

2- Elements of atomic and molecular spectroscopy

Classic Radiation

According to classic electrodynamics, if $\mathbf{P}(P_x, P_y, P_z)$ is the vector 'electric moment' of the charge e , the total radiated power is:

$$W = \frac{2}{3c^3} |\ddot{\mathbf{P}}|^2 \quad \text{erg/s}$$

For example, for a charge oscillating along x with frequency ν :

$$\nu = \omega / 2\pi \quad , \quad P_x = ex = eA \cos(\omega t + b)$$

$$\ddot{P}_x = -e\omega^2 x \quad , \quad \langle W \rangle = \frac{1}{3c^3} e^2 A^2 \omega^4$$

where the last relationship has been obtained by averaging over a cycle

Balmer law (1885)

Atomic hydrogen does **not** radiate according to the previous formula. Its emission lines in the visible region have wavelengths given by Balmer's formula:

$$\lambda_n = \lambda_2 \frac{n^2}{n^2 - 2^2} \quad \text{with } \lambda_2 = 3646.5 \text{ \AA}, \quad n = 3, 4, 5, \dots$$

The following values are found: $\lambda_3 = 6563 \text{ \AA}$ (H α), $\lambda_4 = 4861 \text{ \AA}$ (H β), $\lambda_5 = 4341 \text{ \AA}$ (H γ), $\lambda_6 = 4101 \text{ \AA}$ (H δ), and so on. In high resolution spectra of hot stars, one can count dozens of lines of the Balmer series, converging to the '**Balmer limit**' $\lambda_2 = 3646.5 \text{ \AA}$.

Passing from wavelengths to frequencies ν (in vacuum $\nu = c/\lambda$):

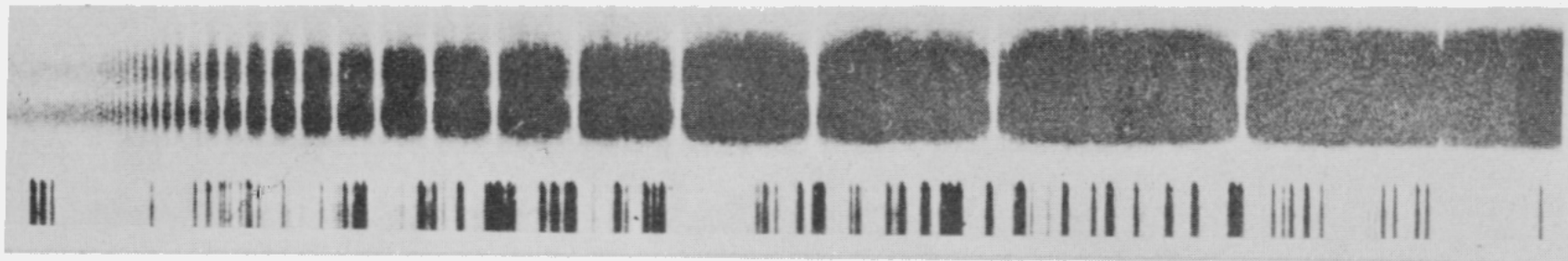
$$\nu_n = \frac{c}{\lambda_n} = \frac{c}{\lambda_2} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where **R** is the so-called Rydberg constant, $R = 3.29 \times 10^{15} \text{ s}^{-1}$.

Another useful unit is the **wave-number** $\sigma = 1/\lambda \text{ cm}^{-1}$, so that $R(\text{cm}^{-1}) = 1.09 \times 10^5$.

The spectrum of the shell star 48 Lybrae

THE SPECTRUM OF THE SHELL STAR 48 LIBRAE. The sharp Balmer absorption lines converge toward the Balmer limit.



H₃₀ H₂₀

H₁₀

H₈

Other series for H

It is apparent from its *term structure*, that Balmer's law could be extended to other possible series by inserting as starting point the values of $n = 1$, $n = 3$, $n = 4$ etc.

These series were indeed soon observed by:

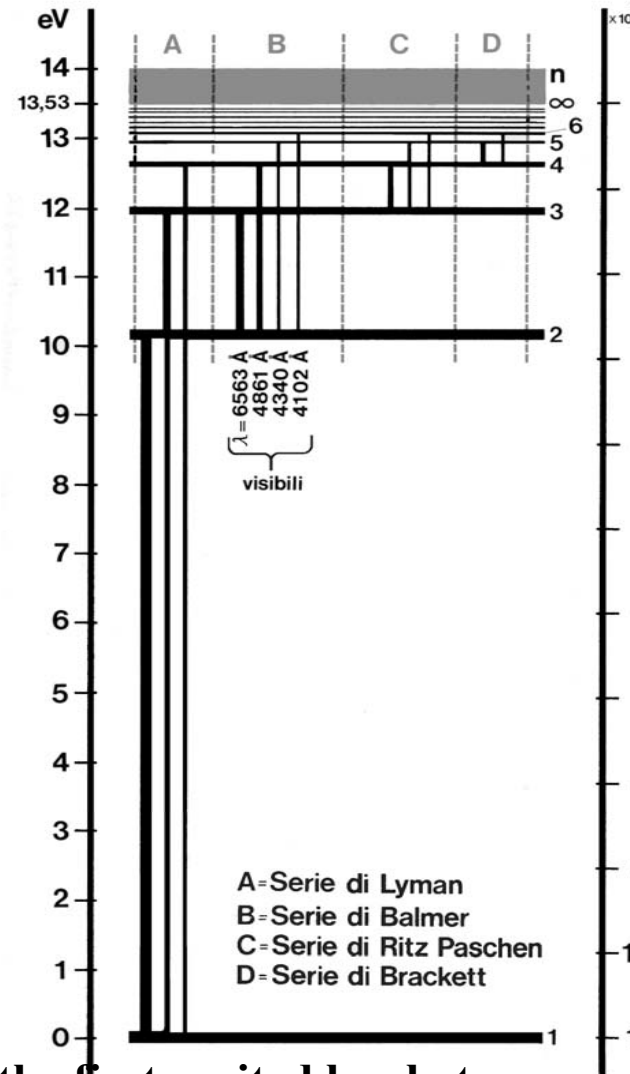
- Lyman ($n = 1$, in the UV, head at 912 Å),
 - Paschen ($n = 3$, in the near Infrared, head at 8208 Å),
 - Brackett ($n = 4$, in the far IR, head at 14600 Å),
- and so on.

The first four series of H.

Left: scale in eV, right scale in cm⁻¹.

The fundamental level is at 13.5 eV below zero, the first excited level at 10.2 eV above the ground level.

Grotrian representation



Ritz extension to Alkali metals

The Balmer-type relationship was almost immediately extended to other elements by Rydberg, Ritz and others, in particular to the alkali elements of the I group of Mendeleef table (Li, Na, Rb, Cs).

The lines of these elements can be grouped in different *series*, named Principal **P**, Sharp **S**, Diffuse **D**, fundamental **F**.

The **P** series is that more easily seen in laboratory absorption spectra; it resembles an *hydrogen-like series*, and it is dominated by an intense line (*resonance line*).

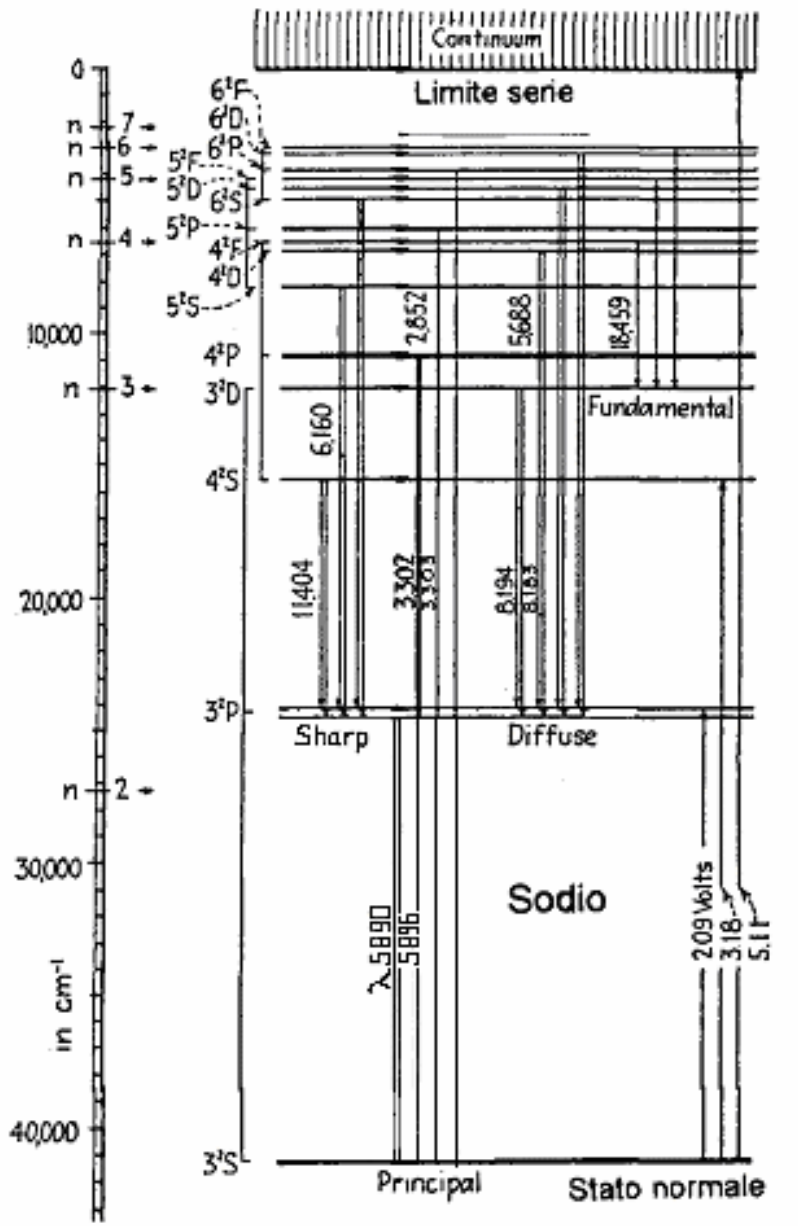
Among the members of the series the following Balmer-like relationship holds:

$$\nu_n^{\text{P}} = \nu_{\infty}^{\text{P}} - \frac{R}{(n + P)^2} \quad n = 2, 3, 4, \dots$$

and similar for the **S**, **D**, **F** series. While **R** is more or less the same for all series and all elements, the constants ν_{∞}^{P} , **P**, ν_{∞}^{S} , **S**, ..., are appropriate to that series, and vary from element to element.

The constants **S**, **P**, **D**, **F** are small corrective terms less than 1.

Terms of Na I



The typical spectrum of alkaline metals is that of Na I.

However, high resolution spectra show that the **P** series is constituted by close *pairs of lines*, the so-called *doublets* (e.g. 5890/96A). Conventionally one can write:

$$\nu_n^P = 1S - nP \quad , \quad n = 2, 3, 4, L$$

$$\nu_n^S = 2P - nS \quad , \quad n = 2, 3, 4, L$$

$$\nu_n^D = 2P - nD \quad , \quad n = 3, 4, 5, L$$

$$\nu_n^F = 3D - nS \quad , \quad n = 4, 5, 6, L$$

where actually each 'line' is a *close doublet*. Notice that the **S** and **D** series have the same head.

Extension to other elements

For more *complex elements* than H and the alkali metals, similar relationships hold. Although they are not as simple as the previous formulae, the same general structure of a series produced by **terms difference** among a fixed term and a running one always holds.

Ritz put forward a so-called *combination principle*, any spectral line can be interpreted as the difference between two terms.

We now know that 'term' means 'energy level' of that particular atom (or ion).

However, it was soon found that not all combinations are actually observed, a **selection effect** must be at work (see later).

Bohr-Sommerfeld semi-classic model - 1

Consider an hydrogen-like atoms (one electron orbiting a nucleus with Z protons), with the electron on the circular orbit of radius a . The potential and kinetic energies of the electron are connected by:

$$V = -\frac{Ze^2}{a} = -2T \quad , \quad T = \frac{1}{2}m_e v^2 = \frac{1}{2}m_e a^2 \omega^2$$

where the arbitrary constant in V has been put = 0 at infinity. The sign minus in front of the potential energy means that the electron is electrostatically **bound** to the nucleus.

A remark about energy units and conversions for photons:

$$1 \text{ eV} = 8066 \text{ cm}^{-1} = 12394 \text{ \AA} = 2.41867 \times 10^{14} \text{ Hz} = 11605 \text{ K} = 1.6 \times 10^{-12} \text{ erg.}$$

Bohr-Sommerfeld semi-classic model - 2

For the hydrogen-like atoms, from the quantization of the harmonic oscillator

$$\int_0^{2\pi} p dq = \int_0^{2\pi} p \varphi d\varphi = nh$$

where h = Planck's constant, one can derive Bohr's radii a_n , the internal energy levels E_n and kinetic energy T_n , and spectroscopic terms \mathbf{T}_n :

$$a_n = \frac{h^2}{4\pi^2 m e^2} \frac{n^2}{Z} ; 0.5 \times 10^{-8} \frac{n^2}{Z} \quad (\text{cm})$$

$$E_n = -T_n = -\frac{1}{2} \frac{4\pi^2}{h^2} m e^4 \frac{Z^2}{n^2} ; -2.18 \times 10^{-11} \frac{Z^2}{n^2} \quad (\text{erg})$$

$$\mathbf{T}_n = -E_n / hc = R \frac{Z^2}{n^2} ; 1.097 \times 10^5 \frac{Z^2}{n^2} \quad (\text{cm}^{-1})$$

Notice how closely the empirically found radii and Rydberg constant are expressed in terms of fundamental physical quantities.

Bohr-Sommerfeld semi-classic model - 3

A slight refinement can be made by inserting the barycentric description of the motion (**recall the 2-body problem**), because then the dependence from the mass of the electron m_e and the mass of the nucleus M (in other words, of the reduced mass μ) will be found:

$$\mu = m_e M / (m_e + M)$$

$$E_n = -R_M \frac{Z^2}{n^2}$$

This dependence of R on the nuclear mass gives the possibility to distinguish among the isotopes of a given element (***at least for the lighter ones***).

Bohr-Sommerfeld semi-classic model - 4

The velocity v on the first orbit is:

$$v = cZ \frac{2\pi e^2}{ch} \approx Z \frac{c}{137} = Z\alpha \quad , \quad \alpha = \frac{2\pi e}{ch} = \frac{e}{ch} \approx \frac{1}{137}$$

where α is the so-called ***fine-structure constant***.

Notice that the velocity is small in comparison with c , but the precision of the spectroscopic measurements is so high that **relativistic corrections** can be appreciated, as shown by Sommerfeld and by Dirac. However, the relativistic corrections are only a partial explanation of the H-line fine structure.

The following paragraph discusses the more recent meaning of α , and its possible cosmic variation over the life of the Universe.

Interested students could read the dedicated .doc file.

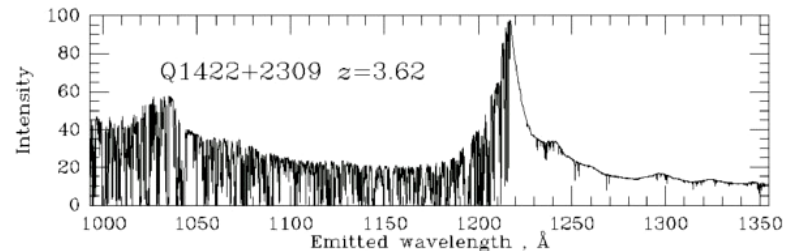
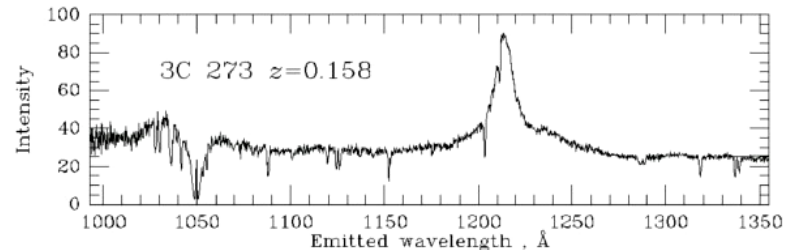
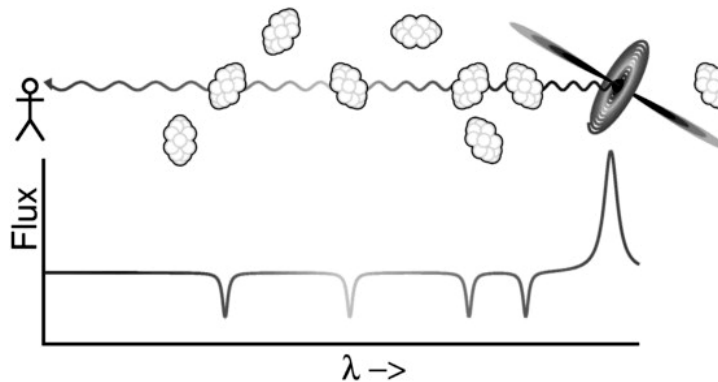
A new meaning of the fine structure constant

In recent theories, our view of α has changed considerably. In the theory of quantum electrodynamics, it represents *the strength of the interaction between electrons and photons*. It is therefore the "coupling constant", or measure of the strength of the electromagnetic force that governs how electrically charged elementary particles (e.g., electron, muon) and light (photons) interact.

We now consider *α similar to the coupling constants* for the other three known fundamental forces or interactions of nature: the gravitational force, the weak nuclear force, and the strong nuclear force.

How constant is the fine-structure constant?

We could ask the following question: how constant is α ? The fine structure constant could *vary over cosmological times*, and spectroscopy affords one powerful mean for deriving limits on that possible variation by taking high resolution spectra of distant cosmological objects, namely of quasars at high redshift z on which intergalactic clouds have superimposed a wealth of absorption lines.

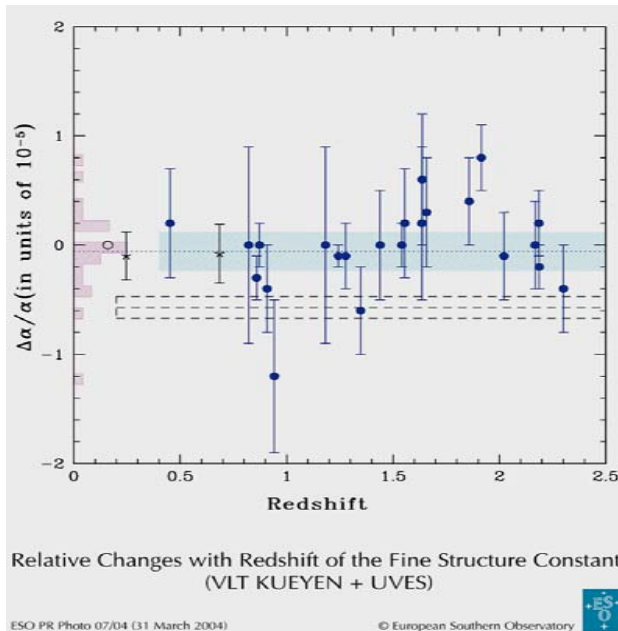


Experimental results

Spectral features, such as the doublet splitting, should vary according to:

$$\Delta\alpha / \alpha = [\alpha(t) - \alpha(t_0)] / \alpha(t_0)$$

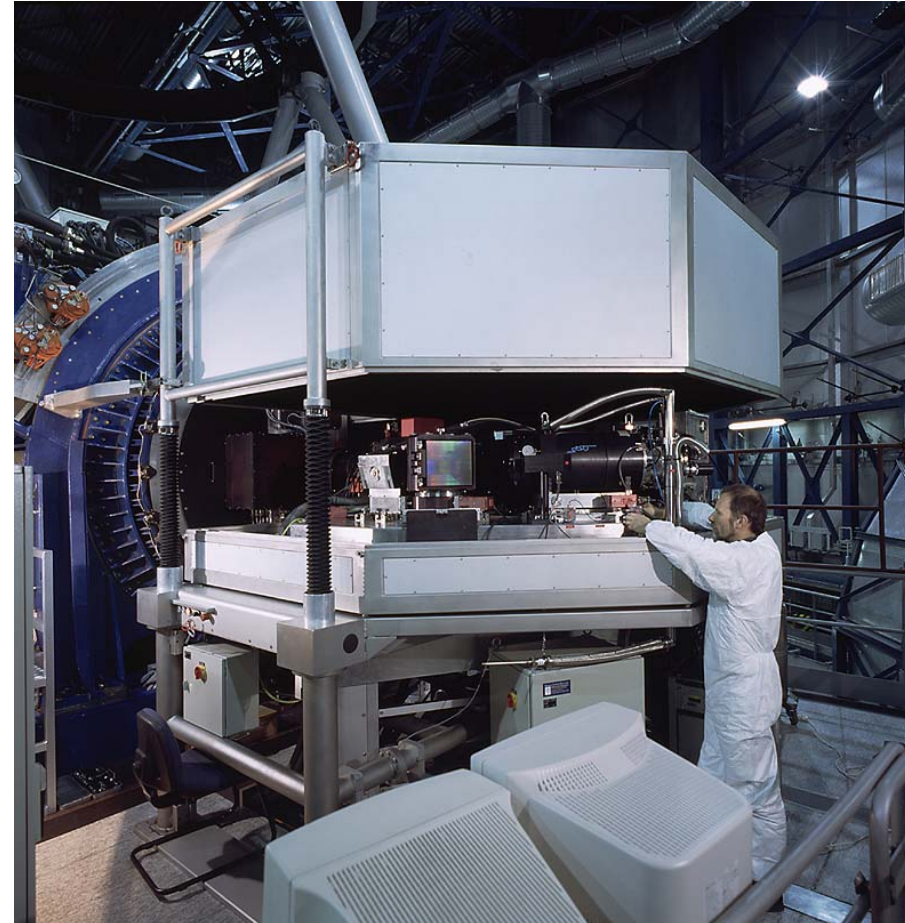
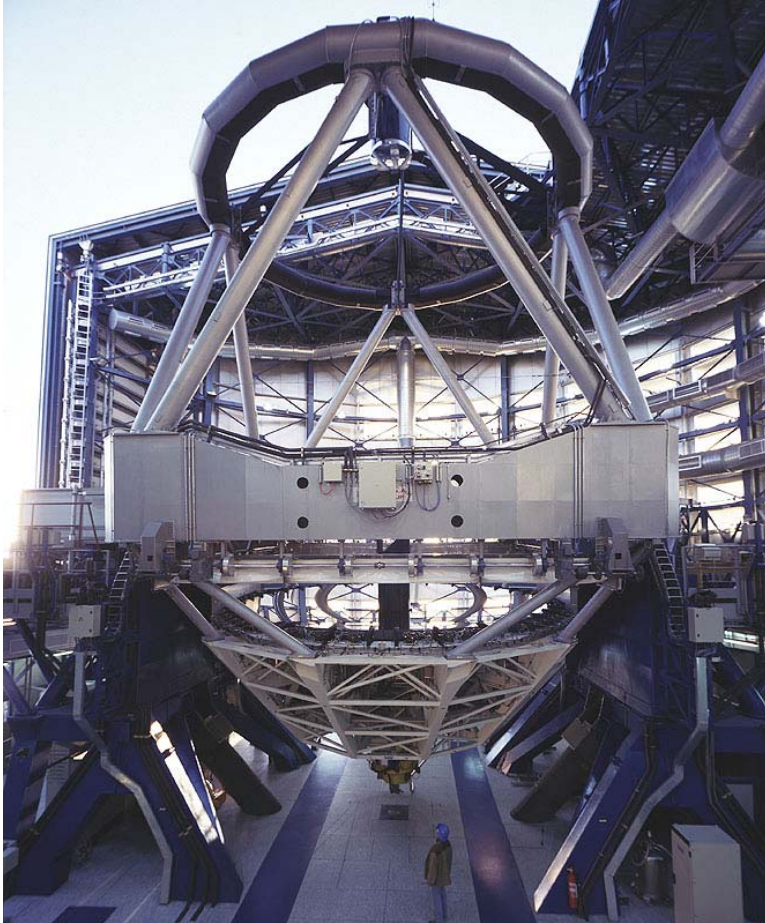
where t_0 is now and t is the cosmological time corresponding at redshift z .



One of the best results (Quast et al., 2003) has been obtained up to $z = 1.15$ with the VLT + UVES:

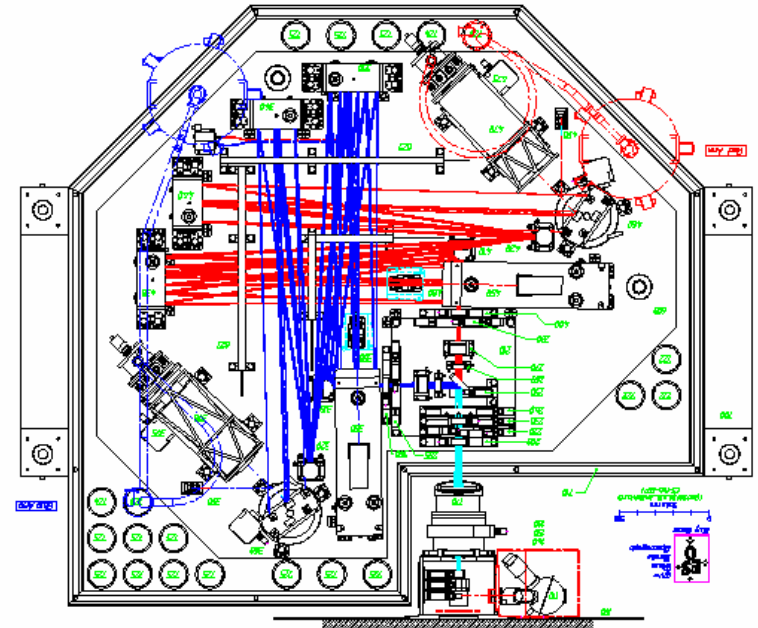
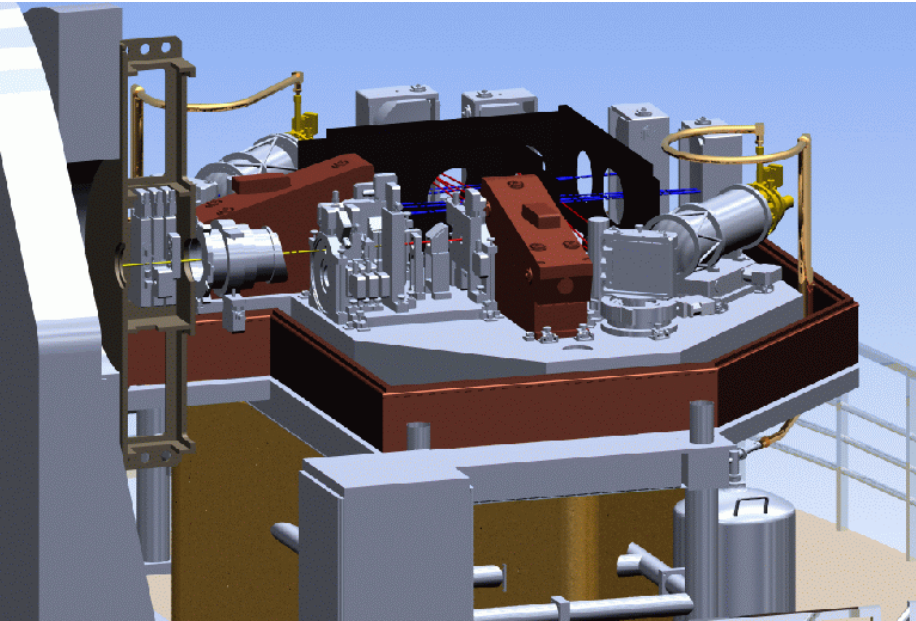
$$\Delta\alpha / \alpha = (-0.5 \pm 2) \times 10^{-6}$$

VLT + UVES - 1



Left, Kuyén (Moon) during the mounting phases. Right: UVES at the Nasmyth focus.

VLT + UVES - 2



UVES is a two-arm cross dispersed *echelle* spectrograph covering the wavelength range 300 - 500 nm (blue) and 420 - 1100 nm (red), with the possibility to use *dichroics*.

The spectral resolution for a 1 arcsec slit is about 40,000. The maximum resolution that can be attained with still adequate sampling, using a narrow slit, is about 110,000 in the red and 80,000 in the blue.

The two arms are equipped with CCD detectors, one single chip in the blue arm and a mosaic of two in the red. Each arm has two cross disperser gratings working in first order.

Fine-structure constant from geophysics

Another stronger limit (Olive et al., 2003) was obtained by an entirely different mean, namely by the **radioactive decay** of long lived nuclei in geophysical and meteoritic data, back to the epoch of Solar System formation (approximately 4.5×10^9 years ago, which would correspond to $z = 0.45$):

$$\Delta\alpha / \alpha = (8 \pm 8) \times 10^{-7}$$

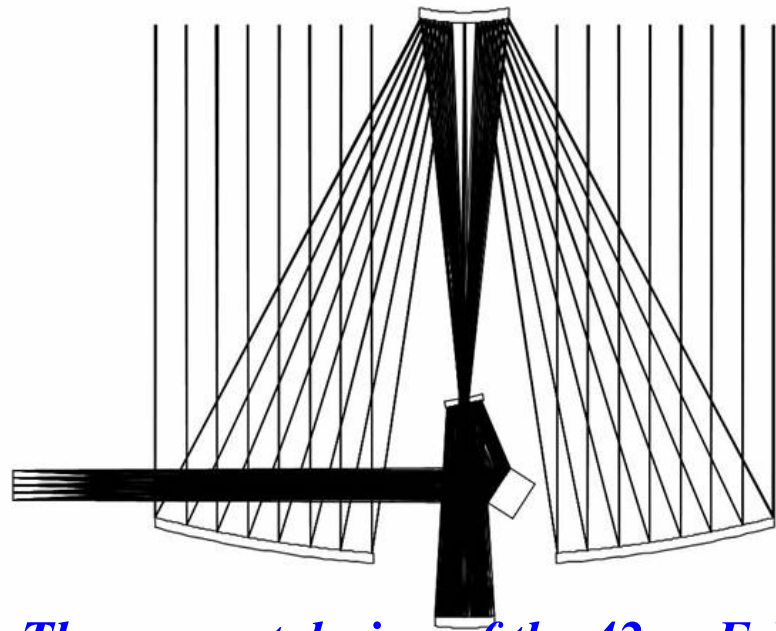
This is one of the many instances when geophysical and astrophysical data give complementary information (in this case, the two are in good agreement).

Other fundamental constants can be probed using quasars. In particular, by studying the wavelengths of molecular hydrogen, one can probe the variations of the ratio between the masses of the proton and the electron.

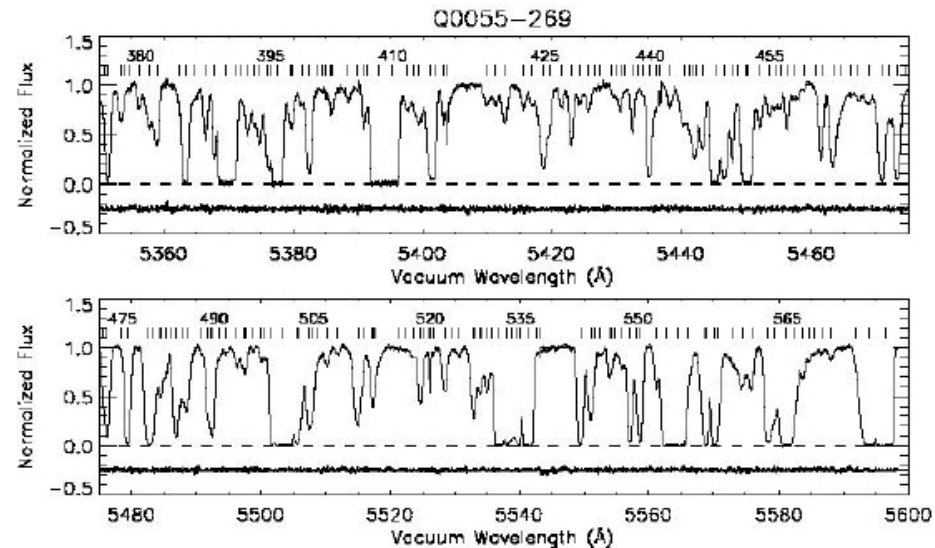
Fine-structure constant at the E-ELT

More stringent limits could be provided by the new instrument (ESPRESSO) being considered for the VLT as a precursor for the instrument named CODEX for the European Extremely Large Telescope (E-ELT).

CODEX should be able to measure directly the *variation of the expansion rate of the Universe over a 10-year period*.



The current design of the 42-m E-ELT.



The Lyman- α forest in the spectrum of a distant quasar.

Line radiation according to Bohr

Following Bohr, assume that the atom radiates (or absorbs) energy only in the ‘jump’ from level n to level m ; the energy difference between the two orbits is:

$$\Delta E_{nm} = -E_n + E_m = R_M Z^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right), \quad n \neq m$$

The radiated (or absorbed) frequency will then be:

$$\nu_{nm} = |\Delta E_{nm} / h| = R_M \frac{Z^2}{h} \left| \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \right|, \quad n \neq m$$

The module has been used in order to have always positive frequencies, irrespective of emission ($n > m$) or absorption ($n < m$).

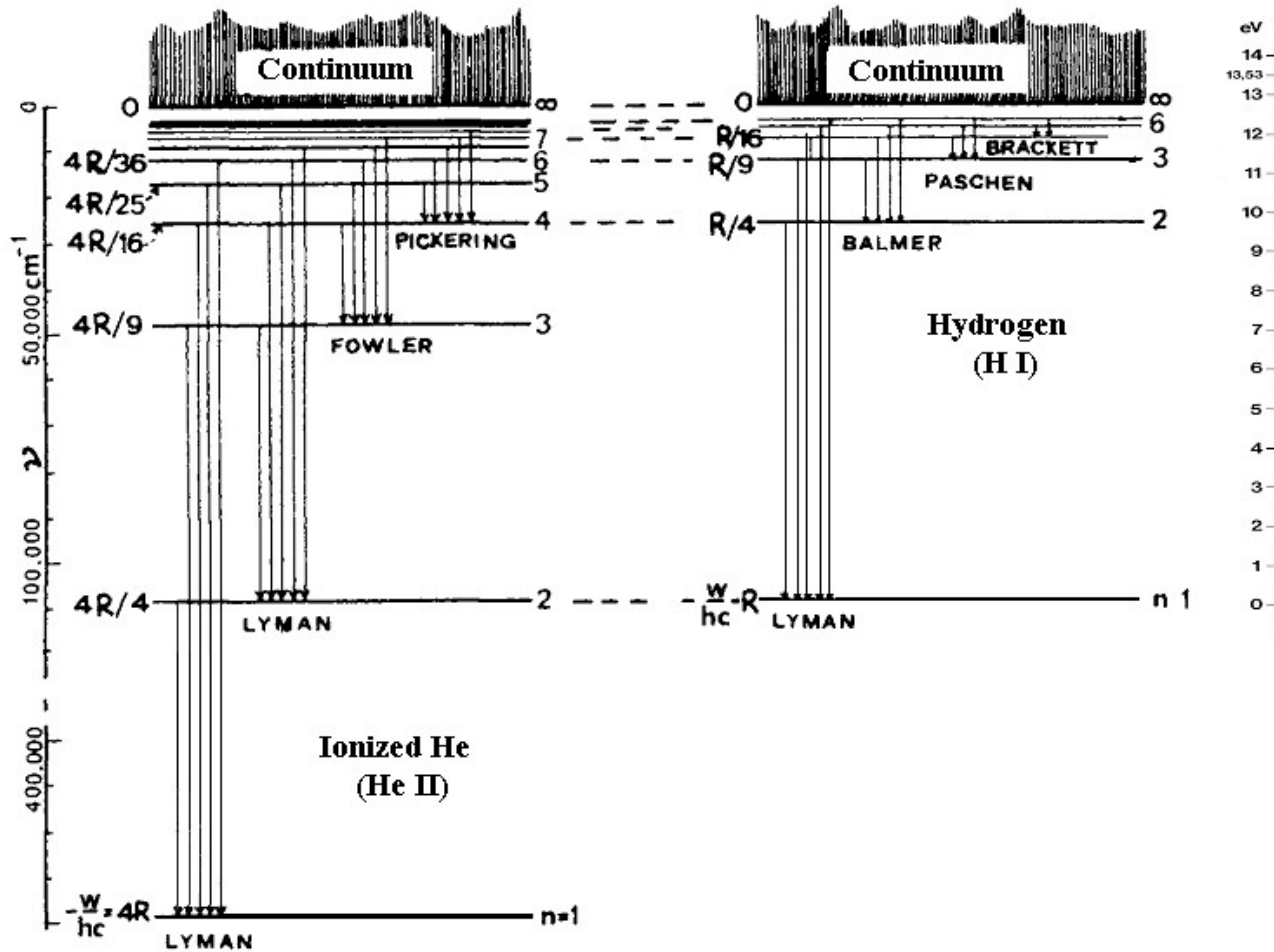
Hydrogen-like Atoms

For He II, the factor $Z^2 = 4$ moves all series to higher frequencies; the line corresponding to Ly- α is then observed at 302 Å. Only if $n = 3$ the He II lines fall in the visible region; they were identified by Pickering in the spectrum of the hot star ζ Pup; the lines corresponding to $E_{34} = 4686$ Å and $E_{35} = 3203$ Å are very important for the spectral classification of the hottest stars. See the He II and H I Grotrian diagram in the following figure.

The energy E_n is also the *energy of ionization* of that element from that level; for instance E_1 for hydrogen is 13.54 eV, for He II is 53.17 eV, for Li III is 123 eV.

It is indeed possible to absorb photons from energy level n greater than E_n ; in this case the electron will reach infinity with kinetic energy greater than 0 (a so-called *bound-free transition*); the reverse process is also possible, giving birth to a photon in the continuum blue-ward of the head of the corresponding series. These processes will be discussed in a following paragraph.

Grotrian Diagram for HI and He II



Transitions from very high levels

Let us consider two levels n, m with n much greater than 1 and $m = n + 1$; the following approximation will hold:

$$\frac{1}{n^2} - \frac{1}{m^2} = \frac{m^2 - n^2}{n^2 m^2} \approx \frac{2n}{n^4} = \frac{2}{n^3}, \quad \nu_{n,n+1} \approx 2 \frac{R_M c Z^2}{n^3} = \frac{\nu_0}{n^3}$$

But this is exactly what is expected on the basis of classic radiation, where the frequency of revolution of the electron is:

$$\nu = \frac{v}{2\pi r} = \frac{2T}{nh} = \frac{2R_M c Z^2}{n^3}$$

This result is also known as **correspondence principle**: when $n \gg$ the quantum results must approach those of classic electrodynamics. Notice the factor 2: qualitatively, the energy is double because the transition from $n + 1$ to n has exactly the same wavelength of the transition from n to $n - 1$.

The possibility to observe transitions from very high levels is offered by the **planetary nebulae** at radio frequencies: the transitions from $n = 110$ to $n = 109$ and from other high levels are indeed well observable (Terzian, 1969, 1974).

Sommerfeld 3-D hydrogen atom

The simple model of circular orbit was extended by Sommerfeld to elliptical orbits of arbitrary orientations in space. The two new degrees of freedom give rise to two new quantum numbers, an azimuthal one l and a magnetic one m .

The azimuthal one is connected with the ellipticity of the orbit; it can assume the integer values:

$$l = 0, 1, \dots, n-1$$

(in total, n values).

The magnetic moment m is connected with the orientation of the orbit in space; it can assume the integer values:

$$m = 0, \pm 1, \dots, \pm l$$

(in total $2l+1$ values).

Degeneracy of the levels

The two new quantum numbers l , m do not correspond to new energy levels; the energy continues to be determined by the principal quantum numbers n . In other words, the energy level E_n corresponds to different possible *configurations* of the electron; the number of these configurations is easily found:

$$\text{number of configurations} = \sum_{l=0}^n (2l+1) = n^2$$

This number is called *degeneracy* of that level.

A treatment taking into account the *relativistic corrections* would show that actually the different l levels do not have exactly the same energy, but the correction is small.

The discovery of the intrinsic *spin of the electron*, which only has the two possible values $\pm 1/2$, doubles that number, **the total degeneracy is $2n^2$** .

Vector Model

It is often convenient to treat the azimuthal, magnetic and spin numbers as modules of **vectors**, and to consider the **two magnetic moments**, the one due to the circulation around the nucleus **l** and the intrinsic one of spin **s**.

The interactions among the two moments is called **spin-orbit interaction**. It amounts approximately to:

$$\Delta E_{ls} \approx \frac{e^2}{a_n} \left(\frac{e^2}{ch} \right)^2 = V\alpha^2 = V$$

where a_n is Bohr's radius, α the fine structure-constant, and V the electrostatic potential. In this approximate treatment, the spin-orbit interaction is always much smaller than the electrostatic one; however, it is evident in the spectra, giving rise to the fine structure of doublets. Every level l can thus be split in two levels $j = l \pm 1/2$, except the level $l = 0$.

The new quantum number j , which can be only an half-integer number, is called the *internal quantum number*.

Electron configurations

The need to use 4 quantum numbers reflects the many possible configurations of the electron in its orbit. The designation of this configuration is therefore fairly complex, especially because it was arrived at before the theoretical comprehension of the problem, simply by the arrangement of the spectral lines into different series. We give here a simple example for the first 3 levels of H I.

<i>n</i>	1	2	3
<i>l</i>	0	0 1	0 1 2
<i>m</i>	0	-1 0 +1	-2 -1 0 1 2
<i>s</i>	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Spectroscopic notation	1s	2s 2p	3s 3p 3d

Spectroscopic notation

The spectral terms are designated with the following general structure:

$$n^{2S+1}L_j^{(\Sigma l)}$$

where:

n = principal quantum number

L = total azimuthal quantum number (= l if there is only one electron); *the designation makes use of letters, not numbers: S* ($L=0$), *P* ($L=1$), *D* ($L=2$), *F* ($L=3$)

S = total spin number (= $\frac{1}{2}$ for a single electron)

$2S+1$ = multiplicity of the level

J = total internal quantum number (= j if there is only one electron)

Σl = total parity (it is explicitly indicated only if odd, and then the letter 'o' is used).

To meaning of this notation will be clearer after some Quantum Mechanics notion and the examination of atoms with more than one electron.

Selection Rules

Electron transitions are described by listing the lower atomic state first, followed by the upper state; e.g. 2S -3P.

Not all possible transitions actually take place, there are selection rules to be obeyed:

- S cannot change, $\Delta S = 0$
- $\Delta L = 0$ or ± 1 ; but for the electron responsible for the emission it is necessarily $\Delta l = \pm 1$ (Laporte's rule), the parity must change by 1, because a photon can be considered a particle with spin = 1
- J behaves like L , however no transition takes place between $J = 0$ and $J = 0$.

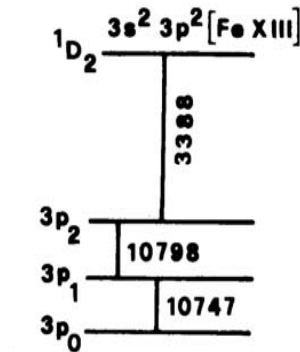
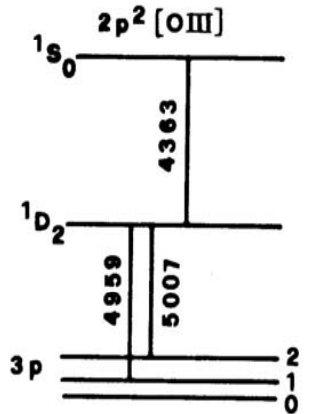
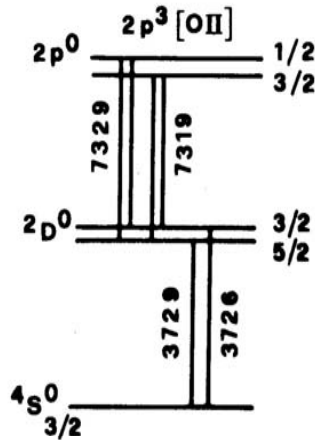
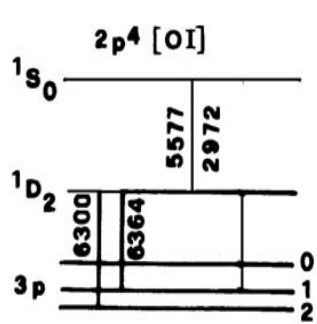
Forbidden lines

However, in several astrophysical situations, 'forbidden' lines appear (in emission) and quite often they are the most intense in the spectrum. This is the case for instance of the solar corona, where are very strong the green line $\lambda 5303 \text{ \AA}$ of [FeXIII] and the red line of $\lambda 6374 \text{ \AA}$ of [FeX], or of the 'nebulium' lines in planetary and diffuse nebulae, due to Oxygen.

A forbidden transition is indicated by inserting in square parenthesis the responsible ion, e.g. $\lambda 3727/29 \text{ [OII]}$, $\lambda 5577 \text{ [OI]}$.

Because of the strong dependence of their intensities from **temperature and density** of the emitting gas, the forbidden lines are *excellent diagnostic instruments for those two variables in diluted, hot gases such as the envelopes of the planetary nebulae.*

Structure of the terms of some forbidden transitions



The Oxygen has many intense forbidden lines. The group of transitions $^3P - ^1D$ is forbidden because $\Delta S = 1$.

The transitions $^3P_0 - ^1D_2$ violate both $\Delta S = 1$ and the rule on ΔJ .

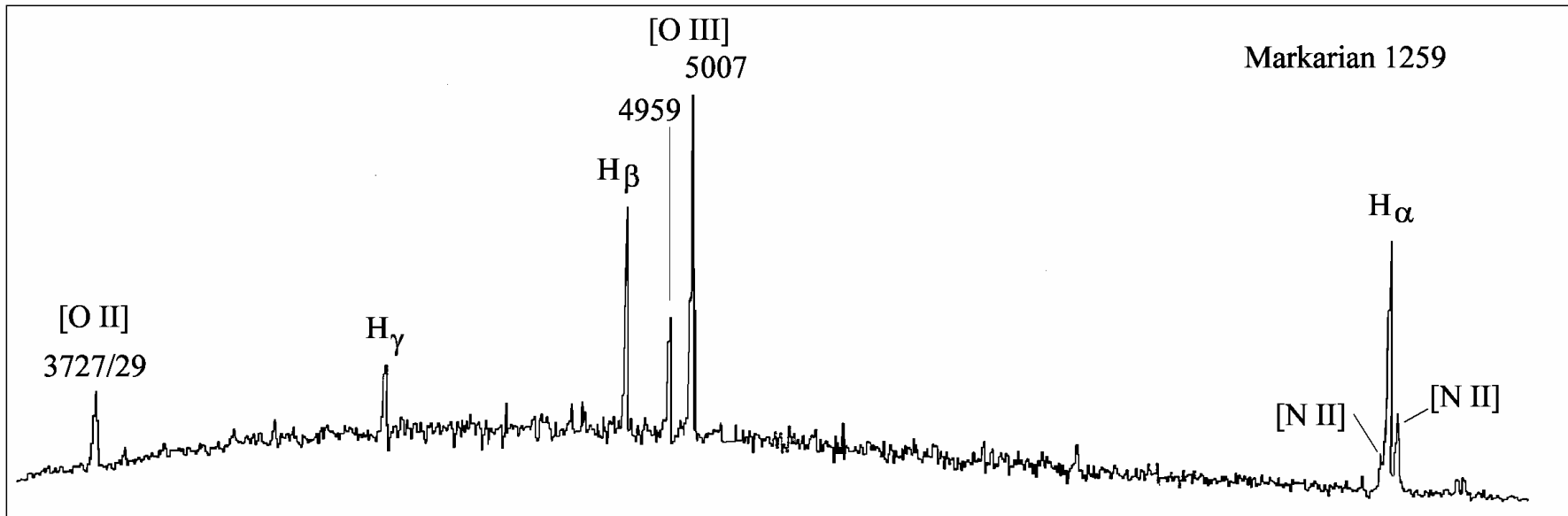
All transitions P - D are said nebular transitions.

The transitions D-S violate both $\Delta S = 1$ and the rule on ΔJ .

The green line [O I] λ 5577 is said *auroral line*.

The levels originating forbidden lines are said '**metastable levels**'.

A galaxy spectrum with forbidden and permitted lines



This spectrum pertains to a Markarian galaxy, discovered by V. Markarian with the Byurakan Schmidt telescope

The nuclear spin and the 21-cm HI line

The nucleus of an atom possesses a spin which can interact with the spin of the electron causing a further splitting of the levels (*hyperfine* structure, not to be confused with the hyperfine splitting due to isotopes). The value of the spin is an integer multiple of $\hbar/2\pi$, indicated with \mathbf{I} .

The nuclear and electronic spin combine to give a further quantum number \mathbf{F} :

$$\mathbf{F} = \mathbf{J} + \mathbf{I}, \mathbf{J} + \mathbf{I}-1, \dots |\mathbf{J}-\mathbf{I}|.$$

In the conditions of the interstellar medium (low temperature $T \approx 100$ K, low densities $\rho \approx 100$ atoms/cm³), the hydrogen gives rise to a very important transition between the possible state of parallel (both spin up) and anti-parallel (one up, one down) situations of \mathbf{I} and \mathbf{J} .

The energy splitting is very low, corresponding to 1420 MHz (21-cm).

The transition is also strongly forbidden, violating the condition $\Delta l = \pm 1$ for the emitting electron.

The life time is therefore extremely long, of the order of 10^7 years: only the very low density and temperature allow its **radiative** emission and not the **collisional de-excitation** of the upper level.

De Broglie's wave

By examining the diffraction figure of a beam of electrons traversing a sheet of crystalline dust, de Broglie made the hypothesis that any particle of mass m and velocity v (or impulse p) has an associated wavelength λ given by:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

which for the electron is: $\lambda_e = \frac{12.36}{\sqrt{E}}$ (Å) if E is in eV.

This wave-particle dualism stems from *Heisenberg's indetermination principle*:

$$\Delta x \Delta p_x \geq h \quad , \quad \Delta E \Delta t \geq h$$

Schroedinger equation -1

The general equation describing the wave propagation is:

$$\nabla^2 \psi = \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} \quad (\nabla^2 = \text{Laplace operator})$$

and the general solution is: $\psi = A(x, y, z)e^{i\omega t} = A(x, y, z)e^{i2\pi\nu t}$

The stationary part is given by: $\nabla^2 A + \frac{\omega^2}{c^2} A = \nabla^2 A + \left(\frac{2\pi}{\lambda}\right)^2 A = 0$

Inserting de Broglie's expression for λ , with the kinetic energy $T = E - V$ (where V is the Coulomb potential and $E < 0$) instead of the square of the velocity, we finally obtain the famous Schroedinger equation:

$$\nabla^2 A + \frac{8\pi^2 m_e}{h^2} (E - V) A = 0$$

Schroedinger equation -2

The meaning of A (which in general is a complex function, the complex conjugate of A being A^*) is the following: the product $A \cdot A^*$ is proportional to the probability to find the electron in position (x, y, z) , a probability which is maximum in correspondence with Boh'r orbits.

Due to the symmetry of the problem, it is convenient to introduce a spherical coordinate system (r, θ, φ) . The function A can then be separated in the product of 3 functions:

$$A(r, \theta, \varphi) = R_{nl} \Theta_{lm} \Phi(\varphi)$$

Schroedinger equation is thus a particular case of the very general class of *auto-values equations, whose solutions are the auto-functions of the problem.*

The three quantum numbers are therefore the spontaneous outcome of the problem itself.

The electron spin is as yet not present; following **Dirac** we could finally write:

$$\psi = \psi(r, \theta, \varphi, s) \quad \text{where } s = \pm 1/2.$$

The He I atom - 1

The presence of two electrons complicates the conceptual treatment, which cannot be solved on classic grounds, as shown by Heisenberg. The interaction between the two electrons is much stronger than what can be predicted by the Coulomb law, and it is called *exchange interaction*.

Basically, no measurement can distinguish between the two electrons, so that if $\psi_A(1)$ is the auto-function of electron A in state 1 of energy E_1 , and $\psi_B(2)$ is the auto-function of electron B in state 2 of energy E_2 , the product $\psi_A(1) \cdot \psi_B(2)$ is the solution of the state $E_1 + E_2$, and so is *any linear combination* of the two.

Among all combinations, of particular importance are the *symmetric* one:

$$\psi^+ = \psi_A(1) \cdot \psi_B(2) + \psi_A(2) \cdot \psi_B(1)$$

and the *anti-symmetric* one:

$$\psi^- = \psi_A(1) \cdot \psi_B(2) - \psi_A(2) \cdot \psi_B(1)$$

The He atom - 2

Those two combinations must have the same energy, because no measurement can distinguish the two electrons; this is a so-called *exchange degeneration*.

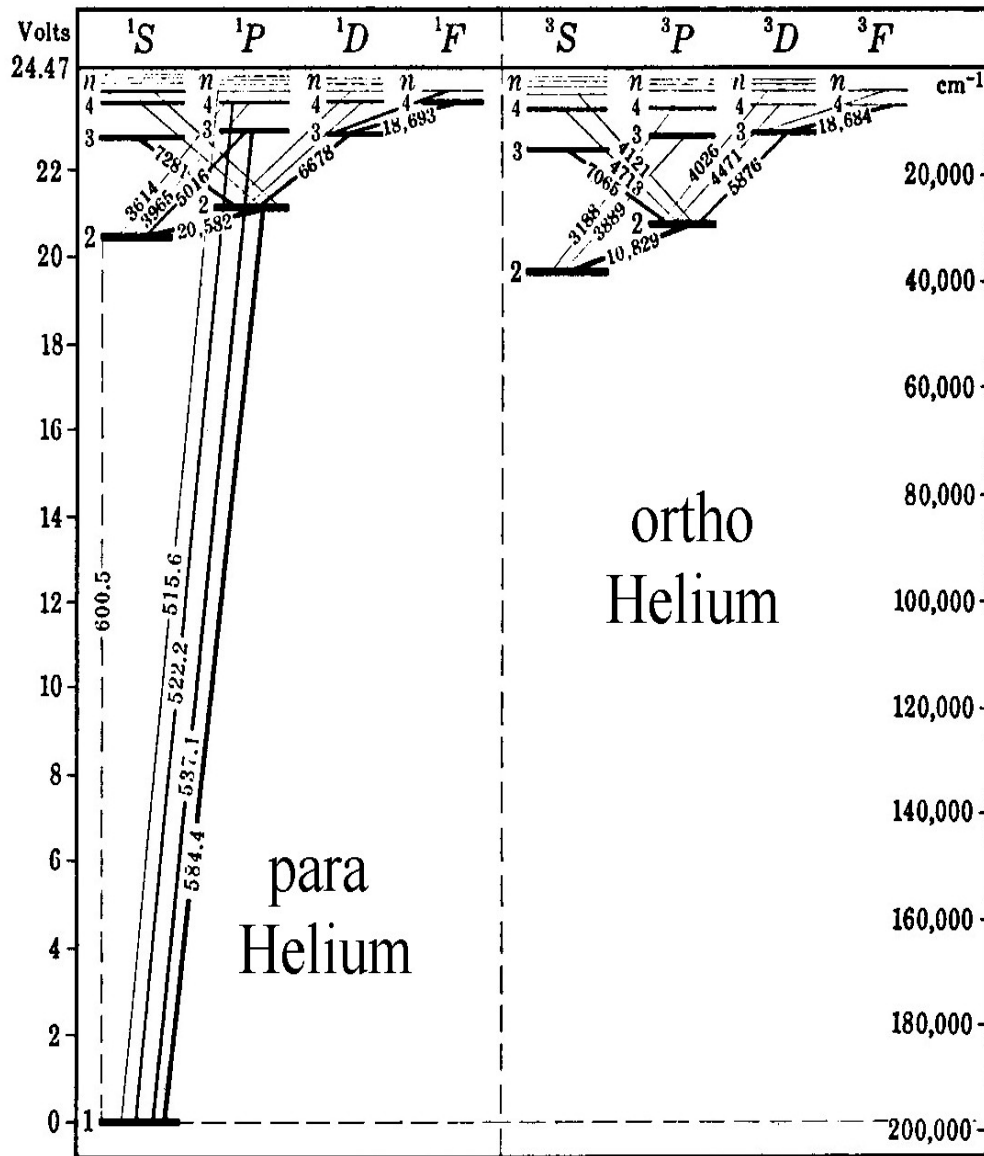
Let us now introduce the **spin** of the electrons, which can be either *parallel or anti-parallel*, combining to give a resultant 0 or 1.

If the resultant is 0, the energy level remains single, if it is equal to 1, the energy level becomes a triplet.

The ground level of He I is of singlet, the He I atom has no associated permanent magnetic moment (the element is indeed diamagnetic, not paramagnetic), the excited levels can be either of singlet or of triplet.

Observations prove that the the levels of singlet do not mix together: the He I spectrum is composed by series of singlets (*para-Helium*) and of triplets (*orto-helium*) (see figure).

The He I atom - 3



Energy Level Diagram for Helium.

Combinations of terms of the *para* system with those of the *ortho* system have not been observed. In particular, the lowest state of ortho helium 2 ³S, which lies 19.72 eV above the ground state 1 ¹S, does not combine with the ground state.

The transition 2 ¹S - 1 ¹S is forbidden (the state is *metastable*) because it violates the rule on Δl ; the metastability of the 2 ³S state is stronger, because it violates also the para-ortho prohibition.

The He atom - 4

The explanation of the para-ortho prohibition cannot be derived from the Bohr-Sommerfeld semiclassical model. It requires the complete quantum mechanical theory.

If we introduce in the wavefunction the Coulomb repulsion between the two electrons, the previous exchange degeneration is removed, but an *exchange interaction* of great amplitude appears, because either electron can be in a *superposition of states*, a property absolutely not present in classic mechanics. The amplitude of the exchange interaction is of the order of the Coulomb energy.

Similar considerations apply to multi-electron atoms and also to the H₂ molecule. The exchange interaction plays indeed a fundamental role in interpreting the homopolar molecules like H₂ and C₂, and also the saturation of the valence (why an H₃ or a CH₅ is not found?).

In classical mechanics we could have an arbitrary number of planets orbiting the Sun.

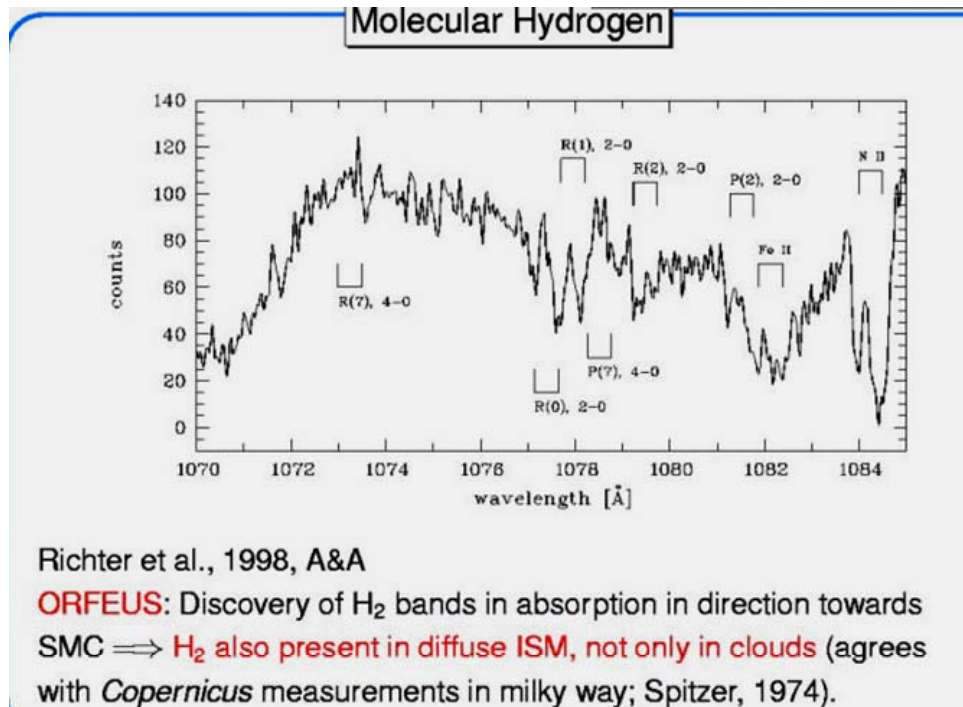
Molecules

In the atmospheres of the cooler bodies (e.g. planets, but also interstellar clouds) the elements are associated in *molecules, not atoms*.

To study astrophysical molecules, the UV and IR regions of the spectrum are particularly important, but then *Space plays a decisive role*.

From the ground, millimeter and radio waves are also extremely important.

The figure below shows the detection of molecular Hydrogen, H_2 in the intergalactic medium.



The name of L. Spitzer, a pioneer in the field of molecular astrophysics, is now associated with the NASA IR telescope.

Molecular spectroscopy

Molecular spectra are very different from atomic ones, being composed by bands, each of which formed by several lines. This is due to the fact that the central field characteristics is usually absent, and to the *vibration* and *rotation* of the whole molecule. **These two energies are also quantized**. Therefore, the three possible forms of energies must be considered independently, but also coupled together to give rise to mixed mode transitions. The situation is very complex, but a first approximation (Born-Oppenheimer) can be obtained by separating the wavefunction and summing the energies:

$$\Psi = \Psi_e \cdot \Psi_v \cdot \Psi_n \quad , \quad E = E_e + E_v + E_r \quad (\textit{usually } E_e \gg E_v \gg E_r)$$

The electron transition therefore are typical of the UV and visible, the vibrational transitions of the red-near IR, the rotations of the infrared and radio domains.

In Astronomy, the word 'molecule' often means *molecular radical*, not a complete molecule; e.g. CN, OH, CH

Electronic energy of diatomic molecules

If the molecule is homonuclear (say H_2), the electron distribution is symmetric, the central field approximation cannot be applied, and the molecule does not possess a permanent electric dipole (and usually not a permanent magnetic dipole).

If the molecule is heteropolar (e.g. HCl), the barycenter of the charge is closer to one of the two ions (in this example it is closer to Cl^-), so that a center can be identified, and the molecule possesses a *permanent electric dipole moment*, which is responsible for the appearance of vibrational and rotational transitions. The presence of the electric dipole does not necessarily imply the existence of a permanent magnetic dipole in the ground energy level, because the total electronic azimuthal numbers tend to sum to zero, and so do also the coupling between the spins.

Spectroscopic Notation for Molecules

Capital Latin and Greek letters are used; L and S are the total angular and spin moments of the electrons of each atom. Their projections along the molecular axis are indicated with Λ and Σ respectively, with $\Lambda = 0, 1, 2, \dots, L$.

The total angular momentum is indicated with $\Omega = L+S$, which is analogous to the inner quantum number J of the atomic case.

The notation is therefore:

$$Z(2S+1)\Lambda_{\Omega}$$

where Z is the electronic state, $2S+1$ the multiplicity.

L is analogous to the atomic meaning, and it is indicated with $\Sigma, \Pi, \Delta, \Phi$ (instead of S,P,D,F of the atomic notation).

The transitions are usually listed with the upper level first and the lower level second, opposite to the atomic case.

The selection rules are: $\Delta\Lambda = 0, \pm 1$, $\Delta\Sigma = 0$, $\Delta\Omega = 0, \pm 1$.

Vibrational energy of a diatomic molecule

The separation between the two molecules can vary around an equilibrium position, according to the internal kinetic energy. At the first order approximation, the vibration is a harmonic motion with frequency:

$$\nu_{\text{vibr}} = \frac{1}{2\pi} \sqrt{\frac{2D}{\mu}}$$

where D is an appropriate potential (Morse potential) and μ the reduced mass. Classically, the energy of the vibration is associated to the amplitude, which quantistically becomes:

$$E_{\text{vibr}} = h\nu_{\text{vibr}} \left(v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots$$

Vibrational level spacing

The vibrational levels are therefore, in this approximation, equally spaced.

A second order approximation would give an expression of the type:

$$T_{\text{vibr}}(v) = \omega \left(v + \frac{1}{2} \right) - \alpha \omega \left(v + \frac{1}{2} \right)^2, \quad v = 0, 1, 2, \dots$$

where $T_{\text{vibr}}(v)$ is the spectral term (in wavenumbers).

Furthermore, there is a zero-level energy which is not present classically, whose value is around 0.1 eV.

With the increase of v , the vibrational levels **do not** usually converge toward the dissociation energy of the molecule.

Rotational Motion of a diatomic molecule

In first approximation, the rotation can be considered a rigid one around a barycentric axis. The moment of inertia, the energy and the spectral term (in wavenumbers) are:

$$I = \mu r_{\text{equil}}^2, \quad E_{\text{rot}} = \frac{1}{2} I \omega_{\text{rot}}^2 = \frac{\hbar^2}{2I} J(J+1), \quad F(J) = BJ(J+1) = \frac{h}{8\pi^2 cI}$$

where B is known as rotational constant of that molecule. The separation between two adjacent levels becomes:

$$\Delta E_{\text{rot}} = \frac{\hbar^2}{2I} [J(J+1) - (J-1)J] = \frac{\hbar^2}{I} J$$

and in wavenumbers: $F(J) = 0, 2B, 6B, 12B, \dots, \Delta F_i = \Delta F_i + 2B$.

In a better approximation, an *oscillating* rotator is considered.

The typical energies vary approximately from 0.01 to 0.0001 eV.

Spectra of diatomic molecules - 1

For each electronic level, there are many vibrational levels, and for any vibrational level many rotational ones.

By neglecting the interactions among them, the energy variation in a radiative transition can be written as:

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_r$$

Therefore the spectrum is a complex of lines which appear grouped in ***bands***.

The pure rotational levels are not observed in a homonuclear molecule such as H₂, O₂, C₂. The permitted transitions, indicated with (r',r''), obey the rule $\Delta J = \pm 1$.

Also the pure vibrational transitions (v',v'') do not take place for homonuclear molecules. The selection rule is $\Delta v = \pm 1$, but is not very strict.

Spectra of diatomic molecules - 2

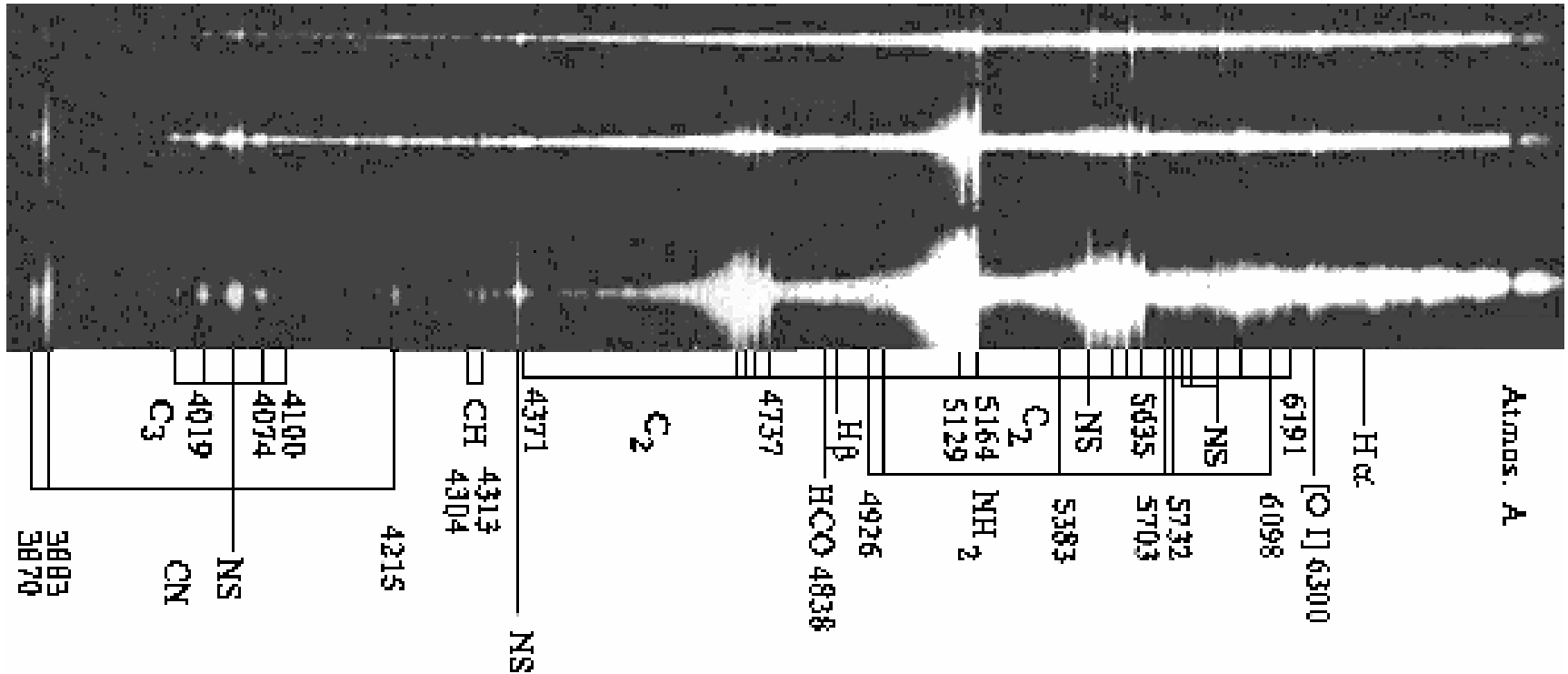
Furthermore, what is usually observed is a vibration-rotation transition: *the vibrational transition determines the region of the spectrum, the rotation the separation of the lines inside the band.*

In other words, any vibrational transition give rise to two symmetric bands separated by B .

The lines at high frequency are known as R-branch, those at lower frequency as P-branch. Sometimes a third branch Q can be observed. In generic spectra, the rotational band structure cannot be resolved; each band is very diffuse.

Notice that the appearance of the bands considerably changes from molecule to molecule: in some cases the bands have the head toward the blue and degrade toward the red. In other cases, just the opposite is seen.

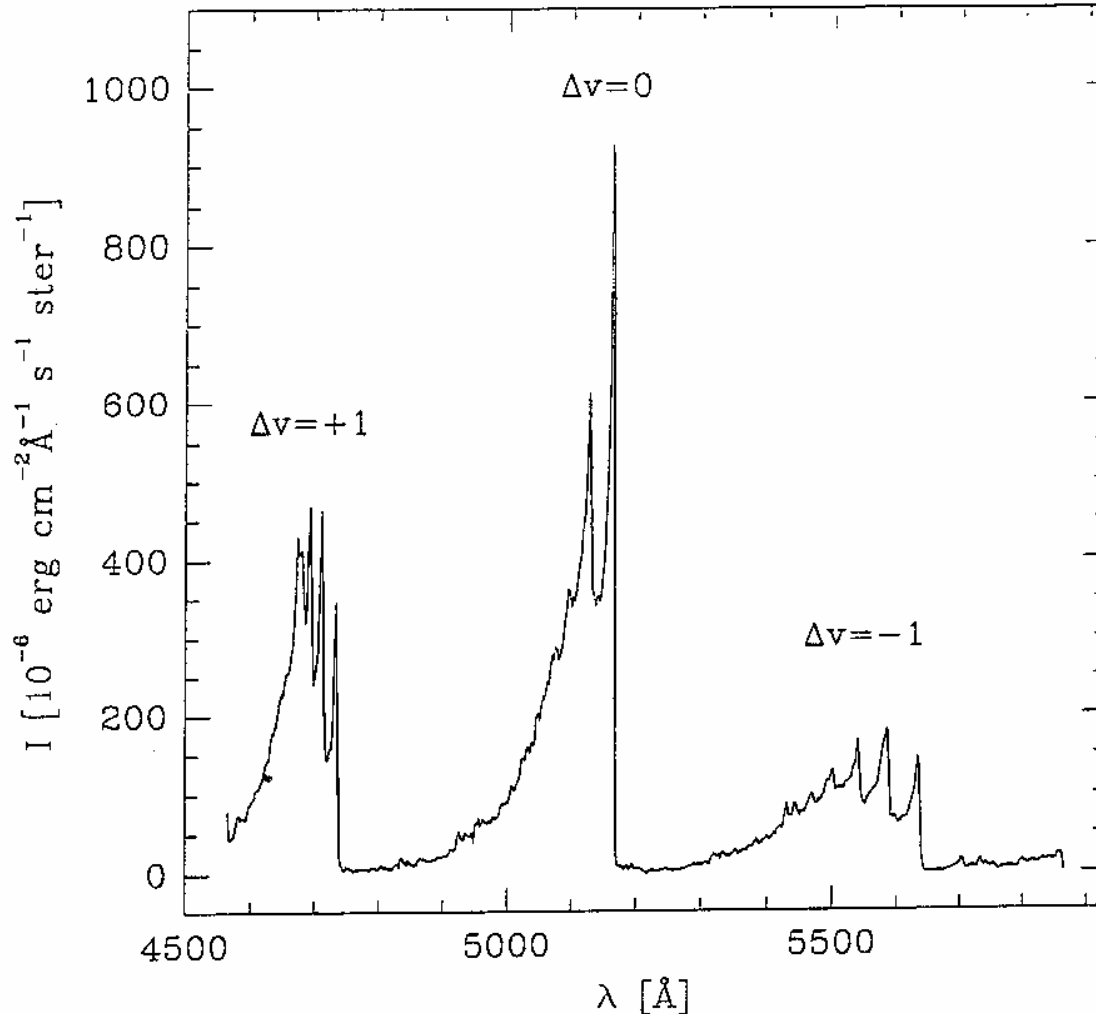
Spectra of Halley's Comet



Three photographic prismatic spectra of Halley's comet taken in 1985-1986. Notice the strong molecular lines, with heads declining to the blue.

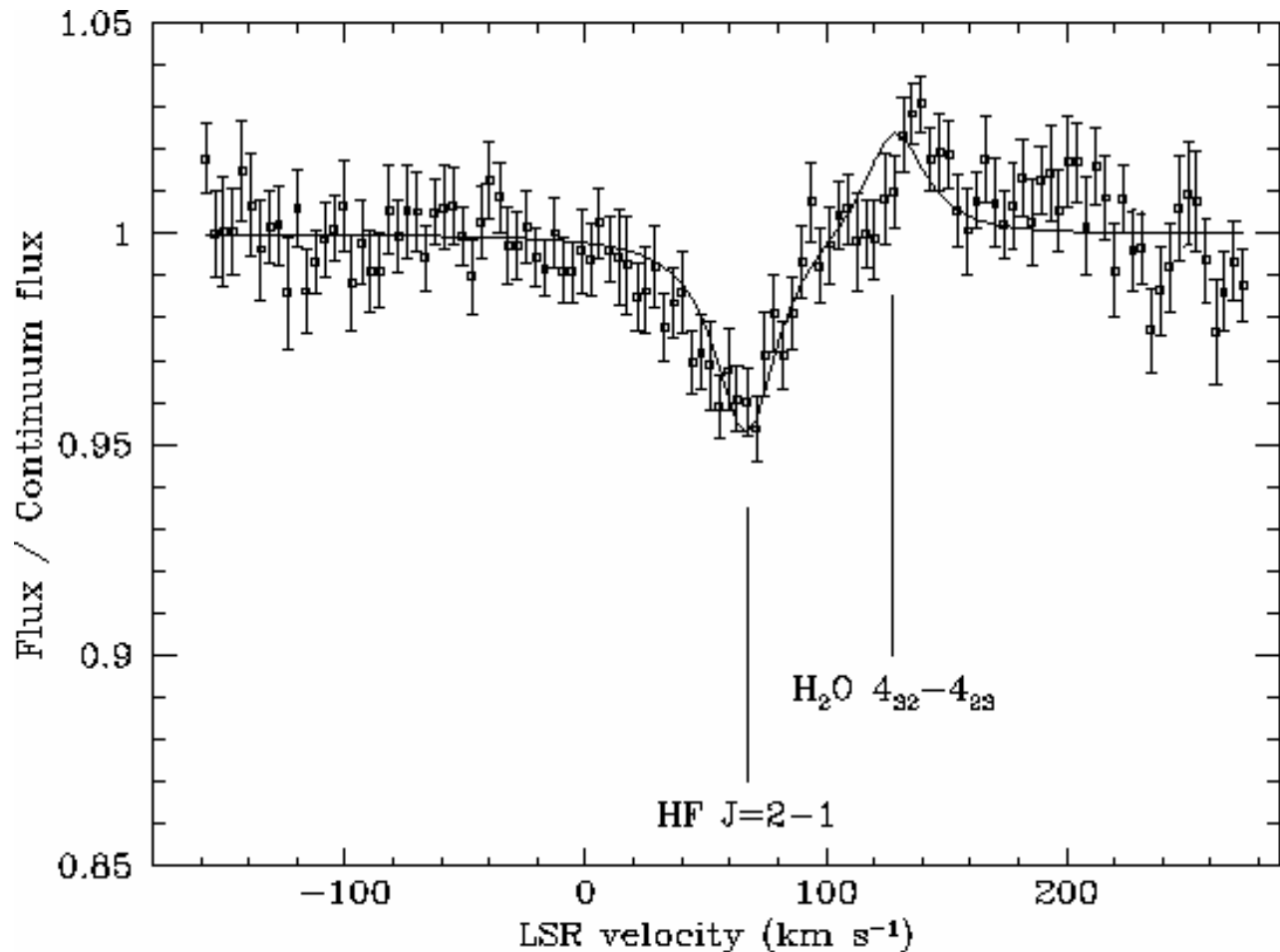
The C₂ (Swan) band in Comet P/Brorsen Metcalf

p/Brorsen-Metcalf 21.03 Agosto 1989



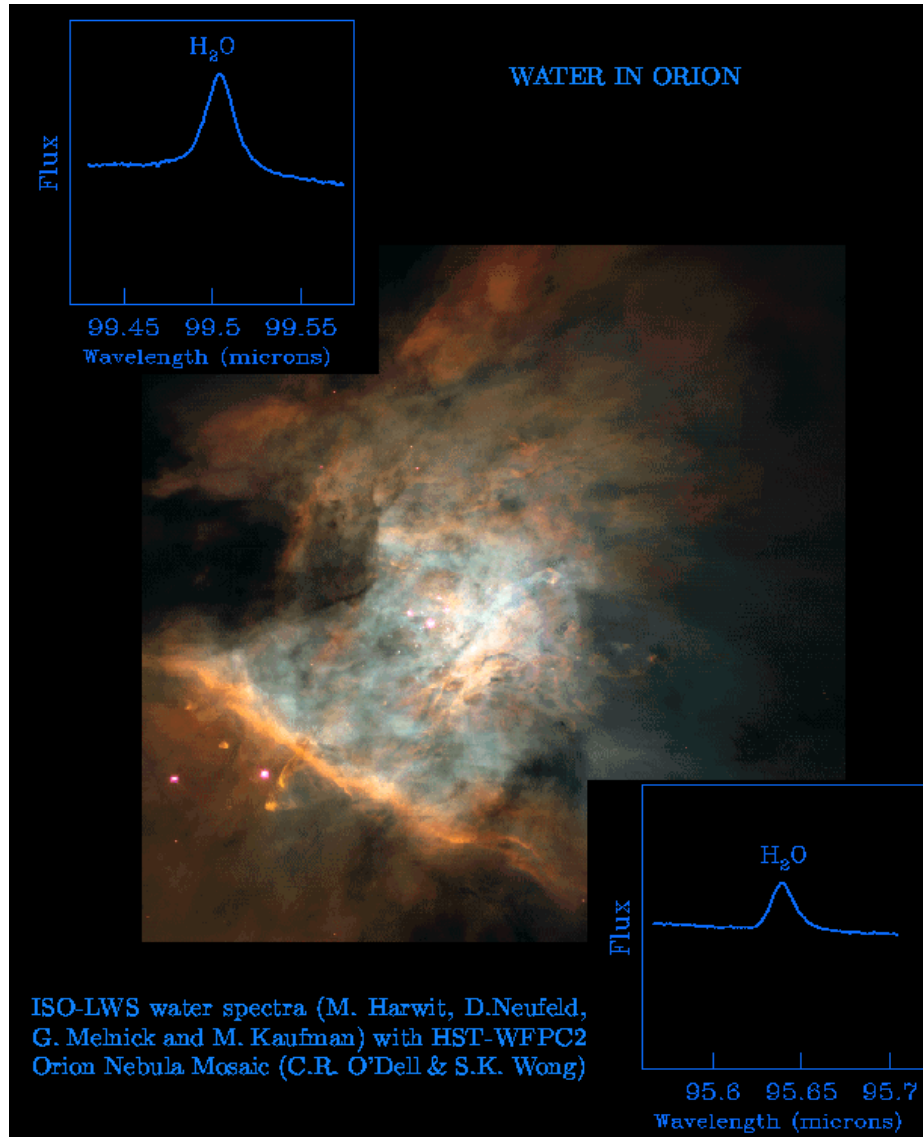
Notice the bands degrading toward the blue.

Observations of HF by ISO



Spectrum of the HF J=2-1 line toward the center of the Milky Way (in Sagittarius) . http://www.iso.vilspa.esa.es/galleries/ism/Hfl_lws.html

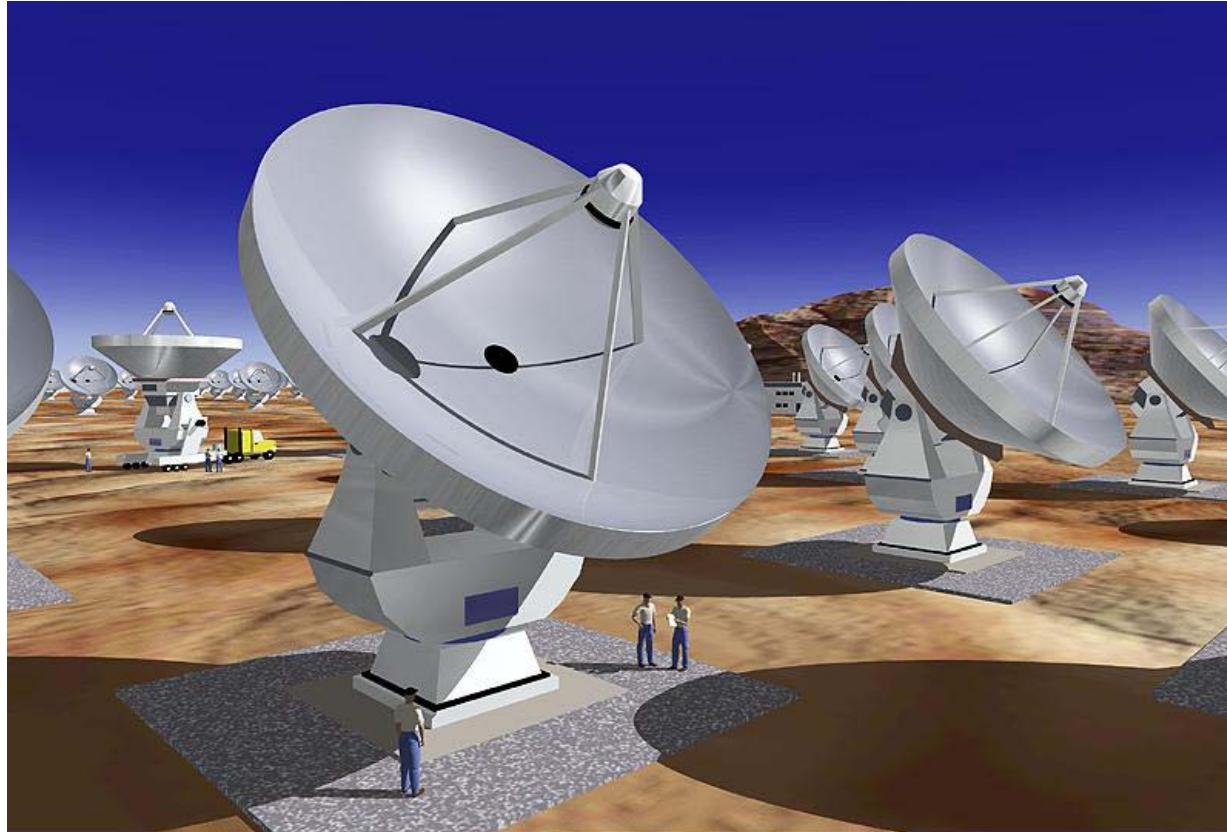
Observation of H₂O in Orion



ISO has found water vapour in many places, from the outer planets to distant galaxies, but the concentration reported in the Orion nebula is twenty times larger than that measured previously in other interstellar gas clouds.

http://www.iso.vilspa.esa.es/outr each/esa_pr/in9812.htm

ALMA, a molecular spectrograph at millimeter wavelengths



<http://www.eso.org/public/astronomy/projects/alma.html>

Semi-classic radiation

In the semi-classic model, the product between the wave function ψ and its complex conjugate ψ^* is interpreted as charge density in (x,y,z) , and the components of the (dipole) electric moment can be defined as:

$$P_x = \int \psi e x \psi^* dx \quad , \quad P_y = \int \psi e y \psi^* dx \quad , \quad P_z = \int \psi e z \psi^* dx$$

For hydrogen-like atoms, not only these moments are stationary, they are also zero for symmetry reasons: the electron on Bohr's orbits do **not** radiate. By analogy, given two levels n (upper) e m (lower), we can define the moment of the transition as :

$$\begin{aligned} P_x^{nm} &= \int \psi_n e x (\psi_m)^* dx = e^{-i2\pi(E_n - E_m)t/h} \int A_n e x (A_m)^* dx = \\ &= e^{-i2\pi\nu t} e R_{nm} \end{aligned}$$

and similar for y and z , where ν is the frequency of the emitted spectral line.

The Einstein A_{nm} coefficient

Derive twice, square with the rule:

$$P_{nm}^2 = P_{nm} (P_{nm})^*$$

and recall the correspondence *principle* (when $n \gg$ the energy emitted from $n-1$ to n is exactly the same between n and $n+1$) which gives rise to a factor of 2:

$$W_{nm} = \frac{64\pi^4 e^2}{3hc^3} R_{nm} R_{mn} h\nu^4 = h\nu \frac{64\pi^4 e^2}{3hc^3} R_{nm} R_{mn} \nu^3 = h\nu A_{nm}$$

erg/s

A_{nm} (proportional to ν^3) is called *Einstein coefficient* for that transition. It has dimensions (time)⁻¹.

The inverse of A_{nm} , τ_{nm} , has then dimension **time**, and it is called lifetime of that level n with respect to the transition to m .

Semi-classic evaluation of the lifetime

An order of magnitude evaluation of τ can be obtained by Bohr's circular orbit:

$$\frac{v^2}{a_n} = \frac{Ze^2}{ma_n^2} \quad , \quad r_n = e a_n = \frac{(2\pi)^4 Z^3 e^7 m}{h^4 n^4}$$

$$\tau_{n,n-1} \approx \frac{E_n - E_{n-1}}{W_n - W_{n-1}} = \frac{3c^3 h^6}{2^2 (2\pi)^6 Z^4 e^{10} m} n^6 \frac{2n-1}{(n-1)^2} \approx 4 \times 10^{-11} n^6 \frac{2n-1}{(n-1)^2} \quad (s)$$

For $n = 2$, $\tau_{2,1} \approx 10^{-8} s$.

The lifetime *augments very rapidly with n* . Consider the radio domain transition $n = 110$ to $n = 109$ of H I ; the lifetime is of the order of seconds, and only the very low densities of the gas ($\approx 10^4$ electrons per cm^3) permit a radiative transition, and not a collisional de-excitation.

Natural width of the lines

A consequence of the finite lifetime is the natural width of the spectral lines. According to Heisenberg principle indeed:

$$\Delta E_{nm} \cdot \tau_{nm} \geq h / 2\pi \quad , \quad \Delta E_{nm} \geq h \cdot A_{nm} / 2\pi$$

which is the *minimum* energy spread of that transition. Therefore:

$$\Delta \nu_{nm} \geq A_{nm}$$

is the **natural width** of the line.

In the visible:

$$\frac{\Delta \lambda}{\lambda} \approx 10^{-6} \div 10^{-7} \quad , \quad \Delta \lambda \approx 0.001 \div 0.0001 \text{ \AA}$$

De-excitation path

The previous considerations allow to answer the following question: given an H I atom excited to level 3, would it de-excite going from 3 to 1 (thus emitting 1 Ly β) or from 3 to 2 and then from 2 to 1 (1 H α + 1 Ly α)? By writing:

$$A_{n,m-1} = A_0 \nu_{n,m-1}^3, \quad A_{nm} = A_0 \nu_{nm}^3$$

we conclude that:

$$A_{n,m-1} / A_{nm} = (\nu_{n,m-1} / \nu_{nm})^3$$

The direct route, with the emission of a single photon of the highest possible energy is *usually* favoured.

Molecular Transitions

The same line of reasoning can be applied to the molecules; one could still write:

$$R_{if}(e\mathbf{r}) = \int \Psi' \left(\sum_k e\mathbf{r}_k \right) \Psi'' d\mathbf{r}$$

with the great added complication of a wave-function product of **three components**, one for electrical, one for vibrational, and one for rotational, transitions. Several lines of approach are possible (e.g. the so-called Franck-Condon principle), however the analysis is extremely complex, and outside the scope of this text.

Detailed Balance Condition

We restrict our considerations to a medium in *thermodynamic equilibrium, at least locally* (LTE): in each volume element of such medium, the temperature has a precise value T , the *population* of states depends only on the temperature, while the density of the medium only affects the *rates of the transitions* between the states. The radiation density u_ν is:

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

where $B_\nu(T)$ is the Planck function.

According to Kirchoff first law, at each place and frequency, the ratio between volume emissivity j and linear absorption coefficient k , namely the *source function*, is a function of temperature only:

$$S_\nu = j_\nu / k_\nu$$

$S_\nu(T)$ can often be identified with Planck's radiation function $B_\nu(T)$. However, there are astrophysical situations where this identification is not legitimate, and therefore we'll continue to keep the formal distinction between S and B .

Balance between Absorption and Emission

In stationary conditions, every transition must be balanced by the inverse, e.g. the **emission** of a photon of energy $h\nu$ by a jump from upper level n to lower level m , is balanced by the **absorption** of a photon of the same energy in a transition from m to n . Consider then the *detailed balance* between those two states, n and m , separated by energy $h\nu$.

- Downward transitions (*emissions*) can take place either by spontaneous or stimulated emission. *Spontaneous emissions* occur at a rate $N_n A_{nm}$ even in the absence of the radiation field. A radiation density u_ν produces *stimulated emission* at a rate $N_n u_\nu B_{nm}$, where N_n is the number of atoms per cm^3 in the n -th level, and B_{nm} is an appropriate Einstein coefficient still to be determined. Notice that the photons produced by stimulated emissions are **coherent with the incident electromagnetic field**.

- Upward transitions (*absorptions*) cannot occur spontaneously, they must be *stimulated* by the incident radiation field, and occur at a rate $N_m u_\nu B_{mn}$.

Einstein's Coefficients A_{nm} , B_{nm} and B_{mn}

The coefficients A_{nm} , B_{mn} are connected by the *detailed balance condition*:

$$N_n (A_{nm} + u_\nu B_{nm}) = N_m B_{mn} u_\nu$$

Stimulated emissions can be treated as *negative absorptions*, and the previous equation becomes:

$$N_n A_{nm} = u_\nu N_n \left(\frac{N_m}{N_n} B_{mn} - B_{nm} \right) \quad , \quad A_{nm} = u_\nu \left(\frac{N_m}{N_n} B_{mn} - B_{nm} \right)$$

In thermodynamic equilibrium, this relative population is given by the Boltzmann law:

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} e^{-\Delta E_{mn}/kT} = \frac{g_n}{g_m} e^{-h\nu/kT}$$

In most conditions of stellar and planetary atmospheres, *stimulated emission is negligible*, so that: $N_n A_{nm} \approx N_m B_{mn} u_\nu$, but this is not necessarily so, nor the distribution is necessarily Boltzmann (see Chapter 1, *masers and lasers*).

Relationships between A_{nm} , B_{nm} and B_{mn}

Therefore, in general:

$$\begin{aligned} A_{nm} &= \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \left(\frac{N_m}{N_n} B_{mn} - B_{nm} \right) = \\ &= \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} g_n (g_m e^{h\nu/kT} B_{mn} - g_n B_{nm}) \end{aligned}$$

which is satisfied if:

$$g_n B_{nm} = g_m B_{mn} \quad , \quad A_{nm} = \frac{8\pi h\nu^3}{c^3} B_{nm} = \frac{8\pi h\nu^3}{c^3} \frac{g_m}{g_n} B_{mn}$$

or else:

$$g_n B_{nm} = g_m B_{mn} = \frac{8\pi^3}{3h^2} S_{nm} \quad , \quad g_n A_{nm} = g_n \frac{8\pi h\nu^3}{c^3} B_{nm} = \frac{64\pi^4}{3h\lambda^3} S_{nm}$$

where we introduced the new quantity S_{nm} .

Oscillator Strength f

Instead of S , the quantities f and gf (named respectively *oscillator strength* and *weighted oscillator strength*) are usually found in the astronomical literature:

$$gf = g_m f_{mn} = -g_n f_{nm} = \frac{m_e h \nu}{\pi e^2} g_m B_{mn} = \frac{8\pi^2 m_e \nu}{3he^2} S_{mn}$$

where m_e and e are respectively mass and electric charge of the electron.

The a-dimensional numbers called *oscillator strengths*, and denoted with the letter f , are often derived from the observed intensities of stellar spectral lines. The f -values are small numbers, and have the useful properties that their sum for emission (or absorption) from a given energy level *is equal to the number of effective electrons*. For instance, for the first 5 lines of the Lyman series, the f -values are: 0.42, 0.079, 0.029, 0.014, 0.0078, and the total sum must be = 1.

Indeed, for the strongest resonance lines, the approximation $f = 1$ is often a good one. The weighted oscillator strengths are symmetric in absorption and emission. They are connected to the Einstein coefficients by:

$$A_{nm} = 0.67 \times 10^8 \cdot \frac{gf}{g_n \lambda^2} \quad (\lambda \text{ in } \mu\text{m}, A \text{ in } \text{s}^{-1})$$

Permitted and forbidden transitions

All previous semi-classical reasoning must be taken with **strong caution**, especially in astrophysical conditions where often the temperatures and densities are very different from those achievable in the laboratory.

In addition to *electric dipole* transitions, we must include higher order moments: the successive terms are called *magnetic dipole* and *electric quadrupole* transitions. If the first term is different from zero, then the transition is called *permitted*; if the first term is zero, the second or the third can still produce radiation, with very low probability but still with non negligible intensity. Those are the so-called *forbidden transitions*.

As an order of magnitude, in the visible region the oscillator strengths for the magnetic dipole transitions are 10^{-5} the f -values of electric dipole transitions, and 10^{-8} for the electric quadrupole transitions.

More precisely, if the wavelength of a transition is expressed as wave-number i in rydberg ($2 \text{ ryd} = 1 \text{ atomic unit} = 4.3598 \times 10^{-11} \text{ erg}$, $1 \text{ ryd} = 2.1799 \times 10^{-11} \text{ erg}$), then $A(\text{electric dipole}) \approx 2.67 \times 10^9 i^3$, $A(\text{magnetic dipole}) \approx 3.6 \times 10^4 i^3$, $A(\text{electric quadrupole}) \approx 2.7 \times 10^3 i^5$.

Exercise: derive Planck law from detailed balance conditions – 1

We use a two-level atom (0=lower, 1=upper). In thermodynamic equilibrium the populations of the two levels N_0 , N_1 are described by Boltzmann law, and the detailed balance condition applies. The number of spontaneous emissions is $N_1 A_{10}$ (per second per unit solid angle per unit volume), the rate of stimulated emission is $N_1 A_{10} I$ (where I is the *intensity of radiation* at that particular frequency). The absorptions from 0 to 1 are $N_0 B_{01} I$.

In addition to radiative transitions, we might have collision induced transitions, but in detailed balance, there are as many up as there are down, and they cancel out in the equilibrium equation.

So we must have:

$$N_1 A_{10} + N_1 B_{10} I = N_0 B_{01} I \quad , \quad I = \frac{A_{10}}{B_{01} (N_1 / N_0) - B_{01}}$$

which is just the ratio of emission to absorption (same structure of the source function).

Exercise: derive Planck law from detailed balance conditions – 2

Substitute in the previous expression the populations as given by Boltzmann, and expand the exponential to *keep only the first term ($h\nu \ll kT$, namely to the conditions of Rayleigh's law)*:

$$I \approx \frac{A_{10}}{\frac{g_0}{g_1} B_{01} - B_{10} + \frac{g_0}{g_1} B_{01} h\nu / kT} = \frac{2kT\nu}{c^2}$$

For this result to be true, it must be:

$$B_{10} = B_{01} \frac{g_0}{g_1} \quad , \quad A_{10} = B_{10} \frac{2h\nu^3}{c^2}$$

Putting these back in the upper expression, we derive that $I = \mathbf{B}(T)$.

Notice that this result has been obtained using only atomic constants, so it must be true for any physical condition satisfying the detailed balance.

Few References - 1

For an introduction on Atomic Spectroscopy see:

<http://physics.nist.gov/Pubs/AtSpec/AtSpec.PDF>

(Atomic Spectroscopy, by W.C. Martin and W.L. Wiese).

A non-astronomical but didactically instructive site on Visual Quantum Mechanics is: <http://phys.educ.ksu.edu/vqm/index.html>

Regarding the *forbidden lines*, I. S. Bowen in 1927 (*The Origin of the Chief Nebular Lines*, Publ. Astronom. Soc. Pacific, Vol. **39**, No. 231, p. 295) was able to identify the so called 'nebulium lines', so prominent in planetary and diffuse nebulae, as forbidden transitions of O II, O III and N II. The forbidden lines in the solar corona were identified by B. Edlén in 1942 (*Zeits. f. Astrophys.* **22**, p. 30). See also R.H. Garstang, 1995, *Radiative Hyperfine Transitions*, *The Astrophys. J.* **447**, 962

Few references - 2

Regarding astrophysical masers and lasers:

Astrophysical lasers and nonlinear optical effects in space

Authors:Johansson, S; Letokhov, V.; New Astronomy Reviews, Volume 51, Issue 5-6, p. 443-523