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 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392 - I

SMR/100 - 7

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(24 January - 25 March 1983)

Atomic Spectra

J. BAUCHE

Laboratoire Aimé Cotton
C.N.R.S. II
Campus d'Orsay, Bâtiment 505
91405 Orsay Cedex
France

These are preliminary lecture notes, intended only for distribution to participants
Missing or extra copies are available from Room 230.

Trieste
1983 Winter College

Lectures on Atom Spectra

I. HYDROGEN ATOM

Hydrogen is the starting point, not only of this series of lectures, but also of the sun (and of the solar system!) and of modern Physics.

1. Beginning of the history of hydrogen.

In the second part of the nineteenth century, physicists were more and more numerous to believe in Atomic Theory. Among the many convincing phenomenons supporting it, there was the fact that identical spectral lines could be emitted, under electrical excitation, by various chemical substances containing the same element. The wavelengths of those lines were characteristic of the atoms of this element, but what could the physicists learn from them?

It was a great surprise when, in 1885, Johann BALMER, a Swiss teacher, showed that the wavelengths of a series of hydrogen lines in the visible range obey a remarkably simple formula: $\lambda_n = \lambda_0 \frac{n^2}{n^2-4}$ with integer $n > 2$. Then physicists worked hard to find similar formulae for other elements, but they did not succeed. Only other series of hydrogen lines, in the ultraviolet and infrared ranges, were found to obey $\lambda_{mn} = \lambda_0 \frac{n^2}{n^2-m^2}$, with $n > m$ and $m = 1$ (Lyman), 3 (Paschen), 4, etc.

After the hydrogen atom was proven to be the association of one nucleus (the proton) of charge $+e$ and one electron of charge $-e$, the mysterious formulae above could still not be understood, until Niels BOHR came.

2. The Bohr model (1913)

It is of interest to recall here Bohr's method, because it yields correct results for the energy, it is simpler to use than Quantum Mechanics and it is easy to memorize. In classical mechanics, the proton-electron pair resembles the sun-earth pair, with the electrostatic force replacing the gravitational force. A continuous variety of orbits are possible, associated with almost any value of the total energy. The first concern of Bohr was to introduce some kind of quantization (= discretization), in accordance with his two famous postulates, suggested by the observation of spectral lines (discrete wavelengths).

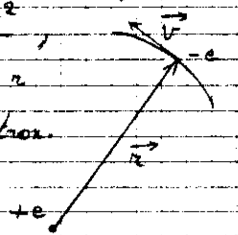
- the energy of an atomic system can only have certain discrete values, called level energies
- This energy can change under emission or absorption of one quantum of electromagnetic energy (one photon)

$$E_2 - E_1 = \overbrace{h\nu}^{\text{photon energy}}$$

ν ← frequency

h ← Planck's constant

For hydrogen, Bohr assumes that the proton is fixed and that the electronic orbit is a circle. Then, from Newton's Second Law $\frac{-e^2}{4\pi\varepsilon_0 r^2} = -m\frac{v^2}{r}$, an equation which links the radius r of the orbit with the velocity v of the electron. Any value of r would be allowed, but Bohr quantizes the system by imposing that the angular momentum J of the electron around



the proton is equal to $n\frac{h}{2\pi}$, n being a positive integer: $J = mvr = n\hbar$. Then the corresponding total energy of the system is

$$E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} = -\frac{Ryd}{n^2} \qquad (1)$$

whence the formulae of Balmer et al. are exactly interpreted. Later, Arnold SOMMERFELD built a refined classical model which allowed for non-circular orbits, but this becomes too complicated for us.

3. Schrödinger's equation (1926)

It is well known that the three-body case is a formidable problem in Astronomy, and this explains that Bohr's breakthrough remained limited to the interpretation of hydrogen. We shall see in Lecture III that an approximate solution for other atoms can be obtained with Quantum Mechanics which is, paradoxically, more complicated than classical mechanics.

For hydrogen, Schrödinger's equation reads

$$H\psi = E\psi \qquad (2)$$

with $H = -\frac{\hbar^2}{2m}\Delta\psi - \frac{e^2}{4\pi\varepsilon_0 r}$, ψ being a function of $\vec{r}$, and the eigenvalue E a constant to be determined. We first suppose that, like Bohr, we are only interested in the discrete values of E.

4. Atomic units.

It must be stressed that H in eq. (2) only contains two dimensioned constants, $\frac{\hbar^2}{m}$ and $\frac{e^2}{4\pi\varepsilon_0}$. Any discrete solution for E is necessarily a function of these constants. More precisely, $E_i = k_i\left(\frac{\hbar^2}{m}\right)^{\alpha}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^{\beta}$ where k_i is a number. For dimensional reasons, $\alpha = -1$ and $\beta = 2$: E is a multiple of $\frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2}$, which is chosen as being the atomic unit (a.u.) for

energy and is called the Hartree (1 Hartree = 2 Rydberg; see eq. (1)).

Another a.u. is defined in the same way, that for length, $a_0 = \frac{\hbar^2}{m}\frac{4\pi\varepsilon_0}{e^2}$, which is precisely the radius of the electronic orbit for $n = 1$ in the Bohr model.

As for the other a.u. of interest (time, velocity, magnetic field, etc.), they are defined, to an arbitrary dimensionless constant, by the fact that they only contain powers of $m, \hbar, e, 4\pi\varepsilon_0$.

Numerical values: 1 Hartree = $43{,}5\ 10^{-19}$ Joule = 27,2 eV, or 219 474 cm^{-1} in the wavenumber scale; $a_0 = 0{,}529\ 10^{-10}$ m.

Problems. Determine atomic units for time and velocity, in formal and numerical values (with $m = 0.9\ 10^{-30}$ kg; $\hbar = 1.05\ 10^{-34}$, $e = 1.6\ 10^{-19}$ and $\frac{1}{4\pi\varepsilon_0} = 9\ 10^{9}$, all in the International System of Units). Compare the velocity a.u. with c, the velocity of light ($c = 3\ 10^{8}$ m/s).

Remark. For the sake of simplicity, we will omit the quantity $\frac{1}{4\pi\varepsilon_0}$ when we are interested only in mechanical results, because we know that it multiplies systematically e^2 for yielding a non-electrical quantity. It can be reintroduced afterwards in the final result.

5. Angular part of ψ.

Because the electric field of the nucleus possesses spherical symmetry, we write the Laplace operator in spherical coordinates:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{(\vec{L})^2}{\hbar^2 r^2},$$

with $r^2 = x^2 + y^2 + z^2$, where $(\vec{L})^2$ is the square of the angular momentum $m\vec{r} \times \frac{d\vec{r}}{dt}$ of the electron around the nucleus, and the only part depending on θ and φ. Looking for solutions ψ of the form $u(r)\,v(\theta,\varphi)$ and rewriting Schrödinger's equation in the form

$$-\frac{\hbar^2}{2m}\frac{\frac{d}{dr}\left(r^2\frac{du}{dr}\right)}{u} + \frac{1}{2m}\frac{(\vec{L})^2 v}{v} - e^2 r = Er^2$$

we see that it can be separated in

an angular equation $(\vec{L})^2 v(\theta,\varphi) = \alpha\, v(\theta,\varphi)$ (3)

and a radial equation $-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{du}{dr}\right)+\frac{\alpha}{2mr^2}u-\frac{e^2}{r}u=Eu$ (4)

where α is a constant to be determined.

Now, the angular equation (eq. 3) is well known in Quantum Mechanics, because it occurs in all the problems where a particle moves in a central field of force. Its solutions are the famous spherical-harmonic functions $Y_{\ell m}(\theta,\varphi)$, for the eigenvalues $\alpha = \ell(\ell+1)\hbar^2$, with integers $\ell \geq 0$ and $-\ell \leq m \leq \ell$. $Y_{\ell m}(\theta,\varphi)$ is also an eigenfunction of L_z, the z component of the angular momentum $\vec{L}$, with $L_z Y_{\ell m}(\theta,\varphi) = m\hbar\, Y_{\ell m}(\theta,\varphi)$.

Note on the spherical harmonics.

In fact $L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$, so that the φ part of $Y_{\ell m}$ is $\frac{e^{im\varphi}}{\sqrt{2\pi}}$, normalized by $\int_0^{2\pi}|Y_{\ell m}(\theta,\varphi)|^2 d\varphi = 1$.

The infinite set of spherical harmonics is a complete basis set for all functions of θ and φ, orthonormalized by

$$\int_{\theta=0}^{\theta=\pi}\int_{\varphi=0}^{\varphi=2\pi} Y^*_{\ell m}(\theta,\varphi).\, Y_{\ell' m'}(\theta,\varphi)\sin\theta\, d\theta\, d\varphi = \delta(\ell,\ell')\delta(m,m')$$

The simplest functions are

$$Y_{00}(\theta,\varphi)=\frac{1}{\sqrt{4\pi}},\quad Y_{10}(\theta,\varphi)=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_{1\pm1}(\theta,\varphi)=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$$

6. Radial part of ψ.

It is convenient to work in atomic units of length and energy. Defining a reduced variable $\rho = \frac{r}{a_0}$ and a reduced constant $\mathcal{E} = \frac{E}{\text{Hartree}}$, we rewrite eq. (4) in the reduced form

$$-\frac{1}{2\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{du}{d\rho}\right)+\frac{\ell(\ell+1)}{2\rho^2}u-\frac{u}{\rho}=\mathcal{E}u$$

Another simplification is obtained through writing $u(r) = \frac{R(\rho)}{\rho}$, whence the equation

$$\left[\frac{1}{2}\frac{d^2}{d\rho^2}-\frac{\ell(\ell-1)}{2\rho^2}+\frac{1}{\rho}\right]R(\rho) = -\mathcal{E}\,R(\rho) \qquad (5)$$

(Note that this radial equation contains ℓ as a parameter.)

The quantization of the energy $\mathcal{E}$, the eigenvalue of equation (5), is a consequence of the very general postulate of Quantum Mechanics that the wavefunction representing a stationary state be square integrable.

For very large values of r, eq. (5) reads approximately $\frac{1}{2}\frac{d^2R}{d\rho^2} = -\mathcal{E}R$, whose general solution is, for $\mathcal{E}<0$ (bound states),

$$R = A\exp(k\rho) + B\exp(-k\rho), \text{ with } k=\sqrt{-2\mathcal{E}}$$

Of course, for R to be square integrable, we must have $A=0$. Then, with $R(\rho) = e^{-k\rho}f(\rho)$, we change to the equation

$$-k\frac{df}{d\rho}+\frac{1}{2}\frac{d^2f}{d\rho^2}-\frac{\ell(\ell+1)}{2\rho^2}f+\frac{f}{\rho}=0 \qquad (6)$$

and we can try and expand $f(\rho)$ in the form of a series $\sum_n a_n\rho^n$. It can be shown that, for R to be square integrable, this series must be a polynomial, with n ranging from its minimum value n_{min} to its maximum n_{max}.

From the cancellation of the term in $\rho^{(n_{max}-1)}$ in eq. (6), we find $-k\, n_{max}+1=0$, whence $k=\frac{1}{n_{max}}$ or $\boxed{\mathcal{E} = -\frac{1}{2n^2}}$, with n integer.

From the cancellation of the term in $\rho^{(n_{min}-2)}$ in eq. (6), we find $\frac{1}{2}n_{min}(n_{max}-1)-\frac{\ell(\ell+1)}{2}=0$, whence $n_{min}=\ell+1$. This shows the behaviour of $f(\rho)$ at very small values of ρ.

The final result reads $R_{n\ell}(\rho)=N_{n\ell}\,\rho^{\ell+1}e^{-\frac{\rho}{n}}P_{n\ell}(\rho)$ where $N_{n\ell}$ is a normalization coefficient such that $\int_0^\infty[R_{n\ell}(\rho)]^2dr=1$ and $P_{n\ell}(\rho)$ a polynomial whose lowest-power term is a constant, called a Laguerre polynomial. (Note that $P_{n\ell}(\rho)$ is just a constant if $n=\ell+1$)

Examples (using the conventional letters s, p, d, f, g, h, i, k, etc. for $\ell = 0,1,2,3,4,5,6,7$, etc.) $R_{10}(\rho)=2\rho\, e^{-\rho}$; $R_{2p}(\rho)=\frac{\rho^2}{2\sqrt{6}}e^{-\frac{\rho}{2}}$; $R_{2s}(\rho)=\frac{\rho}{\sqrt{2}}e^{-\frac{\rho}{2}}\left(1-\frac{\rho}{2}\right)$. (the phases are conventional).

7. Conclusion: energies and states of the hydrogen atom.

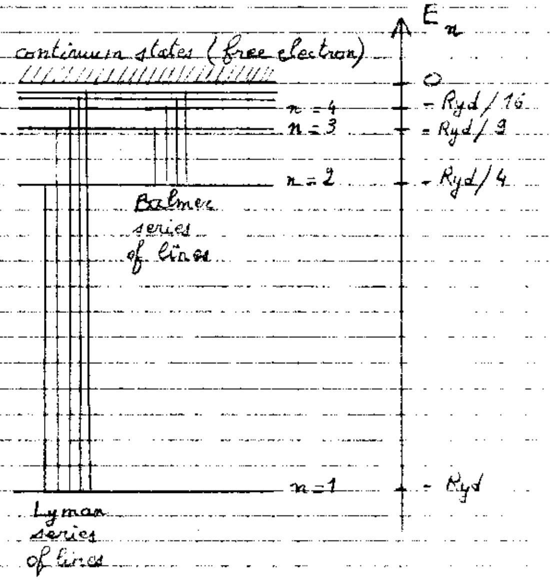
For all n-particle systems (atoms, molecules, even nuclei), it is convenient to call a quantized bound energy a <u>level</u> (or an energy level) and a quantized eigenfunction a <u>state</u>, so that the correspondances are

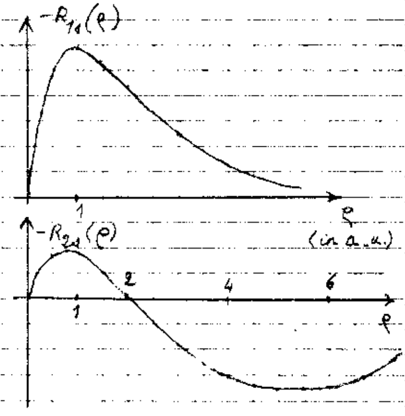
$$\boxed{\begin{array}{c}\text{energy} \leftrightarrow \text{level} \\ \text{wavefunction} \leftrightarrow \text{state}\end{array}}$$

and.

When g states correspond to the same energy, this level is said to be g times degenerate.

In atomic hydrogen, each bound level is characterized by an integer positive number n, called the principal quantum number. The bound states are characterized, in addition, by the orbital quantum number l (integer l, with $l<n$), the magnetic orbital quantum number m (integer m, with $-l \leq m \leq l$), and the magnetic spin quantum number m_s ($m_s = +\frac{1}{2}$ or $-\frac{1}{2}$) if the electronic spin is allowed for. The energy is $E_n = \frac{-1}{2n^2}$ u.a.





(see plots of $[R_{n\ell}(\rho)]^2$ on page 116 of the book "The Theory of Atomic Spectra" by E.U. Condon and G.H. Shortley)

8. Refinements.

Progress in the theory of the hydrogen atom was the main reason for the Nobel Prize being awarded to four physicists:

(Niels) Bohr in 1922
Schrödinger in 1933
Dirac also in 1933
Lamb in 1955

Bohr's method and Schrödinger's method are studied above.

P.A.M Dirac built a theory accounting for the relativity phenomenon and for the electronic spin. We shall see in Lecture II a semi-classical way for adding to the hamiltonian the magnetic interactions, which are absent from our eq. (2).

W.E. Lamb Jr measured, and interpreted by Quantum Electrodynamics, some very fine splittings in the spectrum. The n = 2 example is typical. In Schrödinger's theory, the 8 corresponding states are degenerate. In Dirac's theory, two different levels appear, the one with total angular momentum $j=\frac{1}{2}$ (actually, two $j=\frac{1}{2}$ levels which are degenerate) and the one with $j=\frac{3}{2}$. In Lamb's theory, the two $j=\frac{1}{2}$ levels are no more degenerate.