

# THE BOHR TREATMENT OF ATOMIC SPECTRA

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FILE: BOHR.TEX

MICHAEL C. MACKEY

Institut für Theoretische Physik  
Universität Bremen  
Bremen, Germany  
and  
Mathematical Institute  
University of Oxford  
Oxford, England

These notes summarize the treatment followed by N. Bohr<sup>1-4</sup> in his explanation of the emission and absorption spectra of various elements. This work was later summarized by Bohr in yet a fifth paper<sup>5</sup>.

The impetus for Bohr's work was the observation, by 1913 quite well established, that the spectra of atomic hydrogen can be very accurately described by the formula

$$\bar{\nu} = R_{\infty} \left\{ \frac{1}{n'^2} - \frac{1}{n^2} \right\} \quad n' < n \quad \text{with both being positive integers,} \quad (1)$$

wherein  $\bar{\nu}$  (in units of  $mt^{-1}$ ) is the wavenumber [related to the frequency  $\nu$  ( $sec^{-1}$ ) by  $\nu = c\bar{\nu}$ , where  $c$  is the speed of light], and  $R_{\infty}$  is the *Rydberg constant* appropriate for hydrogen. When  $n' = 1$ , equation (1) describes the *Lyman* series in the ultraviolet region (discovered in 1906); for  $n' = 2$  it describes the visible *Balmer* series first described in 1885; with  $n' = 3$  one recovers a good description of the infrared *Paschen* series of 1908.  $n' = 4$  corresponds to the 1922 *Brackett* series (also infrared); and  $n' = 5$  gives the far infrared *Pfund* series.

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<sup>1</sup>N. Bohr, "On the constitution of atoms and molecules", *Phil. Mag.* (1913), **26**, 1-25.

<sup>2</sup>N. Bohr, "On the constitution of atoms and molecules: II. Systems containing only a single nucleus", *Phil. Mag.* (1913), **26**, 476-502.

<sup>3</sup>N. Bohr, "On the constitution of atoms and molecules: III. Systems containing several nuclei", *Phil. Mag.* (1913), **26**, 857-875.

<sup>4</sup>N. Bohr, "On the effect of electric and magnetic fields on spectral lines", *Phil. Mag.* (1914), **27**, 506-524.

<sup>5</sup>N. Bohr, "On the quantum theory of radiation and the structure of the atom", *Phil. Mag.* (1915), **30**, 394-415.

In trying to understand the phenomenology described by equation (1), Bohr used a mixture of classical physics, and what we now call the “old” quantum mechanics. Let us first examine the classical portion of his treatment.

For an electron-proton system, where the proton is fixed (infinitely massive) and the electron has finite mass  $m_e$ , from Newton’s laws  $m_e a = F$ , where  $a$  is the acceleration and  $F$  is the force, for circular motion we obtain

$$m_e \frac{v^2}{r} = \frac{|A|}{r^2}, \quad (2)$$

where  $r$  is the radius of the orbit,  $v$  is the electron velocity, and the constant  $A$  is given by

$$A = -\frac{e^2}{4\pi\epsilon_0} = -\frac{e^2 c^2}{10^7}. \quad (3)$$

( $e$  is the electronic charge and  $c$  is the velocity of light.)

Since, in a circular orbit,  $v = r\omega$ , where  $\omega$  is the angular frequency, equation (2) can also be written in form

$$m_e r \omega^2 = \frac{|A|}{r^2}, \quad (4)$$

If  $E$  is the total energy of the electron, then it is made up of the sum of the kinetic and potential energy:

$$E = E_{kin} + E_{pot} \quad (5)$$

where the kinetic energy is defined in a usual fashion

$$E_{kin} = \frac{1}{2} m_e v^2. \quad (6)$$

From the customary definition of the potential energy,

$$E_{pot} = -\int_r^\infty \frac{|A|}{r'} dr' = -\frac{|A|}{r}. \quad (7)$$

This potential energy corresponds to the work required to remove the electron from position  $r$  to  $\infty$ , and the point at which the potential energy goes to zero must correspond to the ionization potential for the electron-proton pair. Thus, we can write the total energy of equation (4) as

$$E = \frac{1}{2} m_e v^2 + \frac{A}{2r} = \frac{1}{2} m_e v^2 - \frac{|A|}{2r} = \frac{A}{2r} = -\frac{|A|}{2r}, \quad (8)$$

where we have used (2) to arrive at the final result. Alternately, we can solve (4) for  $r$ :

$$r = \left( \frac{|A|}{m_e \omega^2} \right)^{\frac{1}{3}}, \quad (9)$$

to give

$$E = -\frac{|A|^{\frac{2}{3}}}{2} (m_e \omega^2)^{\frac{1}{3}}. \quad (10)$$

So far, the treatment is entirely classical, and equations (9) and (10) point out the inadequacy of any classical treatment to explain the spectral phenomena described by (1). Namely, from equation (9) in a classical situation all energies are allowed as well as all radii. However, since the electron is moving in a circular orbit, it is under constant acceleration, and consequently should be radiating electromagnetic waves at a frequency equivalent to its orbital frequency, i.e.

$$\nu = \frac{\omega}{2\pi}. \quad (11)$$

Consequently the electron should lose energy in a continuous fashion and eventually spiral into the nucleus. All of this is quite elementary, and simply a summary of the well known classical paradox with respect to the observed discrete spectrum of radiation described by equation (1).

Faced with this impasse from classical theory, Bohr made the following postulates:

- (1) Although the classical equations of motion (as sketched out above for circular orbits) are valid for an electron in an atom, only certain orbits (denoted by the index  $n = 1, 2, \dots$ ) are allowed, and in these orbits the electron has a fixed binding energy  $E_n$ .
- (2) In these allowed orbits (which can be thought of as corresponding to *stationary states*) there is no emission of radiation even though this would be expected on the basis of classical electromagnetic theory.
- (3) An electron going from a stationary state of binding energy  $E_n$  (remember that on a classical basis that the binding energy is negative) at radius  $r_n$  to a second stationary state with a binding energy  $E_{n'} < E_n$  at a smaller radius  $r_{n'}$  will radiate electromagnetic waves at a frequency  $\nu$  proportional to the difference in the binding energies in the two orbits.

$$E_n - E_{n'} \propto \nu.$$

Bohr assumed the constant of proportionality is Planck's constant  $h$ :

$$E_n - E_{n'} = h\nu = hc\bar{\nu}. \quad (12)$$

The adsorption of energy would be described by the reverse process. Through a comparison of equations (1) and (12), Bohr then concluded that the energies in the stationary states must have the form

$$E_n = -\frac{R_\infty hc}{n^2}. \quad (13)$$

- (4) Things in the Bohr papers now become a bit clouded, but the fourth postulate essentially utilizes a primitive form of what he later enunciated as the *correspondence principle*. Bohr argued that in the situation that we are observing a transition from a state  $n - \delta$  to  $n$ , and  $n$  is large relative to  $\delta$ , we should identify  $\nu$  with the classical orbital frequency  $\omega/2\pi$ . In such a circumstance, from equation (1) and the relation

between wavenumber and frequency we have

$$\begin{aligned}\nu &= R_\infty c \left[ \frac{1}{(n-\delta)^2} - \frac{1}{n^2} \right] \\ &= \frac{R_\infty c}{n^2} \left[ \frac{1}{[1-\delta/n]^2} - 1 \right] \\ &\simeq \frac{2R_\infty c\delta}{n^3}.\end{aligned}\tag{14}$$

Thus, in going from the  $n-1$  to  $n$  level with  $n$  large, we have that

$$\nu \simeq \frac{2R_\infty c}{n^3}.\tag{15}$$

Now setting  $\omega = 2\pi\nu$ , with  $\nu$  given by (15), in equation (10), along with equation (13), we immediately obtain an expression for the Rydberg constant, namely

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}.\tag{16}$$

Equation (16) was Bohr's main result, and with the value of  $h$  estimated from black body radiation and experiments on the photoelectric effect, and the other constants, he was able to obtain a numerical value for the Rydberg constant consistent with spectroscopic measurements.

With these relations, we can put some more flesh on the character of these stationary orbits assumed by Bohr. From equation (13) we can write the energy of the  $n^{\text{th}}$  stationary state as

$$E_n = -\frac{|A|}{2r_n},\tag{17}$$

or

$$\boxed{E_n = \frac{E_1}{n^2}}\tag{18}$$

wherein

$$E_1 = -\frac{m_e |A|^2}{2\hbar^2},\tag{19}$$

and we use the now customary notation  $\hbar = h/2\pi$ . Using the expression for the energy in equation (8) we can solve for  $r_n$  to give

$$r_n = \frac{n^2 \hbar^2}{m_e |A|},\tag{20}$$

or

$$\boxed{r_n = n^2 r_1}\tag{21}$$

with

$$r_1 = \frac{\hbar^2}{m_e |A|}. \quad (22)$$

Equation (4) now yields

$$\begin{aligned} \omega_n &= \left( \frac{n\hbar}{m_e} \right) \left( \frac{m_e |A|}{n^2 \hbar^2} \right)^2 \\ &= m_e \frac{|A|^2}{(n\hbar)^3}, \end{aligned} \quad (23)$$

or

$$\boxed{\omega_n = \frac{\omega_1}{n^3}} \quad (24)$$

where

$$\omega_1 = m_e \frac{|A|^2}{\hbar^3}. \quad (25)$$

Since the period  $T_n$  is just  $T_n = 1/f_n$  and  $f_n = 2\pi\omega_n$  it is immediate from (24) that

$$\boxed{T_n = n^3 T_1}, \quad (26)$$

with  $T_1 = 1/2\pi\omega_1$ . The time required for the propagation of effects from electron to proton (the *delay*) is just  $\tau = r/c$ , so from the above relations we find

$$\tau_n = \frac{n^2 \hbar^2}{m_e c |A|} \quad (27)$$

or more simply

$$\boxed{\tau_n = n^2 \tau_1}, \quad (28)$$

with

$$\tau_1 = \frac{\hbar^2}{m_e c |A|}. \quad (29)$$

From equation (2) in conjunction with (21), we may write  $v_n$  as

$$v_n = \frac{|A|}{n\hbar}, \quad (30)$$

or

$$\boxed{v_n = \frac{v_1}{n}} \quad (31)$$

with

$$v_1 = \frac{|A|}{\hbar}. \quad (32)$$

In a circular orbit, the angular momentum is

$$p = m_e v r,$$

which means that

$$m_e v_n r_n = n \hbar \quad (33)$$

so as a consequence of this entire treatment the angular momentum also ends up being quantized. Many authors incorrectly present the Bohr treatment as if quantized angular momentum was one of his postulates, but this is not the case.

Having all of these relations, its instructive to see what the numbers really look like. Taking the best available modern determinations we use (unless otherwise noted, these values are taken from<sup>6</sup>):

- (1) speed of light  $c = 2.99792458 \times 10^8 \text{ ms}^{-1}$ ;
- (2)  $\epsilon_0 = 10^7 / 4\pi c^2 \text{ Fm}^{-1}$ ;
- (3) electronic charge  $e = 1.60217733 \times 10^{-19} \text{ C}$   
or<sup>7</sup>  
 $e = 1.60217670 \times 10^{-19} \text{ C}$  ;
- (4) electron mass  $m_e = 9.1093897 \times 10^{-31} \text{ kg}$ ;
- (5)  $h = 6.6260755 \times 10^{-34} \text{ Js} \implies \hbar = 1.054573 \times 10^{-34} \text{ Js}$   
or<sup>7</sup>  
 $h = 6.6260704 \times 10^{-34} \text{ Js} \implies \hbar = 1.054572 \times 10^{-34} \text{ Js}$ ;
- (6)  $R_\infty = 1.0973731534 \times 10^7 \text{ m}^{-1}$   
or<sup>8</sup>  
 $R_\infty = 1.097373156830 \times 10^7 \text{ m}^{-1}$   
or<sup>9</sup>  
 $R_\infty = 1.097373156841 \times 10^7 \text{ m}^{-1}$

we first find that **calculating**  $h$  from equation (16) using the CODATA<sup>6</sup> values, especially for  $R_\infty$ , that the precise value quoted in the CODATA figures results. Namely,

$$h = 6.6260755 \times 10^{-34} \text{ Js},$$

which is a bit suspicious since in the CODATA report they make no mention of how their best figure for  $h$  was arrived at. Going further we rather easily find, using the 1986 CODATA values, that

- (1) Energy in the first Bohr orbit is  $E_1 = -2.1798741 \times 10^{-18} \text{ J}$ ;

<sup>6</sup>E.R. Cohen & B.N. Taylor, "The 1986 adjustment of the fundamental physical constants", Rev. Mod. Phys. (1987) **59**, 1121-1148.

<sup>7</sup>M.E. Cage, R.F. Dziuba, R.E. Elmquist, B.F. Field, G.R. Jones, P.T. Olsen, W.D. Phillips, J.Q. Shields, R.L. Steiner, B.N Taylor & E.R. Williams, "NBS determination of the fine-structure constant and of the quantized Hall resistance and Josephson frequency to voltage quotient in SI units", IEEE Trans. Instru. Meas. (1989), **38**, 284-289.

<sup>8</sup>F. Nez, M.D. Plummer, S. Bourzeix, L. Julien, F. Biraben, R. Felder, O. Acef, J.J. Aondy, P. Laurent, A. Clairon & M. Abed, "Precise frequency measurement of the 2S-8S/8D transitions in atomic hydrogen: New determination of the Rydberg constant", Phys. Rev. Lett. (1992) **69**, 2326-2329.

<sup>9</sup>T. Andreae, W. König, R. Wynands, D. Leibfried, F. Schmidt-Kaler, C. Zimmerman & D. Meschede, "Absolute frequency measurement of the hydrogen 1S-2S transition and a new value of the Rydberg constant", Phys. Rev. Lett. (1992) **69**, 1923-1926.

- (2) Radius in the first Bohr orbit is  $r_1 = 5.29177249 \times 10^{-11}$  m;
- (3) Angular frequency in the first Bohr orbit is  $\omega_1 = 4.13413732 \times 10^{16}$  s<sup>-1</sup>;
- (4) Period in the first Bohr orbit is  $T_1 = 1.51982989 \times 10^{-16}$  s;
- (5) Delay to the first Bohr orbit is  $\tau_1 = 1.7651453 \times 10^{-19}$  s;
- (6) Velocity in the first Bohr orbit is  $v_1 = 2.18769141 \times 10^6$  ms<sup>-1</sup>;
- (7) Frequency in the first Bohr orbit is  $f_1 = 6.57968374 \times 10^{15}$  sec<sup>-1</sup>;
- (8) Ratio of the period to the delay in the first Bohr orbit is

$$\frac{T_1}{\tau_1} = 2\pi \times 137.03590744504,$$

where 137. . . . is the “fine structure constant”. This last relation can be written in the alternate form

$$\frac{1}{\omega_1 \tau_1} = 137.03590744504.$$

Interestingly, this is not the same value as given in the CODATA report<sup>6</sup>, namely

$$\alpha^{-1} = 137.0359895,$$

nor does it match the recent value<sup>7</sup> determined from measurements on the quantized Hall effect and the Josephson junction carried out at the NBS:

$$\alpha^{-1} = 137.0359940.$$

### A simpler route to the Bohr results.

It is interesting that a much simpler and more transparent way is available to derive the essence of the Bohr results. It is the following.

First, we have equation (4), which I repeat for ease of exposition:

$$m_e r \omega^2 = \frac{|A|}{r^2}. \quad (4)$$

Furthermore, for circular planar motion the angular momentum of the electron is constant, so

$$m_e \omega r^2 = \mathcal{C}, \quad (34)$$

where  $\mathcal{C}$  is an unknown quantity to be determined. Solving (4) and (34) for the pair  $(r, \omega)$  gives

$$r = \frac{\mathcal{C}^2}{m_e |A|} \quad (35)$$

and

$$\omega = \frac{m_e |A|^2}{\mathcal{C}^3} \quad (36)$$

respectively. If we also adopt the Bohr approximation derived from the Rydberg equation:

$$\nu \simeq \frac{2R_\infty c \delta}{n^3}, \quad (14)$$

and assume

$$\omega = 2\pi\nu \simeq \frac{4\pi R_\infty c\delta}{n^3}, \quad (37)$$

then in conjunction with (36) we have after a bit of algebra the result

$$\left(\frac{2\pi\mathcal{C}}{n}\right)^3 = \frac{m_e e^4}{8R_\infty \epsilon_0^2}. \quad (38)$$

The right hand side of equation (38) is numerically equal to the value of the Planck constant raised to the third power:

$$\left(\frac{2\pi\mathcal{C}}{n}\right)^3 = \frac{m_e e^4}{8R_\infty \epsilon_0^2} = h^3. \quad (39)$$

Consequently, we must have

$$\mathcal{C}_n = n \frac{h}{2\pi} = n\hbar, \quad (40)$$

so

$$r_n = \frac{n^2 \hbar^2}{m_e |A|} \quad (41)$$

and

$$\omega_n = \frac{m_e |A|^2}{n^3 \hbar^3} \quad (42)$$

respectively.

Finally, we note that from equation (7), we can write

$$E_n = -\frac{m_e A^2}{2n^2 \hbar^2}, \quad (43)$$

so

$$E_n - E_m = \frac{m_e A^2}{2\hbar^2} \left[ \frac{1}{m^2} - \frac{1}{n^2} \right] = \hbar R_\infty c = \left[ \frac{1}{m^2} - \frac{1}{n^2} \right] = \hbar R_\infty c = h\nu. \quad (44)$$



# BOHR TREATMENT OF ATOMIC SPECTRA

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FILE: BOHRQUAN.TEX

MICHAEL C. MACKEY

Institut für Theoretische Physik  
Universität Bremen  
Bremen, Germany

These notes summarize the assumptions and results of the old Bohr quantization rules, as these provide a touchstone for any alternative treatment of quantum mechanics.

In his work, Bohr made four assumptions that we can summarize as follows:

- (1) Atomic systems have a number of *stationary states*. In a stationary state, there is no emission of radiation even though this would be expected on the basis of classical electromagnetic theory.
- (2) Any emission or absorption of radiation corresponds to a *transition* between stationary states. The frequency ( $\nu$ ) of radiation (either emitted or absorbed) is given by

$$h\nu = E_1 - E_2,$$

where  $h$  is Planck's constant, and  $E_{1,2}$  is the energy of the two stationary states between which the transition is occurring.

- (3) When the system is in a stationary state, the dynamics are governed by classical considerations, **but this is not the case for transitions between stationary states.**
- (4) Different stationary states for an electron orbiting a proton in a circular orbit are determined by

$$p = n \left( \frac{h}{2\pi} \right) = n\hbar,$$

so the angular momentum  $p$  is an integral multiple of  $\hbar$ .

Now, let's put flesh on these assumptions and do some calculations for an electron-proton system, where the proton is fixed (infinitely massive) and the electron has finite mass  $m$ . First, from Newton's laws  $ma = F$ , where  $a$  is the acceleration and  $F$  is the force, for circular motion we obtain

$$m \frac{v^2}{r} = K \frac{e^2}{r^2},$$

where  $r$  is the radius of the orbit,  $v$  is the electron velocity,  $e$  is the electronic charge and the constant  $K$  is given by

$$K = \frac{1}{4\pi\epsilon_0} = \frac{c^2}{10^7}.$$

( $c$  is the velocity of light.) Thus

$$mv^2 = \frac{Ke^2}{r}. \quad (1)$$

If  $E$  is the total energy of the electron, then

$$\begin{aligned} E &= E_{kin} + E_{pot} \\ &= \frac{1}{2}mv^2 - \frac{Ke^2}{r} \end{aligned}$$

or

$$E_T = -\frac{Ke^2}{2r}. \quad (2)$$

Since Bohr assumes that the angular momentum is quantized (assumption 4)  $p_n = n\hbar$  so

$$p_n = np_1,$$

and in a circular orbit the angular momentum is

$$p = mvr,$$

which means that  $mv_n r_n = n\hbar$  so  $v_n = n\hbar/mr_n$  and consequently

$$mv_n^2 = m \left( \frac{n\hbar}{mr_n} \right)^2 = \frac{Ke^2}{r_n}.$$

This, in turn, implies that

$$r_n = \frac{n^2\hbar^2}{mKe^2},$$

or

$$r_n = n^2 r_1 \quad (3)$$

with

$$r_1 = \frac{\hbar^2}{mKe^2}. \quad (3')$$

Furthermore,

$$v_n = \frac{Ke^2}{n\hbar},$$

or

$$v_n = \frac{v_1}{n} \quad (4)$$

with

$$v_1 = \frac{Ke^2}{\hbar}. \quad (4')$$

Since the orbital frequency  $f$  is given by

$$f = \frac{\omega}{2\pi} = \frac{v}{2\pi r},$$

we have

$$\begin{aligned} f_n &= \frac{v_n}{2\pi r_n} \\ &= \left( \frac{n\hbar}{2\pi m} \right) \left( \frac{mKe^2}{n^2\hbar^2} \right)^2 \\ &= \left( \frac{m}{2\pi} \right) \frac{(Ke^2)^2}{(n\hbar)^3}, \end{aligned}$$

or

$$f_n = \frac{f_1}{n^3} \quad (5)$$

where

$$f_1 = \frac{m}{2\pi} \frac{(Ke^2)^2}{\hbar^3}. \quad (5')$$

Since the period  $T_n$  is just  $T_n = 1/f_n$  it is immediate from (5) that

$$T_n = n^3 T_1, \quad (6)$$

with  $T_1 = 1/f_1$ .

The time required for the propagation of effects from electron to proton (the *delay*) is just  $\tau = r/c$ , so from the above relations we find

$$\tau_n = \frac{n^2\hbar^2}{mKce^2}$$

or more simply

$$\tau_n = n^2\tau_1, \quad (7)$$

with

$$\tau_1 = \frac{\hbar^2}{mKce^2}. \quad (7')$$

Finally, the energy of the  $n^{\text{th}}$  stationary state is

$$E_n = -\frac{Ke^2}{2r_n} \quad (8)$$

and from Bohr's assumption 2 the frequency of radiation in going from stationary state  $n_1$  to  $n_2$  is

$$\begin{aligned} h\nu &= E_{n_1} - E_{n_2} \\ &= -\frac{Ke^2}{2r_{n_1}} + \frac{Ke^2}{2r_{n_2}} \\ &= \frac{Ke^2}{2} \left( \frac{1}{r_{n_2}} - \frac{1}{r_{n_1}} \right) \\ &= \frac{m(Ke^2)^2}{2\hbar^2} \left( \frac{1}{r_{n_2}} - \frac{1}{r_{n_1}} \right) \end{aligned}$$

Thus

$$\nu = \frac{m(Ke^2)^2}{4\pi\hbar^3} \left( \frac{1}{r_{n_2}} - \frac{1}{r_{n_1}} \right).$$

Since, from equation (5) we can write

$$\frac{nf_n}{2} = \frac{m(Ke^2)^2}{4\pi n^2 \hbar^2},$$

this last relation becomes

$$\nu = \frac{1}{2} [n_2 f_{n_2} - n_1 f_{n_1}].$$

Having all of these relations, its instructive to see what the numbers really look like.

Taking

- (1) electronic charge  $e = 1.6 \times 10^{-19}$  coulombs;
- (2)  $\hbar = 1.05 \times 10^{-34}$  Joule-sec;
- (3) speed of light  $c = 3 \times 10^8$  meters/sec;
- (4) electron mass  $m = 9.1 \times 10^{-31}$  kg; and
- (5)  $K = 8.99 \times 10^9$  mt<sup>2</sup>/sec<sup>2</sup>

we rather easily find that

- (1) Radius in the first Bohr orbit is  $r_1 = 5.26 \times 10^{-11}$  mt = 0.526A;
- (2) Velocity in the first Bohr orbit is  $v_1 = 2.2 \times 10^6$  mt/sec;
- (3) Delay to the first Bohr orbit is  $\tau_1 = 1.75 \times 10^{-19}$  sec;
- (4) Frequency in the first Bohr orbit is  $f_1 = 6.66 \times 10^{15}$  sec<sup>-1</sup>;
- (5) Period in the first Bohr orbit is  $T_1 = 1.5 \times 10^{-16}$  sec;
- (6) Ratio of the period to the delay in the first Bohr orbit is

$$\frac{T_1}{\tau_1} = 858 = 2\pi \times 137,$$

where 137 is the "fine structure constant". This last relation can be written in the alternate form

$$\omega_1 \tau_1 = \frac{1}{137}.$$