Ref.

INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

H4.SMR/204 - 1

WINTER COLLEGE ON

ATOMIC AND MOLECULAR PHYSICS

(9 March - 3 April 1987)

ATOMIC SPECTRA

Prof. A. Trombetti

Dipartimento di Chimica Fisica ed Inorganica
Università degli Studi di Bologna
Bologna

Lecture 1

Atomic Spectra

Short historical introduction.

1666 I.Newton: "The sun's lights is a heterogeneous mixture of rays"

1752 Thomas Melvill published (Edimburgh) the first description of an emission spectrum: the spectrum of sodium flame.

1800 W.Herschel, the great British astronomer, discovered the infrared spectrum, and J.W.Ritter of Jena revealed the existence of the ultraviolet radiation in 1801

1802 Thomas Young, using Newton's data, computed the wavelengths of the seven colors recognized by Newton and showed that the visible spectrum extends from 675 nm to 424 nm.

1802 W.H.Wollaston observed the darklines which interrupt the continuous spectrum of the sun: the Fraunhofer lines

1814 J.Fraunhofer measured the wavelengths of 700 solar lines and observed stellar and planetary spectra

1823 J.Fraunhofer made the first accurate determination of sodium D-lines (yellow lines) using a diffraction grating

1859 Kirchhoff made the spectral analysis of the solar atmosphere on the basis of the principle that the spectra are characteristic of the atoms and molecules that produce them. In 1861 discovered, from their spectra, the new alkali metals caesium and rubidium.

The spectrum of atomic hydrogen.

In the following figure is shown the visible and u.v. emission spectrum of H.

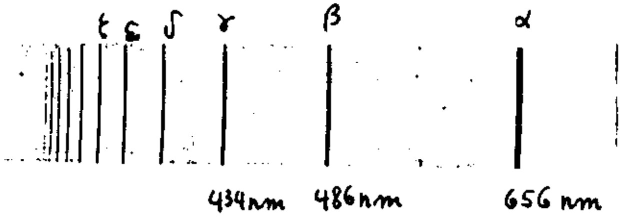


Table 1 reports the measured wavelengths λ, the corresponding wavenumbers $\bar{\nu} = \frac{1}{\lambda}$ and the wavenumbers calculated according to the formula:

$$[1] \qquad \bar{\nu}_i = \frac{1}{\lambda_i} = R\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right) \qquad n_i = 3;4;5;\ldots$$

Table 1

The Balmer series of hydrogen

Symbol	n_i	λ_{air}(nm)	$\bar{\nu}_{vac}$(cm^{-1})	$\bar{\nu}_{calc.}$(cm^{-1})
H_α	3	656.28	15233.2	15233.1
H_β	4	486.13	20564.8	20564.7
H_γ	5	434.05	23032.5	23032.5
H_δ	6	410.17	24373.1	24373.0
H_ε	7	397.01	25181.3	25181.3
H_ζ	8	388.91	25705.8	25705.9
H_η	9	383.54	26065.5	26065.6
H_ϑ	10	379.79	26322.8	26322.8

Symbol	n_i	λ_{air}(nm)	$\bar{\nu}_{vac}$(cm^{-1})	$\bar{\nu}_{calc.}$(cm^{-1})
H_ι	11	377.06	26513.2	26513.2
H_k	12	375.02	26658.0	26658.0
H_λ	13	373.44	26770.6	26770.6
H_μ	14	372.20	26860.0	26860.8
H_ν	15	371.20	26932.1	26932.2
H_ξ	16	370.39	26991.2	26991.2
H_o	17	369.72	27040.2	27040.1
H_π	18	369.16	27081.2	27081.1
H_ρ	19	368.68	27115.8	27115.8
H_σ	20	368.28	27145.4	27145.4

The formula given above was empirically discovered by Balmer (1885) and its real meaning was recognized by Bohr (1911).

According to the Bohr theory of atomic hydrogen, a spectral line is emitted following the transition between two stationary states of energy E_1 and E_2.

The frequency of the line is given by the equation : [2] $h\nu = E_1 - E_2$.

The solution of the Schödinger equation for the internal motion of the hydrogen atom, gives the following expression for the energy of bound states of the electron:

$$[3] \qquad E_i = -\frac{2\pi^2\mu e^4}{h^2} \cdot \frac{1}{n_i^2} \qquad n_i = 1;2;3;\ldots\ldots$$

μ is the reduced mass of the system electron + proton;

e is the elementary electrical charge;

h is the Planck constant.

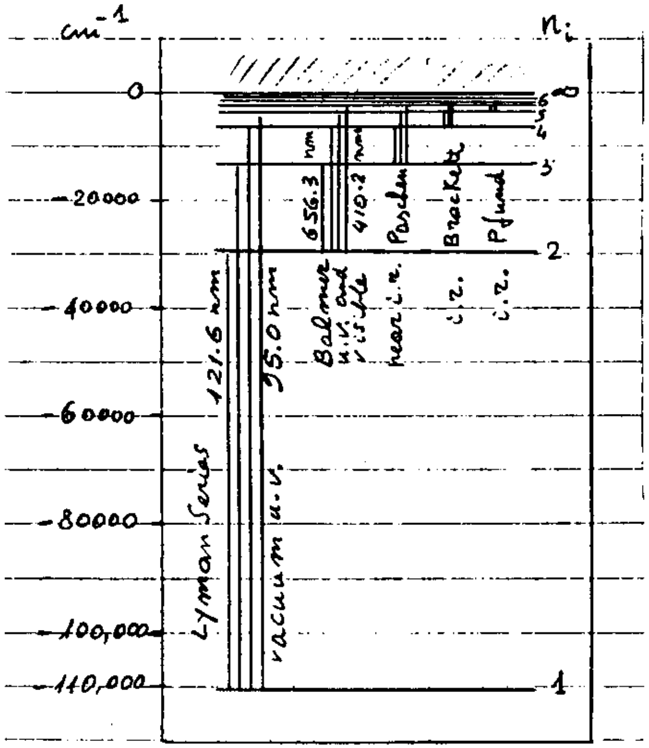
By substitution of [3] in [2], we obtain:

$$[4] \qquad \bar{\nu} = \frac{2\pi^2\mu e^4}{c h^3}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

This is exactly the Balmer formula [1] if the constant R is:

$$R = \frac{2\pi^2\mu e^4}{c h^3} = 109677.6 \text{ cm}^{-1}$$

The following figure presents the energy levels and transitions of the H atom.

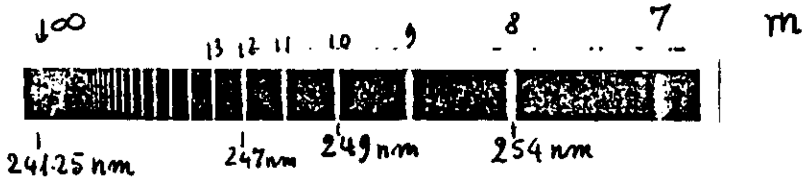


Series with high values of n_2 ($n_2 = 159$; 166) were discovered by radioastronomy in the interstellar medium.

Theoretical interpretation of the alkali atoms series.

The electronic structure of all alkali atoms (Li, Na, K, Rb, Cs) is characterized by inner closed shell(s), where all electrons are paired, plus a single outer electron.

The appearence of the absorption spectra of alkali atoms resembles to that of H, the main difference being their displacement toward much lower frequencies.



The spectrum of sodium vapour (Na) in absorption.

The frequencies of the lines are given by eq.[6]

$$\bar{\nu} = T_{PS} - \frac{R}{(m+p)^2} \qquad [6]$$

T_{PB} = fixed term; R is the Rydberg constant (see eq.[5]); m = integer running number from 2 to ∞; p = Rydberg correction ($p < 1$).

Like in H, there are other series observed in emission:

Principal : $\bar{\nu} = T_{PS} - \frac{R}{(m+p)^2} = 1S - mP$ ($m = 2; 3; \ldots$)

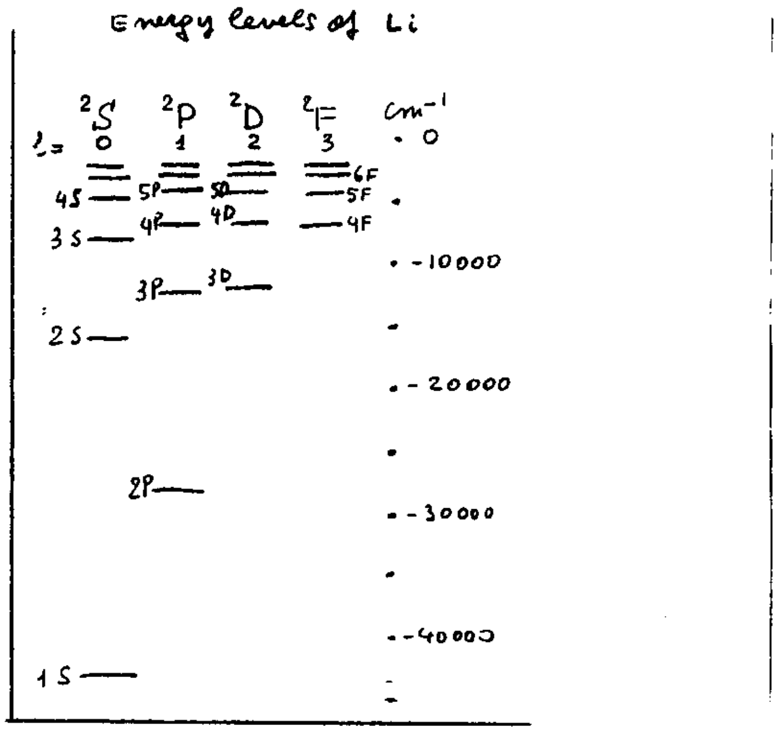
Sharp : $\bar{\nu} = T_{SS} - \frac{R}{(m+s)^2} = 2P - mS$ ($m = 2; 3; \ldots$)

Diffuse : $\bar{\nu} = T_{SS} - \frac{R}{(m+d)^2} = 2P - mD$ ($m = 3; 4; \ldots$)

Bergmann : $\bar{\nu} = T_{BS} - \frac{R}{(m+f)^2} = 3D - mF$ ($m = 4; 5; \ldots$)

The second part of the series equations can be so written, because it was found that: $T_{PS} = \frac{R}{(1+s)^2}$; $T_{SS} = \frac{R}{(2+p)^2}$; $T_{BS} = \frac{R}{(3+d)^2}$.

From these results, it can be concluded that there are four sets of energy levels, S, P, D, F, given in the next figure.



The difference between this energy level diagram and that of H is that, levels, with the same running number m and belonging to different sets, have different energy.

This behaviour is due to the different orbital angular momentum of the outer electron in states S; P; D; F.

As we will see soon, this effect is present in H too, but it is very small in comparison with alkali atoms.

Finer details of spectra of hydrogen and alkali.

Hydrogen.

Fine structure. The Balmer lines of H studied under high resolutions appear to consist of several components.

The splitting of lines correspond to splitting of levels and is due to relativistic and spin-orbital momentum coupling effects.

The splittings involve $n > 1$ and $\ell > 0$ states, and according to Dirac electron theory is given by:

$$\Delta \bar{\nu} = \frac{R \alpha^2 Z^4}{n^3 \ell(\ell+1)}$$

Z = nuclear charge

R = Rydberg constant

n = principal quantum number

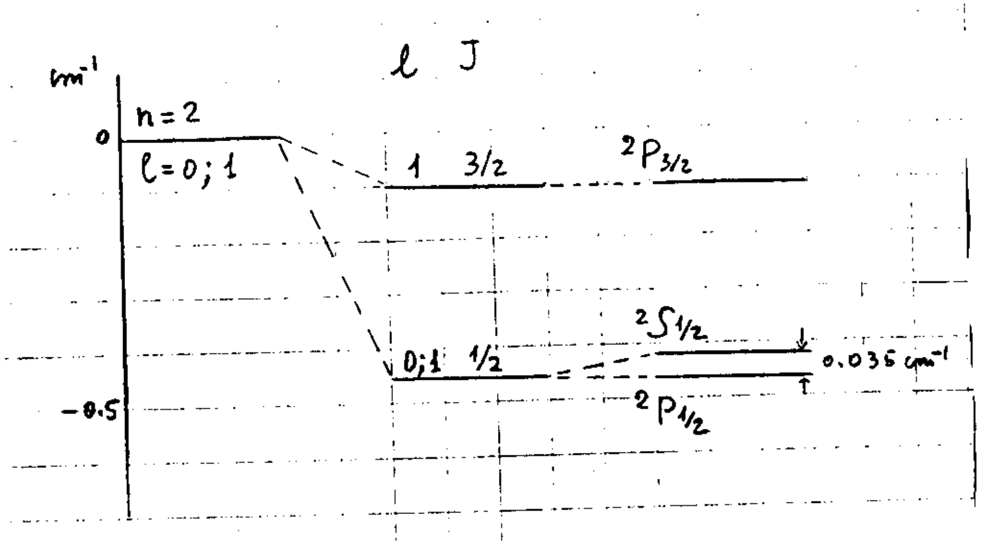
$\ell(\ell+1)$ = square of electron orbital angular momentum

α = fine structure constant $\simeq$ 1/137

For $n=2$, $\ell=1$ in H, $\Delta\bar{\nu} = 0.365\ \mathrm{cm}^{-1}$

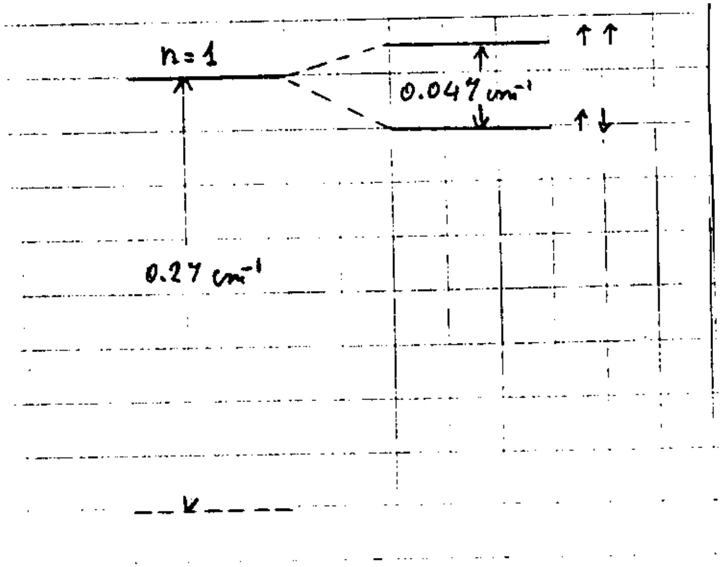
A further splitting of $^2S_{1/2}$ and $^2P_{1/2}$ states in H was discovered by Lamb and Retherford (1947). Dirac theory was unable to explain this effect, which was accounted for by quantum electrodynamics.

In the next figure is illustrated the fine structure of n=2 levels of H.



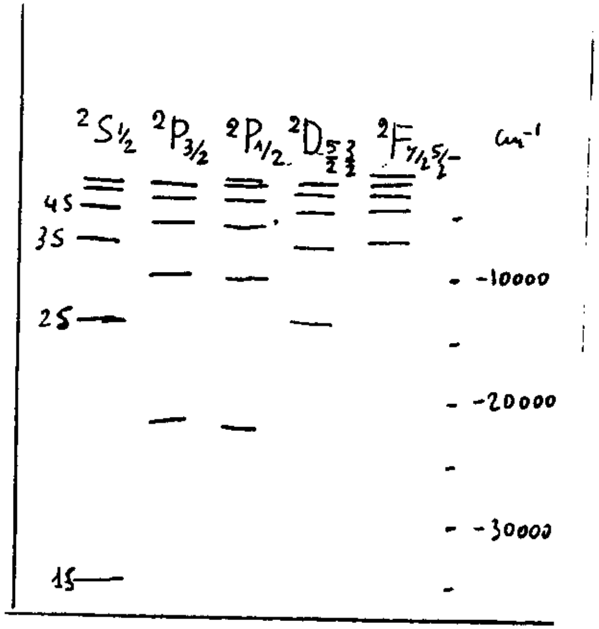
Hyperfine structure.

Hyperfine structure in the ground state of H is due to a doubling of this level corresponding to the 2 possible orientations of electron and proton spins (see the nex figure)



The splitting amounts to 1420 MHz (0.0474 cm^{-1}), corresponding to a wavelength of 21 cm: this is the rather famous 21 cm radiation, discovered in 1951 as emission of the interstellar medium. Measurements at this frequency allowed to bild a map of H distribution in interstellar space.

The D-line of sodium (Na) at 589.3 nm is a doublet with 0.6 nm splitting. A splitting in a spectral line correspond to a splitting of electronic energy levels. In the following figure are presented the energy levels of potassium and it is clear that all, except the S levels, are double.



Generally speaking, the multiplet splitting is the result of coupling of the electron orbital momentum L and spin angular momentum S.

The vectorial sum $\mathcal{L} + \mathcal{S} = \mathcal{J}$, can take the values:

$J = (L+S);\ (L+S-1)\ \ldots\ldots\ |L-S|$

when $L > S$ $\quad 2S+1$ possible J-values

$L < S$ $\quad 2L+1$ possible J-values

The possible J-values for doublets are given in the following table.

L	Term	J	
0	S	1/2	
1	P	1/2	3/2
2	D	3/2	5/2
3	F	5/2	7/2

For one-emission electron the doublet splitting is, to a very crude approximation, proportional to Z^4, (Z = atomic number): for ^2P-splittings, Li ($Z = 3$) 0.34 cm^{-1}, Cs ($Z = 55$) 5540 cm^{-1}.

Many-electron atoms: spectra and structure.

We will discuss very briefly the present subject, presenting as example the spectrum of oxygen.

^3P, ^1D and ^1S terms correspond to the lowest energy electron configuration $1S^2 2S^2 2p^4$, ^3P being the lowest in energy. In order to discuss the terms arising from excited electron configuration, we start from the lowest energy electron configuration of the ion O^+. Using the rules of vectorial addition of angular momenta, we obtain electronic states for O, by adding one electron to the ion.

The terms of the ion are ^4S; ^2D; ^2P.

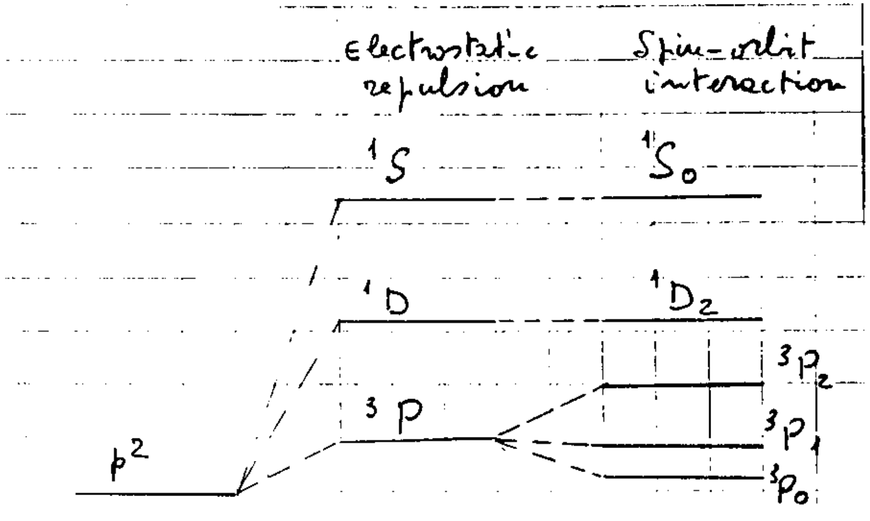
electron

$$^4S + \left\{\begin{matrix} s \\ p \end{matrix}\right\} = \begin{matrix} ^3S \;;\; ^5S \\ ^3P \;;\; ^5P \end{matrix}$$

$$^2D + \left\{\begin{matrix} s \\ p \end{matrix}\right\} = \begin{matrix} ^1D \;;\; ^3D \\ ^1P \;;\; ^3P \;;\; ^1D \;;\; ^3D \;;\; ^1F \;;\; ^3F \end{matrix}$$

$$^2P + \left\{\begin{matrix} s \\ p \end{matrix}\right\} = \begin{matrix} ^1P \;;\; ^3P \\ ^1S \;;\; ^3S \;;\; ^1D \;;\; ^3D \end{matrix}$$

Series going to different limits are expected for each different configuration of the ion O^+. This results in a very complicated spectrum, if, in addition, the multiplet splitting is considered. The following figure are schematically represented the energy levels for an atom with electron configuration p^2, that is 2 electrons in p-orbitals.



Intensity of spectral lines.

Electronic energy levels of an atom cannot be connected by an electronic transition, unless certain conditions concerning the quantum numbers, are satisfied. These conditions are known as selection rules.

For electric dipole radiation transition, usually the stronger, the selection rules are:

$\Delta J = 0 \;;\; \pm 1$ ($\Delta J = 0$ only if $J \neq 0$)

$\Delta S = 0$

$\Delta L = 0 \;;\; \pm 1$

$\Delta \ell = \pm 1$ for the electron making the quantum jump.

J = total angular momentum
S = spin angular momentum
L = orbital angular momentum
} of the atom

l = orbital angular momentum of the electron