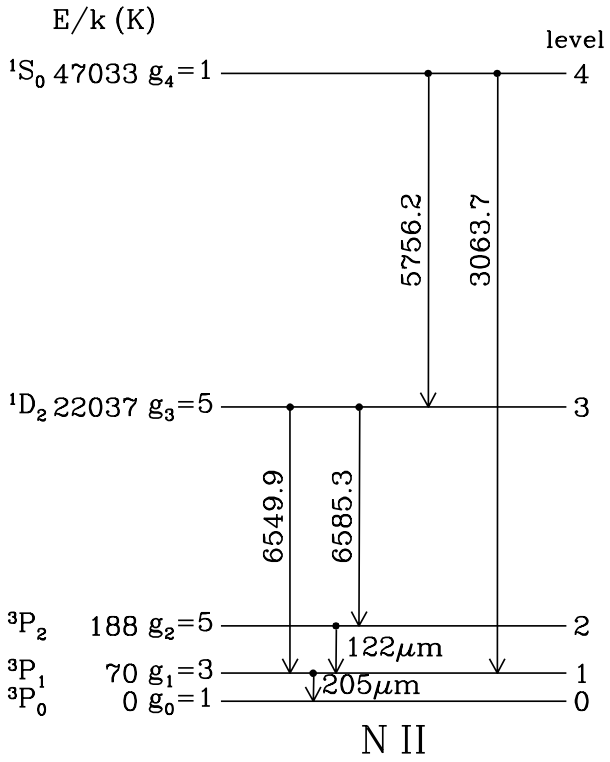
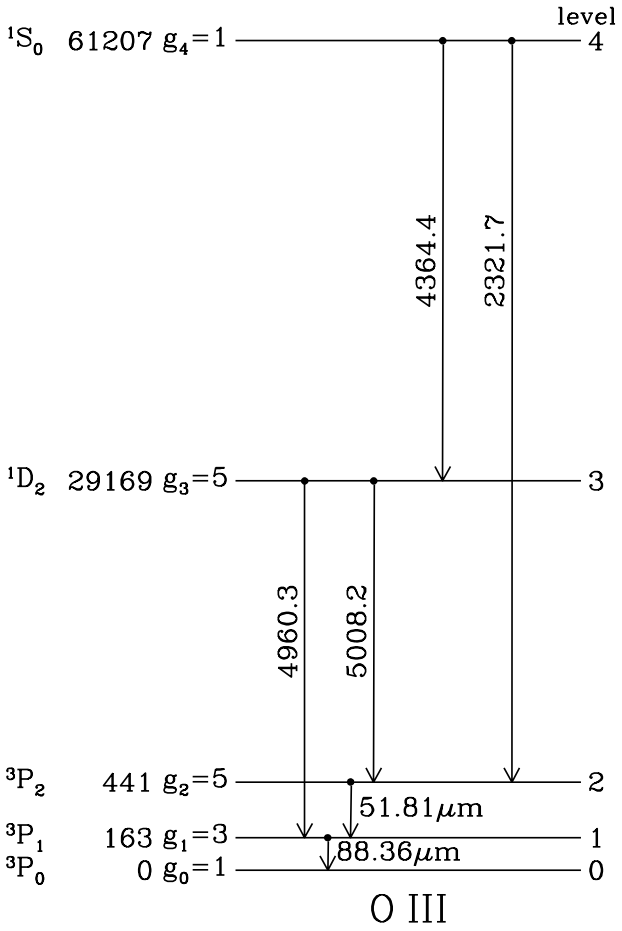
INTERSTELLAR MEDIUM

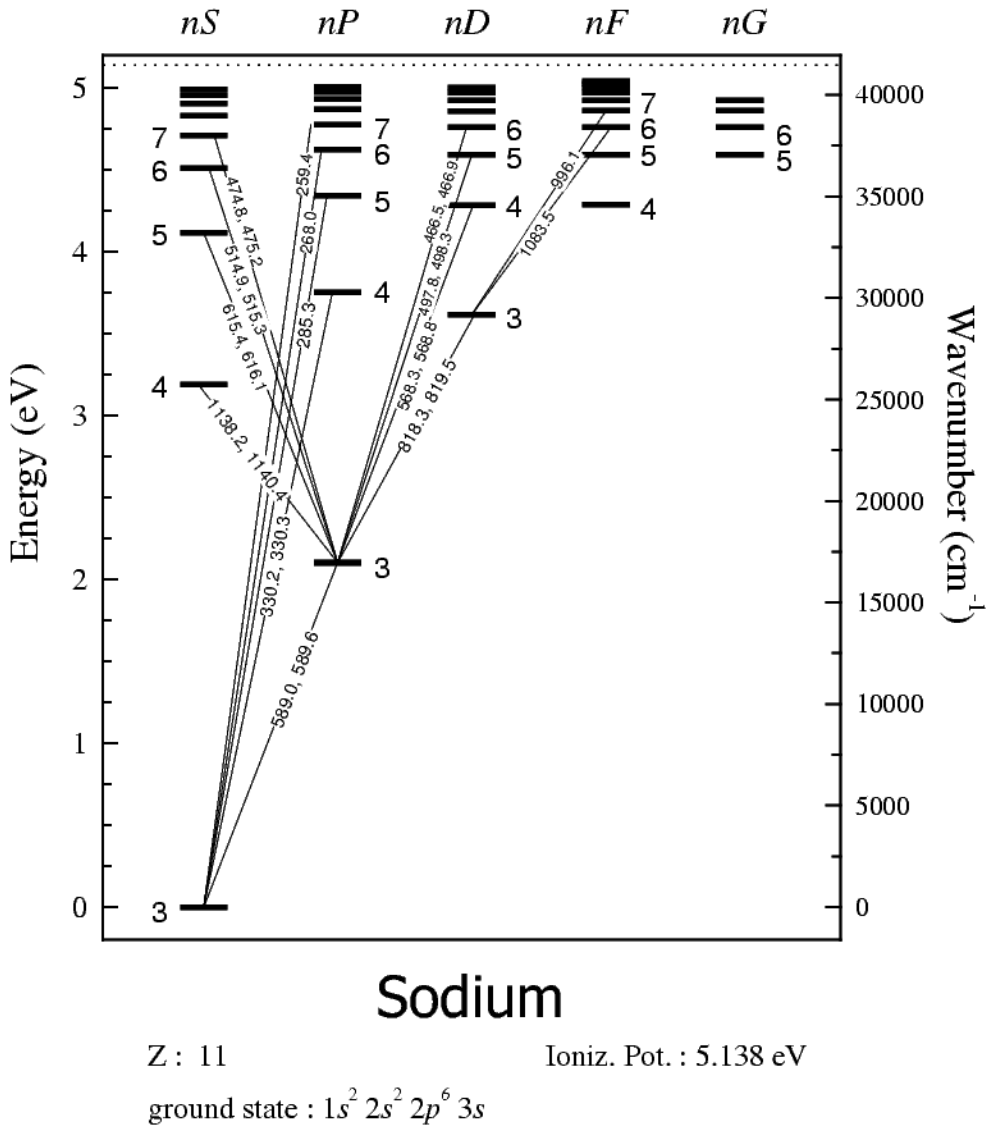
- Stefano Bovino -

Atomic Structure II

Goal: Understanding these diagrams!



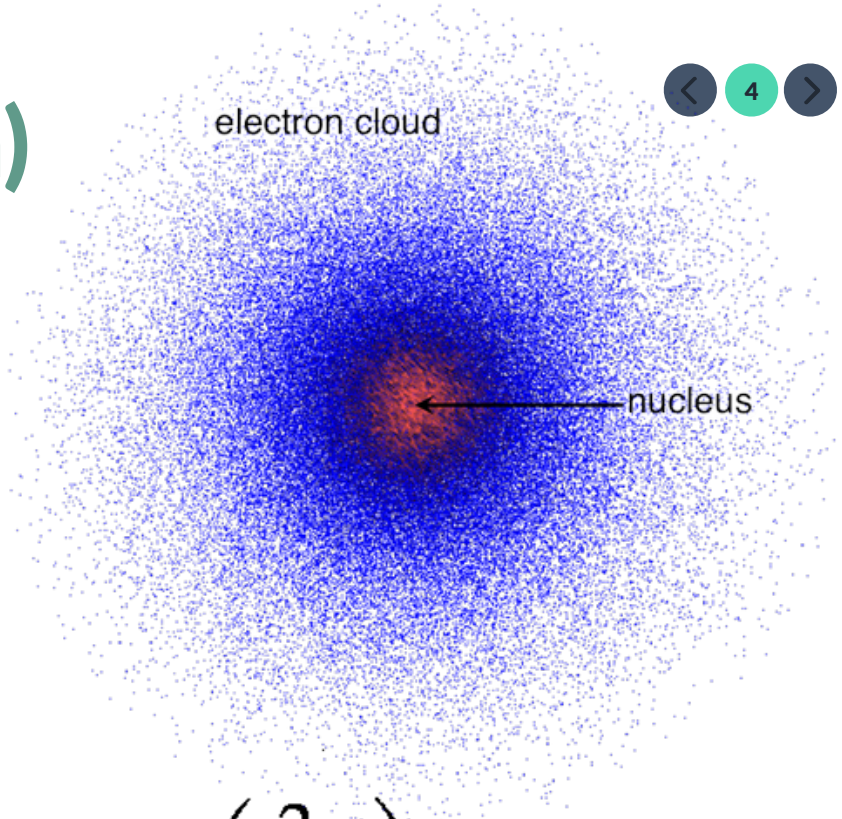




Atomic structure in a nutshell

- Electrons behave both as particles and waves (De Broglie)
- Quantisation of energy (Planck, Bohr)
- Wave function and energy of an atom (solving the S.E.)
- Wavefunction squared represents a probability (Born)

Hydrogen atom (single electron)



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

Radial

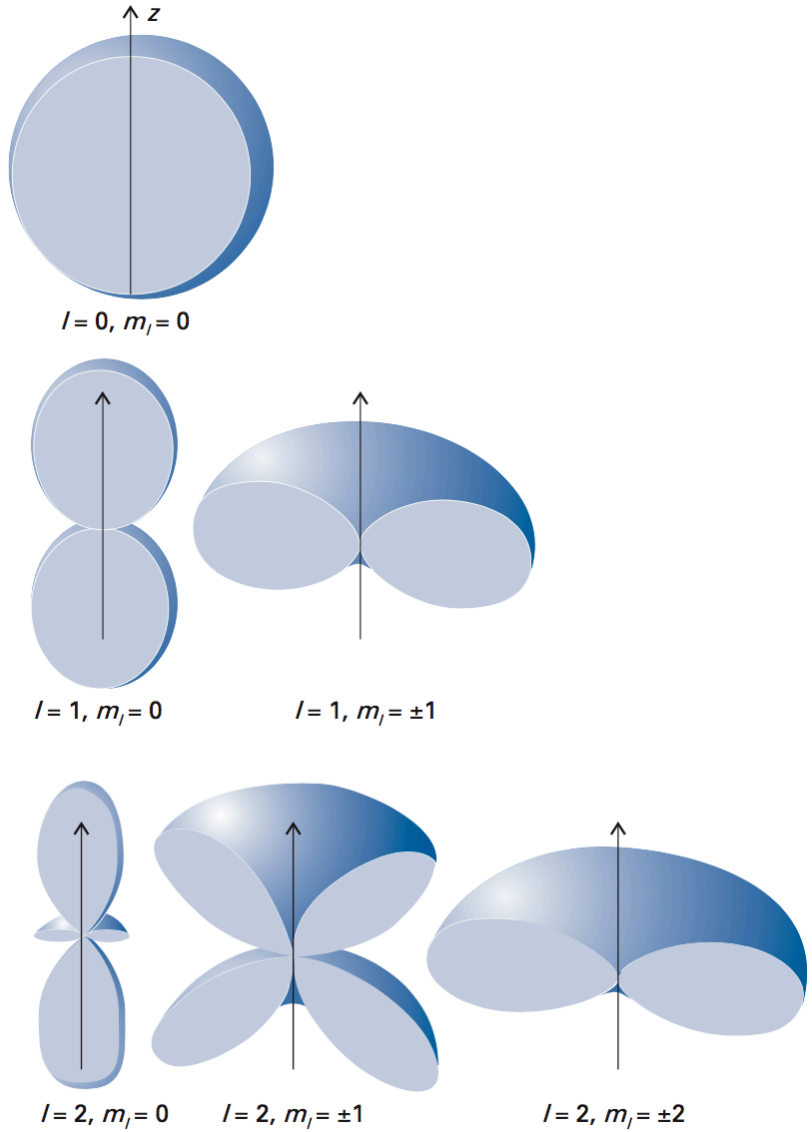
$$Y_l^m(\theta,\phi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$

Angular

Quantum numbers describe orbitals

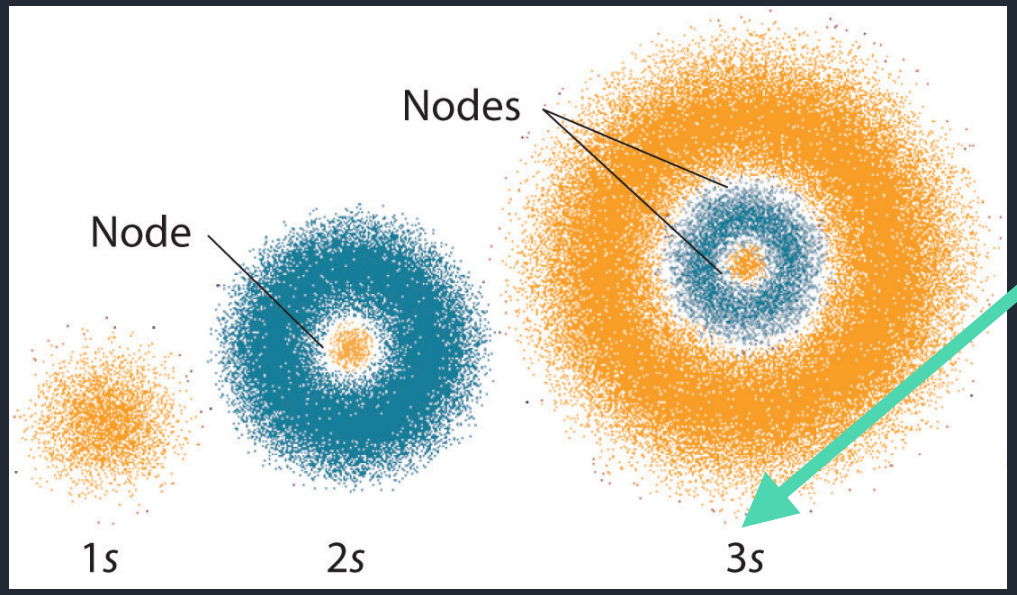
Orbitals represent regions of probability where an electron can be found

Each orbital can hold up to a maximum of 2 electrons (Pauli principle)



- n → principal quantum number
- Specifies the energy of the orbital and the shell
- Assume values n = 1, 2, 3…
- Larger the value of n further away from the nucleus the electron is

Energy →

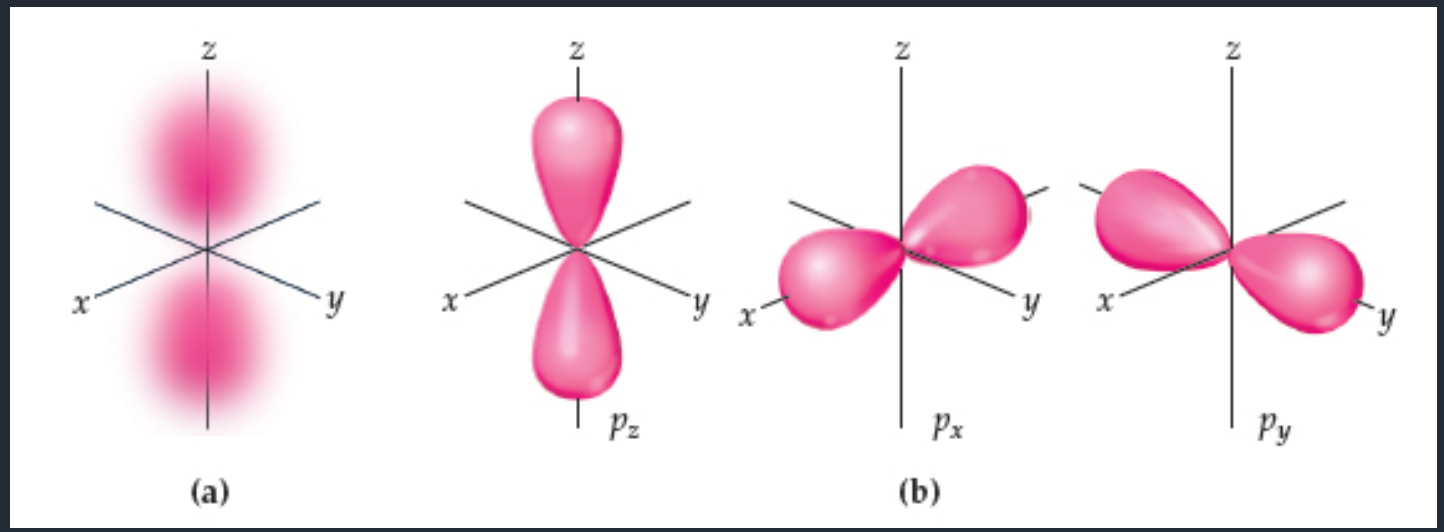


Principal quantum number

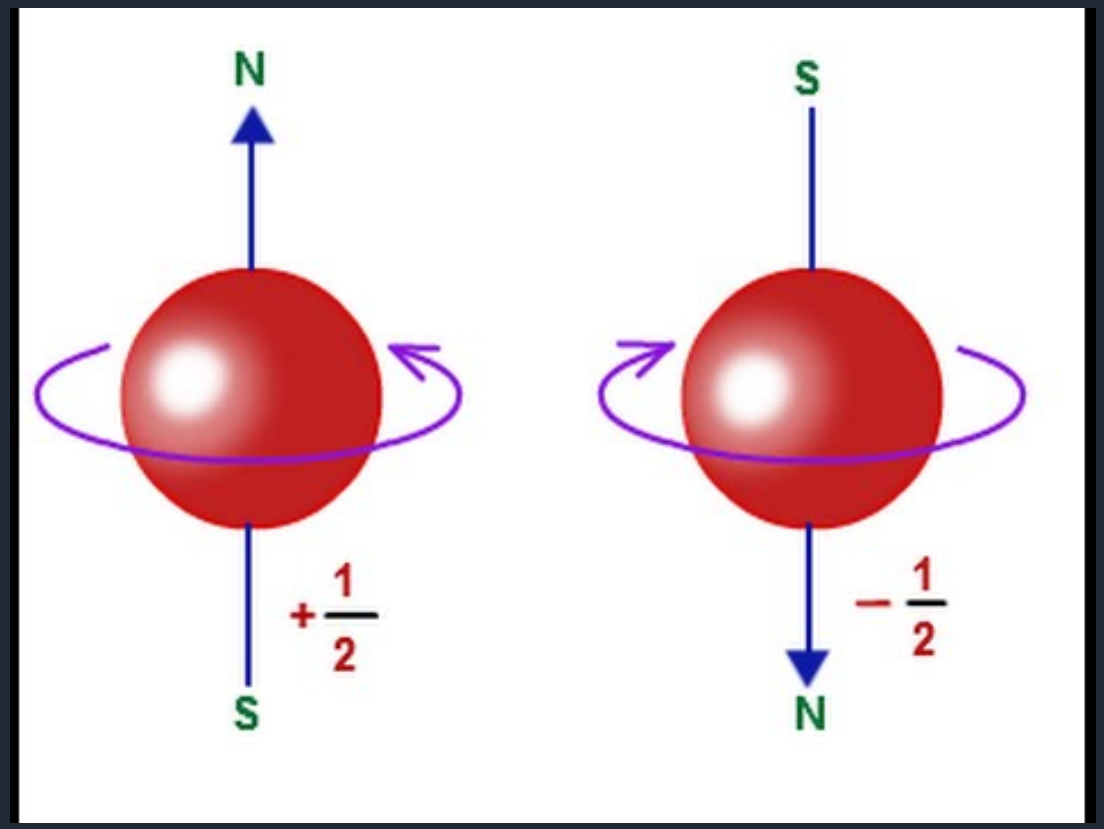
- l → orbital (angular momentum) quantum number
- Defines the shape of the orbitals
- Assume values l = 0, 1, 2, n-1

0	1	2	3
s-orbital	p-orbital	d-orbital	f-orbital

- m_l ⟶ magnetic quantum number
- Orientation of the angular momentum around the nucleus
- How many orbitals of that kind exist per energy level
- Assume values m_l = l, l-1,-l
- 2l + 1 values of m_l for a given value of l



- s, m_s → spin magnetic quantum number (z-component)
- Intrinsic angular momentum of the electron
- Assume values m_s = -1/2, +1/2



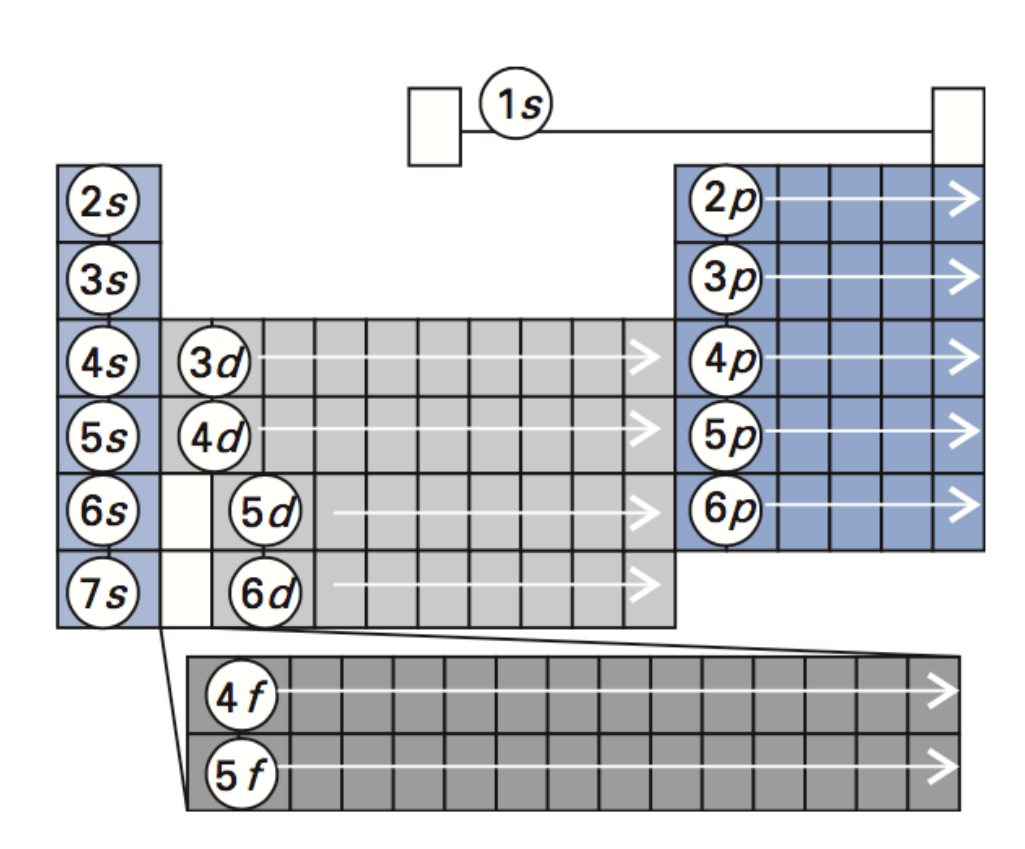
Electronic configuration

- Configuration specifies the orbitals that electrons occupy
- H ($1s^1$) means one electron occupies a 1s-orbital
- A single configuration (e.g. $2p^1$) can split in more levels (different j)

Hund's rules
Pauli principle

Multielectrons systems

Aufbau principle



Hund's rules
Pauli principle

Example: CI or NII

Six electrons

$1s^2 2s^2 2p^2$

Multielectrons systems

- Chemists (and spectroscopists) introduced the term symbols

$$\text{multiplicity} \rightarrow 2S+1 \{L\}_{J \leftarrow \text{Level}} \leftarrow \text{orbital angular momentum}$$

Example: Hydrogen atom

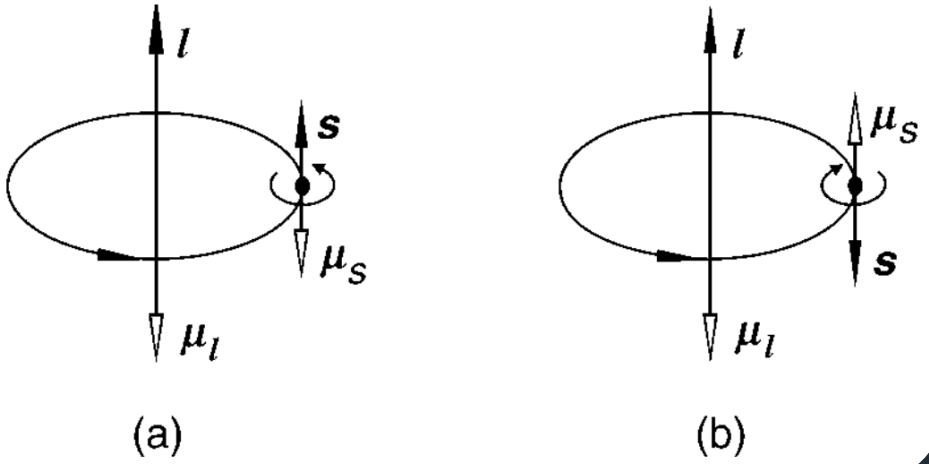
One electron

$1s^1$

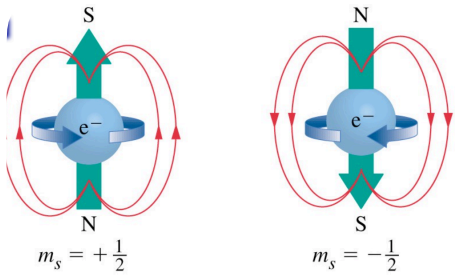
What is the term symbol of the ground state?

Spin-orbit coupling

- Rotation of an electrical charge generates a magnetic dipole (classical electrodynamics)
- The spin and orbital angular momenta (e-) couple
- This generates a splitting of a given energetic level (fine structure)
- This can be further split by the presence of a magnetic field (hyperfine structure)



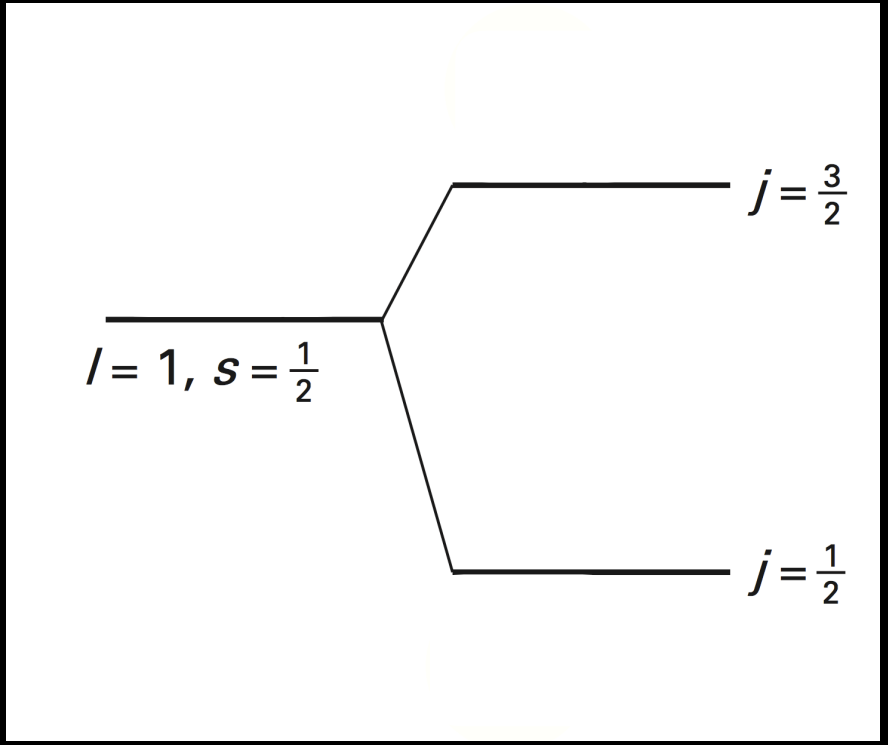
The energy shift depends on L and S

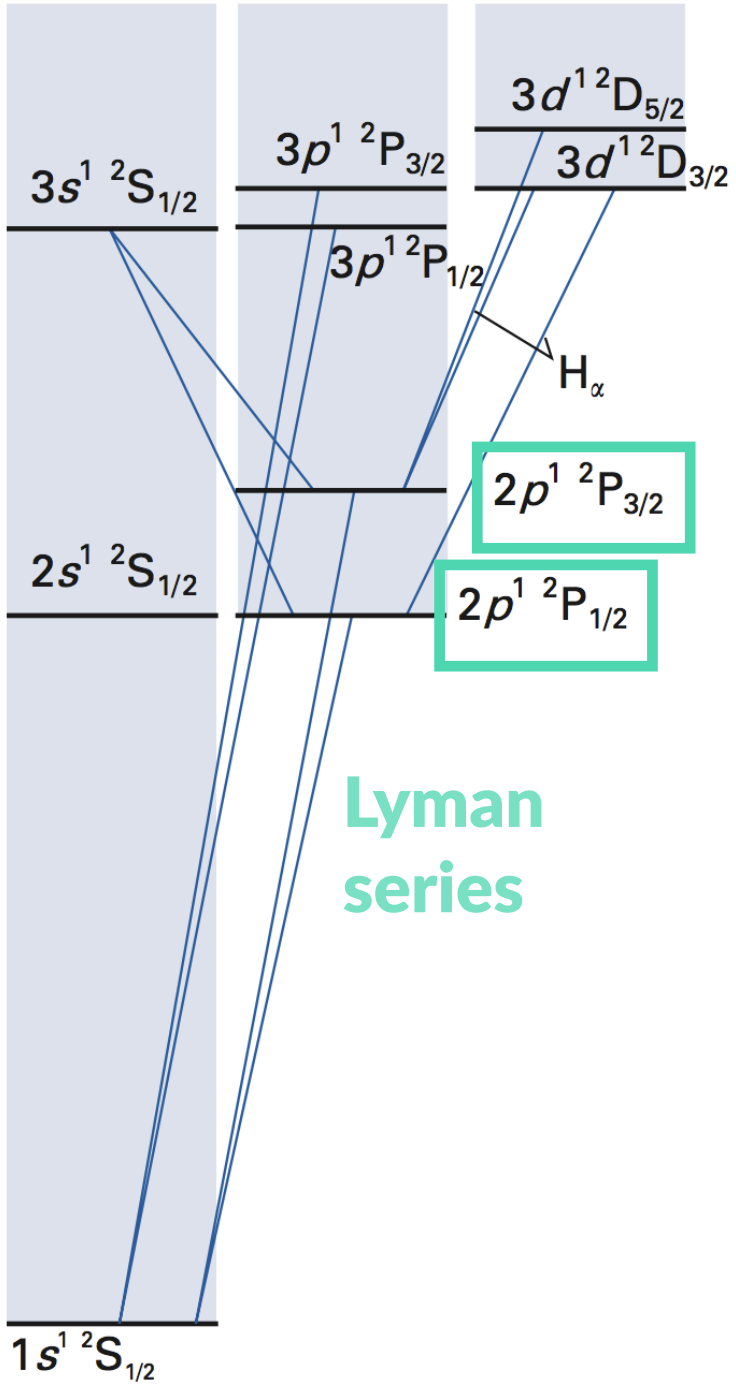


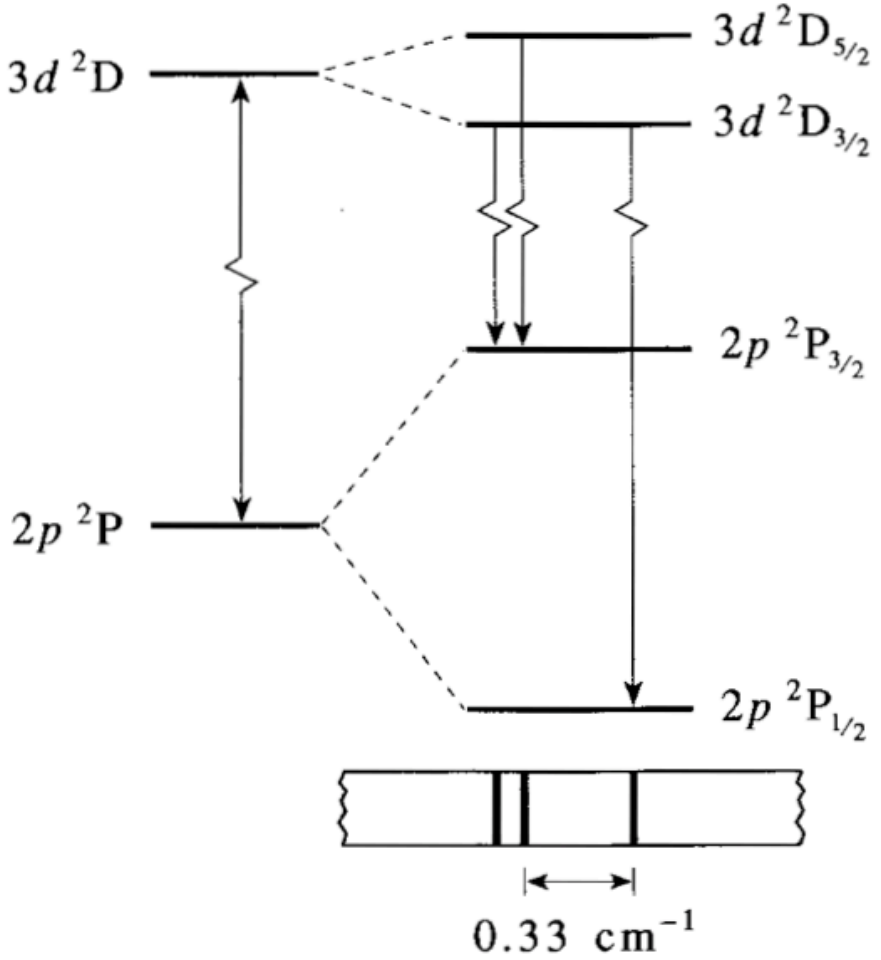
Spin-orbit coupling (fine)

$j = l + s$

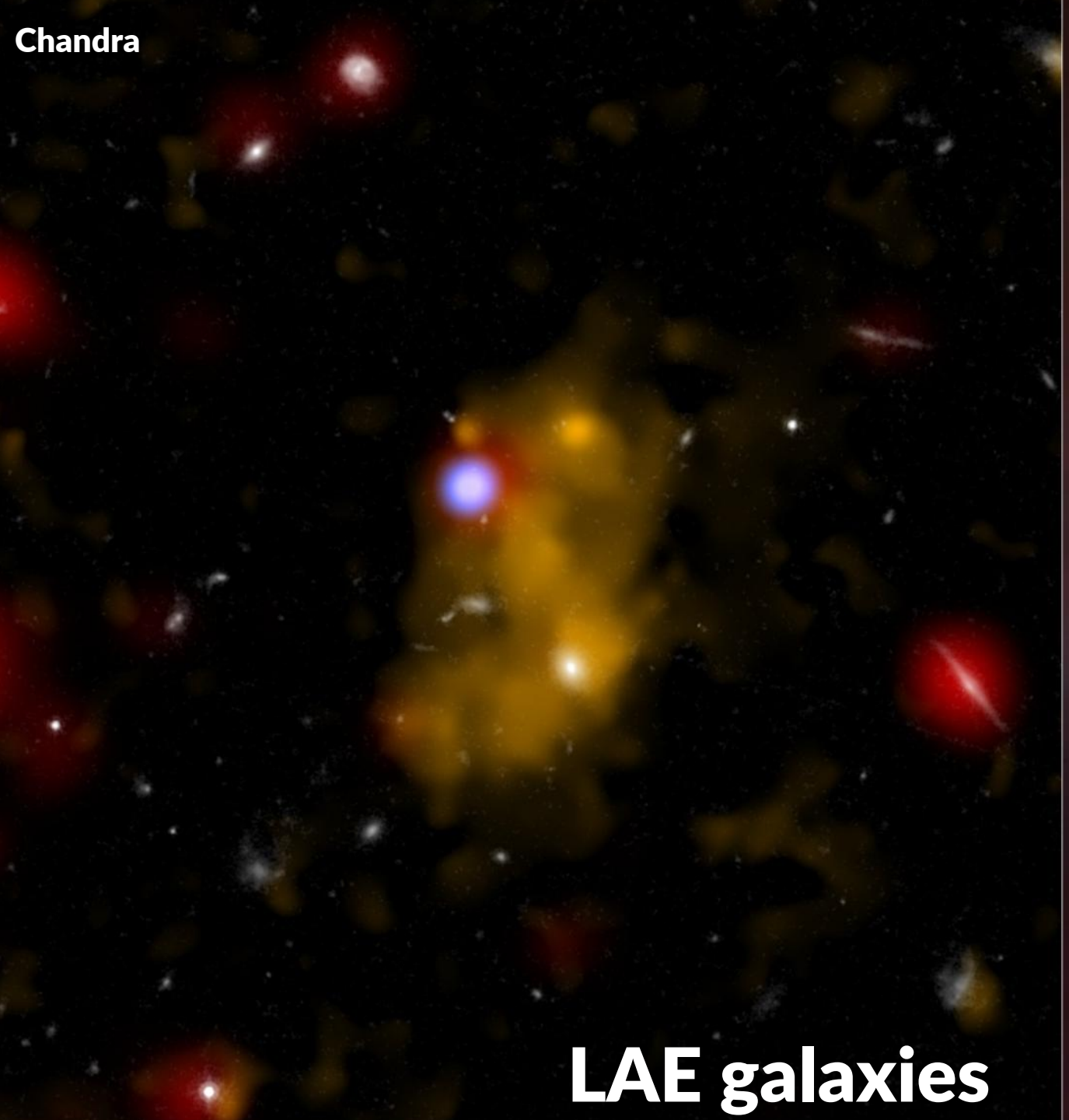
Doublet

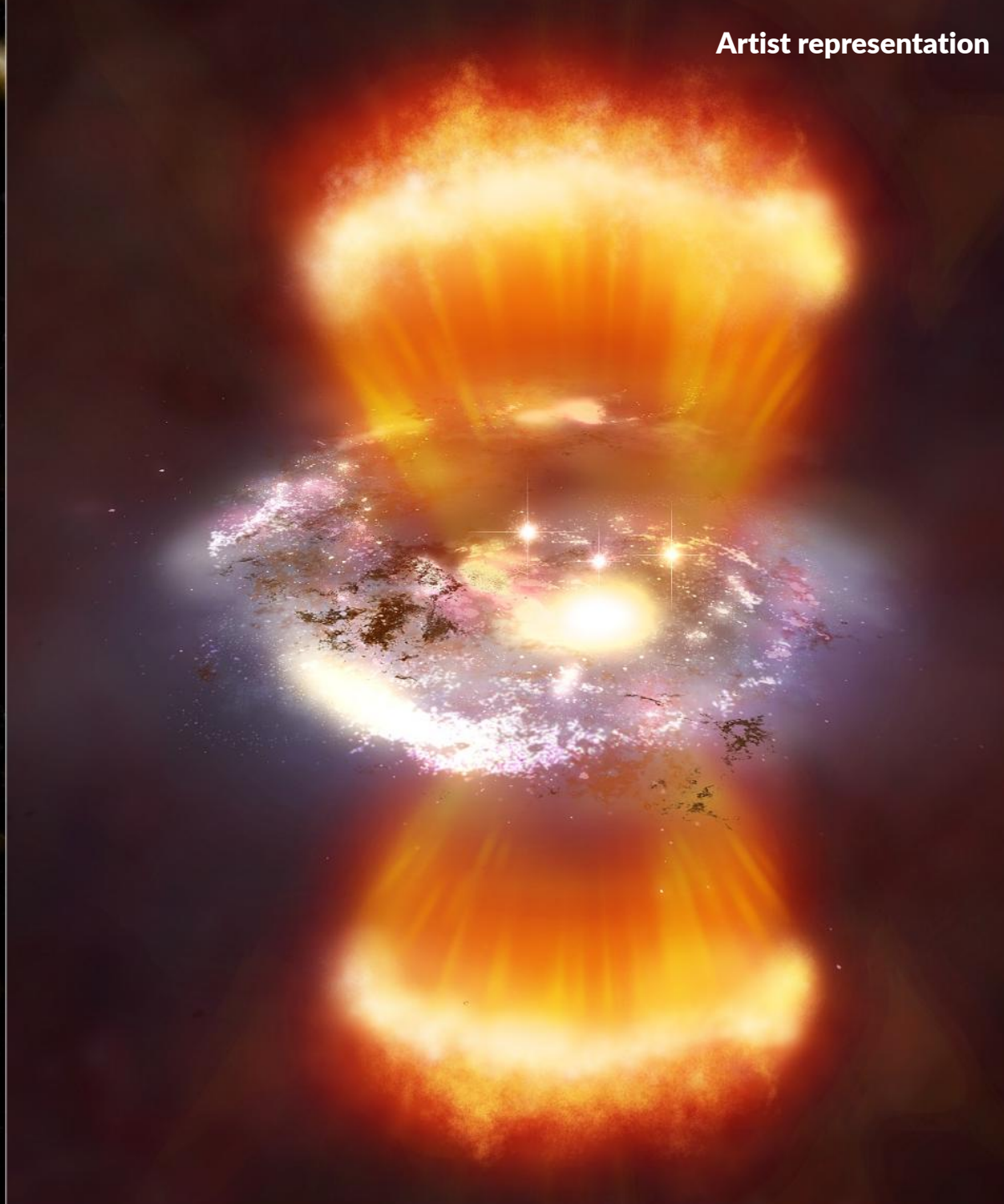




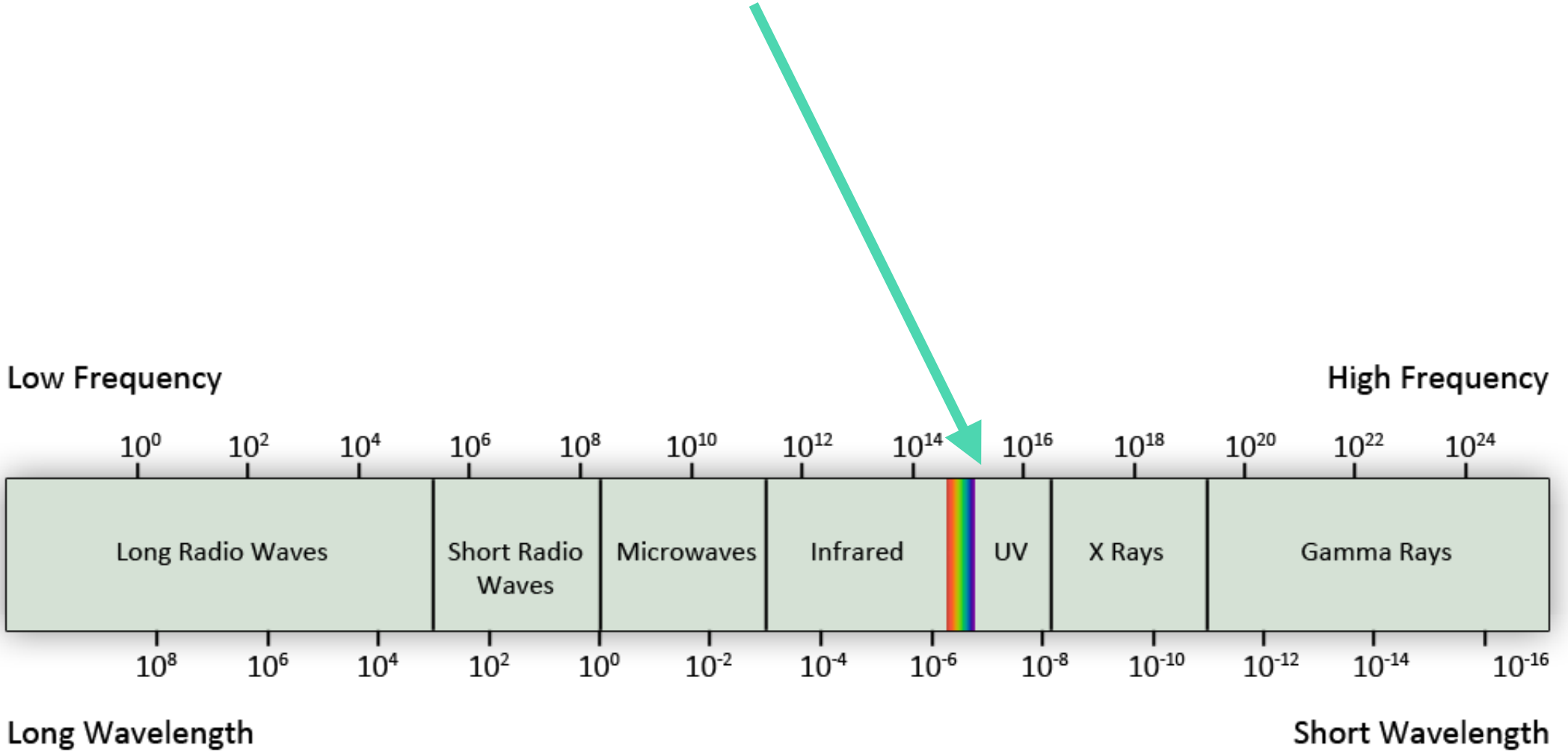


Spin-orbit coupling

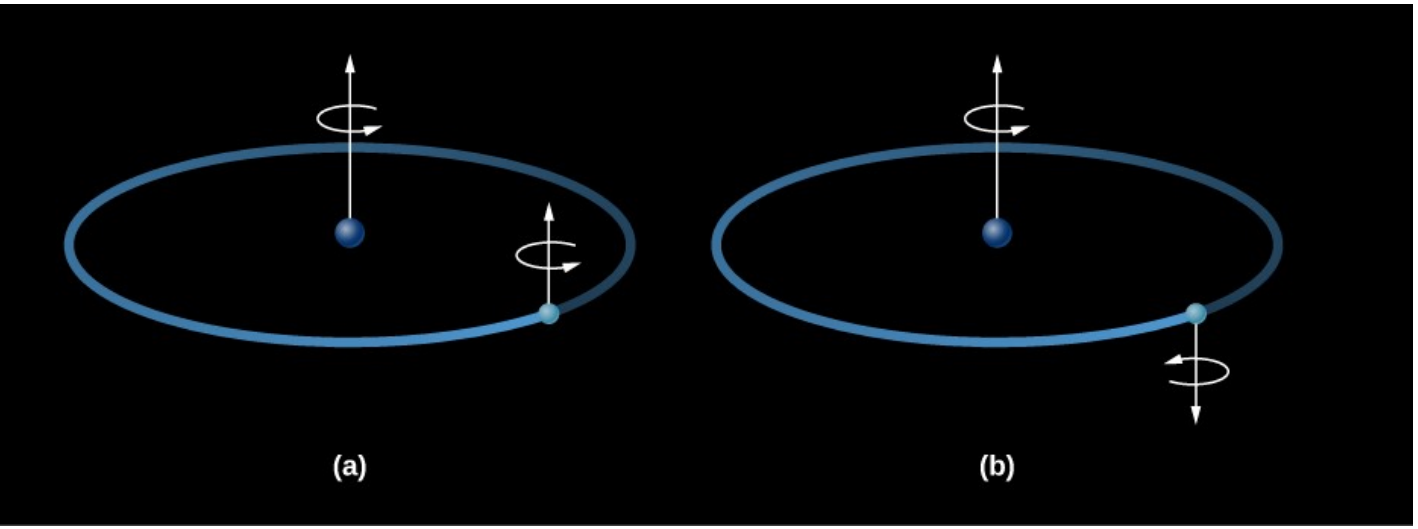

Chandra
LAE galaxies

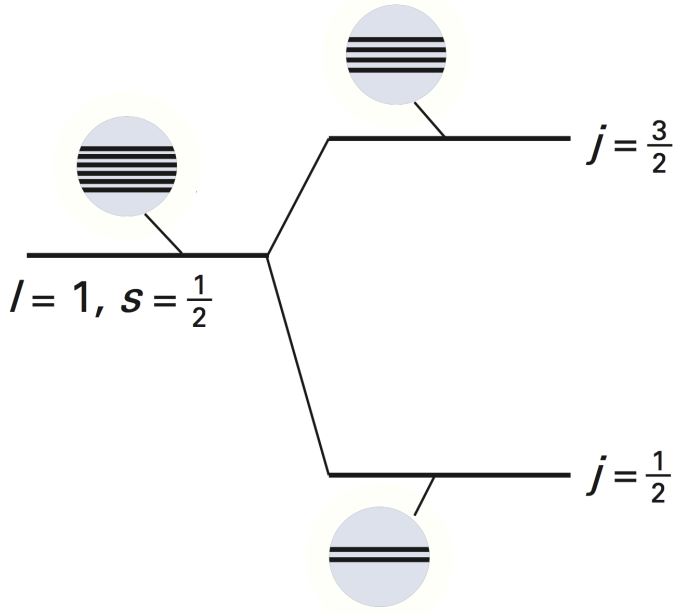

Artist representation

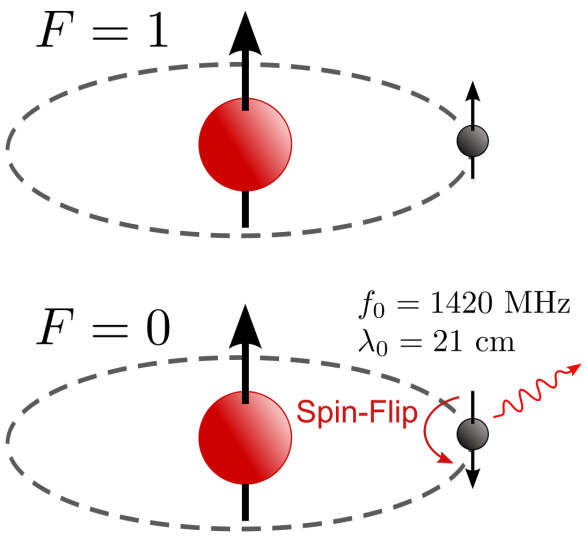
Ly-alpha observable in UV: 2.45 x 10^{15} Hz

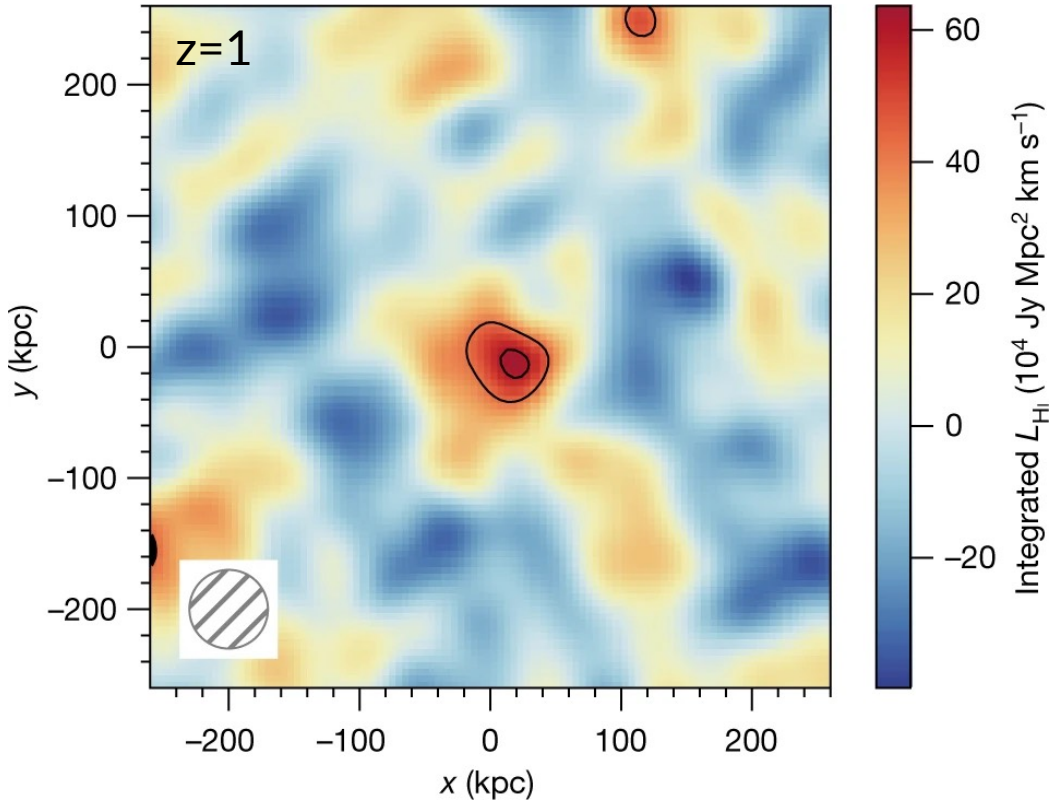


Spin-orbit coupling (hyperfine)









Chowdhury+, Nature, 2020

Obtained with
Giant Metrewave Radio Telescope (PUNA)

Multielectrons systems

- Chemists (and spectroscopists) introduced the term symbols

$$\text{multiplicity} \rightarrow 2S+1 \{L\}_{J \leftarrow \text{Level}} \leftarrow \text{orbital angular momentum}$$

Example: CI or NII

Six electrons

$1s^2 2s^2 2p^2$

^3P (L=1, S=1), ^1D (L=2, S=0), ^1S (L=0, S=0)

Symbol	Name	Allowed Range
L	Total orbital angular momentum	$\lvert l_1 + l_2\rvert, \ldots, \lvert l_1 - l_2\rvert$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, \ldots, -m_{l1} - m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\lvert m_{s1} + m_{s2}\rvert, \ldots, \lvert m_{s1} - m_{s2}\rvert$
S	Inherent Spin Number	$\lvert s_1 + s_2\rvert, \ldots, \lvert s_1 - s_2\rvert$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, \ldots, \lvert L - S\rvert$

Multielectrons:

1. Non-equivalent → Electrons with different n and/or l ($3p^1 3d^1$)
2. Equivalent → Electrons with same n and l ($2p^2$)

Table 7.2 Terms arising from some configurations of non-equivalent and equivalent electrons

Non-equivalent electrons		Equivalent electrons	
Configuration	Terms	Configuration	Terms[a]
s^1s^1	$^{1,3}S$	p^2	$^1S, ^3P, ^1D$
s^1p^1	$^{1,3}P$	p^3	$^4S, ^2P, ^2D$
s^1d^1	$^{1,3}D$	d^2	$^1S, ^3P, ^1D, ^3F, ^1G$
s^1f^1	$^{1,3}F$	d^3	$^2P, ^4P, ^2D(2), ^2F,$
p^1p^1	$^{1,3}S, ^{1,3}P, ^{1,3}D$		$^4F, ^2G, ^2H$
p^1d^1	$^{1,3}P, ^{1,3}D, ^{1,3}F$	d^4	$^1S(2), ^3P(2), ^1D(2),$
p^1f^1	$^{1,3}D, ^{1,3}F, ^{1,3}G$		$^3D, ^5D, ^1F, ^3F(2),$
d^1d^1	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G$		$^1G(2), ^3G, ^3H, ^1I$
d^1f^1	$^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G, ^{1,3}H$	d^5	$^2S, ^6S, ^2P, ^4P, ^2D(3),$
f^1f^1	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G,$		$^4D, ^2F(2), ^4F, ^2G(2),$
	$^{1,3}H, ^{1,3}I$		$^4G, ^2H, ^2I$

[a] The numbers in brackets indicate that a particular term occurs more than once.

Table 7.3 Derivation of terms arising from two equivalent p electrons

Quantum number	Values														
$(m_\ell)_1$	1	1	1	1	1	1	1	1	1	0	0	0	0	0	−1
$(m_\ell)_2$	1	0	0	0	0	−1	−1	−1	−1	0	−1	−1	−1	−1	−1
$(m_s)_1$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$
$(m_s)_2$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$M_L = \sum_i (m_\ell)_i$	2	1	1	1	1	0	0	0	0	0	−1	−1	−1	−1	−2
$M_s = \sum_i (m_s)_i$	0	1	0	0	−1	1	0	0	−1	0	1	0	0	−1	0

Pairs of values of M_L and M_S can be rearranged as follows:

M_L	2	1	0	−1	−2	1	0	−1	1	0	−1	1	0	−1	0
M_S	0	0	0	0	0	1	1	1	0	0	0	−1	−1	−1	0
	^1D					^3P									^1S

Hund's rules

- The state with the largest value of S is the most stable
- For states with the same S, the state with largest L is the most stable
- If the states have same S and L, the state with the smallest J is the most stable (if half filled)
- If more than half filled the state with largest J is the most stable

Term symbols: more

- Degeneracy factor **g = (2S + 1) x (2L + 1)**
- Example: ^{3}P term (S = 1, L = 1) has a **g** = 3 x 3 = 9
- If we take into consideration spin-orbit coupling these states are split into different fine structure levels
- We have then **degeneracy** g = 2J + 1

$$\text{multiplicity} \rightarrow {}^{2S+1}\{L\}_{J \leftarrow \text{Level}} \leftarrow \text{orbital angular momentum}$$

Selection rules

Are restrictions that govern the possible (or allowed) transitions from a state to another

$\Delta L = \pm 1$	**Follow conservation of angular momentum**
$\Delta S = 0$	**Spin can only change by B**
$\Delta J = 0, \pm 1$	**Follow conservation of angular momentum**

Selection rules: Spin

Singlet-Singlet, Doublet-Doublet etc. allowed

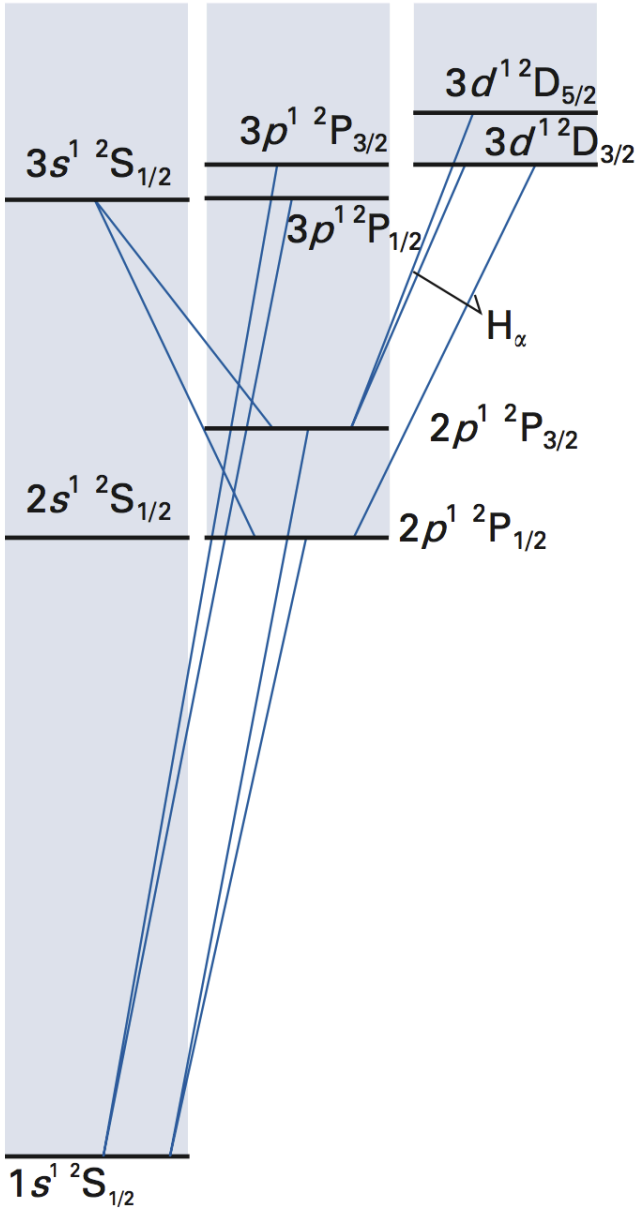
Singlet-Triplet etc. forbidden

It is also a consequence of the Pauli principle

allowed: $s \leftrightarrow p,\ p \leftrightarrow d$

forbidden: $\boldsymbol{d \leftrightarrow d},\ p \leftrightarrow p$

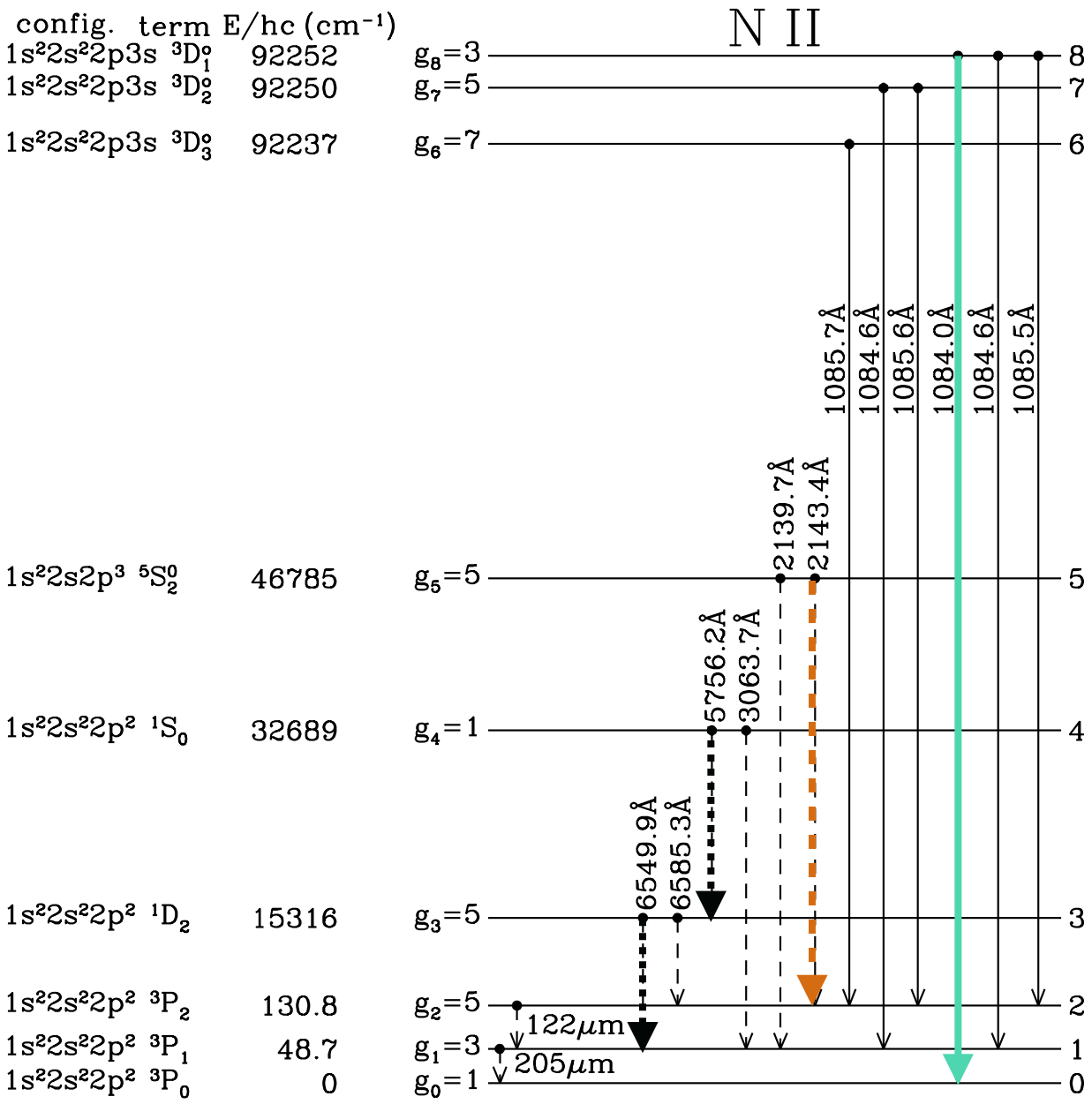
Selection rules Lyman series of H



$$np\,^2\mathrm{P}_{1/2} \rightarrow 1s\,^2\mathrm{S}_{1/2} \qquad \begin{pmatrix} \Delta L = 1 \\ \Delta S = 0 \\ \Delta J = 0 \end{pmatrix}$$

$$np\,^2\mathrm{P}_{3/2} \rightarrow 1s\,^2\mathrm{S}_{1/2} \qquad \begin{pmatrix} \Delta L = 1 \\ \Delta S = 0 \\ \Delta J = -1 \end{pmatrix}$$

$$\Delta L = \pm 1$$
$$\Delta S = 0$$
$$\Delta J = 0, \pm 1$$



Allowed transition

$^3D_1$ - $^3P_0$

$A_{ul} = 2.18 \times 10^8\ s^{-1}$

Spin forbidden transition

$^5S_2$ - $^3P_2$

$A_{ul} = 1.27 \times 10^2\ s^{-1}$

Forbidden transition

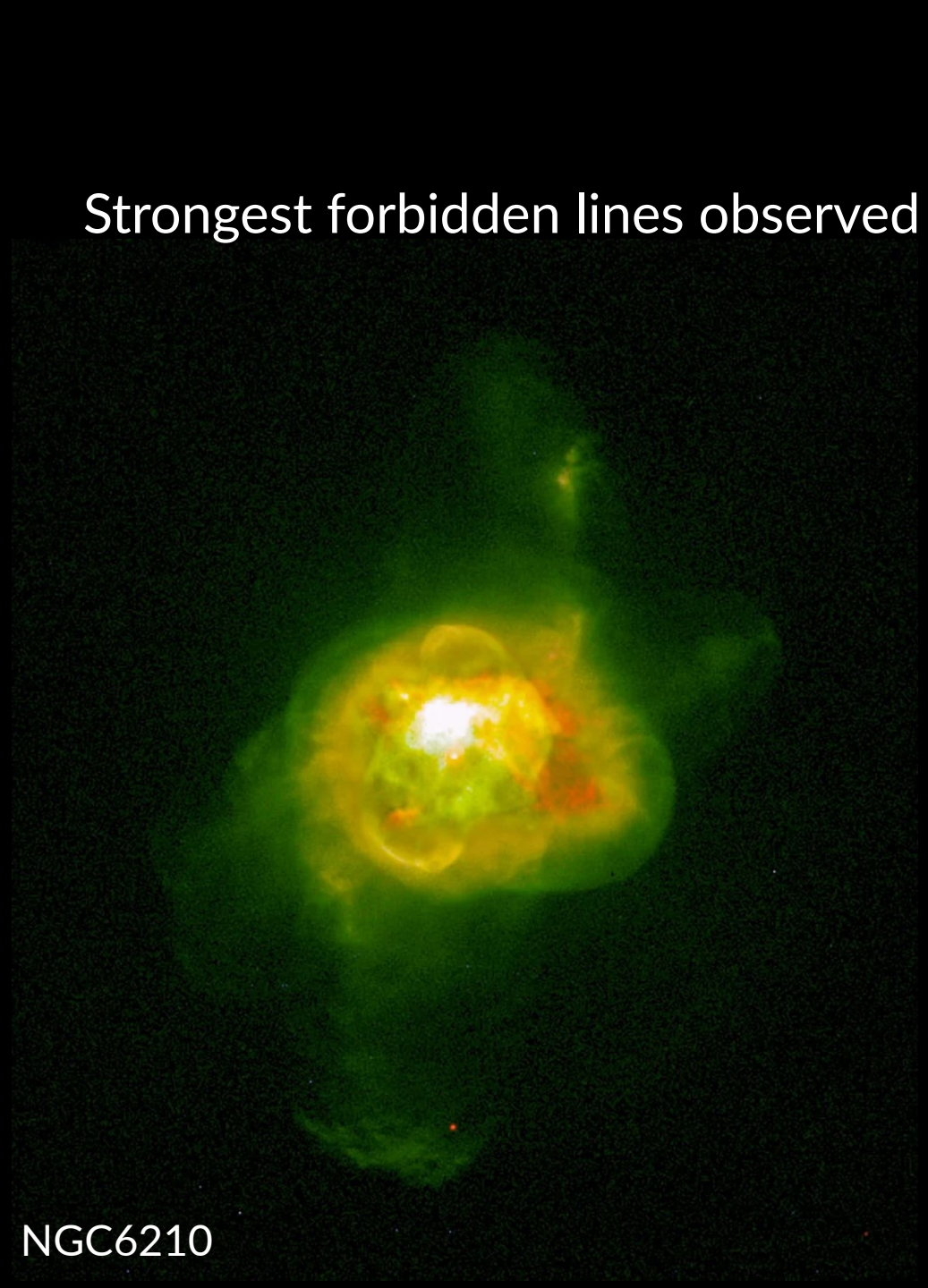
$^1D_2$ - $^3P_1$

$A_{ul} = 1.17 \times 10^0\ s^{-1}$

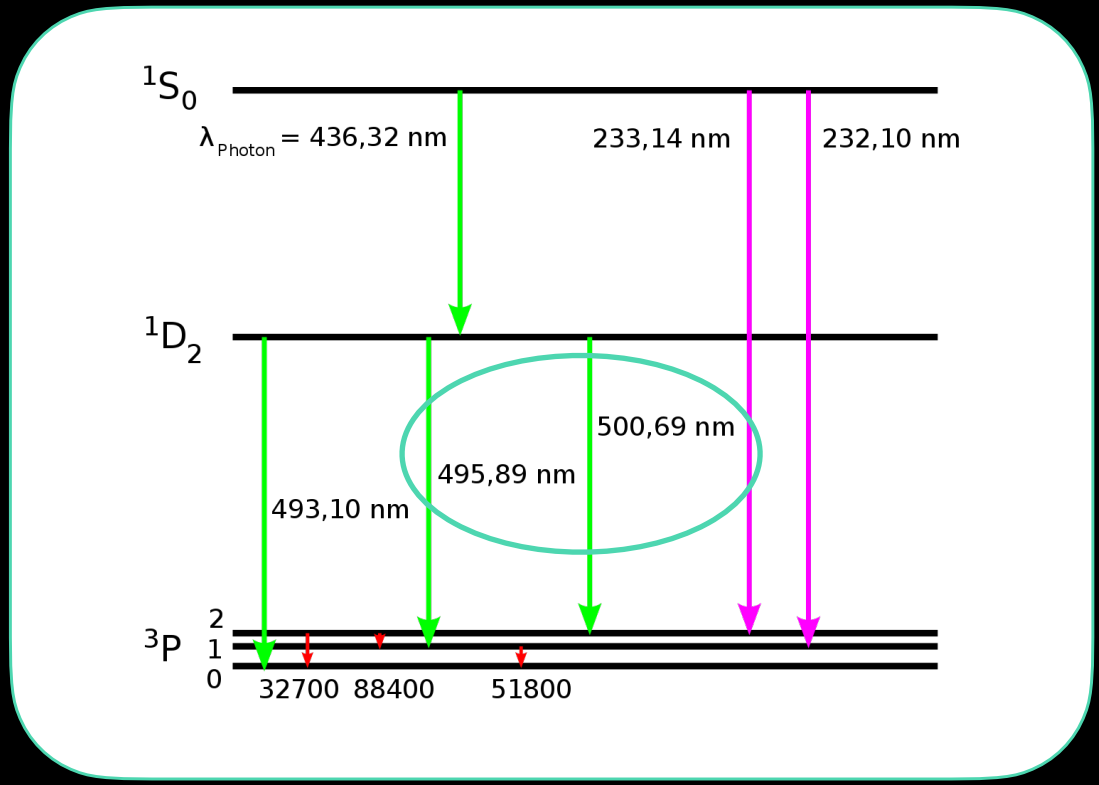
General rules

- Intersystem lines are 10^6 times weaker than permitted transitions
- Forbidden transition are 10^2-10^6 times weaker than intersystem ones
- **Forbidden transitions** are important in astrophysics in particular in the low-dense environment where timescales are much longer and slow decay could occur (collisions very rare)

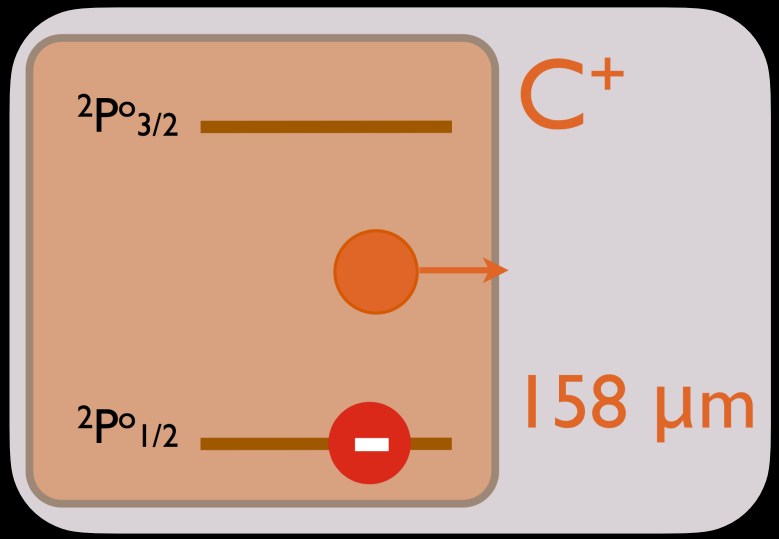
Strongest forbidden lines observed in the ISM are from doubly ionized oxygen [OIII]

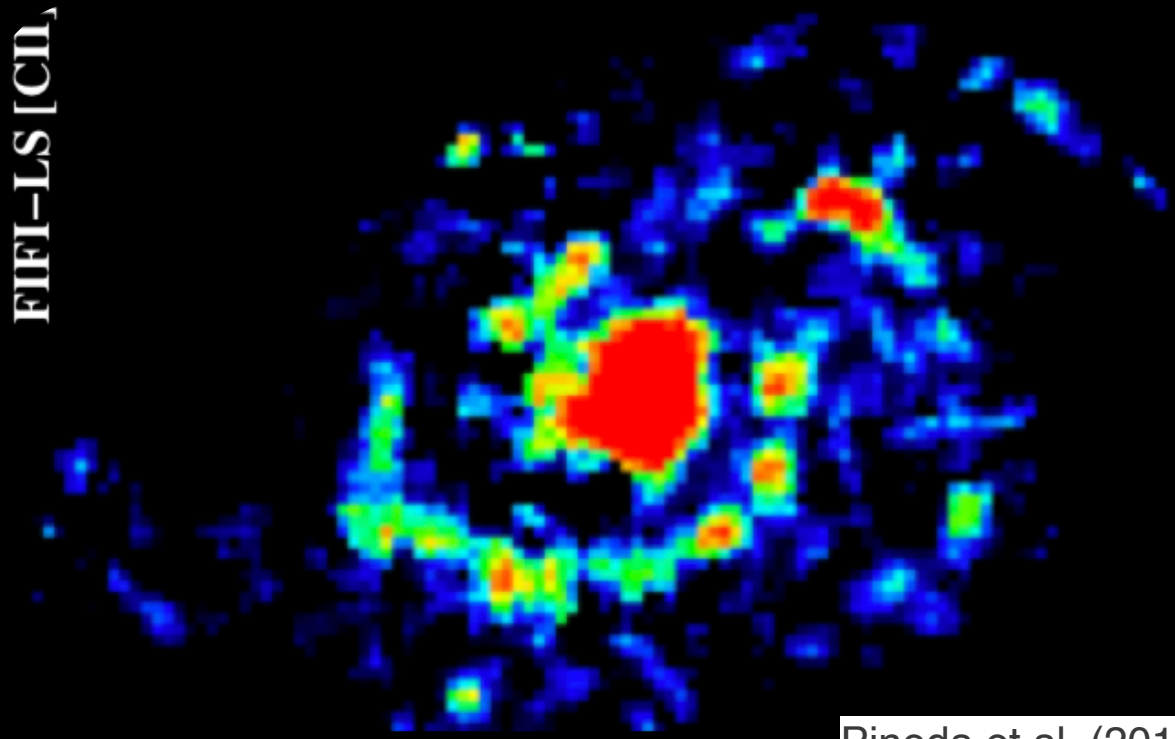


NGC6210



158 micron [CII] transition





Pineda et al. (2018)

Term symbols: Na doublet (exercise)

Sodium, Na, Z=11

Spin $\mathbf{S}$

$^{2\mathbf{S}+1}\mathcal{L}^{\mathrm{p}}_{\mathbf{J}}$

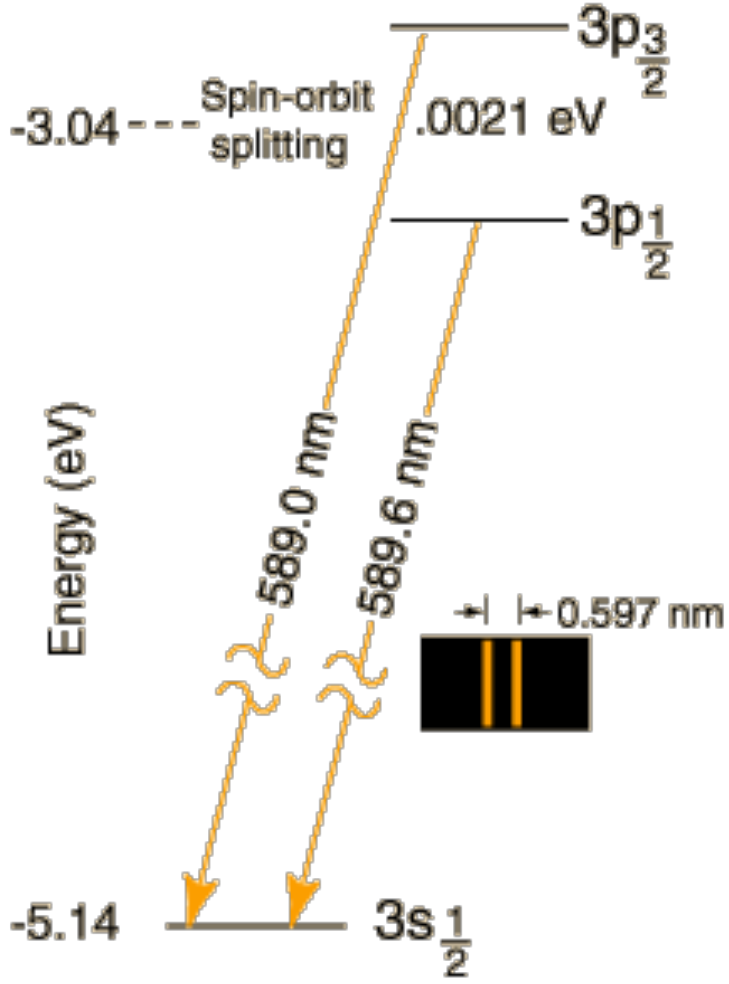
"parity" = $\Sigma \boldsymbol{l}_i$

blank if even, "o" if odd

for $1s^2\ 2s^2\ 2p^2$
parity = 0+0+0+0+1+1
= 2

Orbital Angular Momentum
S, P, D, F (for $\mathbf{L}$=0,1,2,3)

Total angular momentum
$\mathbf{J} = \mathbf{L} + \mathbf{S}$



Most of this information

Molecular Quantum Mechanics (Atkins & Friedman)

Modern Spectroscopy (Hollas)