



Physics and Chemistry of the Interstellar Medium

Lecture 5

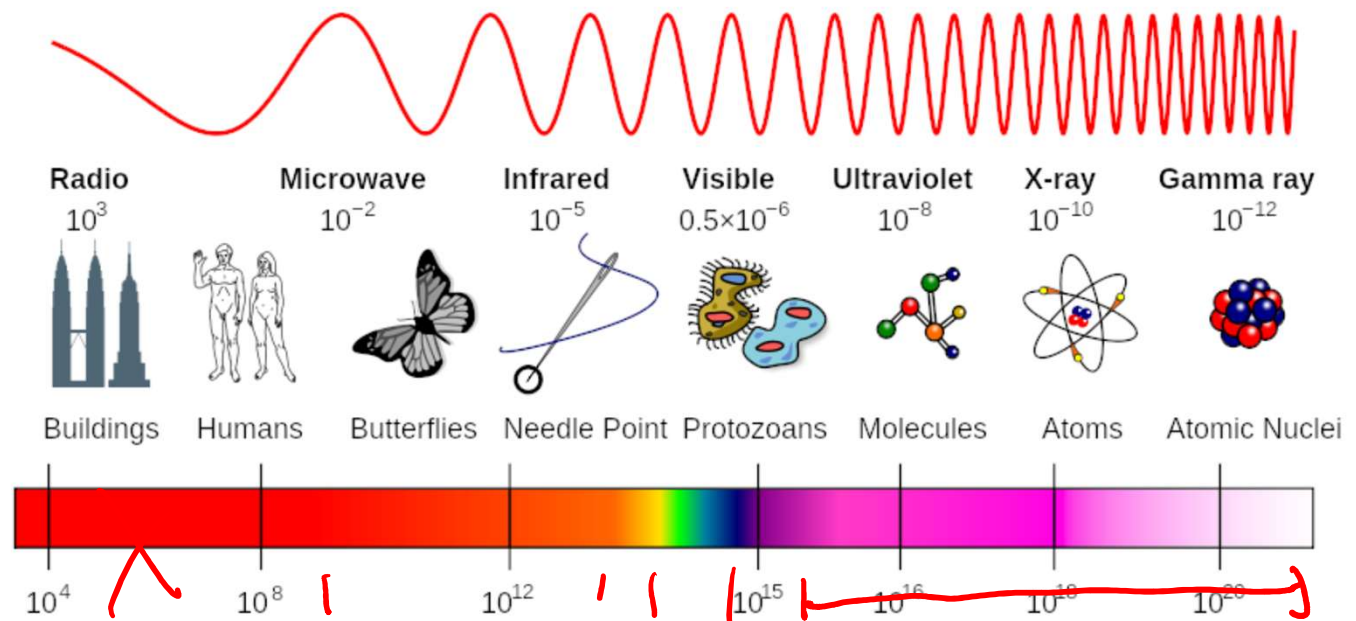
Radiation

Lecture V

3.1. Dirac perturbation theory

3.2. Discrete systems

- The hydrogen atom
- Fine structure
- Hyperfine structure
- Multiple electrons
- Molecules



Radiation

Motivation

- **Fundamentals**

- Interaction of the electromagnetic free-field with matter

- **Diagnostics**

- Radiation is our only way to obtain information from astrophysical systems
- Imprint of the properties of the interstellar matter on the photon field
- All analysis in this lecture is based on inverting the radiative transfer problem

- **Energy Balance**

- Radiative contributions Λ, Γ dominate the energy balance in many regions
- Emission and absorption needs to be understood

Radiation

Basic Physics

• Dirac Perturbation Theory

- Atomic system with Hamiltonian \hat{H}_{at}^0 and eigenstates $|a_{at}\rangle$
 - Eigenvalues : $E_{a,at}$
- Free photon field with eigenstates $|n_\lambda\rangle$ corresponding to n_λ photons of wavelength λ
 - Eigenvalues

$$E_{\text{Free-Field}} = \sum_{\lambda} \frac{hc}{\lambda} n_{\lambda} = \sum_{\lambda} h\omega n_{\lambda}$$

$$\omega = 2\pi \frac{c}{\lambda}$$

- Total Hamiltonian

$$\hat{H}^0 = \hat{H}_{at}^0 + \hat{H}_{\text{Free-Field}}^0$$

- with eigenstates

$$|a\rangle = |a_{at}\rangle |n_{\lambda}\rangle$$

- Interaction \hat{H}_i

- As perturbation term $\hat{H}_i \ll \hat{H}^0$

Radiation

Dirac Perturbation theory

- **Interaction**

- Transition from state $|a\rangle$ to state $|a'\rangle$ determined by Fermi's Golden Rule:

$$W_{a,a'} = \frac{2\pi}{\hbar} |\langle a' | \hat{H}_i | a \rangle|^2 \delta(E_{a'} - E_a)$$

$W_{a,a'}$: Transition probability
 δ : function from energy conservation

$E_a, E_{a'}$: Eigenvalues of unperturbed system given by Hamiltonian \hat{H}^0

- **Computation of interaction matrix** $\langle a' | \hat{H}_i | a \rangle$

- Through Maxwell equations
- Without prove here (see QM II)

Radiation

Interaction matrix

$$\sqrt{n_\lambda + 1}$$

$$\langle a' | \hat{H}_i | a \rangle = \sum_\lambda \frac{e}{m_{at}} \sqrt{\frac{\hbar}{2\omega\epsilon_0}} \vec{E}_{\text{phot}} \cdot$$

$$\left\{ \sqrt{n_\lambda + 1} \langle a'_{at} | \vec{p} e^{i\vec{k}\vec{r}} | a_{at} \rangle \langle n'_\lambda | n_\lambda + 1 \rangle + \right.$$

$$\left. + \sqrt{n_\lambda} \langle a'_{at} | \vec{p} e^{-i\vec{k}\vec{r}} | a_{at} \rangle \langle n'_\lambda + 1 | n_\lambda \rangle \right.$$

$$\text{with } \omega = 2\pi \frac{c}{\lambda} = c |\vec{k}|$$

Change of the free field characterized by the change of the photon number:

$$\langle n'_\lambda | n_\lambda + 1 \rangle = \delta(n'_\lambda - [n_\lambda + 1]) : n_\lambda \text{ must increase by 1} \rightarrow \text{emission}$$

$$\langle n'_\lambda + 1 | n_\lambda \rangle = \delta([n'_\lambda + 1] - n_\lambda) : n_\lambda \text{ must decrease by 1} \rightarrow \text{absorption}$$

Fermi condition $\delta(E_a - E_{a'})$ requires that energy of atomic system changes in opposite way:

$$E_{a,at} = E_{a',at} \pm \hbar\omega \rightarrow \text{Energy conservation}$$

Radiation

Interaction matrix

- Transition strength

- Strength of the coupling given by electromagnetic interaction term $\frac{e}{m_{at}} \vec{p} \cdot \vec{E}_{photo}$

- $\frac{e}{m_{at}} \vec{p} = e \dot{\vec{r}}$ = charge momentum of the atomic system
coupling to the photon electric field

- Apart from the energy conservation rule, only the properties of the atomic system determine the transition probabilities

→ Selection rules

- Consider series expansion: $e^{\pm i\vec{k}\vec{r}} = 1 \pm i\vec{k}\vec{r} - \frac{k^2 r^2}{2} \mp \dots$

- Interaction terms: $\left\langle a'_{at} \left| \frac{e}{m_{at}} \vec{p} e^{\pm i\vec{k}\vec{r}} \right| a_{at} \right\rangle = \left\langle a'_{at} \left| e \dot{\vec{r}} \right| a_{at} \right\rangle \pm \left\langle a'_{at} \left| e i\vec{k} (\vec{r} \times \dot{\vec{r}}) \right| a_{at} \right\rangle - \dots$

Aufspaltung in symmetrischen und antisymmetrischen Anteil

Radiation

Selection rules

- **First order term** $\langle a'_{at} | e\dot{\vec{r}} | a_{at} \rangle$

- Interpretation:

- $e\dot{\vec{r}}$ must change between $|a_{at}\rangle, |a'_{at}\rangle$ to provide a non-zero expectation value
- $e\ddot{\vec{r}} \neq 0$
- **Charge accelerated/decelerated** \rightarrow trivial knowledge confirmed
- Change must happen resonantly for states $|a_{at}\rangle, |a'_{at}\rangle \rightarrow$ frequency ω_λ
- Precondition: Dipole moment $\vec{d} = e\vec{r}$ must exist

- Dipole transition:

$$\langle a'_{at} | e\dot{\vec{r}} | a_{at} \rangle \sim \vec{d} \cdot \omega$$

- **Next terms:**

- $e(\vec{r} \times \dot{\vec{r}}) = \vec{M}$ = magnetic moment \rightarrow magnetic dipole transition
- \vec{Q} = electric quadrupole ...

Radiation

Transition probability

- **Combine everything for dipole transition and emission case:**

$$W_{a,a'} = \sum_{\lambda} \frac{2\omega^2}{3\hbar c^3 \epsilon_0} |\langle d_{a,a'} \rangle|^2 (1 + n_{\lambda})$$

- **Express in terms of Einstein coefficients:**

- Spontaneous emission: $A_{a,a'} = W_{a,a'}(n_{\lambda} = 0) \times \frac{\omega}{2\pi} = \frac{\omega^3}{3\hbar c^3 \epsilon_0} |d_{a,a'}|^2$

- Induced emission: $B_{a,a'} = \frac{W_{a,a'}(n_{\lambda}-1)}{u_{\omega}} \times \frac{\omega}{2\pi}$

- with radiative energy density

$$u_{\omega} = \int_{4\pi} I_{\omega} d\Omega$$

I_{ω} : intensity

Radiation

Einstein coefficients

- $W_{a,a'} = \sum_{\lambda} \frac{2\omega^2}{3\hbar c^3 \epsilon_0} |\langle d_{a,a'} \rangle|^2 (1 + n_{\lambda})$

- Spontaneous emission: $A_{a,a'} = W_{a,a'}(n_{\lambda} = 0) \times \frac{\omega}{2\pi} = \frac{\omega^3}{3\pi\hbar c^3 \epsilon_0} |d_{a,a'}|^2$

- Induced emission: $B_{a,a'} = \frac{W_{a,a'}(n_{\lambda}-1)}{u_{\omega}} \times \frac{\omega}{2\pi}$

- using the photon density:

$$n_{\lambda} = \frac{\pi^2 c^3}{h\omega^3} u_{\omega}$$

- **Result:**

$$B_{a,a'} = \frac{\pi^2 c^3}{h\omega^3} A_{a,a'} = \frac{\pi}{3h^2 \epsilon_0} |d_{a,a'}|^2$$

Radiation

Einstein coefficients

- **Absorption case:**

$$W_{a,a'} = \sum_{\lambda} \frac{2\omega^2}{3\hbar c^3 \epsilon_0} |\langle d_{a,a'} \rangle|^2 (n_{\lambda})$$

- Analogously:

$$B_{a',a} = \frac{\pi}{3\hbar^2 \epsilon_0} |d_{a',a}|^2 = B_{a,a'} \frac{|d_{a',a}|^2}{|d_{a,a'}|^2}$$

- With dipole moment of inverse transition

- **Higher moments:**

- Magnetic dipole

$$A_{a,a'} = \frac{\omega^3}{3\pi \hbar c^3 \mu_0} |\vec{M}|^2$$

- Electric quadrupole

$$A_{a,a'} = \frac{\omega^5}{40\pi \hbar c^5 \epsilon_0} |\vec{Q}|^2$$

Radiation

Einstein coefficients

- No assumptions were made about the atomic system!
 - Only requirements:
 - Energy conservation $\delta(E_a - E_{a'})$
 - Selection rules=Harmonic variation of $|d_{a,a'}|, |M_{a,a'}|, |Q_{a,a'}|$
 - **Einstein notation valid for any interaction of radiation with matter!**
 - Representation of the solution of the Dirac equation
 - Can be used for all radiative processes in the ISM
 - Atoms
 - Molecules
 - Plasma
 - Dust
- **Start: discrete systems**

Discrete systems

Basic atomic physics:

The H-atom

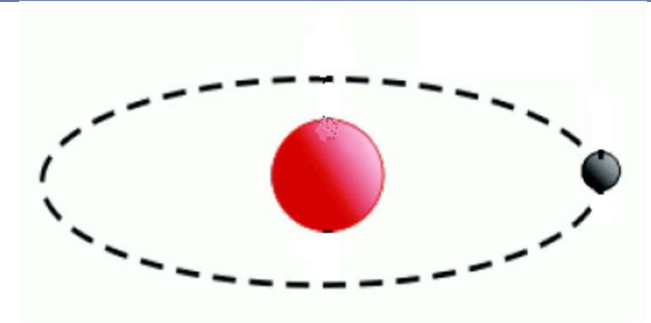
- Simple problem: $p + e^-$
 - Pure Coulomb problem:
 - With reduced mass
 - Solution has eigenvalues
- With Rydberg constant

$$\hat{H} = \frac{\vec{p}^2}{2m_r} - \frac{(Z)e^2}{4\pi\epsilon_0|\vec{r}|}$$

$$m_r = \frac{m_e m_p}{m_e + m_p}$$

$$E = -R \frac{Z^2}{n^2}$$

$$R = \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_r}{\hbar^2} \approx 13.605 \text{ eV}$$



$$\frac{m_e}{m_p} = \frac{1}{1836}$$

Z = charge for more general case of multiple protons

n = main quantum number

Basics of spectroscopy

Repetition of basic atomic physics

The H-atom

- **Orbits:** Solution of the full spatial problem
- Provides in total 3 quantum numbers: n, l, m
 - l = orbital quantum number $l = 0, \dots, n - 1$
 - m_l = projection of l on z-axis: $m_l = -l, \dots, l$
 - Corresponding eigenvector: $|n, l, m_l\rangle$ **!**
 - **Energy levels n are degenerate with respect to l and m_l**
 - Level of degeneracy = statistical weight of energy level

$$g_n = n^2$$

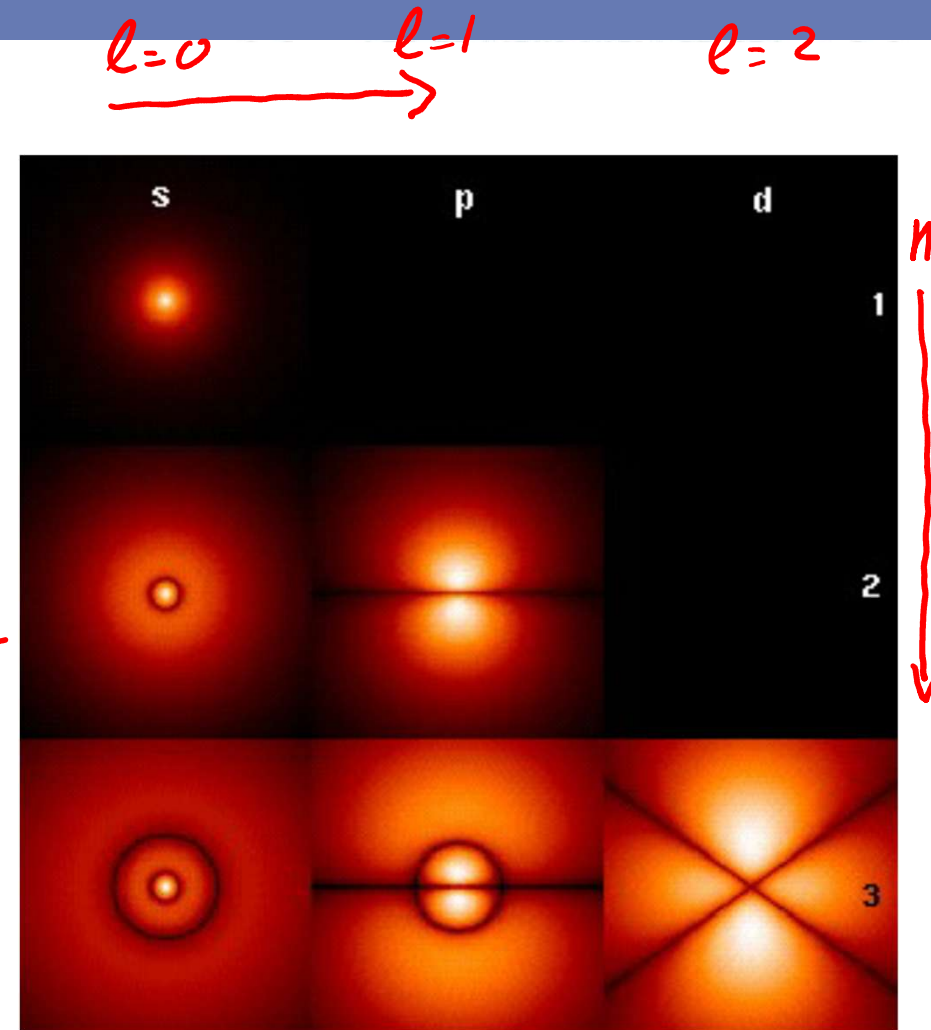
$$n = 1: l = 0, m_l = 0 \quad \rightarrow g = 1$$

$$n = 2: l = 0, m_l = 0$$

$$l = 1, m_l = -1, 0, 1 \quad \rightarrow g = 1 + 3 = 4$$

$$n = 3: l = 0, 1, 2, \dots \quad \rightarrow g = 9$$

$n=2$



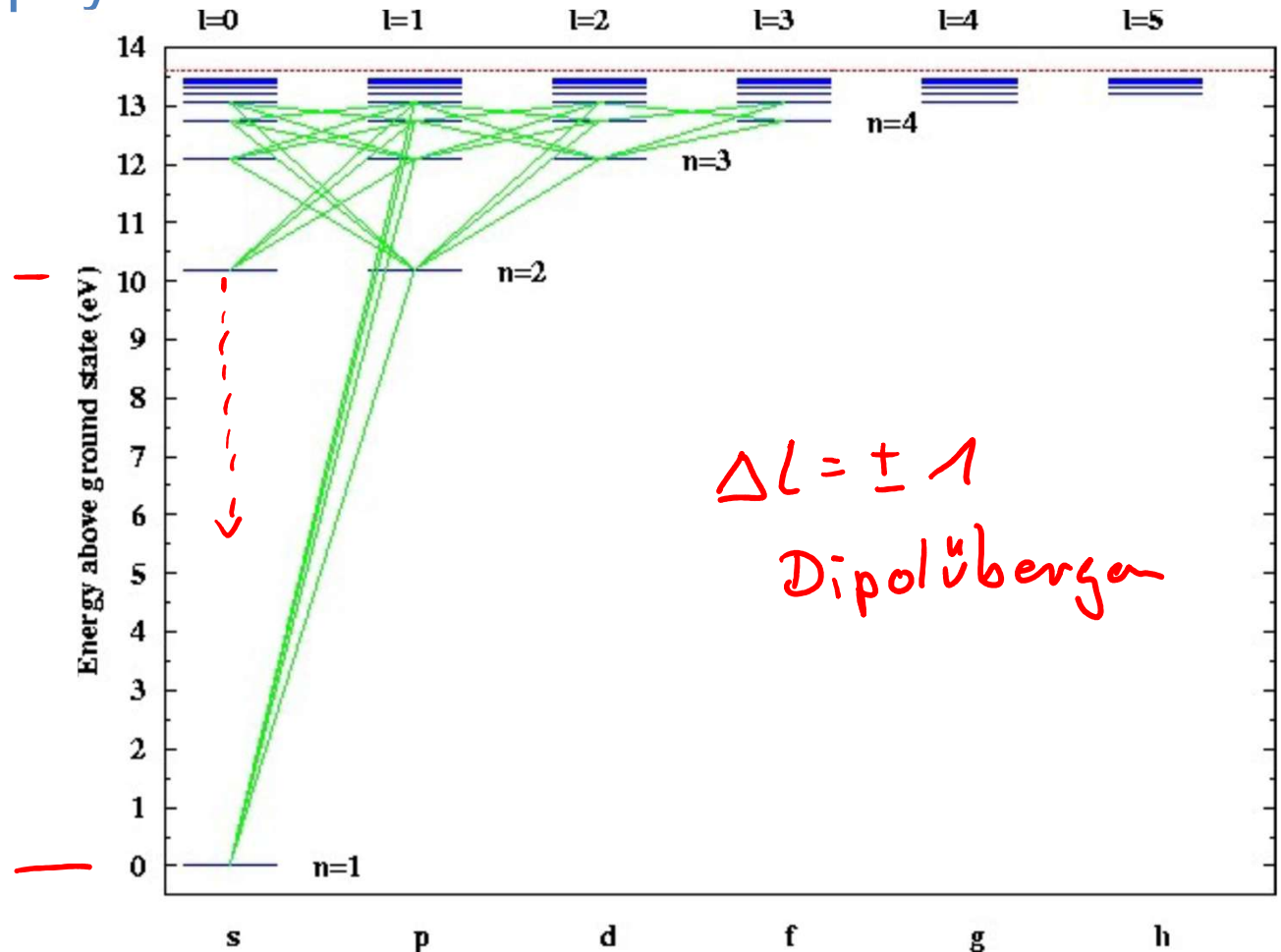
Basics of spectroscopy

Repetition of basic atomic physics

- The H-atom

$$E_n - E_{n'} = (-Z^2)R \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

- Possible transitions
 - from level n to n'



Basics of spectroscopy

Repetition of basic atomic physics

- The H-atom ($Z=1$)
- Possible transitions
 - from level n to n'

$$\Delta E = -R \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

- Gives series for different n'
 - $n' = 1$ - Lyman
 - $n' = 2$ - Balmer
 - $n' = 3$ - Paschen
 - $n' = 4$ - Brackett
 - $n' = 5$ - Pfund

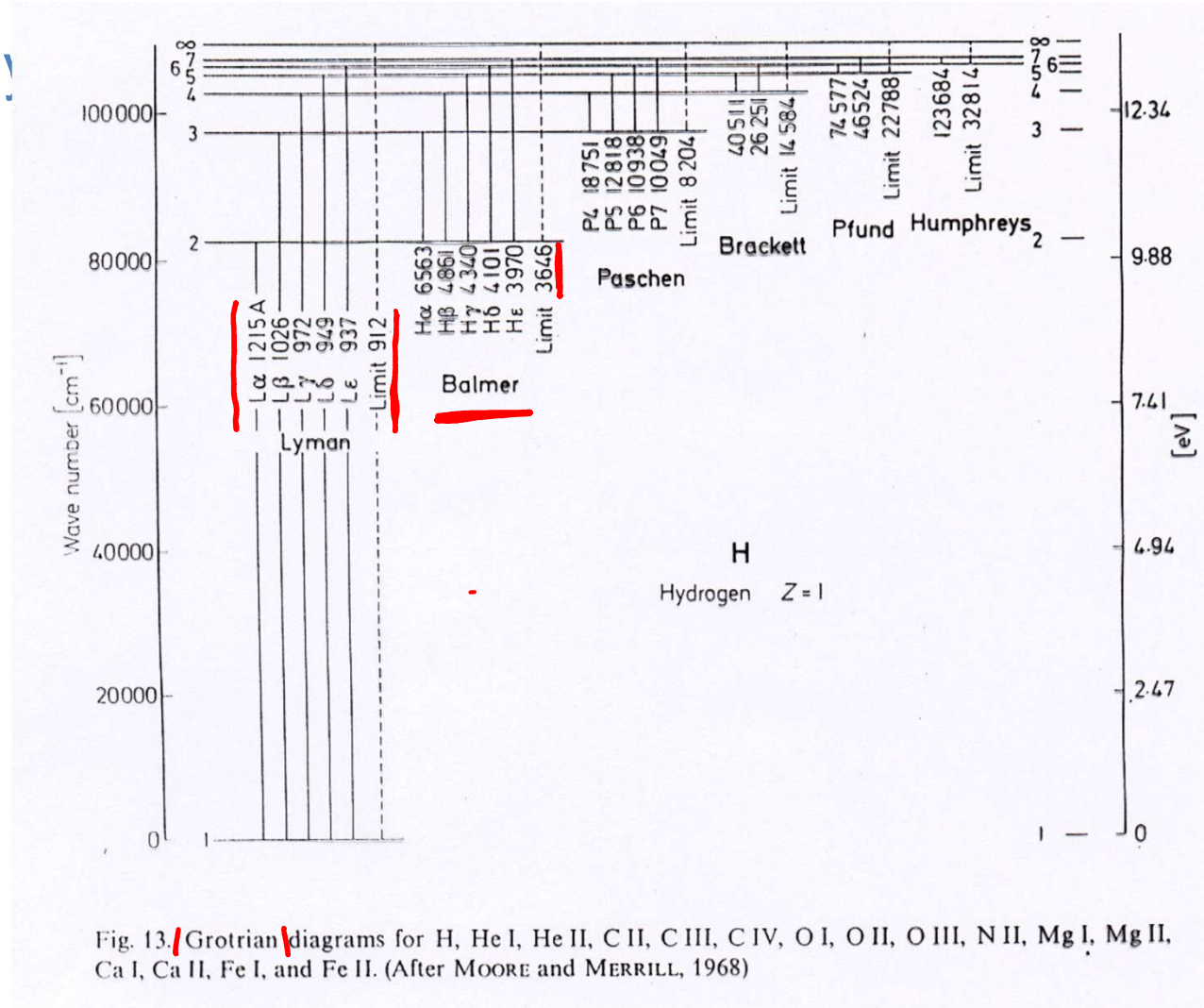


Fig. 13. Grotrian diagrams for H, He I, He II, C I, C II, C III, C IV, O I, O II, O III, N II, Mg I, Mg II, Ca I, Ca II, Fe I, and Fe II. (After MOORE and MERRILL, 1968)

Fine structure

The electron spin

- Adds spin system $|s, m_s\rangle$ with $s = 1/2$
- Provides additional coupling term between orbital momentum and spin

$$\hat{H}_{FS} = \frac{e}{2m_e^2 c^2} \left(-\frac{1}{r} \frac{\partial (Ze^2)}{\partial r} \right) \hat{S} \cdot \hat{L}$$

- Solution has eigenvalues

$$E_{FS} = \alpha^2 R \frac{Z^4 j(j+1) - l(l+1) - s(s+1)}{l(l+1)(2l+1)}$$

- $j =$ total angular momentum from $\vec{j} = \vec{l} + \vec{s} \rightarrow j = \underline{l - s, \dots, l + s}$

- $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$ Sommerfeld fine structure constant

Fine structure

The electron spin

- Fine structure energies are scaled by α^2 relative to main level energies

- H-atom

- No split for $n = 1, l = 0, s = 1/2$ because $j = 1/2$ independent of m_s

- First split for $n = 2, l = 1, s = \frac{1}{2}$

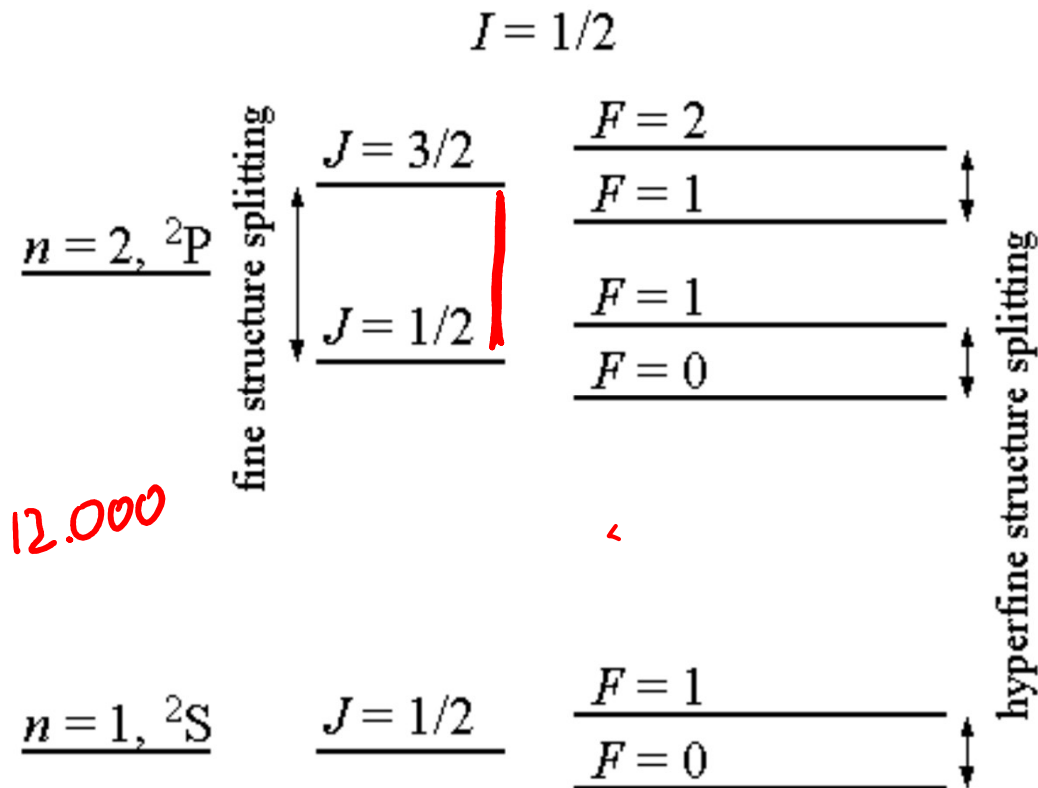
$$\rightarrow j = 1/2, 3/2$$

$$\Delta E_{fs} = 4.53 \times 10^{-5} eV$$

$$= 10.9 GHz$$

- Radio frequency range
- Requires $n = 2$ excitation:
10.2 eV = 120 000 K
- Not directly observable due to other splits

1 eV \approx 12.000 K



Basics of spectroscopy: Notation

Spectroscopy notation

$$2s+1 \underset{j}{l} (P)$$

- l encrypted in letters
 - $0=s, 1=p, 2=d, 3=f, 4=g, 5=h, \dots$
- p =parity
 - Blank for parity=even, o for parity = odd
 - Characterizes whether wave function changes sign under reflection of all electron positions through the origin.
- Examples:
 - ${}^2s_{1/2}$ = ground state
 - ${}^2p_{1/2}, {}^2p_{3/2}$ = first excited state (Balmer level) + ${}^2s_{1/2}, n=2$

Hyperfine splitting

The nuclear spin

- Adds nuclear spin system $|i, m_i\rangle$ with $i = 1/2$ for every nucleon
- Treatment equivalent to fine-structure splitting

- New operator: $\vec{f} = \vec{j} + \vec{i}$ and corresponding quantum number f
 - $f =$ total angular momentum from $\rightarrow j - i, \dots, j + i$

- Eigenvalues of hyperfine coupling

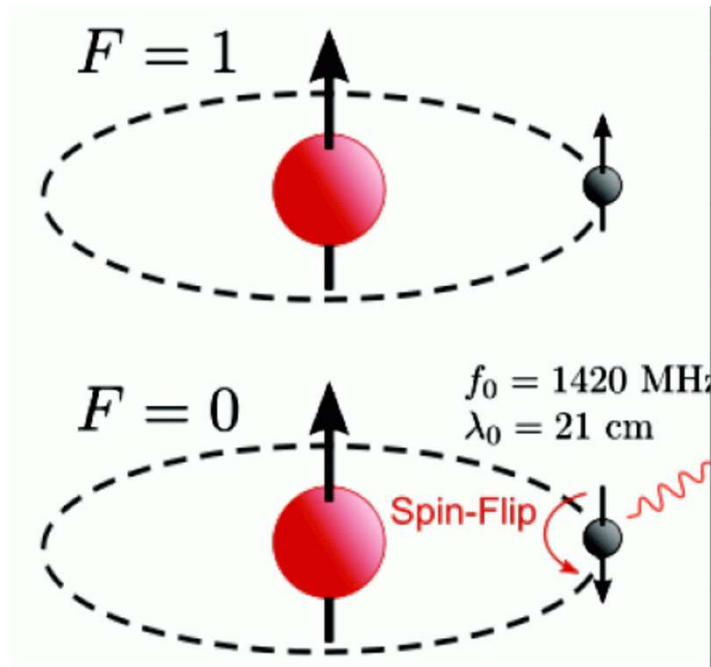
$$E_{HF} = g_N \left(\frac{m_e}{m_p} \right) \alpha^2 R \frac{Z^4}{n^3} \frac{f(f+1) - j(j+1) - i(i+1)}{j(j+1)(2j+1)}$$

- Hyperfine splitting typically lower than fine-structure splitting by factor m_e/m_p
- g_N – Landé-g-factor of the core
- Spectroscopic notation: explicit writing of f

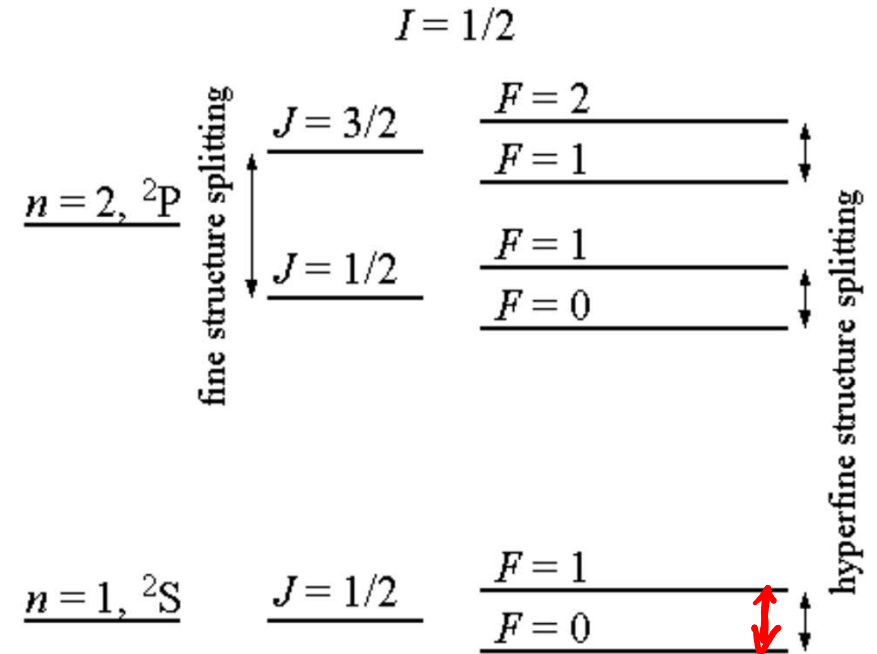
Hyperfine structure splitting

Hyperfine structure

- H-atom
- for $n = 1$ (ground state $l = 0$): $^2S_{1/2}: F = 1 \rightarrow 0$
- can be observed for “cold hydrogen”



$$\vec{F} = 1 - 0$$



famous 21cm line = 1.42GHz
allows for mapping of the Milky Way

magnetic dipole transition \rightarrow forbidden

$$A = 2.9 \times 10^{-15} \text{ s}^{-1} \quad (\vec{F} = 1 \rightarrow \vec{F} = 0)$$

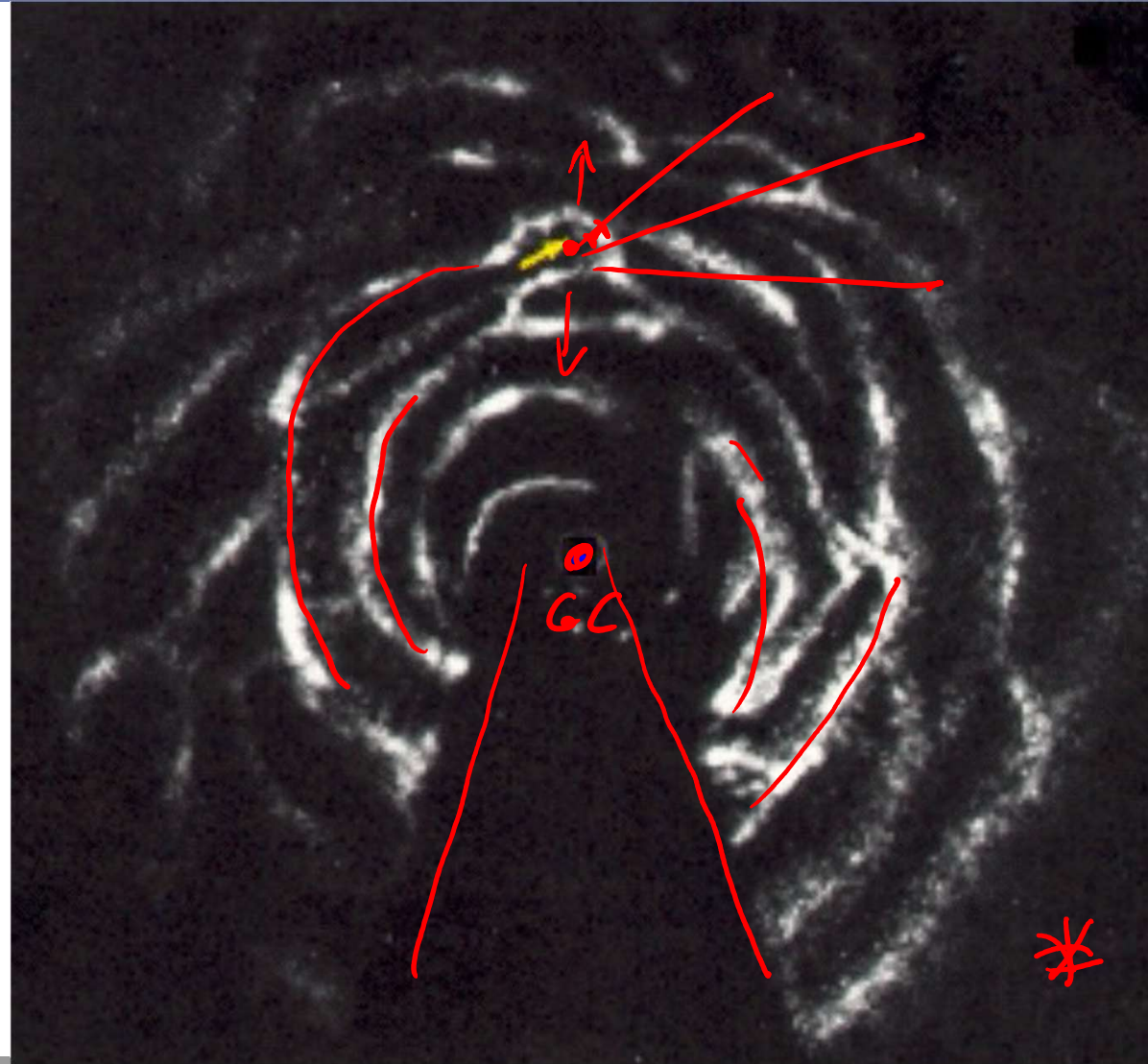
$$t = 10^7 a$$

Hyperfine structure splitting

Hyperfine structure

- H-atom
- for $n = 1$ (ground state $l = 0$):
 $^2S_{1/2}: F = 1 - 0$
- can be observed for “cold hydrogen”
- allows for mapping of neutral interstellar gas

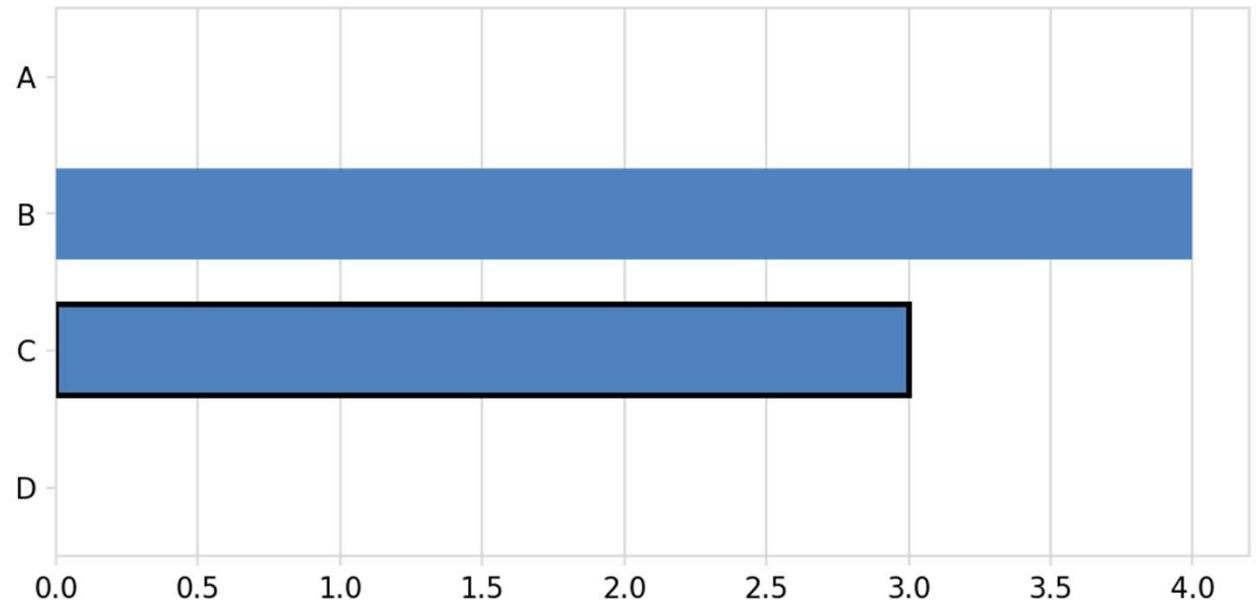
1958 Oort, Kerr, Westerhout :
The galactic system as a spiral nebula



Kurze Frage...

For an allowed electric-dipole transition, the spontaneous emission rate scales with the transition frequency as:

- A) $A \propto \omega$
- B) $A \propto \omega^2$
- C) $A \propto \omega^3$
- D) $A \propto \omega^5$



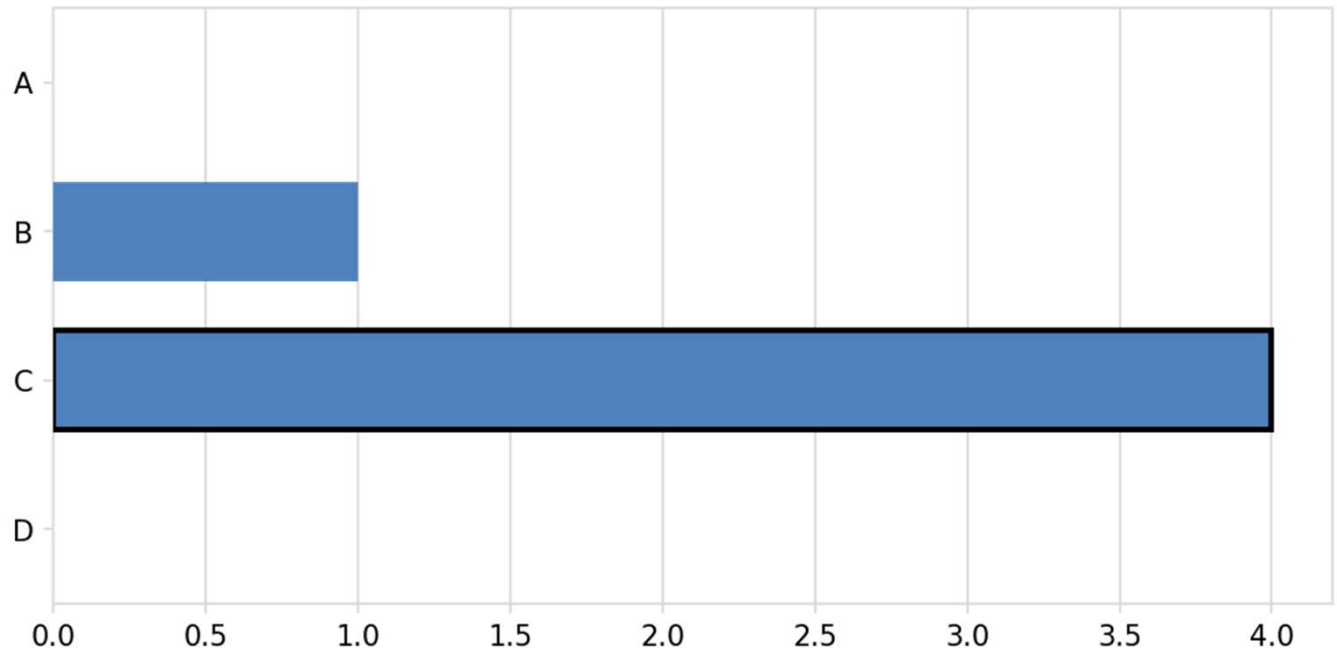
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7 Teilnehmer / Umfrage geschlossen

Kurze Frage...

Ignoring electron spin, what is the statistical weight g of the $n = 4$ level of atomic hydrogen?

- A) 4
- B) 8
- C) 16
- D) 32

$g_n = n^2$
 $n=4 : l = 0, 1, 2, 3$
 $2l+1$



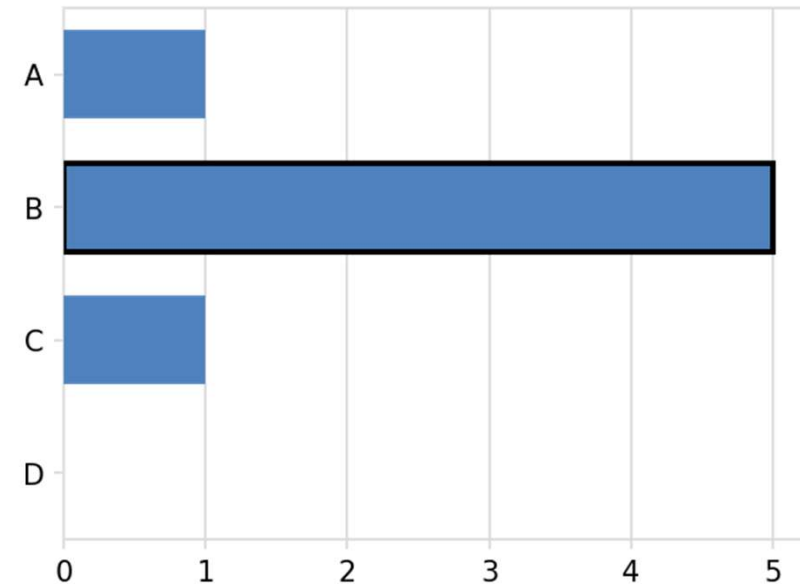
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5 Teilnehmer / Umfrage geschlossen

Kurze Frage...



The 21 cm hyperfine line of atomic hydrogen has an extraordinarily long radiative lifetime ($\sim 10^7$ yr). The main reason is:

- A) The energy gap is too small compared to typical thermal energies.
- B) It is a magnetic-dipole transition — both levels are $^2S_{1/2}$, so it is electric-dipole forbidden ($\Delta l = 0$, same parity).
- C) The upper state $F = 1$ is not appreciably populated in cold neutral gas.
- D) Hyperfine transitions violate conservation of total angular momentum.



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7 Teilnehmer / Umfrage geschlossen

Atoms

Multiple electrons

- **Arrangement in subshells with increasing energy level**
= increasing main and orbital quantum numbers n, ℓ
degeneracy through $m_\ell \rightarrow$ number of electrons that can populate subshell
- Example: $C^+ = 1s^2 2s^2 2p^1$
 - 3 subshells occupied
 - Closed shells: Sum of orbital momenta and spins always = 0
 - No contribution to radiative interaction
 - Can be ignored
 - 3rd subshell is open
 - can take 6 electrons: $m_\ell = -1, 0, 1$ $m_s = -1/2, 1/2$
 - dominates radiative interaction as only electrons in open shell need to be considered

Multiple electrons

- **Coupling between different electrons**

- Provides additional term to Hamiltonian
- No analytic solution
- Approximation through Russell-Saunders coupling
 - Inter-electron coupling stronger than spin-orbit coupling
 - Individual orbital momentums and spins add up $\sum \vec{l} = \vec{L}$ and $\sum \vec{s} = \vec{S}$
 $\vec{J} = \vec{L} + \vec{S}$
 - Remember: approximation only $\rightarrow L, S$ are no “good” quantum numbers
 - Different approximation for heavy elements ($\vec{j} - \vec{j}$ coupling) Fe, Co, Ni

- Spectroscopic notation:

- capital letters for sum over multiple electrons in open shell
- explicit writing of F for sum of total angular momentum including nuclear spin

Multiple electrons

Astrophysically relevant subterms

- Remember H-atom: $2s+1l_j^{(p)}$
- Equivalently for multi-electron atoms: $2S+1L_J^{(P)}$
 - Capital letter for sum over multiple electrons in open shell
 - $2S + 1 =$ “multiplicity” = statistical weight of the state without fine structure

Ground configuration	Terms (in order of increasing energy)	Examples
$\dots ns^1$	$^2S_{1/2}$	<u>HI, He II</u> , CIV, NV, OVI
$\dots ns^2$	1S_0	He I, CIII, NIV, OV
$\dots np^1$	$^2P_{1/2,3/2}^o$	x CII, NIII, OIV
$\dots np^2$	$^3P_{0,1,2}, ^1D_2, ^1S_0$	x CI, NII, OIII, Ne V, SIII
$\dots np^3$	$^4S_{3/2}^o, ^2D_{3/2,5/2}^o, ^2P_{1/2,3/2}^o$	NI, OII, Ne IV, SII, ArIV
$\dots np^4$	$^3P_{2,1,0}, ^1D_2, ^1S_0$	OI, 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

I : neutral
II : einf. ionis.
III : zweifach ionisiert
CII : C⁺

Multiple electrons

Russell-Saunders coupling

- Solution

- “Hund rules”:

- 1) higher S → lower energies
- 2) higher L → lower energies
- 3) lower J and shell ≤ half-full → lower energies
- shell > half-full → higher energies

wichtigste kühl linie *des warme neutrale Mediums*

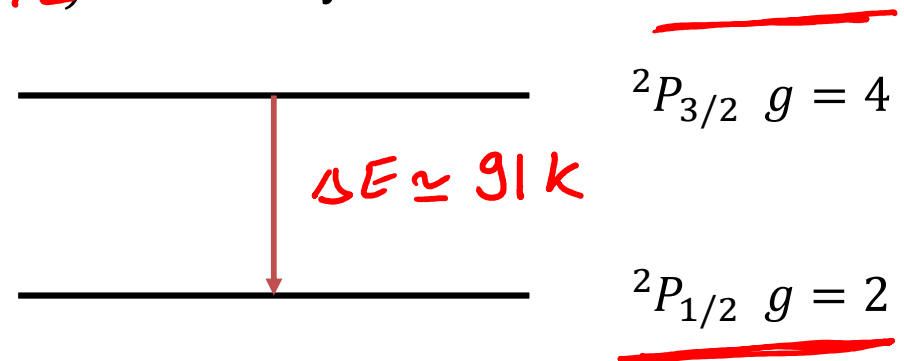
Geben Sie hier eine Formel ein.

- Example: $C^+ = 1s^2 2s^2 2p^1$

- 2p electron has $S = 1/2, L = 1$
- gives $J = 1/2, (m_J = -1/2, 1/2)$
or $J = 3/2, (m_J = -3/2, -1/2, 1/2, 3/2) = 2\text{-level system}$
- Only 3rd Hund rule applies

$\Delta E = 7.86 \text{ meV}$
 $= 1900.536 \text{ GHz}$
 $= 157.7 \mu m$

- Equivalent for N^{++} : $\Delta E = 57 \mu m$

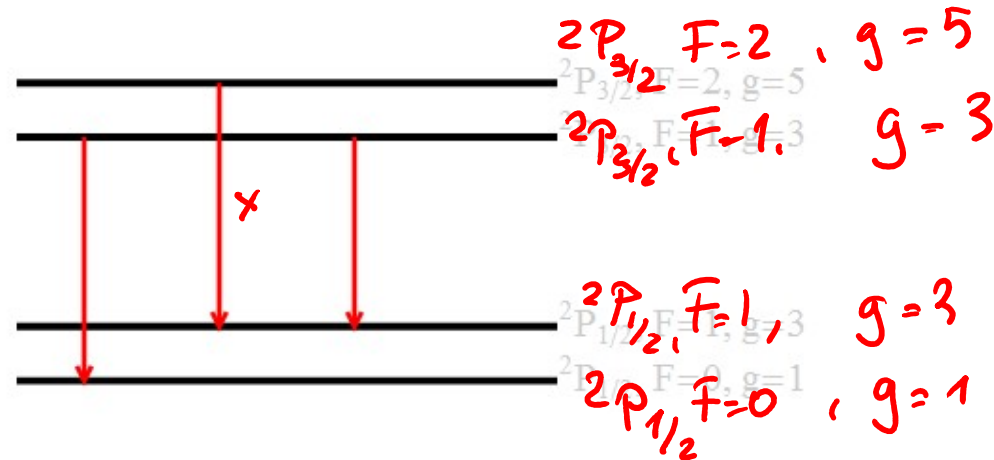


Hyperfine structure in atoms

Hyperfine structure

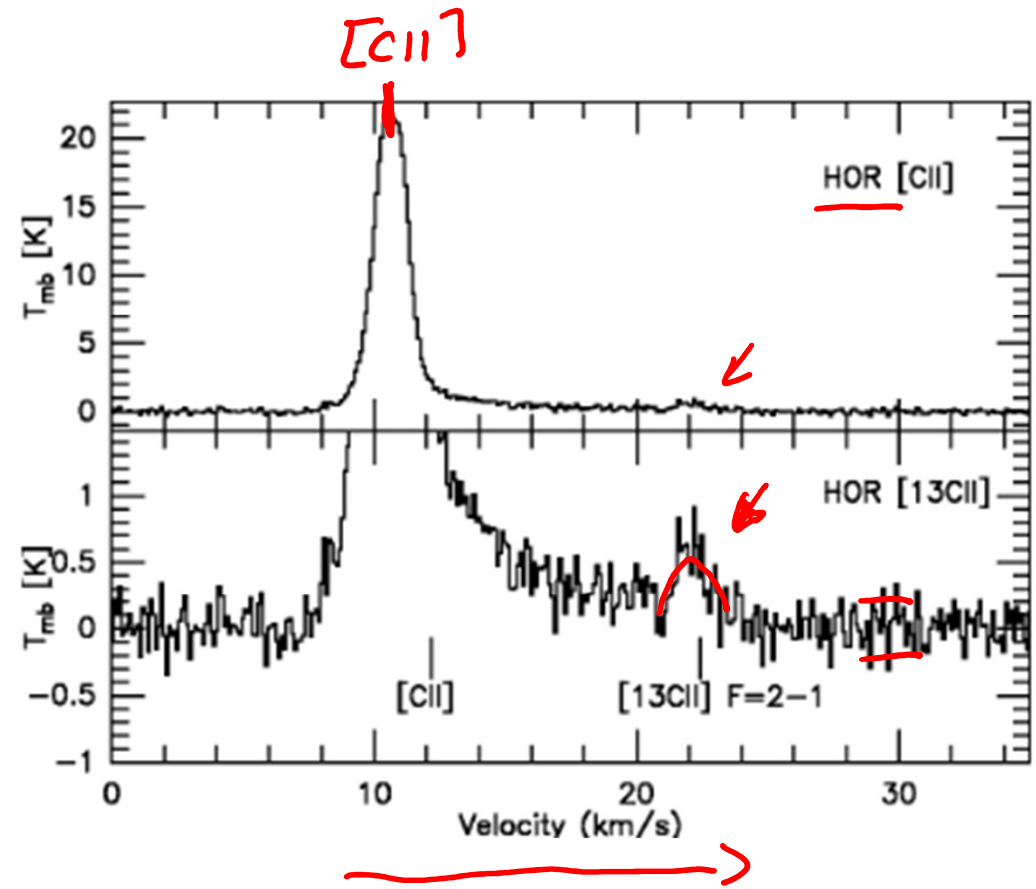
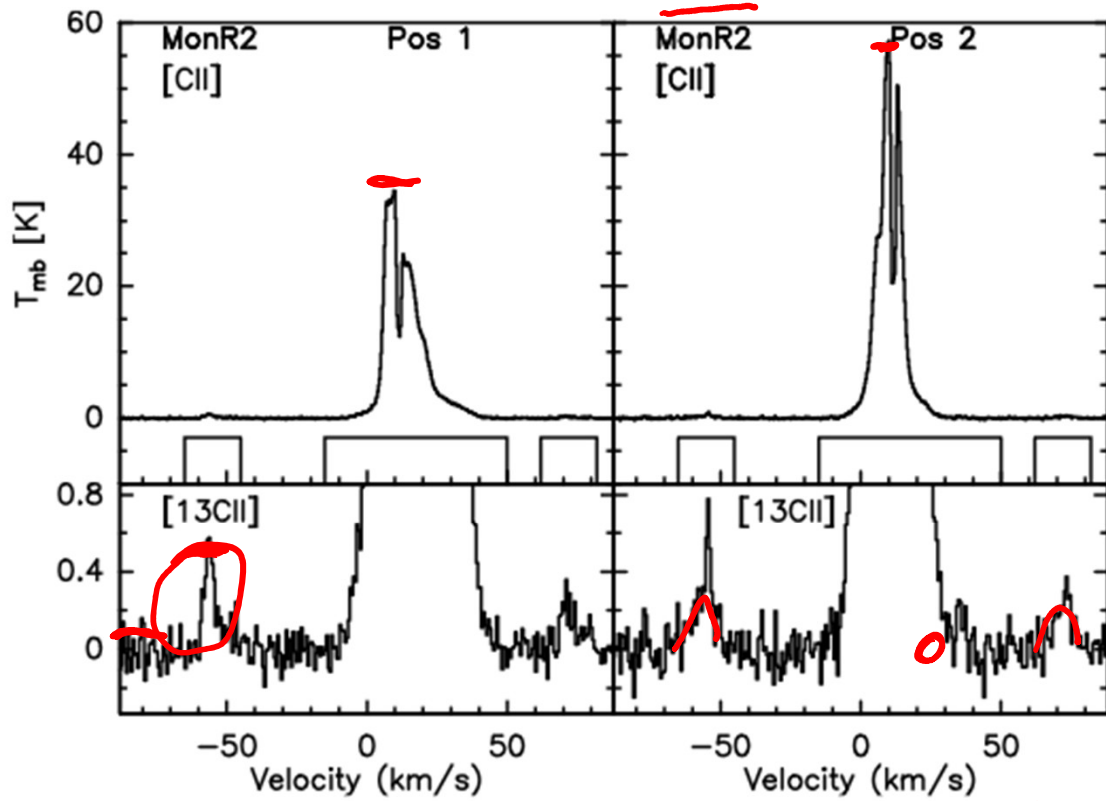
- Superimposed if nuclear spin does not sum up to 0
- Example: $^{13}\text{C}^+$
 - $I = 1/2$ combines with $J = 1/2$ to $F = 0$ ($m_F = 0$) or $F = 1$ ($m_F = -1, 0, 1$)
 - with $J = 3/2$ to $F = 1$ ($m_F = -1, 0, 1$) or $F = 2$ ($m_F = -2, -1, 0, 1, 2$)
 - C^+ levels split up

Line	Statistical g_u	Weight g_l	Frequency ν (GHz)	Vel. offset $\delta \nu_{F \rightarrow F'}$ (km s^{-1})	Relative intensity $S_{F \rightarrow F'}$
$^{12}\text{C II } ^2\text{P}_{3/2} - ^2\text{P}_{1/2}$	4	2	1900.5369	0	-
$^{13}\text{C II } F = 2 \rightarrow 1$	5	3	1900.4661	+11.2	0.625
$^{13}\text{C II } F = 1 \rightarrow 0$	3	1	1900.9500	-65.2	0.250
$^{13}\text{C II } F = 1 \rightarrow 1$	3	3	1900.1360	+63.2	0.125



- 3 possible transitions, $F=2 \rightarrow 0$ is forbidden ($F = 0 \leftrightarrow F = 0$)

[13CII] Observations



Guevara et al. 2020

Multiple electrons in one subshell

Combination of states

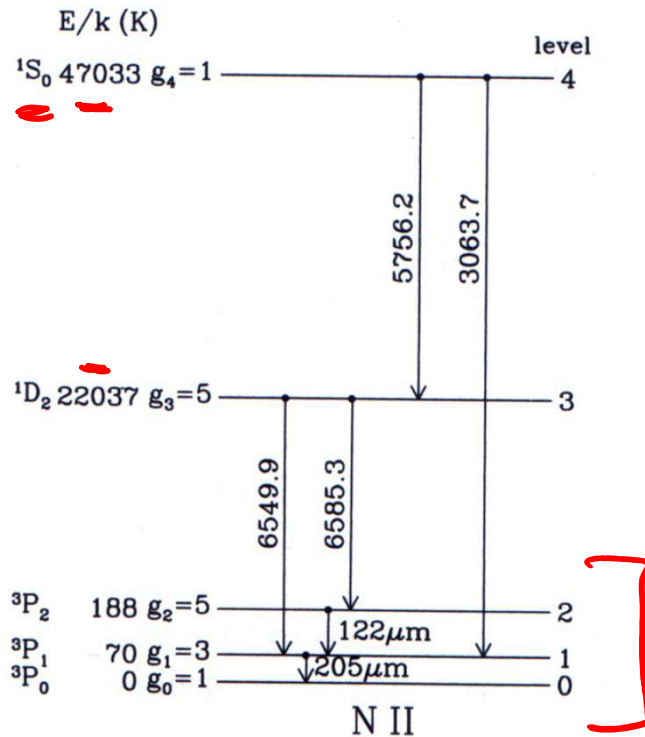
- Example: $N^+ = 1s^2 2s^2 2p^2$
 - Combination of two electrons with $s=1/2$ ($m_s=-1/2, 1/2$), $l=1$ ($m_l=-1, 0, 1$)
→ gives $6 \times 6 = 36$ possible combinations
 - Pauli exclusion principle:
 - 2 electrons never in same state
 - Electrons indistinguishable, i.e. wave functions antisymmetric with respect of exchange of 2 electrons
 - 15 allowed combinations remaining
 - $l_1 \uparrow\uparrow l_2, s_1 \uparrow\downarrow s_2: L = 2, S = 0$ → $J = 2$ ($m_J = -2, -1, 0, 1, 2$) → 1D_2 $g = 5$
 - $l_1 \uparrow\downarrow l_2, s_1 \uparrow\downarrow s_2: L = 0, S = 0$ → $J = 0$ ($m_J = 0$) → 1S_0 $g = 1$
 - $l_1 \perp l_2, s_1 \uparrow\uparrow s_2: L = 1, S = 1$
 - $J = 0$ ($m_J = 0$) → 3P_0 $g = 1$
 - $J = 1$ ($m_J = -1, 0, 1$) → 3P_1 $g = 3$
 - $J = 2$ ($m_J = -2, -1, 0, 1, 2$) → 3P_2 $g = 5$

Combination of states



$N^+ : 14.3 \text{ eV}$
IP

- “Hund rules”
 - 1) higher S → lower energies
 - 2) higher L → lower energies
 - 3) lower J and shell \leq half-full → lower energies
 - shell $>$ half-full → higher energies



The S=0 states need very high excitation energy
→ usually not relevant for ISM physics

→ **treat N^+ as 3-level system**

Only 2 radiative transitions ($J=2 \rightarrow 0$ forbidden)

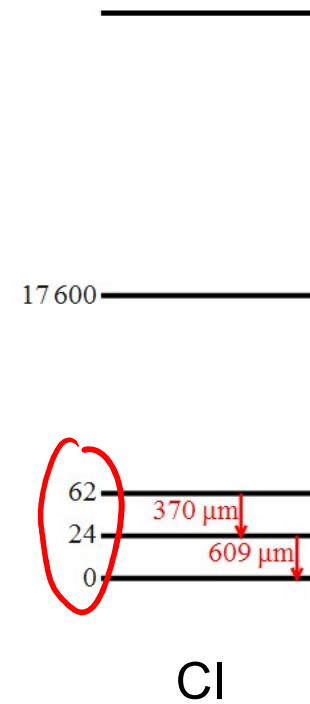
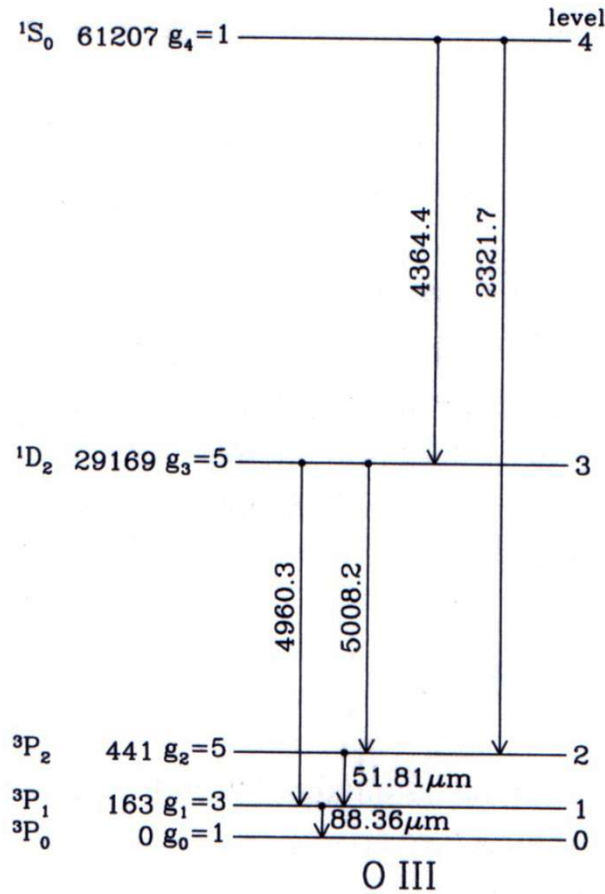
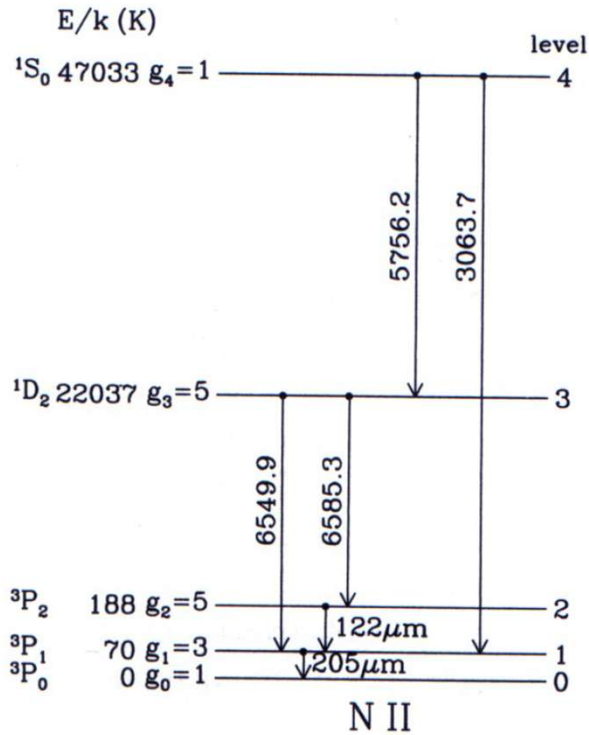
122 $\mu\text{m} = 2457 \text{ GHz}$

205 $\mu\text{m} = 1458 \text{ GHz}$

Combination of states

Other atoms with same configuration: $^3P_{0,1,2}$

- $N^+ = O^{++} = C$

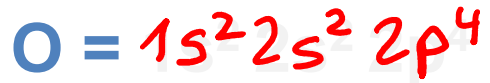


traces cold molecular clouds

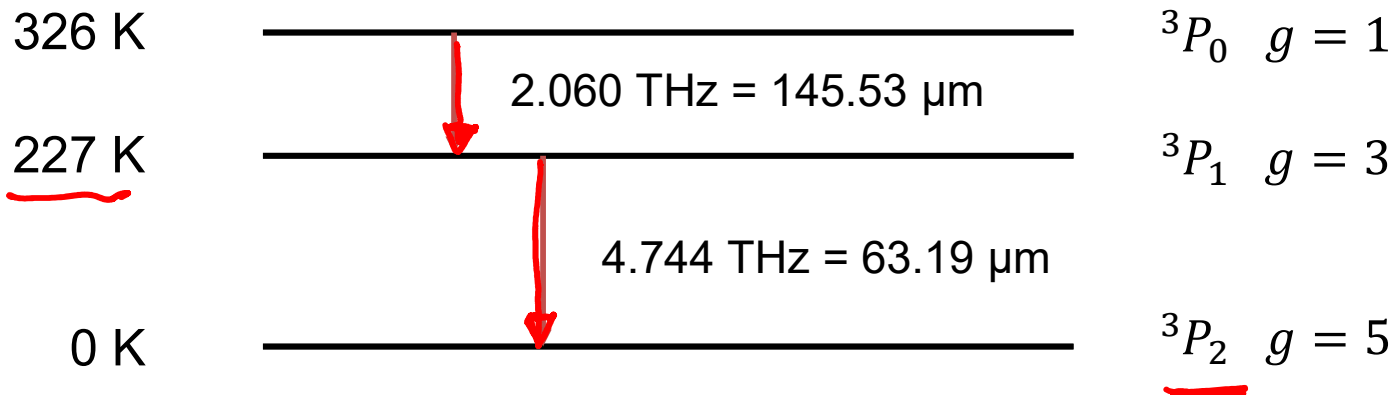
8106 Hz
4906 Hz

Combination of states

PDR
Photo-Dissociation
Regions



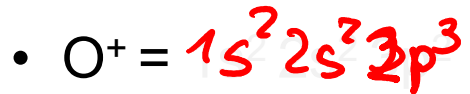
- Similar addition of configurations for all 4 electrons
- But: third Hund rule with “shell > half-full” applies → reverse order: ${}^3P_{2,1,0}$
- Only $S=1$ states excited at moderate temperatures (below 20000K)
 - Effectively 3-level system as well
 - Radiative transitions only $J = 2 \rightarrow 1$ and $J = 1 \rightarrow 0$



$$n_{\text{crit}} \approx 10^5 \text{ cm}^{-3}$$

Multiple electrons in one subshell

- **Combination of states**



- 1. Hund rule: higher $S \rightarrow$ lower energies
- Ground state \rightarrow combination of three electrons with same $m_s \rightarrow m_l = -1, 0, 1$
 \rightarrow single state $S = 3/2, L = 0 \rightarrow J = 3/2 \rightarrow {}^4S_{3/2}, g = 2J + 1 = 4$

- Other combinations:

$$S = 1/2, L = 2 \rightarrow J = 3/2, 5/2 \rightarrow {}^2D_{3/2, 5/2}$$

$$S = 1/2, L = 1 \rightarrow J = 1/2, 3/2 \rightarrow {}^2P_{1/2, 3/2}$$

- 2. Hund rule: higher $L \rightarrow$ lower energies

- ${}^2P_{1/2, 3/2}$ above ${}^2D_{3/2, 5/2}$

- But ${}^2D_{3/2}$ already 20000K above the ${}^4S_{3/2}$ state

- No split of the ${}^4S_{3/2}$ state from the 3rd Hund rule

- Minimum fine-structure transition energy 20000K \rightarrow **"Dark" in the ISM**

Atomic spectroscopy: Summary

Few cases to distinguish:

- 2-level systems: HI, C⁺, N⁺⁺
- 3-level systems: C, N⁺, O⁺⁺, O
 - $^3P_{0,1,2}$ (C, N⁺, O⁺⁺): ground-state transition has lower frequency
 - $^3P_{2,1,0}$ (O): ground-state transition has higher frequency
- 4-level systems: $^{13}\text{C}^+$
- $2p^3$ systems: N, O⁺ → “Darkness”
 - no fine-structure transitions excited at temperatures $\ll 20000\text{K}$

CNM: 21 cm
PDR/CMM: [C II], [O I]
H II: [N II], [O II], [O III]
warm

