

Chapter 3B

3-3A. The Bohr Atom

Begin by equating Coulomb's Law and Newton's 2nd Law of Motion for the force provided by the nucleus of an atom, with atomic number Z , on its outermost electron:

$$F_c = m_e a_c = -Ze^2/r^2 \quad (3-1)$$

The subscript c in (3-2) indicates that the force is centripetal and e is the electrical charge on the electron. Now assume the electron is moving in a circular orbit around the nucleus under this force. The centripetal force on the electron is then $-m_e v_e^2/r$, and from (3-1) we get:

$$m_e v_e^2 = Ze^2/r \quad (3-2)$$

or

$$v_e = (Ze^2/mr)^{1/2} \quad (3-3)$$

This relates the orbital speed of an electron to its distance r from the nucleus. Now the potential energy of the electron is

$$PE_e = - \int_{\infty}^r F dr = - Ze^2/r \quad (3-4)$$

The total energy of the electron in the atom is then the sum of its kinetic and potential energies:

$$E_{\text{Tot}} = 1/2 m_e v_e^2 - Ze^2/r \quad (3-5)$$

Substituting for $m_e v_e^2$ from (3-2), we get

$$E_{\text{Tot}} = 1/2 Ze^2/r - Ze^2/r = - Ze^2/2r \quad (3-6)$$

This says that the total energy of an electron depends inversely on its orbital radius r .

Bohr then assumed that an electron occupies an orbit with its angular momentum, L , quantized such that

$$L = mvr = nh/2\pi \quad (3-7)$$

where n is an integer called the principal quantum number and h is Planck's constant. Now solve for v in (3-7) and substitute in (3-2) or (3-3). Again, solving for r , now associated with n , we get:

$$r_n = n^2 h^2 / 4\pi^2 m_e Z e^2 \quad (3-8)$$

$$r_n = n^2 (0.53 \times 10^{-8}) Z \text{ (cm)} \quad (3-9)$$

So the orbital radii permitted for an electron are discrete values determined by the value of n . The energy of the n th orbit may then be found from 3-6 as:

$$E_{\text{Tot}} = E_n = -2\pi^2 m_e Z^2 e^4 / n^2 h^2 = -13.6 (Z^2 / n^2) \text{ (ev)} \quad (3-10)$$

1 ev = 1.60 x 10⁻¹² ergs.

3-3 B. The Hydrogen Atom

For hydrogen, Z=1, in which case (3-10) become $E_n = -R' / n^2$, where $R' = -13.6 \text{ ev} = 2.18 \times 10^{-11} \text{ erg}$. Now, the difference between two electron energy states a and b , where b is the lower energy state and a is a higher energy state is

$$\Delta E_{ab} = hv = hc/\lambda, \quad (3-11)$$

where the difference in energy corresponds to an absorbed or emitted photon with a corresponding wavelength λ . We now define wave number to be $1/\lambda$. Combining (3-10) and (3-11) for any two electron states of hydrogen we have:

$$1/\lambda_{ab} = (R'/ch)[1/n_b^2 - 1/n_a^2] = R[1/n_b^2 - 1/n_a^2] \quad (3-12)$$

State b is the lower energy state, and $R = 109,737.31 \text{ cm}^{-1}$, is called the Rydberg constant. Equation (3-12) is called the Balmer Equation, who empirically devised it from spectroscopic studies.

For each value of n_b and different values of n_a , a series of spectral lines is produced

n_b	SERIES NAME	
1	Lyman	UV; All transitions to ground state from higher energy states
2	Balmer	VISIBLE; All transitions to 1st excited state from higher states
3	Paschen	IR
4	Brackett	IR
5	Pfund	IR
6	Ritz	IR

Consider the Balmer series of spectral lines, most of which are the visible portion of the spectrum but merge to the Balmer limit in the UV. The first line of the series is referred to as the H_α line and represents the transition from $n_a = 3$ to $n_b = 2$. Let us compute the wavelength of this line. From (3-13) we have:

$$1/\lambda_{H_\alpha} = R[1/n_b^2 - 1/n_a^2] = R[1/2^2 - 1/3^2] = 15,241.3 \text{ cm}^{-1}$$

$$\lambda_{H_\alpha} = 6.5611 \times 10^{-5} \text{ cm} = 6561.1 \text{ \AA}, \text{ since } 1 \text{ \AA} \text{ is } 10^{-8} \text{ cm}.$$

The actual measured value is 6562.85 Å. What may contribute to the difference? (Reduced mass) Sommerfeld added a relativistic correction for the electron.

As n gets larger, the energy states get closer together until they finally merge into a continuum as n goes to infinity. The wavelength for $n_a = \infty$ is called the **series limit**, which is given by:

$$\frac{1}{\lambda_{lim}} = R \left(\frac{1}{n_b^2} - \frac{1}{\infty} \right) = \frac{R}{n_b^2} \quad (3-13)$$

For the Balmer Series:

$$\frac{1}{\lambda_{lim}} = \frac{R}{2^2} = \frac{R}{4} = \frac{109737.31}{4}$$

$$\lambda_{lim} = \frac{4}{109737.31} \text{ cm} = 3.64510 \times 10^{-5} \text{ cm}$$

$$\lambda_{lim} = 3645.10 \text{ \AA}, \text{ which is in the UV.}$$

The Balmer limit is the beginning of the **Balmer continuum** or **Balmer confluence** of spectral lines. Similar terms are used for the other spectral series.

One way of representing the different energy levels and transitions in an atom is shown in Figure 5, where the energy states or levels are depicted as circles of radius r . The downward arrows depict

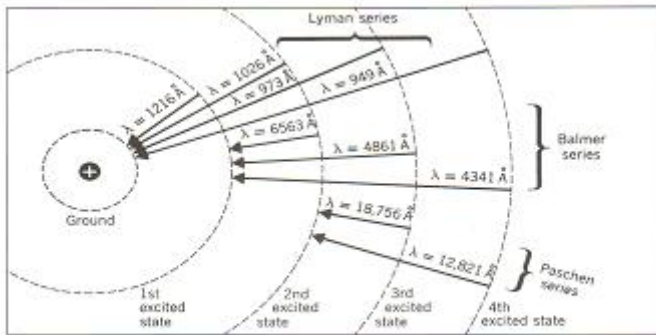


Fig. 5. Energy transitions for Hydrogen

emission transitions for three of the spectral series for hydrogen. Figure 6 is a schematic of a spectrogram for the Balmer series. The Balmer limit is indicated by H_{∞} .

If we display the different energy levels for an atom as horizontal lines in a plane where distance along the vertical axis is proportional to energy, we get what is called a **Grotrian Diagram** or **term Diagram**. Such a diagram for Hydrogen is shown on the right. There the energy levels have been normalized to positive values by subtracting the ground state energy E_1 from all values of E_n .

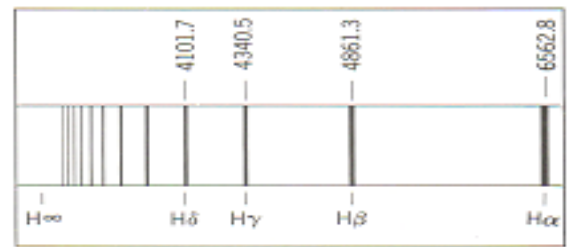
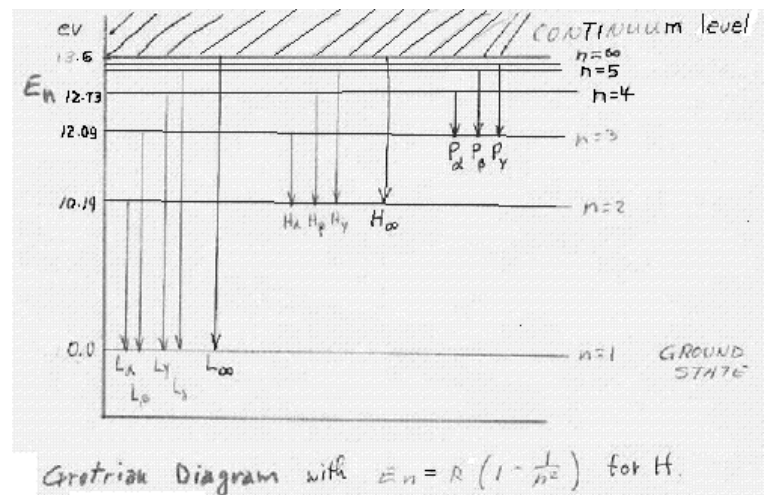


Fig. 6. A schematic spectrogram for the first few spectral lines of the Balmer Series.

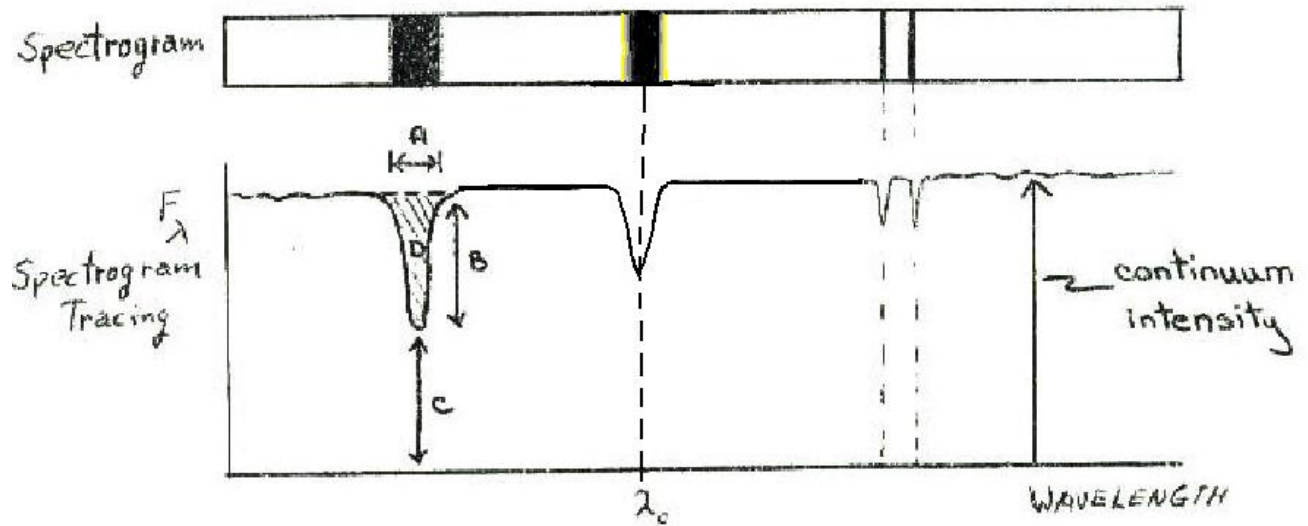


Grotrian Diagram with $E_n = R \left(1 - \frac{1}{n^2} \right)$ for H.

3-3 B. Spectral Line Characteristics

Before we can begin to discuss the quantitative aspects of the theory of spectral line formation, we must first become acquainted with the terminology that spectroscopists use in describing the measurable properties of spectral lines. A schematic spectrogram and its spectrophotometric scan are depicted in the diagram below. Several different spectral absorption lines of different properties are

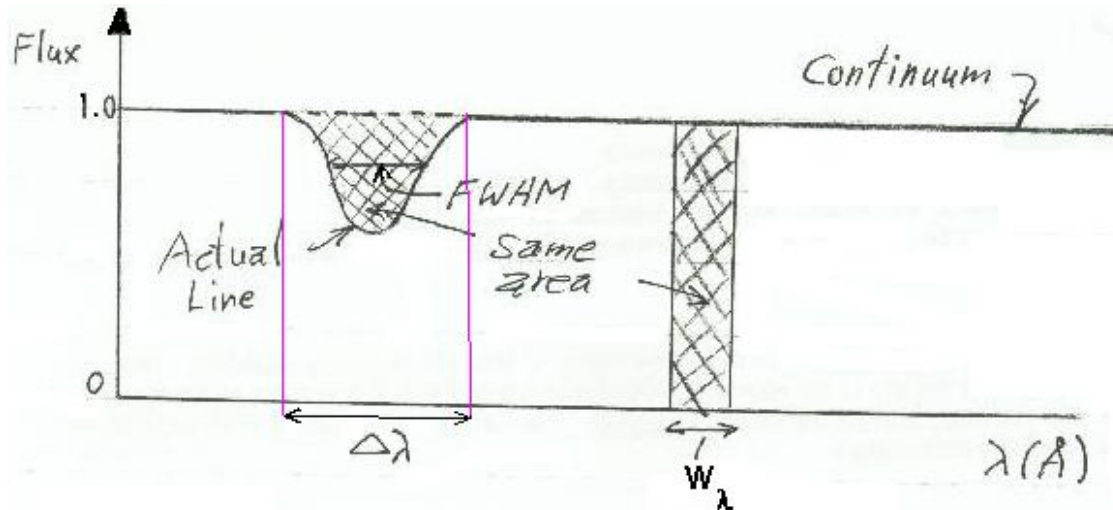
drawn. The term "line profile" is used to refer to the actual shape of the conical dip in brightness of the continuum for the representation of a line in a spectrophotometric tracing or scan. The geometric properties of the profile for the leftmost absorption line are labeled A, B, etc., which are defined as follows:



- A. **Full width of the line in Angstroms.** Sometimes spectral line widths at half the maximum depth of the line are quoted and are referred to as "FWHM" values. The minimum width of a line depends on the Heisenberg uncertainty principle. This is called the **natural width**, which is a very small fraction of an Angstrom. If the width of the line is broader than the natural width, the line is said to be broadened. One broadening mechanism is the pressure in the gas. This mechanism is called **Stark broadening**. Lines are also broadened by several Doppler effects:
1. The star's rotation. Rotational broadening usually dominates in stellar spectra.
 2. Thermal motions in the gas.
 3. Turbulence in the gas.
 4. Convective motions in the atmosphere.
- Doppler motions do not affect the strength of a line.
- B. The depth of the line. This is sometimes given as a fraction of the continuum flux level or intensity. E.G., 0.48. A line's depth is sometimes given in place of line strength but is otherwise not very useful.
- C. The flux level at the bottom of the line. This is usually given as a fraction of the continuum level. E. G., 0.52. This parameter has limited use also.
- D. Line strength, which is the total area within the line profile and represents the total amount of flux or energy absorbed by the atoms in the gas. Line strength depends on the total number of photons that have been absorbed or emitted along the line of sight. This in turn depends on:
1. The temperature of the atmosphere of the star *vis a vis* the mechanisms of excitation and ionization of the element.
 2. The "oscillator strength" or transition probability for a line. This comes from quantum mechanical considerations.
 3. The number density of atoms in the atmosphere and, hence, the abundance of the element.

Also λ_c indicates the central wavelength of a line. This is the quoted wavelength of a line or the value that is computed from the Balmer equation (3-12). A line profile may or may not be symmetrical about the central wavelength depending on several complex matters.

Line strength is often given in terms of its "equivalent width", W_λ , which is used in conjunction with a normalized continuum level. The diagram below shows a representative absorption line on the left with its strength indicated by the shaded area in the line's profile and its total width $\Delta\lambda$. The



FWHM of the line is also indicated. The rectangular absorption feature on the right has the same profile area as the actual line on the left but with a total line width of W_λ . Notice that W_λ is less than $\Delta\lambda$. Equivalent widths, W_λ , are given in Angstroms and defined by:

$$W_\lambda = \int_{\Delta\lambda} (I_c - I_\lambda) / I_c d\lambda \quad (3-14)$$

Here the integration is over the full width of the line, $\Delta\lambda$.

3-4. Theory of Excitation and Ionization

3-4 A. Basic Concepts and Terminology

According to the second law of thermodynamics, a system tends towards its lowest energy state. So normally, electrons tend to be in the lowest energy level ($n=1$) or ground state. When this is the case, atoms do not emit radiation, but they can absorb. However, since atoms are in constant motion, even at very low temperatures, they often collide with one another. Such collisions may then impart energy to the electrons in an atom and cause them to undergo transitions to a higher energy state. This is called **collisional excitation**. After about 10^{-8} secs., an excited electron spontaneously jumps to a lower energy level. This is called a **bound-bound transition**. In so doing, the electron rids itself of its excitation energy by emitting a photon of radiation. The wavelength of this photon is given by Plank's equation:

$$\Delta E = h\nu = hc/\lambda = \quad (3-15)$$

Here h is called Planck's constant and c is the speed of light. The value of h is 6.625×10^{-27} erg-sec. If the temperature is too low, collisions may not be able to deliver sufficient energy to an electron to excite it to a high energy state.

At high temperatures, a collision may cause an atom to become ionized when the energy imparted to an electron results in the electron to be ejected from the atom into what are called the continuum energy levels. This is called a **bound-free transition**. Free electrons may undergo any energy transition. This gives rise to what is called **free-free transitions**, when an electron is accelerated in an electromagnetic field.

An electron may also absorb a photon of radiation and undergo a transition to a higher energy state, but only if the photon carries exactly the energy difference between the two states. This is called **photo-excitation**. Again, downward transitions are usually spontaneous with a lifetime of about 10^{-8} seconds. This number is derived from the Heisenberg uncertainty principle.

The important point here is that the energy absorbed for an upward transition is exactly the same energy radiated away in a downward transition. However, downward transitions from energy levels where $n > 3$ may occur in steps, resulting in the production of several different photons each with a different energy that adds up to the energy of the original upward transition. When the latter happens, it is called "**cascading**." Hence, very energetic upward transitions may result in the production of several spectral lines.

In general, all electromagnetic radiation is produced by charged particles undergoing transitions from a higher energy state to a lower energy state. Classically, this includes electrons that are undergoing accelerations in an electric or magnetic field or any charged particle moving in a magnetic field. The latter is usually referred to as **synchrotron radiation**. For example, electrons accelerated by an alternating electric field in an antenna radiate radio waves (this is not synchrotron radiation).

3-4B. Boltzmann Excitation Theory

We have defined the strength of a given spectral line in terms of how much energy is absorbed or emitted. This depends on the number of atoms in a particular energy state from which a transition may occur. For a system in thermodynamic equilibrium, TDE, classical physics says that the probability that an atom in the system has energy E is proportional to the Boltzmann factor, $e^{-E/kT}$. As temperature in a gas increases, the more energetic the atomic collisions become and the higher the density of high energy photons. This results in the higher energy levels of an atom to become more frequently populated.

Consider two energy levels or states of a particular atomic species in a gas in TDE (a layer in the atmosphere of a star for example). Let state B be a higher energy level than state A and let N be the number density of atoms in a particular state. Then the Boltzmann theory of excitation gives:

$$N_B/N_A = g_B/g_A \exp[(E_A - E_B)/kT] \quad (3-16)$$

The quantity $(E_A - E_B)$ is called the **excitation potential**, and E_B must be greater than E_A so that the argument of the exponential is negative. The factor g gives the **multiplicity** of a level or statistical weight. It is also called the **degeneracy** of a state. Now this is purely classical physics. In quantum physics, the multiplicity is a result of the same energy being associated with different quantum numbers for an electron. For hydrogen, $g=2n^2$, where n is the principle quantum number.