the excited level. Thus, we can balance the collisional feeding into level 2 by the rate of radiative transition back down to level 1. The collision rate is

$$R_{12} = A_{21} n_2$$

$$n_2 = \frac{n_e n_1 q_{12}}{A_{21}}$$

where  $A_{21}$  is the Einstein coefficient for spontaneous emission. Emission line flux is

$$F_{21} = E_{12} A_{21} n_2 = E_{12} R_{12}$$

$$= n_e n_1 E_{12} \frac{8.62942 \times 10^{-6}}{T^{1/2}} \left( \frac{\Omega_{12}}{g_1} \right) \exp \left( -\frac{E_{12}}{kT} \right) \text{ erg cm}^{-3} \text{ s}^{-1}$$

$$\simeq \chi n_e^2 \beta E_{12} T^{-1/2} \left( \frac{\Omega_{12}}{g_1} \right) \exp \left( -\frac{E_{12}}{kT} \right)$$

For low temperature, the exponential term dominates. At high temperature, the  $T^{-1/2}$  term controls the cooling rate.

- 
- ♦ In high-density limit, the level population are set by the Boltzman equilibrium,

$$\begin{aligned}
 F_{21} &= E_{12} A_{21} n_2 \\
 &= n_1 E_{12} A_{21} \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{kT}\right) \\
 &\simeq \chi n_e E_{12} A_{21} \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{kT}\right)
 \end{aligned}$$

- ♦ Critical density defined as the density where the radiative depopulation rate matches the collisional de-excitation for the excited state.

$$\begin{aligned}
 A_{21} n_2 &= R_{21} \\
 A_{21} n_2 &= n_e n_2 \frac{\beta}{T^{1/2}} \frac{\Omega_{21}}{g_2} \\
 n_{\text{crit}} &= \frac{A_{21} g_2 T^{1/2}}{\beta \Omega_{12}} \text{ cm}^{-3}
 \end{aligned}$$

At around this density, the line emissivity plotted in log-scale changes slope from +2 to +1.

# [Line diagnostics]

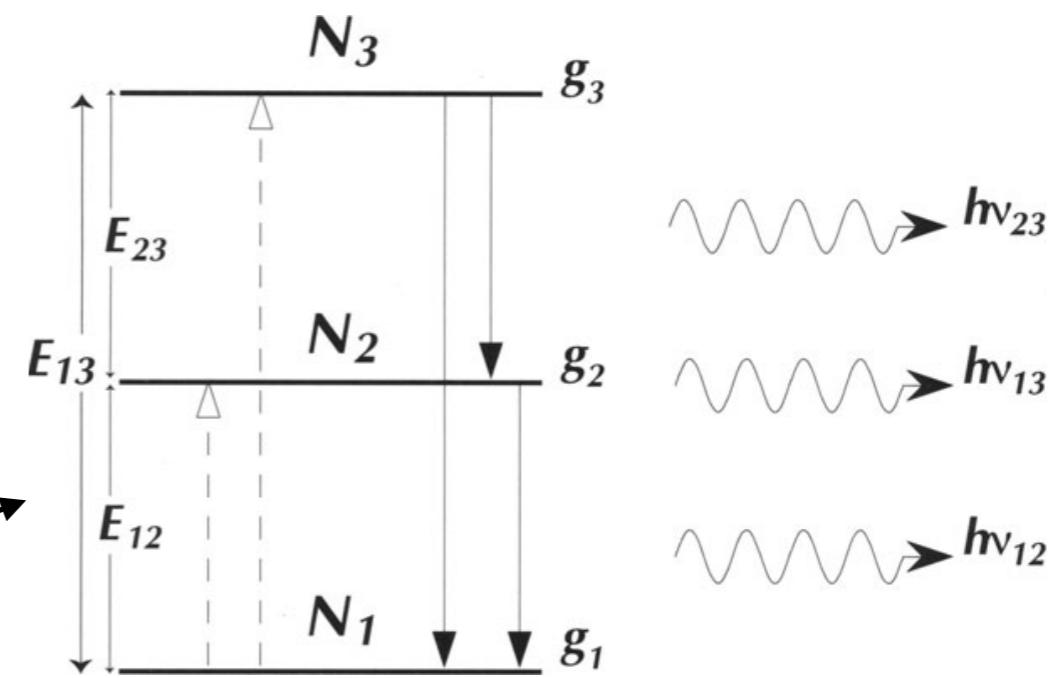
- **The Three-Level Atom (Line diagnostics)**

- Let  $C_{ij}$  be the collision rate ( $C_{ij} = n_e q_{ij} \text{ s}^{-1}$ ) between any two levels. The equations of statistical equilibrium for a three level atom are

$$N_1 C_{13} + N_2 C_{23} = N_3 (C_{31} + C_{32} + A_{32} + A_{31})$$

$$N_1 C_{12} + N_3 (C_{32} + A_{32}) = N_2 (C_{23} + C_{21} + A_{21})$$

$$N_1 + N_2 + N_3 = 1$$



- **Electron temperature**

- ◆ Ions in which  $E_{12} \sim E_{23}$
- ◆ In the low density limit, collisional de-excitation of the excited levels can be ignored. Therefore,

$$C_{31} \sim C_{32} \sim 0.$$

Also, because of the increasing threshold energies to excite each level,  $N_3 \ll N_2 \ll N_1$  so that the equations are reduced to

$$N_3 = \frac{N_1 C_{13}}{(A_{32} + A_{31})}$$

$$N_2 = \frac{N_1 C_{12}}{A_{21}}$$

---

If we now form the line intensity ratio for the  $3 \rightarrow 2$  and  $2 \rightarrow 1$  transitions, we have

$$\begin{aligned}\frac{F_{32}}{F_{21}} &= \frac{E_{23}N_3A_{32}}{E_{12}N_2A_{21}} \\ &= \frac{E_{23}A_{32}C_{13}}{E_{12}(A_{32} + A_{31})C_{12}} \\ &= \frac{E_{23}A_{32}q_{13}}{E_{12}A_{31}q_{12}} \\ &= \frac{E_{23}A_{32}\Omega_{13}}{E_{12}A_{31}\Omega_{12}} \exp\left(-\frac{E_{23}}{kT}\right)\end{aligned}$$

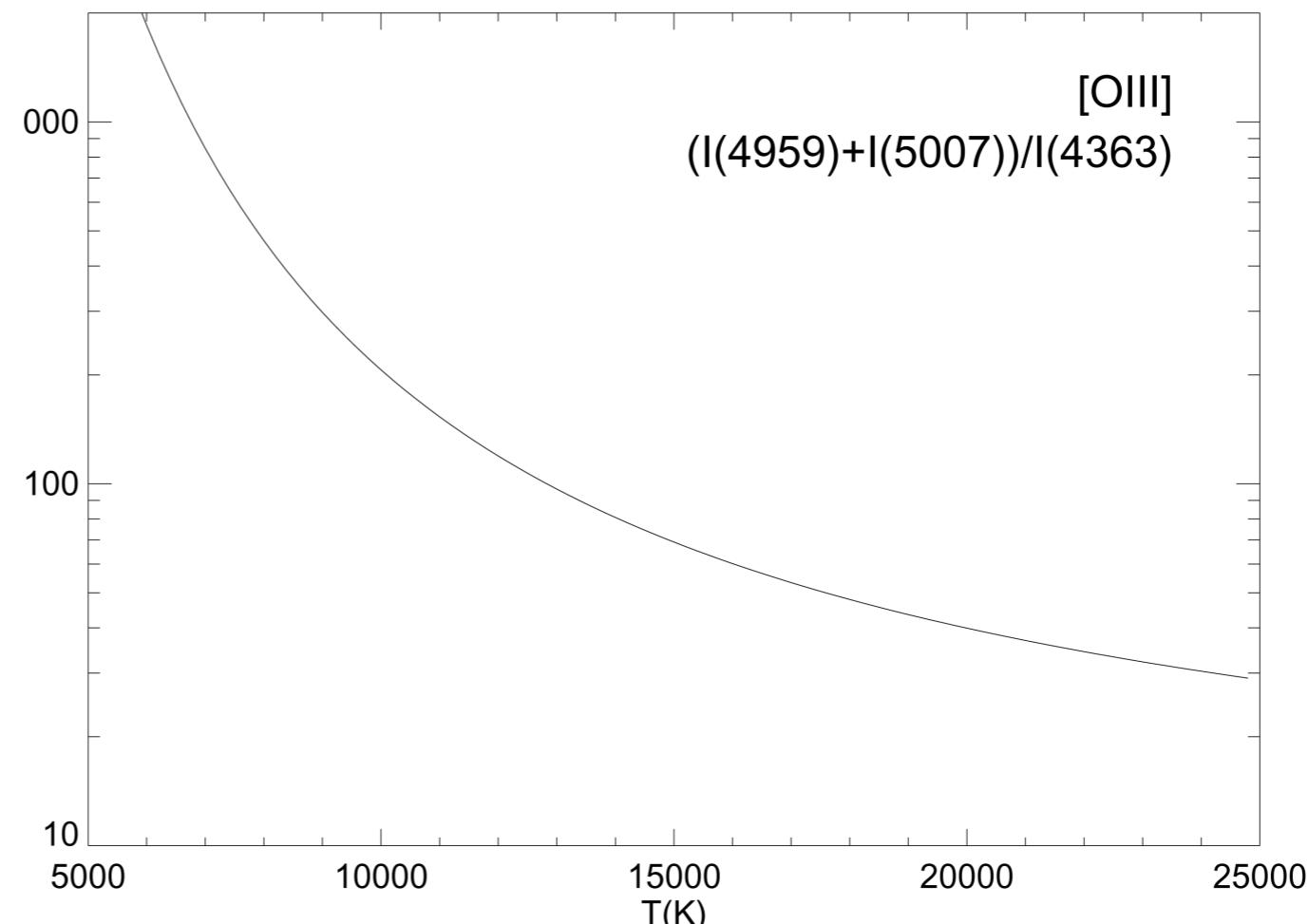
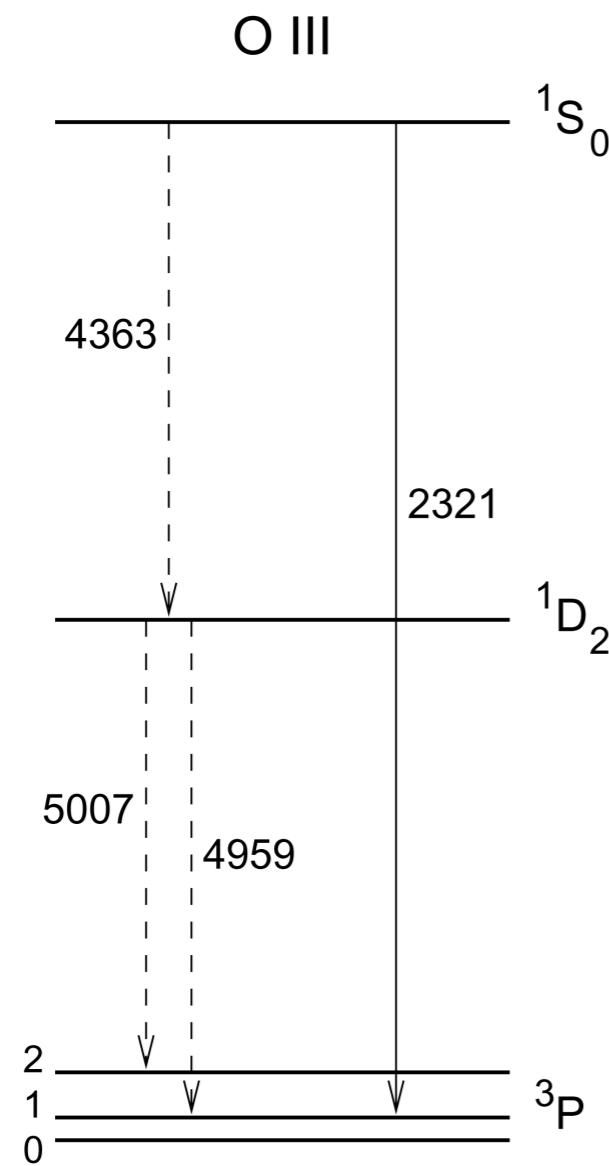
provided that  $A_{32}$  is very much less than  $A_{31}$ .

Because this line ratio depends on the temperature, it can be used to measure the electron temperature in the plasma.

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Temperature

Use two levels with different excitation energy.



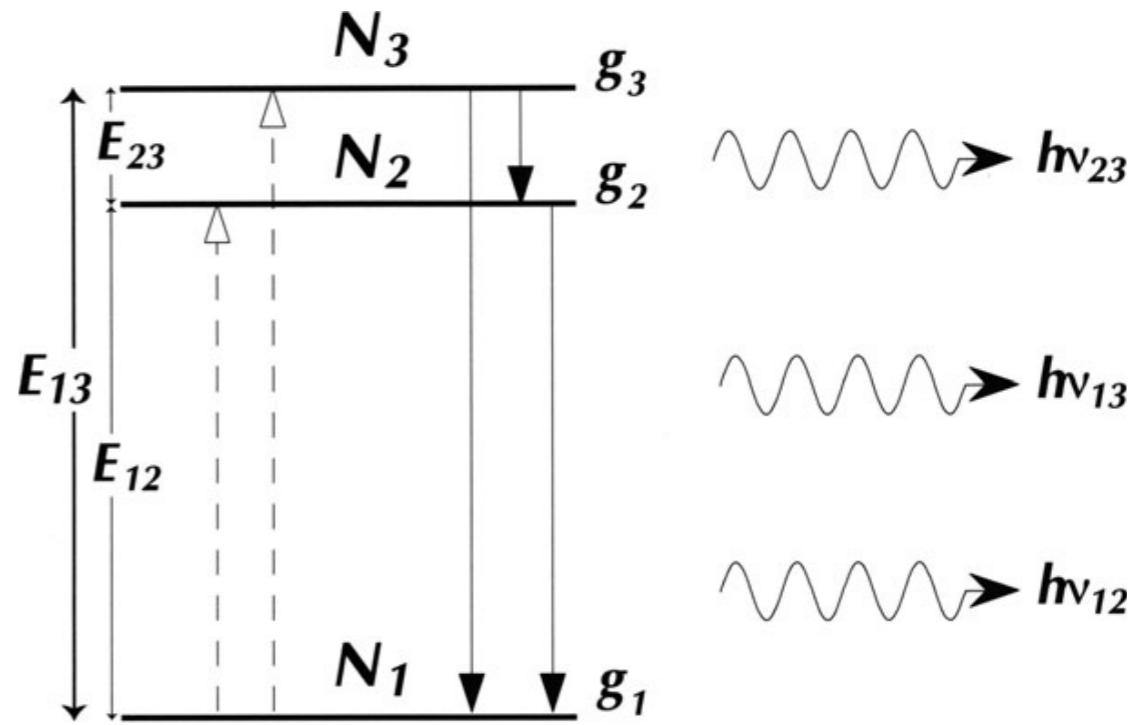
$$\frac{I(4959 + 5007)}{4363} = \frac{7.7 \exp(3.29 \times 10^4 / T)}{1 + 4.5 \times 10^{-4} n_e T^{-1/2}}$$

- **Electron density**

- ♦ Ions in which  $E_{23} \ll E_{12}$
- ♦ In low density limit,  
we can neglect collisional induced transitions  
between the higher levels.

$$N_1 C_{13} = N_3 A_{31}$$

$$N_1 C_{12} = N_2 A_{21}$$



$$\frac{F_{31}}{F_{21}} = \frac{E_{31} A_{31} N_3}{E_{21} A_{21} N_2} = \frac{E_{31} C_{13}}{E_{21} C_{12}} \sim \frac{\Omega_{31}}{\Omega_{21}} \exp\left(-\frac{E_{21}}{kT}\right) \sim \frac{\Omega_{31}}{\Omega_{21}} = \frac{g_3}{g_2}$$

using the quantum-mechanical sum rule for collision strengths.

- ♦ In high density limit, the upper levels are populated according to their Boltzmann ratios,

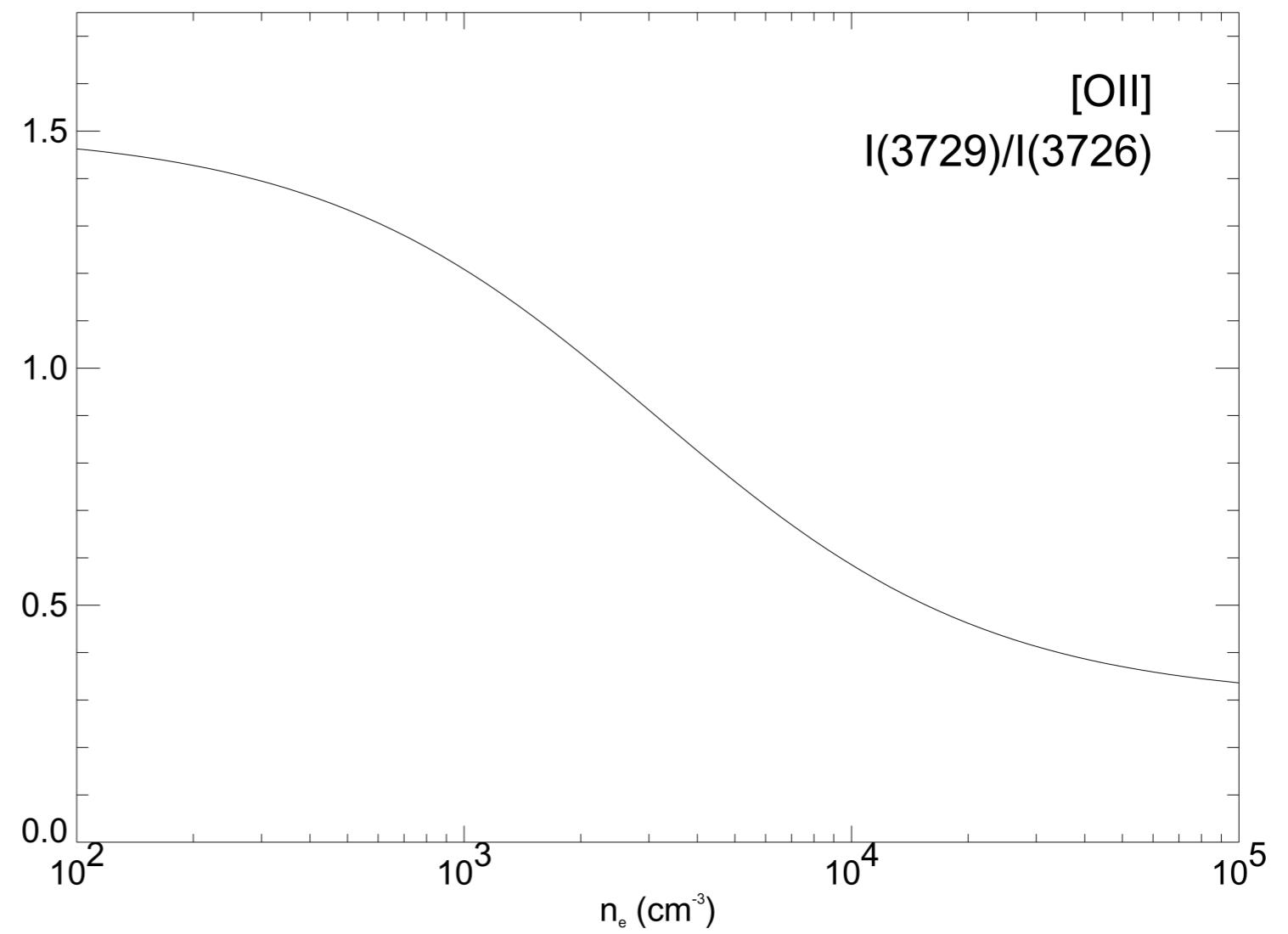
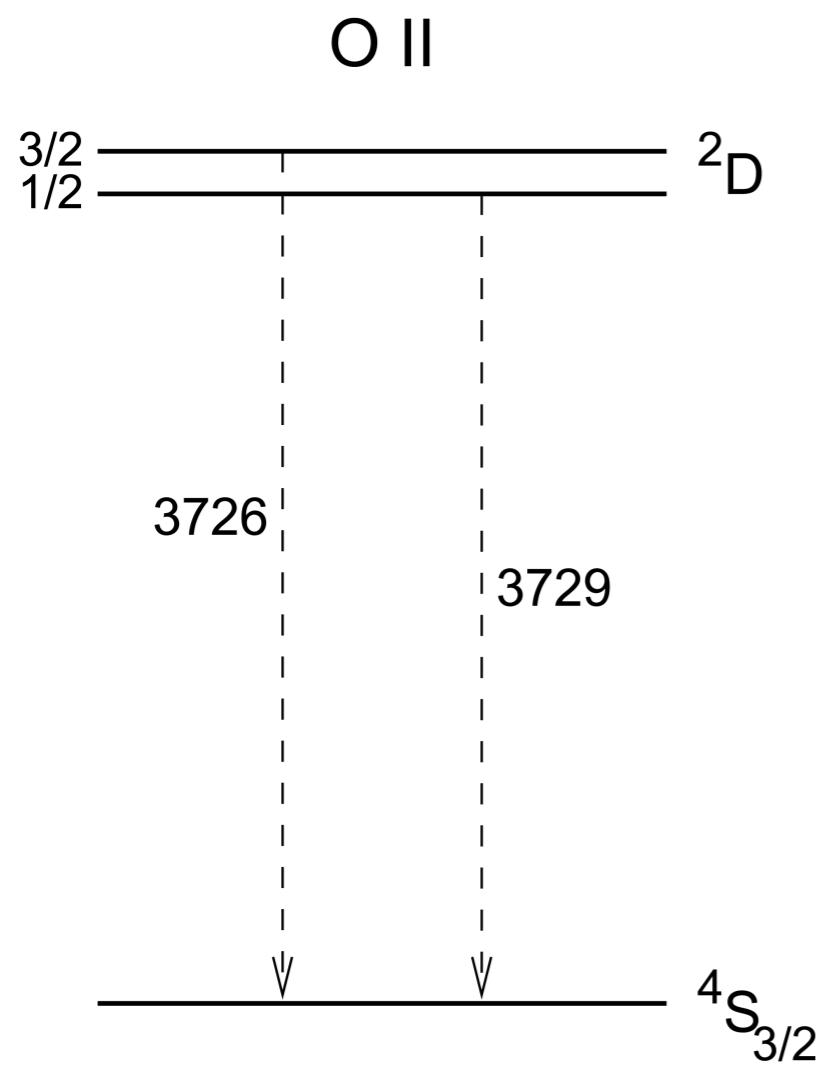
$$\frac{F_{31}}{F_{21}} = \frac{E_{31} A_{31} N_3}{E_{21} A_{21} N_2} \sim \frac{A_{31} g_3}{A_{21} g_2}$$

- ♦ Therefore, the line ratio can be used as density diagnostics in the regime between the critical densities for de-excitation of each of the transitions.

---

Density

Choose atom with two levels with almost same excitation energy.



# [Einstein Coefficients and Oscillator Strengths]

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- Recall resonance scattering cross-section and the Einstein relations:

$$\sigma_{lu}(\nu) = \frac{\pi e^2}{mc} \frac{\gamma/4\pi^2}{(\nu - \nu_0)^2 + (\gamma/4\pi)^2}$$
$$g_l B_{lu} = g_u B_{ul}$$
$$A_{ul} = \frac{2h\nu_{lu}^3}{c^2} B_{ul}$$
$$\text{where } \nu_{lu} \equiv \frac{E_u - E_l}{h} \quad (\nu_0)$$

- The Einstein (absorption)  $B$  coefficient associated with a classical oscillator can be defined in terms of the total energy extracted from a beam of radiation.

$$\int_0^\infty \sigma_{lu}(\nu) d\nu = \frac{\pi e^2}{mc} \equiv B_{lu}^{\text{classical}} \frac{h\nu_{lu}}{4\pi} \quad \rightarrow \quad B_{lu}^{\text{classical}} = \frac{4\pi}{h\nu_{lu}} \frac{\pi e^2}{mc}$$

It is convenient to define the **absorption and emission oscillator strengths** ( $f_{lu}$  and  $f_{ul}$ ) by the formulae:

$$B_{lu} = B_{lu}^{\text{classical}} f_{lu} = \frac{4\pi^2 e^2}{h\nu_{lu} mc} f_{lu}$$
$$B_{ul} = \frac{4\pi^2 e^2}{h\nu_{ul}} f_{ul} \quad (\text{note that } \nu_{ul} = -\nu_{lu} < 0 \text{ and } f_{ul} < 0)$$

The oscillator strength (or  $f$  value) is the factor which corrects the classical result. The quantum mechanical process can be interpreted as being due to a (fractional) number  $f$  of equivalent classical electron oscillators of the same frequency.

- 
- In quantum mechanics, the absorption oscillator strength is given by

$$f_{lu} = \frac{2m}{3\hbar^2 g_l e^2} (E_u - E_l) \sum |d_{lu}|^2 \quad d_{lu} \equiv \langle \phi_u | e\mathbf{r} | \phi_l \rangle$$

where the sum is over all substates of the upper and lower levels.

We also have the following relations.

$$\begin{aligned} g_l f_{lu} &= -g_u f_{ul} \\ g_u A_{ul} \equiv -\frac{8\pi^2 e^2 \nu_{ul}^2}{mc^3} g_u f_{ul} &= \frac{8\pi^2 e^2 \nu_{lu}^2}{mc^3} g_l f_{lu} \\ \sigma(\nu) &= \frac{\pi e^2}{mc} f_{lu} \\ &= \frac{\pi e^2}{mc} f_{lu} \phi(\nu) \end{aligned}$$

- *Thomas-Reiche-Kuhn sum rule*

$$\sum_{n'} f_{nn'} = N = \text{ total number of electrons in the atom}$$

Here, the summation is over all states of the atom. Where there is a close shell and a smaller number  $q$  of electrons outside the closed shells that are involved in a more limited set of transitions, we also have

$$\sum_{n'} f_{nn'} = q$$

where the sum is now only over those states involve transitions of these outer electrons.

We note that  $f \sim 1$  for strong allowed transitions.

# [Line Broadening Mechanisms]

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- Atomic levels are not infinitely sharp, nor are the lines connecting them.
  - (1) Doppler Broadening
  - (2) Natural Broadening
  - (3) Collisional Broadening
- **Doppler Broadening**

The simplest mechanism for line broadening in the Doppler effect. An atom is in thermal motion, so that the frequency of emission or absorption in its own frame corresponds to a different frequency for an observer.

Each atom has its own Doppler shift, so that the net effect is to spread the line out, but not to change its total strength.

The change in frequency associated with an atom with velocity component  $v_z$  along the line of sight (say, z axis) is, to lowest order in  $v/c$ , given by

$$\nu - \nu_0 = \nu_0 \frac{v_z}{c}$$

Doppler shift:  $\left[ \frac{\nu}{\nu_0} = \frac{1}{\gamma(1 - \beta \cos \theta)} \rightarrow \nu \approx \nu_0 (1 + \beta \cos \theta) \rightarrow \nu - \nu_0 = \frac{\nu_0 v_z}{c} \right]$

Here,  $\nu_0$  is the rest-frame frequency.

---

The number of atoms having velocities in the range  $(v_z, v_z + dv)$  is proportional to

$$f(v_z)dv_z = \exp\left(-\frac{mv_z^2}{2kT}\right)dv_z$$

From the Doppler shift formula, we have

$$v_z = \frac{c(\nu - \nu_0)}{\nu_0} \rightarrow dv_z = \frac{cd\nu}{\nu_0}$$

Therefore, the strength of the emission is proportional to

$$\exp\left(-\frac{mv_z^2}{2kT}\right)dv_z \propto \exp\left[-\frac{mc^2(\nu - \nu_0)^2}{2\nu_0^2 kT}\right]d\nu$$

Then, the normalized profile function is

$$\phi(\nu) = \frac{1}{\Delta\nu_D\sqrt{\pi}}e^{-(\nu-\nu_0)^2/(\Delta\nu_D)^2} \quad \text{where } \Delta\nu_D = \frac{\nu_0}{c}\sqrt{\frac{2kT}{m}}$$

---

**The line-center cross section for each atom**, neglecting stimulated emission, is therefore

$$\begin{aligned}\sigma_{\nu_0} &= B_{12} \frac{h\nu}{4\pi} \phi(\nu_0) = \frac{1}{\Delta\nu_D \sqrt{\pi}} \frac{h\nu_0}{4\pi} B_{12} \\ &= \frac{\pi e^2}{mc} f_{12} \frac{1}{\Delta\nu_D \sqrt{\pi}}\end{aligned}$$

In addition to thermal motions, there can be turbulent velocities associated with macroscopic velocity fields. **When the scale of the turbulence is small in comparison with a mean free path (microturbulence)**, the turbulent motions are accounted for by an effective Doppler width.

$$\Delta\nu_D = \frac{\nu_0}{c} \left( \frac{2kT}{m} + v_{\text{turb}}^2 \right)^{1/2}$$

where  $v_{\text{turb}}$  is a root-mean-square measure of the turbulent velocities. This assumes that the turbulent velocities also have a Gaussian distribution.

---

- **Natural Broadening**

A certain width to the atomic level is implied by the uncertainty principle, namely, that the spread in energy  $\Delta E$  and the duration  $\Delta t$  in the state must satisfy  $\Delta E \Delta t \sim \hbar$ .

The spontaneous decay of an atomic state  $n$  proceeds at a rate

$$\gamma = \sum_{n'} A_{nn'}$$

where the sum is over all states  $n'$  of lower energy. The coefficient of the wave function of state  $n$  is of the form  $e^{-\gamma t/2}$  and then the energy decays proportional to  $e^{-\gamma t}$ . We then have an emitted spectrum determined by the decaying sinusoid type of electric field. The spectral profile is of the form, which is called a Lorentz (or natural, or Cauchy) profile,

$$\phi(\nu) = \frac{\gamma/4\pi^2}{(\nu - \nu_0)^2 + (\gamma/4\pi)^2}$$

The above profile applies to cases in which only the upper state is broadened.

If both the upper and lower state are broadened, then the appropriate definition for  $\gamma$  is

$$\gamma = \gamma_u + \gamma_l \quad \text{Note that } \gamma_l = 0 \text{ for the ground state.}$$

where  $\gamma_u$  and  $\gamma_l$  are the widths of the upper and lower states involved in the transition.

The longer an excited state exists, the narrower the line width so that metastable states can have very narrow lines (if the thermal Doppler broadening is not important).

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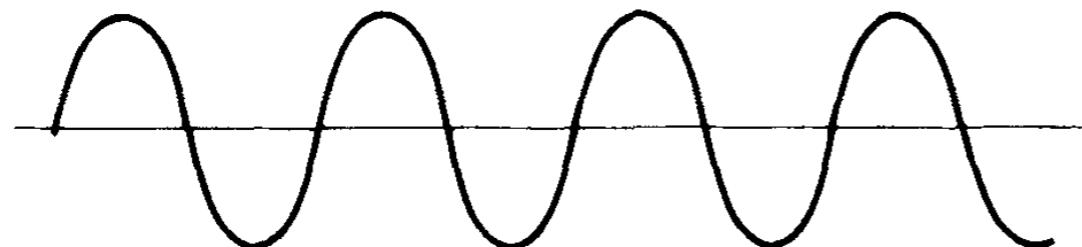
- **Collisional Broadening**

The Lorentz profile applies even to certain types of collisional broadening mechanisms.

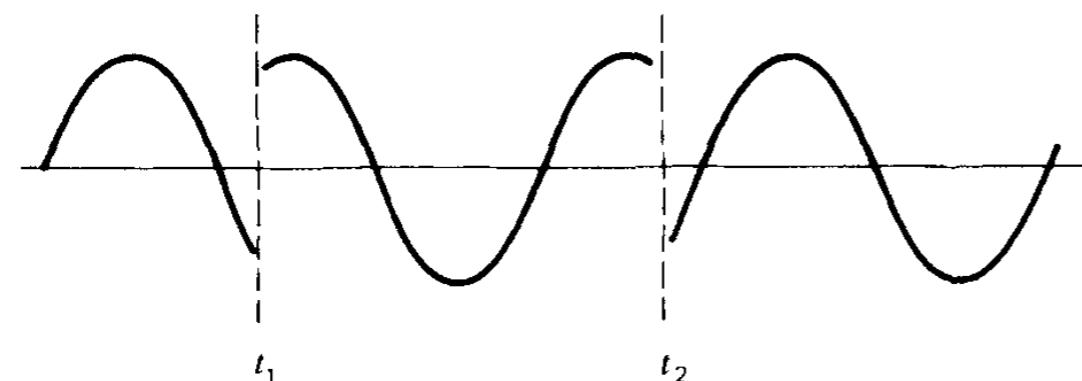
If the atom suffers collisions with other particles while it is emitting, the phase of the emitted radiation can be altered suddenly. If the phase changes completely randomly at the collision times, then information about the emitting frequencies is lost.

If the collisions occur with frequency  $\nu_{\text{col}}$ , that is, each atom experiences  $\nu_{\text{col}}$  collisions per unit time on the average, then the profile is

$$\phi(\nu) = \frac{\Gamma/4\pi^2}{(\nu - \nu_0)^2 + (\Gamma/4\pi)^2} \quad \text{where} \quad \Gamma = \gamma + 2\nu_{\text{col}}$$



purely sinusoidal



random phase interruptions  
by atomic collisions

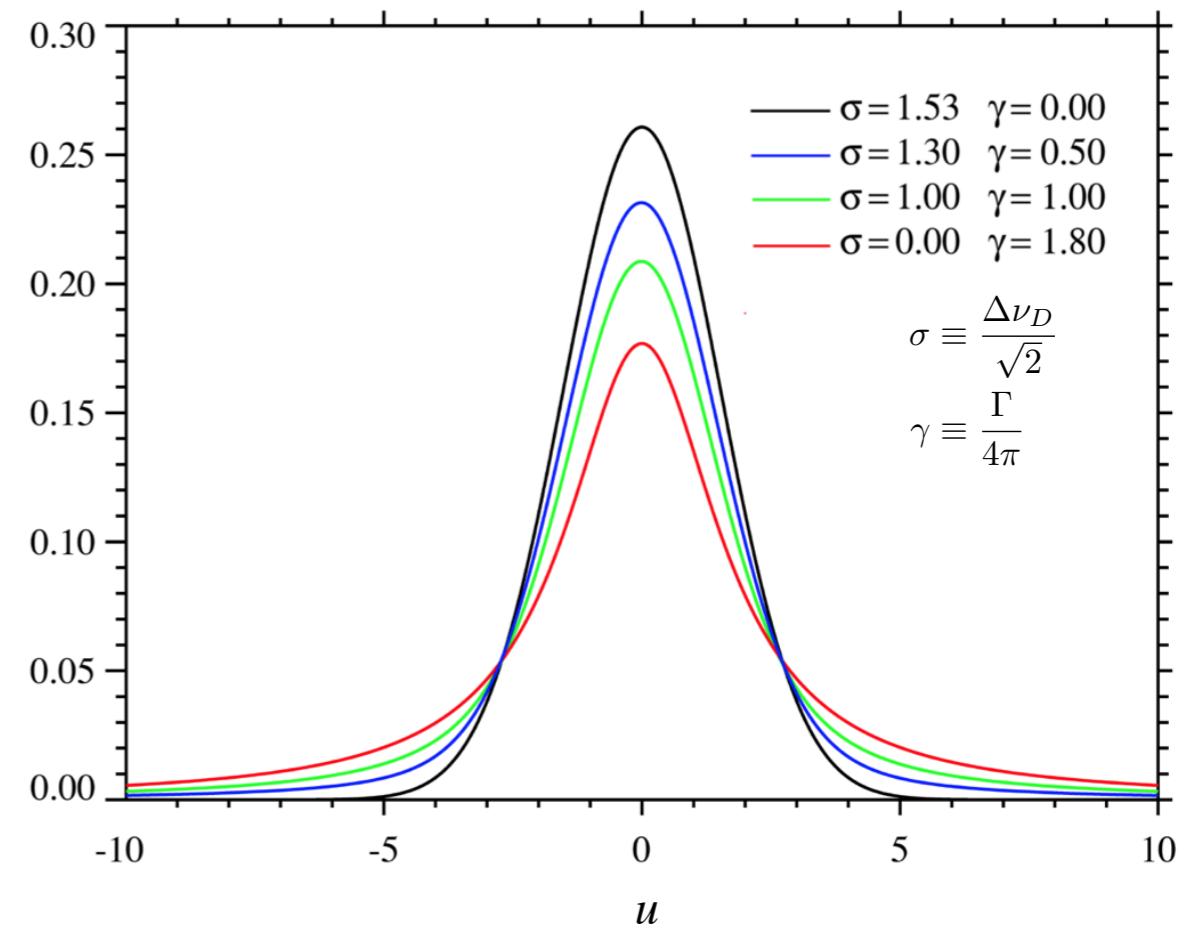
## • Combined Doppler and Lorentz Profiles

Atoms shows both a Lorentz profile plus the Doppler effect. In this case, we can write the profile as an average of the Lorentz profile over the various velocity states of the atom:

$$\phi(\nu) = \frac{\Gamma}{4\pi^2} \int_{-\infty}^{\infty} \frac{(m/2\pi kT)^{1/2} \exp(-mv_z^2/2kT)}{(\nu - \nu_0(1 + v_z/c))^2 + (\Gamma/4\pi)^2} dv_z$$

The profile can be written using the Voigt function.

$$\begin{aligned}\phi(\nu) &= \frac{1}{\Delta\nu_D \sqrt{\pi}} H(a, u) \\ H(a, u) &\equiv \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a^2 + (u - y)^2} \\ a &\equiv \frac{\Gamma}{4\pi \Delta\nu_D} \\ u &\equiv \frac{\nu - \nu_0}{\Delta\nu_D} \\ \nu_D &= \frac{\nu_0}{c} \sqrt{\frac{2kT}{m}}\end{aligned}$$



For small  $a$ , the center of the line is dominated by the Doppler profile, whereas the “wings” are dominated by the Lorentz profile.

# Molecular Structure

# [Bohn-Oppenheimer Approximation]

---

- **Bohn-Oppenheimer approximation:**

- The motions of the electrons and nuclei could be treated separately.
- *This come about because of the great difference between the masses of the electron and a typical nuclei.*
- The slowly moving nuclei only sense the electrons as a kind of smoothed-out cloud. As the nuclei move the electrons have sufficient time to adjust to adiabatically the new nuclear positions. The nuclei then feel only an equivalent potential that depends on the internuclear distance and on the particular electronic state.
- Due to very different energies of the electronic, vibrational, and rotational states, these interactions can be assumed to be decoupled. The separation of wavefunctions is referred to as the Born-Oppenheimer approximation. Under the Born-Oppenheimer approximation, the total wavefunction is a product of the nuclear, electronic, vibrational, and rotational wavefunctions.

$$\psi_{\text{tot}} = \psi_{\text{nuc}} \psi_{\text{el}} \psi_{\text{vib}} \psi_{\text{rot}}$$

- **Order of magnitude of energy levels**

- *Electronic energy:*

Let  $a$  be a typical molecular size. Then, the electron energy will be given by

$$E_{\text{elect}} \sim m_e v^2 = \frac{p^2}{m_e} \sim \frac{\hbar^2}{m_e a^2} \quad (\leftarrow \quad p \times a \sim \hbar, \text{ uncertainty relation}) \quad \Rightarrow \text{UV (a few eV)} \\ (a \sim 1 \text{ \AA})$$

- Vibrational energy:

For stable molecules, the internuclear potential has a minimum at some point. Vibration about the minimum can occur and can be estimated roughly by comparing to a harmonic oscillator. Then, the potential energy of the harmonic oscillator must be similar to the electronic energy:

$$\frac{1}{2}M\omega^2a^2 \sim \frac{\hbar^2}{2m_e a^2}$$

where  $\omega$  = frequency of vibration.  
 $M$  = mass of the molecule.

Then, the vibrational energy is

$$E_{\text{vib}} \sim \hbar\omega \sim \left(\frac{m_e}{M}\right)^{1/2} \frac{\hbar^2}{m_e a^2} \sim \left(\frac{m_e}{M}\right)^{1/2} E_{\text{elect}} \quad \Rightarrow \text{IR}$$

Recall that the energy levels of a harmonic oscillator:

$$E_{\text{osc}} = \left(n + \frac{1}{2}\right) \hbar\omega$$

- Rotational energy:

The nuclei can also rotate about each other. Then, the energy of rotation is

$$E_{\text{rot}} \sim \frac{L^2}{2I} \sim \frac{\hbar^2 \ell(\ell + 1)}{2I} \quad \Rightarrow \text{IR or radio}$$

where I is the moment of inertia of the molecule:  $I = Ma^2$ . Therefore, we obtain

$$E_{\text{rot}} \sim \left(\frac{m_e}{M}\right) E_{\text{elect}}$$

In summary,  $E = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}}$

$$E_{\text{elect}} : E_{\text{vib}} : E_{\text{rot}} = 1 : \left(\frac{m_e}{M}\right)^{1/2} : \left(\frac{m_e}{M}\right)$$

# [Schrodinger equation for a diatomic molecule]

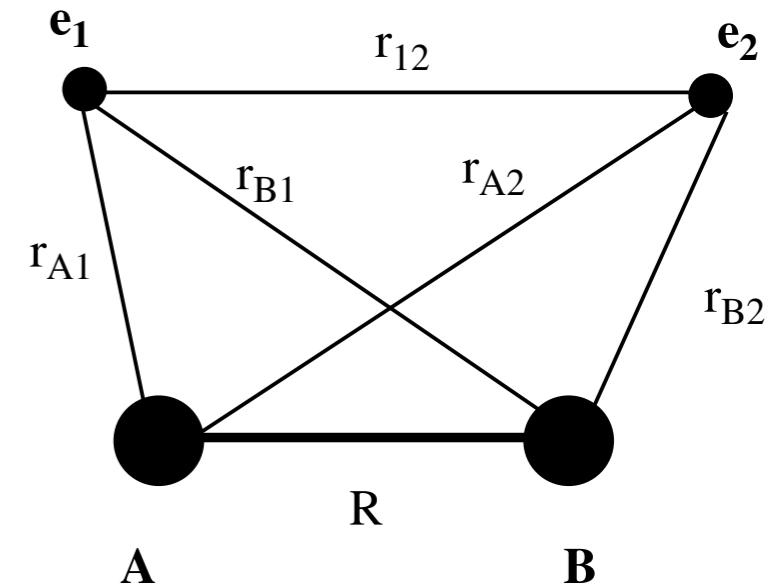
For a diatomic molecule with  $N$  electrons,

$$\left( -\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E \right) \Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_i) = 0$$

$$V_e = - \sum_{i=1}^N \frac{Z_A e^2}{r_{Ai}} - \sum_{i=1}^N \frac{Z_B e^2}{r_{Bi}} + \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{1}{r_{ij}} \frac{e^2}{r_{ij}} + \frac{Z_A Z_B e^2}{R}$$

The potential terms are:

- (1) attraction of the electrons by nucleus A
- (2) attraction of the electrons by nucleus B
- (3) electron-electron repulsion
- (4) nuclear-nuclear repulsion



- Bohn-Oppenheimer approximation: We write the wave function as a product of electronic and nuclear wave functions.

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_i) = \psi_e(\mathbf{r}_i) \psi_n(\mathbf{R}_A, \mathbf{R}_B)$$

- The **electronic wavefunction** satisfies the following equation:

$$\left( -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E_e \right) \psi_e(\mathbf{r}_i) = 0$$

This equation is solved separately for each value of the internuclear separation  $R$ . Then, the resulting eigenvalue  $E_e$  is given as a function of  $R$ .

- 
- The nuclear wave function satisfies the Schrodinger equation:

$$\left( -\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V(R) - E \right) \psi_n(\mathbf{R}_A, \mathbf{R}_B) = 0 \quad \text{where } V(R) \equiv E_e.$$

There are three motions of the nuclei: (1) translation of the whole system, (2) vibrations, and (3) rotations. The motions can be separated into the translational motion of the center-of-mass of the system plus the internal motion of one body in a ‘central’ potential, which depends on the distance between the particles. The effective mass of this one-body problem is the reduced mass:

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

The Schrodinger equation for nuclear motion, neglecting the translational motion, becomes:

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(R) - E \right] \psi_n(\mathbf{R}) = 0$$

where  $\mathbf{R} = (R, \theta, \phi)$ .  $R$  is the internuclear operation,  $(\theta, \phi)$  is the orientation of the molecular axis.

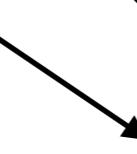
As a good first approximation, the vibration and rotational motion may be separated.

$$\psi_n(\mathbf{R}) = \psi_{\text{vib}}(R) \psi_{\text{rot}}(\theta, \phi)$$

---

Then, we obtain two equations for the rotational motion and vibrational motion:

angular eq:  $\left\{ -\frac{\hbar^2}{2\mu R^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - E_r \right\} \psi_{\text{rot}}(\theta, \phi) = 0$

 the angular part of the Laplacian operator  $\nabla^2$

radial eq:  $\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) - E_v \right] \psi_{\text{vib}}(R) = 0$

(1) The solution of the angular equation is:

$$\begin{aligned} \psi_{\text{rot}}(\theta, \phi) &= Y_{JM}(\theta, \phi) \\ E_r &= \frac{\hbar^2}{2\mu R^2} J(J+1) \end{aligned}$$

(2) The potential  $V(R)$  is not a simple function and thus the radial equation has no general algebraic solution. But, we can approximate  $V(R)$  about its minimum by a parabola:

$$\begin{aligned} V(R) &= V(R_e) + \frac{1}{2} \left. \frac{d^2V}{dR^2} \right|_{R=R_e} (R - R_e)^2 + \mathcal{O}((R - R_e)^3) \\ &= V_0 + \frac{1}{2} k(R - R_e)^2 + \dots \end{aligned}$$

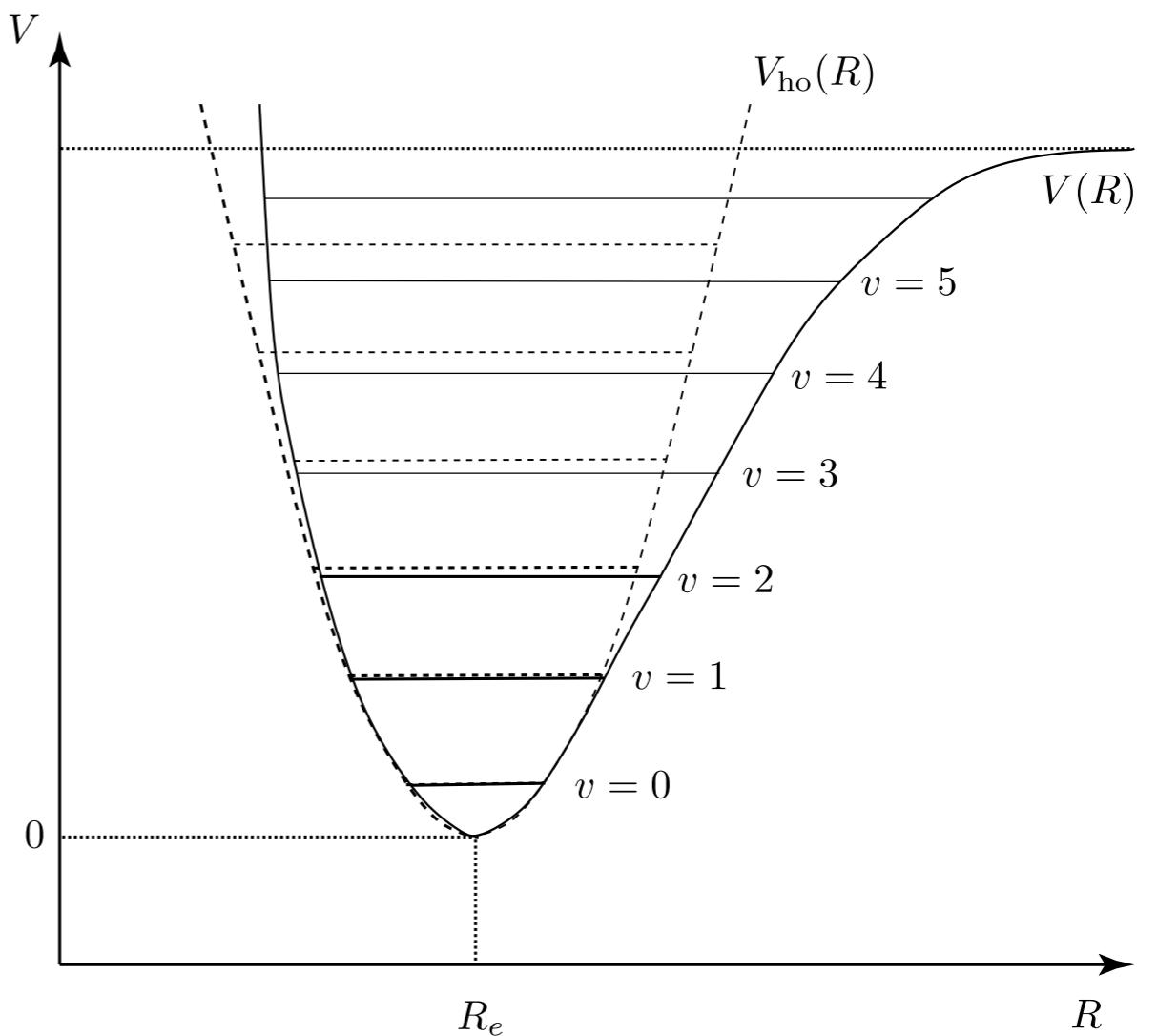
Setting the zero of energy at the minimum potential,  $V_0 = V(R_e) = 0$ , the radial equation becomes

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_e)^2 - E_v \right] \psi_{\text{vib}}(R) = 0$$

This is the QM equation for the harmonic oscillator with the spring constant  $k$ . The energy levels of this equation are:

$$E_v = \hbar\omega \left( v + \frac{1}{2} \right)$$

$$\text{where } \omega = \left( \frac{k}{\mu} \right)^{1/2}, \quad v = 0, 1, 2, \dots$$



# [Electronic Structures of Diatomic Molecules]

- The notation of the electronic structure of a diatomic molecule is similar to that for atomic structure under  $LS$  coupling. Each electronic state is designated by the term symbol.

$$2S+1 \mathcal{L} J_z$$

In most literatures, the following symbol is used.

$$2S+1 \Lambda_{\Omega}$$

$S$  = total electronic spin

$\mathcal{L}$  = projection of the total electronic “orbital” angular momentum along the internuclear axis ( $\rightarrow L_z$ )

$J_z$  = projection of the total electronic angular momentum onto the internuclear axis  
 $= \mathcal{L} + S_z$  ( $\rightarrow J_z = L_z + S_z$ )

- The uppercase Greek letters to denote the total “orbital” angular momentum.

$$\mathcal{L} = \Sigma, \Pi, \Delta, \dots \quad (\text{for } L_z = 0, 1, 2, \dots)$$

- If the term symbol  $\mathcal{L}$  is  $\Sigma$  ( $L_z = 0$ ), then additional superscript  $\pm$  is applied.

$$\pm = \begin{cases} + & \text{if symmetric under reflection through (all) planes} \\ & \text{containing the nuclei,} \\ - & \text{if antisymmetric under reflection through a plane} \\ & \text{containing the nuclei.} \end{cases}$$

Nearly all states are  $\Sigma^+$ .  
One exception is O<sub>2</sub>, of which the lowest electronic state is  $^3\Sigma_g^-$ .

- The electronic states of diatomic molecules are also labelled with letters:

X labels the ground electronic state

A, B, C, ... label states of same spin multiplicity as the ground state

a, b, c, ... label states of different spin multiplicity to the ground state

- Diatomc molecules with identical nuclei ( $H_2$ ,  $N_2$ ,  $O_2$ ,  $C_2$ ) are referred to as homonuclear. The energy levels of homonuclear diatomic molecules are designated by

$$2S+1 \Lambda_{u,g}$$

$$u, g = \begin{cases} g & (\text{"gerade"}) \text{ if symmetric under reflection through the} \\ & \text{center of mass, } \Rightarrow \text{even} \text{ (계하드)} \\ u & (\text{"ungerade"}) \text{ if antisymmetric under reflection through the} \\ & \text{center of mass. } \Rightarrow \text{odd} \text{ (운계하드)} \end{cases}$$

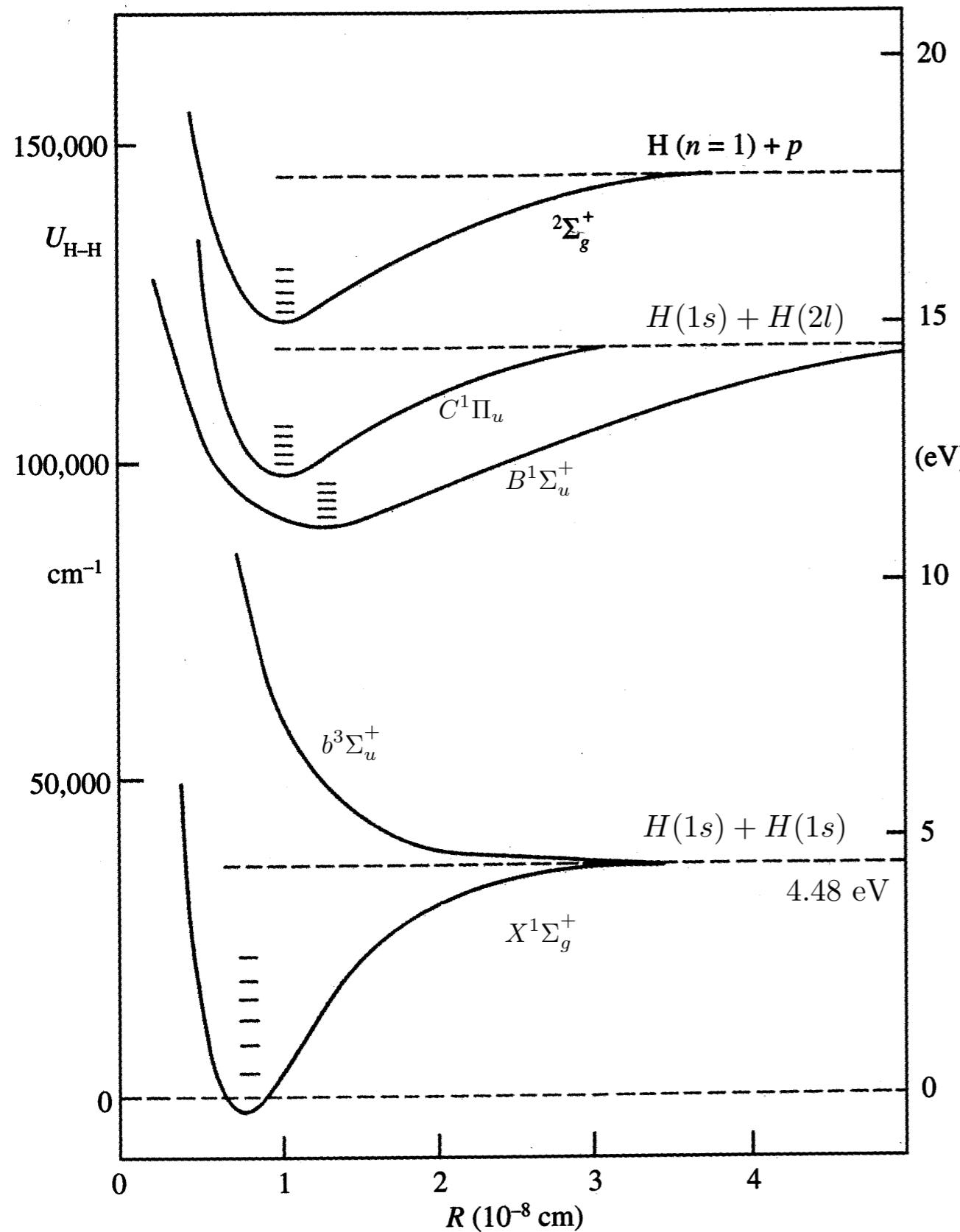
- For the special case of  $\Sigma$  state, a superscript + or - is added.

$$2S+1 \Sigma_{u,g}^{\pm}$$

- In the case of a heteronuclear diatomic molecule (e.g., HD, OH, or CO), the energy levels are designated:

$$2S+1 \mathcal{L}_{J_z}$$

# [Energy levels of Molecular Hydrogen]



- The short horizontal lines in each of the bound states indicate the vibrational levels.
- The transition from the ground state  $X^1\Sigma_g^+$  to the excited states  $B^1\Sigma_u^+$  and  $C^1\Pi_u$  are called **Lyman and Werner bands**.

Werner band:  $C^1\Pi_u - X^1\Sigma_g^+$  at about 1100 Å;  
 Lyman band:  $B^1\Sigma_u^+ - X^1\Sigma_g^+$  at about 1010 Å.

In principle, states are labelled alphabetically in ascending energy order. However, there are many exceptions.

The lowest triplet state of  $\text{H}_2$  is the  $b^3\Sigma_u^+$  with the  $a^3\Sigma_g^+$  lying somewhat higher.

# Other molecules

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	Ground term
H <sub>2</sub>	$^1\Sigma_g^+$
CH	$^2\Pi_{1/2,3/2}$
CH <sup>+</sup>	$^1\Sigma_0^+$
OH	$^2\Pi_{3/2,1/2}$
CN	$^2\Sigma_{1/2}^+$
CO	$^1\Sigma_0^+$
SiO	$^1\Sigma_0^+$
CS	$^1\Sigma_0^+$

The electronic ground state of H<sub>2</sub> (two electrons) has zero electronic orbital angular momentum ( $L_e = 0$ ), has zero electron spin ( $S_e = 0$ ), is symmetric under reflection through the center of mass (*g*), and is symmetric under reflection through planes containing the nuclei (+). The ground state is X  $^1\Sigma_g^+$ .

CO has 2 *p* electrons contributed by C and 4 *p* electrons contributed by O; together, these 6 *p* electrons fill the 2*p* subshell, and as a result, the ground electronic state of CO has zero electronic angular momentum and zero electronic spin:  $^1\Sigma_0^+$ , just like H<sub>2</sub>. The reduced mass of CO is  $(12 \times 16/28)$  amu  $\approx$  6.9 amu. The C=O

OH is an example of a molecule with the ground electronic state having nonzero electronic orbital angular momentum: with seven electrons, the OH ground state has  $L_{ez} = 1$  and  $S_{ez} = 1/2$ , and is therefore designated by  $^2\Pi_{1/2,3/2}$ . The electron spin and orbital angular momenta can couple to give  $J_e = 1/2$  or  $3/2$ , with energies that are separated due to spin-orbit coupling (i.e., fine-structure splitting in atoms or ions); the  $J_e = 3/2$  state has the lower energy.

# [Pure rotational & ro-vibrational transitions]

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- **Energy Levels**

An electronic transition consists of vibrational bands, which in turn are made up of rotational transitions.

$$E_q(v, J) = V_q(r_0) + h\nu_0 \left( v + \frac{1}{2} \right) + B_v J(J+1)$$
$$\nu_0 \equiv \frac{\omega_0}{2\pi} \quad B_v = \frac{\hbar^2}{2m_r r_0^2} .$$

Here, q denotes an electronic state.

- **Pure rotational spectrum:** In the lowest vibrational and electronic states, it is possible to have transitions solely among the rotational states. Such transitions give rise to a pure rotational spectrum.
- **Rotational-vibration spectrum:** Because the energies required to excite vibrational modes are much larger than those required to excite rotation, it is unlikely to have a pure vibrational spectrum in analogy to the pure rotational spectrum. The transitions then yield a rotation-vibrational spectrum, in which both the vibrational state and the rotational state can change together.

# [Selection Rules]

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- Electric-dipole selection rules for electronic transitions in a diatomic molecule.
  - (1)  $\Delta\mathcal{L} = 0, \pm 1$ , e.g.,  $\Sigma - \Sigma$ ,  $\Pi - \Sigma$ ,  $\Delta - \Pi$ , etc.
  - (2)  $\Delta S = 0$
  - (3)  $\Delta J_z = 0, \pm 1$
  - (4)  $\Sigma^+ - \Sigma^+$ ,  $\Sigma^- - \Sigma^-$ , but not  $\Sigma^+ - \Sigma^-$
  - (5)  $g \longleftrightarrow u$
  - $\Delta\Lambda = 0, \pm 1$ , e.g.,  $\Sigma - \Sigma$ ,  $\Pi - \Sigma$ ,  $\Delta - \Pi$ , etc.
  - $\Delta S = 0$
  - $\Delta\Omega = 0, \pm 1$
  - $\Sigma^+ - \Sigma^+$ ,  $\Sigma^- - \Sigma^-$ , but not  $\Sigma^+ - \Sigma^-$
  - $g \leftrightarrow u$
- Electric-dipole selection rule for ro-virational transitions:  
 $\Delta v = \text{any}$   
 $\Delta J = 0, \pm 1$  not  $J = 0 \leftrightarrow 0$
- But, note that  $H_2$  has no electric-dipole. The electric-quadrupole are allowed for  $\Delta J = \pm 2$ .

# O, P, Q, R, and S transitions

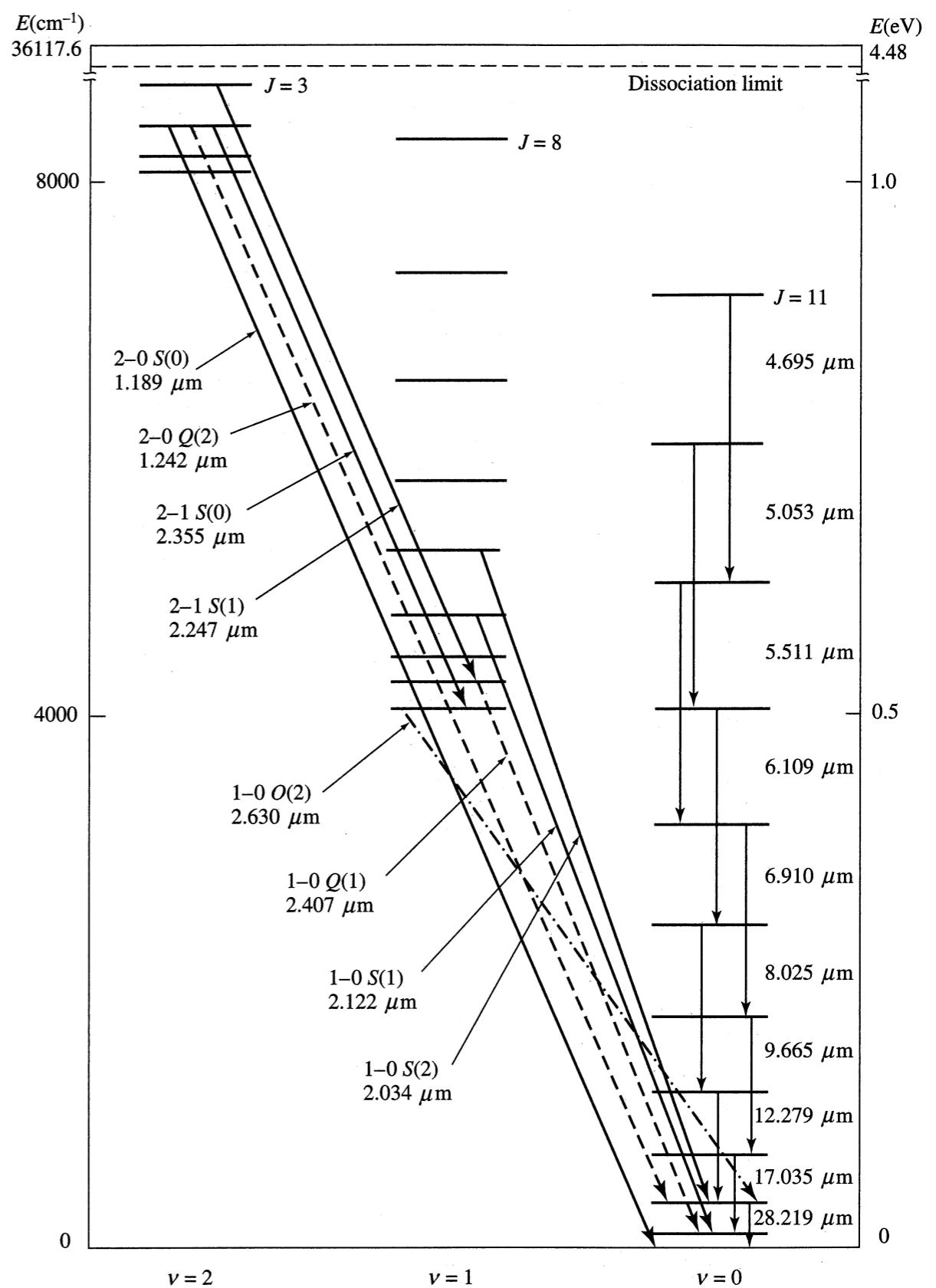
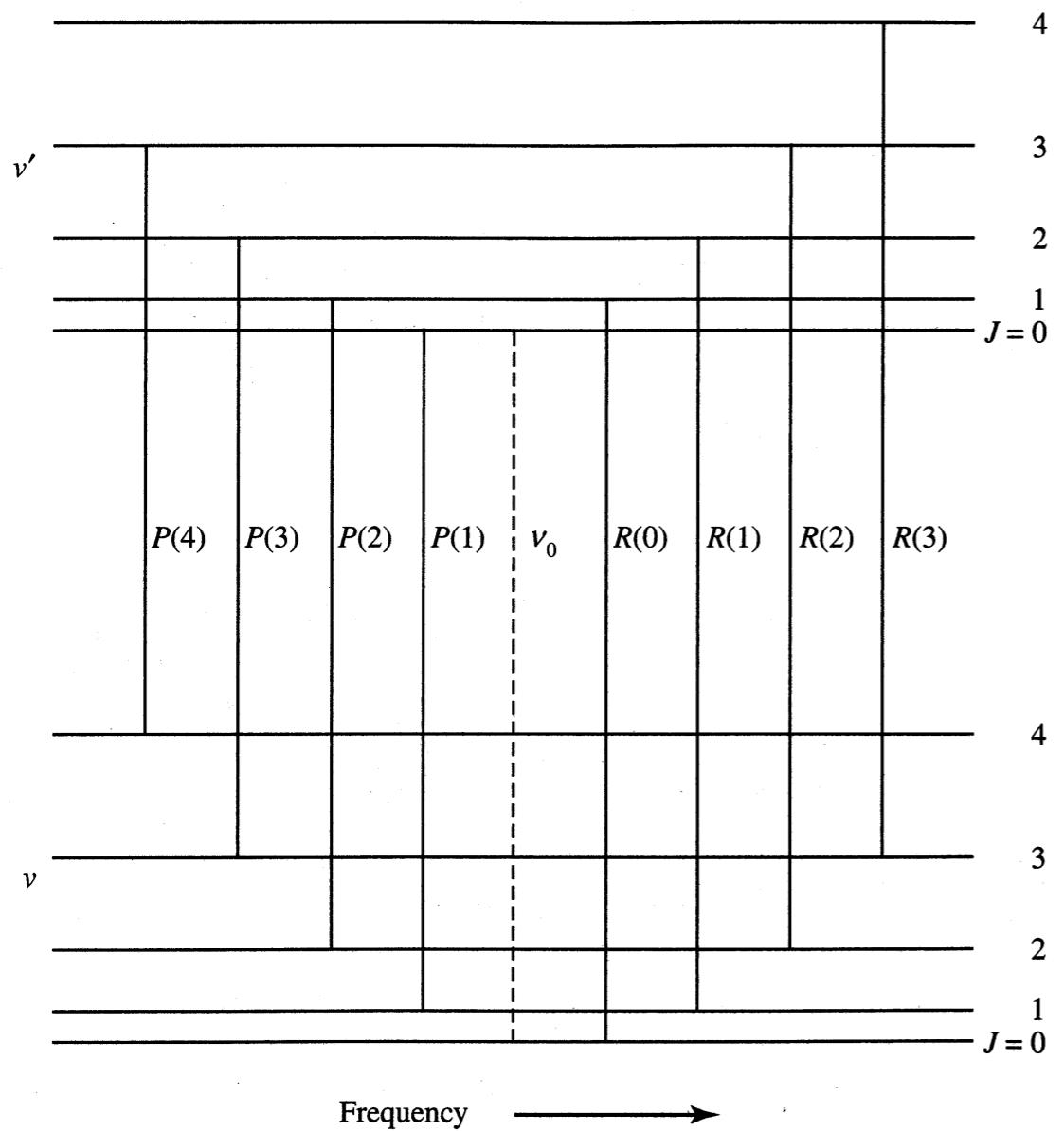
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- The rotational levels of diatomic molecules are specified by a single vibrational quantum number  $v$  and rotational quantum number  $J$ .
  - **Transitions will change  $J$  by either  $0, \pm 1$  or  $\pm 2$ .**
  - It is customary to identify transitions by specifying the upper and lower electronic states, upper and lower vibrational states, and one of the follows:  $O(J_\ell)$ ,  $P(J_\ell)$ ,  $Q(J_\ell)$ ,  $R(J_\ell)$ ,  $S(J_\ell)$
  - The usage of the symbols are shown in the following table.

Designation $(J_u - J_\ell)$	Note
$O(J_\ell)$	-2 Electric quadrupole transition
$P(J_\ell)$	-1 Electric dipole transition
$Q(J_\ell)$	0 Electric dipole or electric quadrupole; $Q(0)$ is forbidden
$R(J_\ell)$	+1 Electric dipole transition
$S(J_\ell)$	+2 Electric quadrupole transition

- For instance, a transition from the the  $v_\ell = 0, J_\ell = 1$  level of the ground electronic state to the  $v_u = 5, J_u = 2$  level of the first electronic excited state would be written

B-X 5-0  $R(1)$



# [Hyperfine Splitting & Ortho-H<sub>2</sub> and Para-H<sub>2</sub>]

- **Hyperfine splitting:** If one or more nuclei have nonzero nuclear spin and  $J_{ez} \neq 0$ , then there will be an interaction between the nuclear magnetic moment and the magnetic field generated by the electrons, resulting in “hyperfine splitting.” The energy will depend on the orientation of the nuclear angular momentum relative to the axis.
- **Ortho-H<sub>2</sub> and Para-H<sub>2</sub>**

In the case of H<sub>2</sub>, the electronic wave function is required to be antisymmetric under exchange of the two electrons.

The two protons, just like electrons, are identical fermions, and therefore, the Pauli exclusion principle antisymmetric requirement also applies to exchange of the two protons. The protons are spin 1/2 particles - the two protons together can have total spin 1 (parallel) or total spin 0 (antiparallel).

The consequence of the antisymmetry requirement is that

If the protons have spin 0, the rotational quantum number  $J$  must be even.  $\Rightarrow$  para-H<sub>2</sub> (even  $J$ )

(an antisymmetric nuclear spin wave function ( $I = 0$ ) and a symmetric spatial wave function involving even values of the rotational quantum number  $J$ )

If the protons have spin 1, the rotational quantum number  $J$  must be odd.  $\Rightarrow$  ortho-H<sub>2</sub> (odd  $J$ )

(a symmetric nuclear spin wave function ( $I = 1$ ) and an antisymmetric spatial wave function involving odd values of the rotational quantum number  $J$ )

Because the nuclear spins are only weakly coupled to the electromagnetic field, ortho-H<sub>2</sub> and para-H<sub>2</sub> behave as almost distinct species.

- 
- **H<sub>2</sub> has no permanent electric dipole moment.**
  - The vibrational states and the rotational states radiate very weakly, via the time-variation of the electric quadrupole moment and the molecule vibrates or rotates.
  - Because the nuclear spin state does not change, the ro-vibrational radiative transitions of H<sub>2</sub> must have  $\Delta J = 0$  or  $\Delta J = \pm 2$ , i.e., ortho  $\rightarrow$  ortho or para  $\rightarrow$  para  
(not  $J = 0 \leftrightarrow J = 0$ )

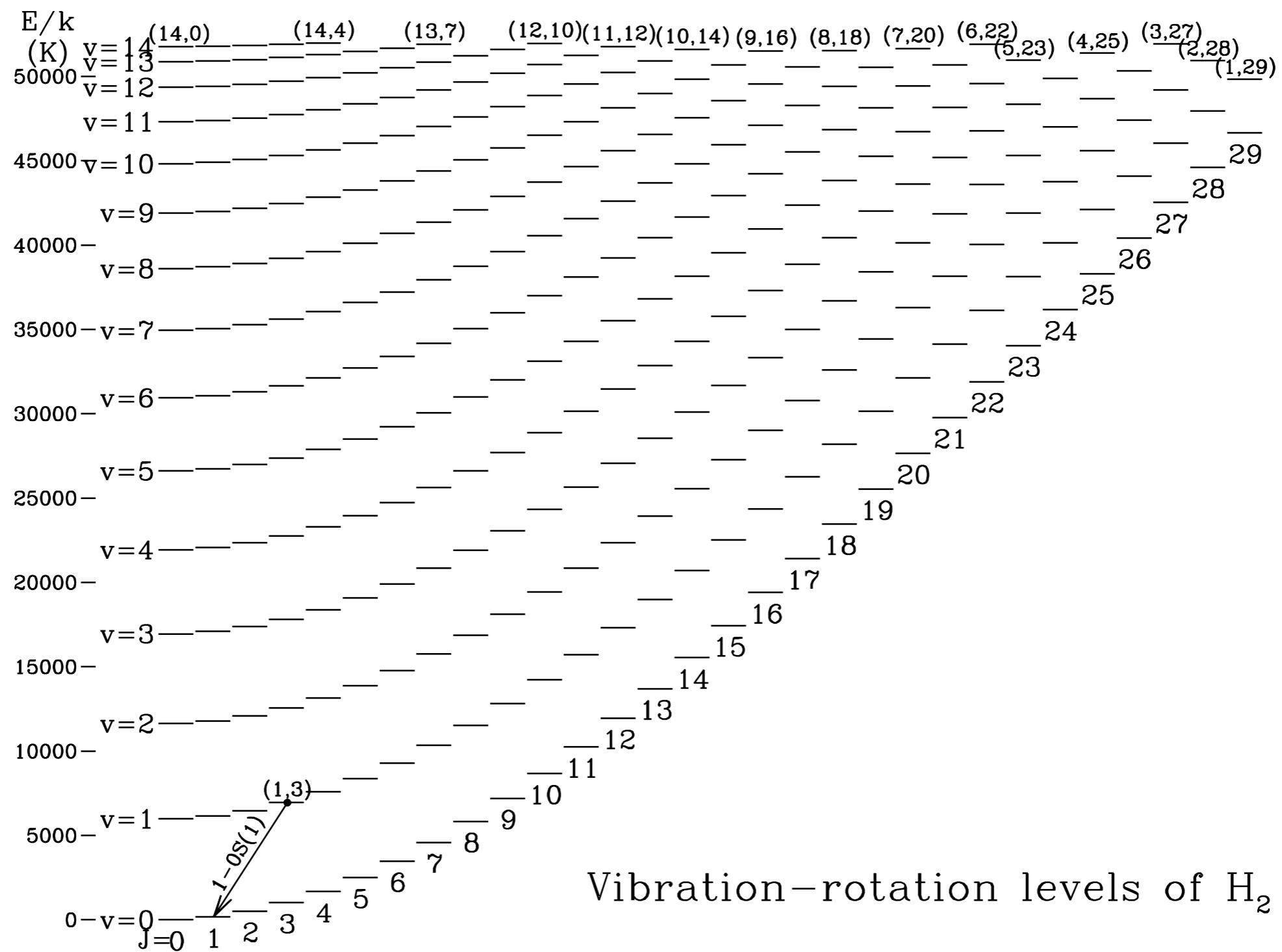
The vibration-rotation emission spectrum of H<sub>2</sub> therefore consists of electric quadrupole transitions. Therefore, the H<sub>2</sub> emission lines are faint and hard to detect. The downward transitions are identified by

$$\begin{aligned} v_u - v_\ell \ S(J_\ell) &\quad \text{if } J_\ell = J_u - 2 \ , \\ v_u - v_\ell \ Q(J_\ell) &\quad \text{if } J_\ell = J_u \ , \\ v_u - v_\ell \ O(J_\ell) &\quad \text{if } J_\ell = J_u + 2 \ . \end{aligned}$$

For example, 1-0 S(1) refers to the transition  $(v = 1, J = 3) \rightarrow (v = 0, J = 1)$ .

- Spin-exchange collisions with H<sup>0</sup> or H<sup>+</sup>, and a process in which H<sub>2</sub> is captured on a grain surface, can cause an ortho-para conversion.
- The statistical weight of an ortho-H<sub>2</sub> rotational level  $J$  is  $3(2J+1)$ . [because  $S_{\text{nucleus}} = 1$ ]

For a para-H<sub>2</sub> it is  $(2J+1)$ . [because  $S_{\text{nucleus}} = 0$ ]



# Maser Emissions

- Microwave amplification stimulated emission of radiation (maser) action is observed from at least 36 molecules including SiO, OH and water, usually at IR and microwave frequencies.
- The population inversion necessary to cause maser action can be created by a number of mechanisms including optical pumping, radiation trapping in certain long-lived levels and selective collisional excitation of the masing molecule.
- In the righthand side figure, the levels are vibration-rotation levels of the electronic ground state. If level A is excited in some collision process, such as scattering with  $H_2$ , and level B is not, then the population of level A can be greater than the population of level B. The situation gives a non-thermal population and can lead to maser action.

