

# Physics 4617/5617: Quantum Physics Course Lecture Notes

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**Edition 5.1**

## **Abstract**

These class notes are designed for use of the instructor and students of the course **Physics 4617/5617: Quantum Physics**. This edition was last modified for the Fall 2006 semester.

# I. Introduction: Atoms and Light

## A. The Classical Point of View.

1. A **system** is a collection of particles that interact among themselves via internal forces and that may interact with the world outside via external fields.
  - a) To a classical physicist, a **particle** is an indivisible mass point possessing a variety of physical properties that can be measured.
    - i) **Intrinsic Properties:** These don't depend on the particle's location, don't evolve with time, and aren't influenced by its physical environment (*e.g.*, rest mass and charge).
    - ii) **Extrinsic Properties:** These evolve with time in response to the forces on the particle (*e.g.*, position and momentum).
  - b) These measurable quantities are called **observables**.
  - c) Listing values of the observables of a particle at any time  $\implies$  specify its **state**. (A **trajectory** is an equivalent way to specify a particle's state.)
  - d) The *state of the system* is just the collection of the states of the particles comprising it.
2. According to classical physics, all properties, intrinsic and extrinsic, of a particle *could* be known to infinite precision  $\implies$  for instance, we could measure the precise value of both position and momentum of a particle at the same time.

3. Classical physics predicts the outcome of a measurement by calculating the **trajectory** (*i.e.*, the values of its position and momentum for all times after some initial (arbitrary) time  $t_o$ ) of a particle:

$$\{\vec{r}(t), \vec{p}(t); t \geq t_o\} \equiv \text{trajectory}, \quad (\text{I-1})$$

where the linear momentum is, by definition,

$$\vec{p}(t) \equiv m \frac{d}{dt} \vec{r}(t) = m \vec{v}(t), \quad (\text{I-2})$$

with  $m$  the mass of the particle.

- a) Trajectories are *state descriptors* of Newtonian physics.
- b) To study the evolution of the state represented by the trajectory in Eq. (I-1), we use Newton's Second Law:

$$m \frac{d^2}{dt^2} \vec{r}(t) = -\nabla V(\vec{r}, t), \quad (\text{I-3})$$

where  $V(\vec{r}, t)$  is the potential energy of the particle.

- c) To obtain the trajectory for  $t > t_o$ , one only need to know  $V(\vec{r}, t)$  and the **initial conditions**  $\implies$  the values of  $\vec{r}$  and  $\vec{p}$  at the initial time  $t_o$ .
- d) Notice that classical physics tacitly assumes that we can measure the initial conditions without altering the motion of the particle  $\implies$  *the scheme of classical physics is based on precise specification of the position and momentum of the particle.*
4. From the discussion above, it can be seen that classical physics describes a **Determinate Universe**  $\implies$  knowing the initial conditions of the constituents of any system, however complicated, we can use Newton's Laws to predict the future.

5. If the Universe is determinate, then for every *effect* there is a *cause*  $\implies$  the **principle of causality**.

## B. The Quantum Point of View.

1. The concept of a *particle* doesn't exist in the quantum world — so-called particles behave both as a particle and a wave  $\implies$  **wave-particle duality**.
  - a) The properties of quantum particles are not, in general, well-defined until they are measured.
  - b) Unlike the classical state, the quantum state is a conglomeration of several *possible* outcomes of measurements of physical properties.
  - c) Quantum physics can tell you only the *probability* that you will obtain one or another property.
  - d) An observer cannot observe a microscopic system without altering some of its properties  $\implies$  the interaction is *unavoidable*: The effect of the observer *cannot be reduced to zero*, in principle or in practice.
2. This is not just a matter of experimental uncertainties, *nature itself will not allow position and momentum to be resolved to infinite precision* (see Figure I-1)  $\implies$  **Heisenberg Uncertainty Principle (HUP)**:

$$\Delta x(t_o) \Delta p_x(t_o) \geq \frac{1}{2} \frac{h}{2\pi} = \frac{\hbar}{2}, \quad (\text{I-4})$$

where  $h = 6.62620 \times 10^{-27}$  erg-sec =  $6.626 \times 10^{-34}$  J-sec is **Planck's Constant**.

- a)  $\Delta x(t_o)$  is the *minimum* uncertainty in the measurement of the position in the  $x$ -direction at time  $t_o$ .

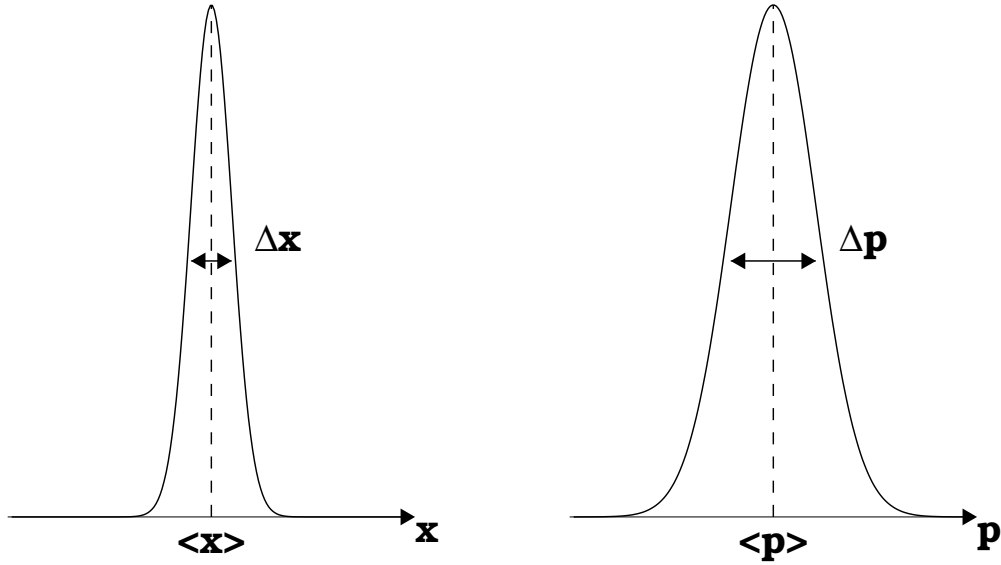


Figure I-1: The results of measurement of the  $x$  components of the position and momentum of a large number of identical quantum particles. Each plot shows the number of experiments that yield the values on the abscissa. Results for each component are seen to fluctuate about a central peak, the *mean value*  $\langle x \rangle$  and  $\langle p \rangle$ .

- b)  $\Delta p_x(t_o)$  is the *minimum* uncertainty in the measurement of the momentum in the  $x$ -direction at time  $t_o$ .
- c) Similar constraints apply to the pairs of uncertainties  $\Delta y(t_o)$ ,  $\Delta p_y(t_o)$  and  $\Delta z(t_o)$ ,  $\Delta p_z(t_o)$ .
- d) Position and momentum are *fundamentally incompatible observables*  $\implies$  the Universe is inherently uncertain!
- e) The HUP strikes at the very heart of classical physics: the trajectory  $\implies$  obviously, if we cannot know the position and momentum of a particle at  $t_o$ , we cannot specify the initial conditions of the particle and hence cannot calculate the trajectory.
- f) Once we throw out trajectories, we can no longer use Newton's Laws, new physics must be invented!

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**Example I-1.** Derive the **energy-time uncertainty relation** from the Heisenberg (position-momentum) Uncertainty Relation.

**Solution:**

A particle moves a distance  $\Delta x$  in a time interval  $\Delta t$ . These are related via the velocity equation

$$\Delta x = \frac{p}{m} \Delta t .$$

Plugging this into Eq. (I-4) gives

$$\Delta x \Delta p = \frac{p}{m} \Delta t \Delta p \geq \frac{\hbar}{2} .$$

Special relativity gives the energy of a particle is related to its momentum by

$$E^2 = p^2 c^2 + m_o^2 c^4 ,$$

where  $m_o$  is the rest mass of the particle. Taking the derivative of this equation with respect to momentum gives

$$2E \frac{dE}{dp} = 2pc^2 .$$

Replacing the infinitesimal differentials with small changes in both  $E$  and  $p$  gives

$$p \Delta p = \frac{E}{c^2} \Delta E .$$

Substituting above gives

$$\frac{E}{mc^2} \Delta E \Delta t \geq \frac{\hbar}{2} .$$

Finally, using Einstein's well known equation  $E = mc^2$ , we see that

$$\Delta E \Delta t \geq \frac{\hbar}{2} . \tag{I-5}$$

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3. Since Newtonian and Maxwellian physics describe the macroscopic world so well, physicists developing quantum mechanics demanded that when applied to macroscopic systems, the new physics must reduce to the old physics  $\implies$  this **Correspondence Principle** was coined by Neils Bohr.
  
4. Due to quantum mechanics probabilistic nature, only *statistical* information about *aggregates of identical systems* can be obtained. Quantum mechanics can tell us nothing about the behavior of individual systems. Moreover, the statistical information provided by quantum theory is limited to the results of measurements  $\implies$  *thou shall not make any statements that can never be verified.*

### C. Blackbody Radiation

1. In the early part of the 20th century, Max Planck asked the question: *What is the spectrum of electromagnetic (EM) radiation inside a heated cavity?* More specifically, how does this spectrum depend on the temperature  $T$  of the cavity, on its shape, size, and chemical makeup, and on the frequency  $\nu$  of the EM radiation in it?
  - a) Earlier in the mid-19th century, Kirchhoff found that the energy inside such a cavity is independent of the physical characteristics of the cavity (*i.e.*, size and shape), only  $\nu$  and  $T$  were important.
  
  - b) Planck was interested in the energy density in the cavity and sought an expression for the **radiative energy density per unit volume**  $\rho(\nu, T)$  and this density in the frequency range  $\nu$  to  $\nu + d\nu$ :  $\rho(\nu, T) d\nu$ .
  
  - c) Kirchhoff called his model of a heated cavity in *thermal equilibrium* a “black-body radiator.” A **blackbody** is

simply anything that absorbs all radiation incident upon it. Thus a blackbody radiator neither reflects nor transmits energy; it just absorbs or emits it.

2. Wien had already experimentally ascertained that the radiative energy density of a blackbody was proportional to  $\nu^3$  and, from the work of Stefan, that the *integrated energy density*  $\int_0^\infty \rho(\nu, T) d\nu$  is proportional to  $T^4$ .
  - a) Planck realized that  $\rho(\nu, T)$  could not solely depend upon  $\nu^3$  since this would imply that the energy density would blow up at small frequencies (*i.e.*, long wavelengths).
  - b) Planck focused on the exchange of energy between the radiation field and the walls of the cavity.
    - i) He developed a simple model of this process by imagining that the molecules of the cavity walls are *resonators* — electrical charges undergoing simple harmonic motion.
    - ii) As a consequence of their oscillations, these charges emit EM radiation at their oscillation frequency, which at thermal equilibrium, equals the frequency  $\nu$  of the radiation field.
    - iii) According to classical electromagnetic theory, energy exchange between the resonators and the energy field is a continuous process  $\implies$  the oscillators can exchange any amount of energy with the field, provided that the energy is conserved in the process.

- c) Planck deduced an empirical formula for the radiative energy density:

$$\rho(\nu, T) = \frac{A\nu^3}{e^{B\nu/T} - 1} . \quad (\text{I-6})$$

- i)  $A$  and  $B$  are constants that were to be determined by fitting experimental data.
- ii) The functional form of Eq. (I-6) agreed beautifully with observations.
- iii) In the limit of  $\nu \rightarrow \infty$  and  $T \rightarrow 0$ , Eq. (I-6) reduces to Wien's law.
- iv) However, when Planck developed this functional form for blackbody radiation, he didn't have a clue as to how to prove it theoretically.
- v) Planck made a second assault on the energy density by adopting a statistical method based upon the concept of entropy as interpreted probabilistically by Boltzmann. He also assumed in this treatment that *only discrete amounts of energy can be absorbed or emitted by the resonators that comprise the walls of the blackbody.*
- vi) He called these discrete amounts of energy **quanta**. To each quantum, Einstein took Planck's idea and assigned an energy equal to an integral multiple of  $h\nu$ , where  $h$  is now referred to as **Planck's constant**.

- d) Having made this assumption, Planck easily derived the radiation law:

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}, \quad (\text{I-7})$$

where  $k$  is the above mentioned Boltzmann's constant. As can be seen, Eq. (I-7) agrees with the empirical relation expressed in Eq. (I-6).

- e) The *radiative energy density*,  $\rho(\nu, T)$ , is related to the monochromatic **radiative energy flux**  $B_\nu(T)$  (*i.e.*, the “brightness” of a glowing object) with the relation

$$\rho(\nu, T) = \frac{4\pi}{c} B_\nu(T). \quad (\text{I-8})$$

- f) As such, the monochromatic energy flux (or brightness) of a blackbody is

$$B_\nu(T) = \frac{2h\nu^3/c^2}{e^{h\nu/kT} - 1} \quad (\text{I-9})$$

in frequency space, where  $B_\nu$  is measured in J/s/m<sup>2</sup>/Hz/sr (‘sr’ is the steradian unit) in SI units and erg/s/cm<sup>2</sup>/Hz/sr in the cgs unit system. Since  $B_\nu d\nu = B_\lambda d\lambda$  and  $\nu = c/\lambda$ , we can also write this function in wavelength space as

$$B_\lambda(T) = \frac{2hc^2/\lambda^5}{e^{hc/\lambda kT} - 1}. \quad (\text{I-10})$$

Both Eqs. (I-9) and (I-10) are called the **Planck function** (in frequency and wavelength space, respectively).

3. Planck's radiation law not only solve the problem of blackbody radiation, it also opened the door to a new understanding of radiation energy in physics  $\implies$  quantum physics, also called *quantum mechanics*.

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**Example I-2.** One of the early advances in the study of blackbody radiation was the **Stefan-Boltzmann Law**. This law is simply a formula for the power radiated from the surface of a blackbody. It expresses the radiated power  $P$  per unit surface area in terms of the temperature as

$$P = \sigma T^4 , \quad (\text{I-11})$$

where  $T$  is the temperature in Kelvins of the blackbody and  $\sigma$  is the **Stefan-Boltzmann constant**:  $\sigma = 5.6696 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} = 5.6696 \times 10^{-5} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ K}^{-4}$ . Deduce Eq. (I-11) from Planck's Law (e.g., Eq. I-7). The incident radiant solar flux arriving at the Earth's outer atmosphere is  $1.4 \times 10^3 \text{ J m}^{-2} \text{ s}^{-1}$ , where the Sun's diameter is  $1.4 \times 10^9 \text{ m}$  and the Earth-Sun distance is about  $1.5 \times 10^{11} \text{ m}$ . From this, estimate the atmospheric temperature of the Sun.

**Solution:**

Power is defined by

$$P = \frac{c}{4} \int_0^\infty \rho(\nu, T) d\nu .$$

Plugging Eq. (I-7) into this expression and solving the integral gives:

$$\begin{aligned} P &= \frac{c}{4} \int_0^\infty \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} d\nu \\ &= \frac{2\pi h}{c^2} \int_0^\infty \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu . \end{aligned}$$

Let  $y = h\nu/kT$ , then  $dy = (h/kT) d\nu$  or

$$\nu = \frac{kT}{h} y, \quad d\nu = \frac{kT}{h} dy .$$

$$\begin{aligned} P &= \frac{2\pi h}{c^2} \int_0^\infty \frac{(kT/h)^4 y^3}{e^y - 1} dy \\ &= \frac{2\pi h}{c^2} \left( \frac{kT}{h} \right)^4 \int_0^\infty \frac{y^3}{e^y - 1} dy . \end{aligned}$$

Looking up the integral above in a Table of Integrals, we find:

$$\int_0^{\infty} \frac{x^{n-1}}{e^x - 1} dx = \Gamma(n) \left( \frac{1}{1^n} + \frac{1}{2^n} + \frac{1}{3^n} + \dots \right)$$

(from Schaum's Mathematical Handbook, page 98, Eq. 15.80).

For our case  $n = 4$  and  $\Gamma(n) = (n - 1)!$ , so

$$\Gamma(4) = (4 - 1)! = 3! = 3 \cdot 2 \cdot 1 = 6 ,$$

and

$$\left( 1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \dots \right) = \frac{\pi^4}{90} \quad (\text{Eq. 19.20 from Schaum's}).$$

So,

$$\begin{aligned} P &= \frac{2\pi k^4 T^4}{h^3 c^2} \int_0^{\infty} \frac{y^3}{e^y - 1} dy \\ &= \frac{2\pi k^4 T^4}{h^3 c^2} (6) \left( \frac{\pi^4}{90} \right) = \frac{2\pi k^4 T^4}{h^3 c^2} \frac{\pi^4}{15} \\ &= \frac{2\pi^5 k^4}{15 h^3 c^2} T^4 . \end{aligned}$$

Let

$$\begin{aligned} \sigma &= \frac{2\pi^5 k^4}{15 h^3 c^2} \\ &= \frac{2\pi^5 (1.38062 \times 10^{-23} \text{ J/K})^4}{15 (6.62620 \times 10^{-34} \text{ J s})^3 (2.9979 \times 10^8 \text{ m/s})^2} \\ &= 5.6697 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4} . \end{aligned}$$

Hence,

$$P = \sigma T^4 .$$

Now, the power as defined in Eq. (I-11) has the same meaning as **flux** (*i.e.*,  $P = F$ , see any radiative transfer book), where  $F$  is the total flux integrated over all wavelengths at the Sun's surface and is related to the observed flux  $f$  by

$$4\pi R_{\odot}^2 F = 4\pi d_{\oplus}^2 f ,$$

where  $R_{\odot}$  is the Sun's radius ( $= 0.5 D_{\odot}$ ) and  $d_{\oplus}$  is the Earth-Sun distance. From this,

$$F = \left( \frac{d_{\oplus}}{R_{\odot}} \right)^2 f = 6.43 \times 10^7 \text{ J m}^{-2} \text{ s}^{-1} .$$

Hence, the temperature of the Sun is

$$\begin{aligned} T &= \left( \frac{F}{\sigma} \right)^{1/4} = \left( \frac{6.43 \times 10^7 \text{ J m}^{-2} \text{ s}^{-1}}{5.6697 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}} \right)^{1/4} \\ &= 5800 \text{ K} , \end{aligned}$$

which is the actual solar effective temperature.

**Example I-3.** Wien also empirically derived a *displacement law* which states

$$\lambda_{max} = \frac{0.0029 \text{ m K}}{T} , \quad (\text{I-12})$$

where  $\lambda_{max}$  is the wavelength where the maximum amount of light is emitted for a blackbody of temperature  $T$ . For stars with their temperature range from 2000 K to 50,000 K,  $\lambda_{max}$  is ranges from UV to IR wavelengths. Derive Eq. (I-12) from Planck's law as applied to stellar atmospheres.

**Solution:**

$\lambda_{max}$  occurs when  $dF_{\lambda}/d\lambda = 0$ , where  $F_{\lambda}$  is the energy flux of the radiation field. Note that one cannot analytically solve for the derivative of the Planck function outright — one is left with a transcendental function. This transcendental function can be solved numerically and I leave it up to you to try this numerical solution to see if it agrees with the analytic solution derived below which is based upon a certain assumption.

For this problem, we need to express the energy density in terms of wavelength  $\lambda$  instead of frequency. The energy flux must be conserved whether integrating over  $\nu$  or  $\lambda$ , hence (note that  $F_{\nu} = c\rho(\nu, T)/4\pi$ )

$$F_{\lambda}(T) d\lambda = F_{\nu}(T) d\nu .$$

We need to replace  $\nu$  with  $\lambda = c/\nu$  in the Planck function and replace

the differential with

$$d\nu = \frac{c}{\lambda^2} d\lambda ,$$

note that we have ignored the negative sign in this differential since the limits in the defining integral equation get swapped

$$\int_0^\infty F_\nu(T) d\nu = - \int_\infty^0 F_\lambda(T) d\lambda = \int_0^\infty F_\lambda(T) d\lambda = \sigma T^4 .$$

The flux integrand becomes

$$\begin{aligned} F_\lambda(T) d\lambda &= \frac{8\pi c(c/\lambda)^2}{4\pi c^3} \frac{hc/\lambda}{e^{hc/\lambda kT} - 1} \frac{c}{\lambda^2} d\lambda \\ F_\lambda(T) d\lambda &= \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} d\lambda , \end{aligned}$$

hence the energy flux as a function of wavelength is just

$$F_\lambda(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} .$$

At UV, optical, and near-IR wavelengths for typical stellar temperatures,  $hc/\lambda \gg kT$ , so  $e^{hc/\lambda kT} \gg 1$  and

$$F_\lambda(T) = \frac{2hc^2}{\lambda^5} e^{-hc/\lambda kT} .$$

$\lambda_{max}$  occurs where  $dF_\lambda/d\lambda = 0$ , so

$$\begin{aligned} \frac{dF_\lambda}{d\lambda} &= 2hc^2 \left( \frac{1}{\lambda^5} \frac{d}{d\lambda} e^{-hc/\lambda kT} + e^{-hc/\lambda kT} \frac{d}{d\lambda} \lambda^{-5} \right) = 0 \\ \lambda^{-5} \left( \frac{hc}{\lambda^2 kT} e^{-hc/\lambda kT} \right) - 5\lambda^{-6} e^{-hc/\lambda kT} &= 0 \end{aligned}$$

or

$$\begin{aligned} \lambda^{-5} \left( \frac{hc}{\lambda^2 kT} e^{-hc/\lambda kT} \right) &= 5\lambda^{-6} e^{-hc/\lambda kT} \\ \frac{hc}{\lambda^7 kT} &= \frac{5}{\lambda^6} \quad (\text{note } \lambda = \lambda_{max} \text{ here}). \end{aligned}$$

Finally,

$$\lambda_{max} = \frac{hc}{5kT} = \frac{(6.62620 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})}{5(1.38062 \times 10^{-23} \text{ J/K}) T}$$

or

$$\lambda_{max} = \frac{0.002898 \text{ m K}}{T}.$$

In units of Ångstroms ( $1 \text{ Å} = 10^{-10} \text{ m}$ ):

$$\lambda_{max} = \frac{2.898 \times 10^7 \text{ Å K}}{T}.$$

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**Example I-4.** Another early advance in understanding the physics of blackbody radiation was the derivation by Rayleigh and Jeans of a formula for the radiation density function  $\rho$ . These physicists used classical arguments to obtain this quantity as a function of wavelength of the radiation and the temperature of the cavity. They obtained

$$\rho(\nu, T) = \frac{8\pi kT}{\lambda^4}. \quad (\text{I-13})$$

- (a) Compare the **Rayleigh-Jeans Law** given in Eq. (I-13) with Planck's result as expressed as a function of  $\lambda$ . Are the two in agreement for any ranges of  $\lambda$  and  $T$ ? If so, determine *quantitatively* where the two expressions agree.
- (b) Derive the total energy density from the Rayleigh-Jeans formula. Why was this result called the *ultraviolet catastrophe*?

**Solution (a):** From our example above,

$$\rho(\lambda, T) = \frac{4\pi F_\lambda(T)}{c} = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}.$$

Opposite of what we assumed for Wien's displacement law, let's assume that  $hc/\lambda \ll kT$ , hence  $hc/\lambda kT \ll 1$ . This will occur either when temperatures are very high and/or when  $\lambda$  is very big (*e.g.*, radio wavelengths). Under this assumption, we can expand the exponential term as

$$\begin{aligned} e^{hc/\lambda kT} &= 1 + \frac{hc}{\lambda kT} + \frac{1}{2!} \left( \frac{hc}{\lambda kT} \right)^2 + \dots \\ &\approx 1 + \frac{hc}{\lambda kT} \quad (\text{when } hc/\lambda \ll kT) \end{aligned}$$

The energy density then becomes

$$\begin{aligned}\rho(\lambda, T) &= \frac{8\pi hc}{\lambda^5} \frac{1}{1 + (hc/\lambda kT) - 1} \\ &= \frac{8\pi hc}{\lambda^5} \frac{\lambda kT}{hc} \\ &= \frac{8\pi kT}{\lambda^4},\end{aligned}$$

which is Rayleigh-Jeans Law.

**Solution (b):** The total energy density is

$$\begin{aligned}\rho(T) &= \int_0^\infty \frac{8\pi kT}{\lambda^4} d\lambda \\ &= 8\pi kT \int_0^\infty \frac{d\lambda}{\lambda^4} \\ &= \frac{8\pi kT}{3\lambda^3} \Big|_\infty^0\end{aligned}$$

which obviously blows up at  $\lambda = 0 \implies$  the integral diverges at short wavelengths, the so-called *ultraviolet catastrophe!*

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## D. The Semi-Empirical Model of Hydrogen.

1. Work that lead to an understanding of the spectrum of the hydrogen atom took place at the end of the 19th and beginning of the 20th century. As such, much of what of the work described in this and the next few subsections is presented in the cgs unit system since those are the units that were being used in physics at the time.
2. Rydberg (1890), Ritz (1908), Planck (1910), and Bohr (1913) were all responsible for developing the theory of the spectrum of the H atom. A transition from an upper level  $m$  to a lower level  $n$  will radiate a photon at frequency

$$\nu_{mn} = c R_A Z^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right), \quad (\text{I-14})$$

Table I-1: Atomic Masses and Rydberg Constants

Atom	Atomic Mass, $M_A$ (amu)	Rydberg Constant, $R_A$ ( $\text{cm}^{-1}$ )
Hydrogen, $^1\text{H}$	1.007825	109,677.6
Helium, $^4\text{He}$	4.002603	109,722.3
Carbon, $^{12}\text{C}$	12.000000	109,732.3
Nitrogen, $^{14}\text{N}$	14.003074	109,733.0
Oxygen, $^{16}\text{O}$	15.994915	109,733.5
Neon, $^{20}\text{Ne}$	19.992440	109,734.3

where the velocity of light,  $c = 2.997925 \times 10^{10}$  cm/s,  $Z$  is the *effective* charge of the nucleus ( $Z_H = 1$ ,  $Z_{He} = 2$ , etc.), and the atomic Rydberg constant,  $R_A$ , is given by

$$R_A = R_\infty \left(1 + \frac{m_e}{M_A}\right)^{-1}. \quad (\text{I-15})$$

a) The Rydberg constant for an infinite mass is

$$R_\infty = \frac{2\pi^2 m_e e^4}{c h^3} = 109,737.31 \text{ cm}^{-1}, \quad (\text{I-16})$$

where  $e = 4.80325 \times 10^{-10}$  esu is the electron charge in cgs units.

b) In atomic mass units (amu), the electron mass is  $m_e = 5.48597 \times 10^{-4}$  amu whereas the atomic mass,  $M_A$ , can be found on a periodic table (see also Table I-1).

c) Eq. (I-6) can also be expressed in wavelengths (vacuum) by the following

$$\frac{1}{\lambda_{mn}} = R_A Z^2 \left(\frac{1}{n^2} - \frac{1}{m^2}\right). \quad (\text{I-17})$$

3. Lines that originate from the same level in a hydrogen-like atom/ion are said to belong to the same series. Transitions out of (or into) the ground state ( $n = 1$ ) are lines of the **Lyman series**,  $n = 2$

corresponds to the **Balmer series**, and  $n = 3$ , the **Paschen series**.

4. For each series, the transition with the longest wavelength is called the *alpha* ( $\alpha$ ) transition, the next blueward line from  $\alpha$  is the  $\beta$  line followed by the  $\gamma$  line, etc.
  - a) Lyman  $\alpha$  is the  $1 \leftrightarrow 2$  transition, Lyman  $\beta$  is the  $1 \leftrightarrow 3$  transition, Lyman  $\gamma$  is the  $1 \leftrightarrow 4$  transition, etc.
  - b) Balmer or  $H\alpha$  is the  $2 \leftrightarrow 3$  transition,  $H\beta$  is the  $2 \leftrightarrow 4$  transition,  $H\gamma$  is the  $2 \leftrightarrow 5$  transition, etc.
5. Lines that go into or come out of the ground state are referred to as **resonance lines**.

## E. Emission and Absorption of Radiation.

1. Electromagnetic Waves.
  - a) An electromagnetic (EM) wave consists of a transverse, and mutually perpendicular, oscillating electric and magnetic fields (see Figure I-2).
  - b) An atom, in the presence of a passing EM wave, responds primarily to the electric component of the EM wave.
    - i) If the wave is long as compared to the size of the atom, the *spatial* variation of the electric field can be ignored during the interaction.
    - ii) This is the same thing as saying that the period of oscillation is long as compared to the time it takes the charge to move around (or within) the atom.

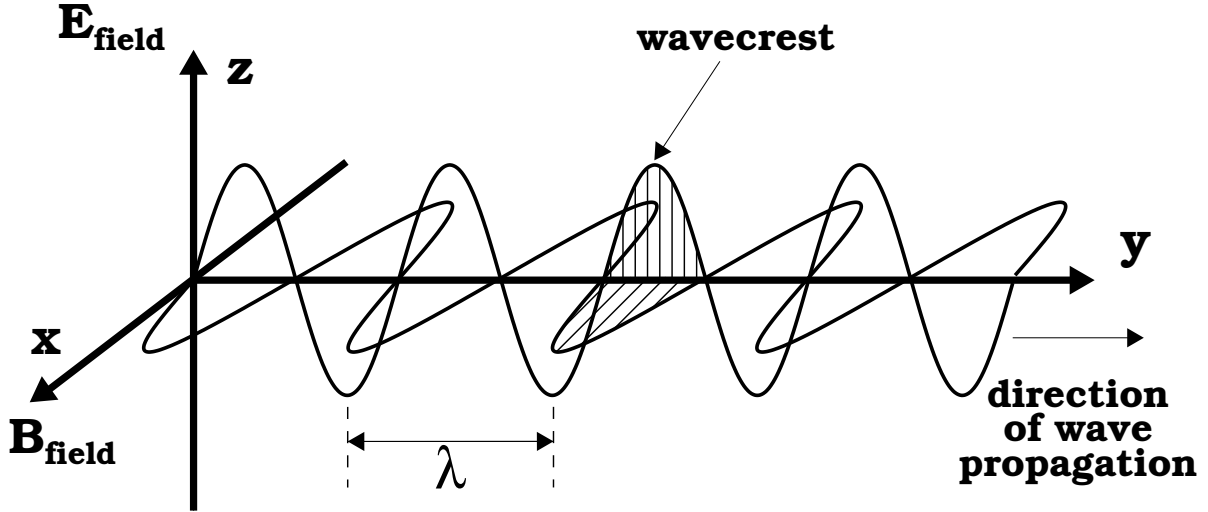


Figure I-2: An electromagnetic wave.

- c) As a result, the atom is essentially exposed to a purely sinusoidal oscillating electric field,  $\mathbf{E}$ , of the form

$$\mathbf{E} = E_o \cos(\omega t) \hat{z} , \quad (\text{I-18})$$

where here the electric wave oscillates about the  $z$  axis with an amplitude of  $E_o$  with an angular frequency  $\omega = 2\pi\nu$ .

- d) The potential,  $\phi$ , is related to the  $E$  field by

$$\mathbf{E} = -\nabla\phi , \quad (\text{I-19})$$

hence the potential must be a sinusoidal function as well.

- e) The potential of an EM wave passing a bound electron can *perturb* the potential energy  $V_e$  of said electron via the potential energy equation from classical EM theory:

$$V_e = \frac{1}{2}q\phi , \quad (\text{I-20})$$

where  $q$  is the charge of the electron. This oscillating perturbation then can cause the bound electron to change its *state*.

## 2. Absorption, Stimulated Emission, and Spontaneous Emission.

- a) We shall see later in the course that bound electrons in an atom are only found in certain **energy states** or levels. Each of these states are described by **wave functions** (see §II of these notes).
  - i) The form of an electron wave function is solved with the partial differential equation called the **Schrödinger equation** (see §III).
  - ii) The solution of this equation depends upon the potential energy of the given state.
- b) Bound electrons will jump from one state to another based upon the probability of the transition occurring.
  - i) This probability is calculated from the wave function of the particle/state (see §II).
  - ii) By the end of the course, the student will be able to prove that this probability for a bound electron being perturbed by a passing photon takes the following form:

$$P_{i \rightarrow j} = \left( \frac{\mathcal{P} E_o}{\hbar} \right)^2 \frac{\sin^2[(\omega_{ij} - \omega)t/2]}{(\omega_{ij} - \omega)^2}, \quad (\text{I-21})$$

where  $\mathcal{P}$  is the *electric dipole moment* of the induced by the transition when the atom absorbs energy  $E_j - E_i = \Delta E_{ij} = h\nu_{ij} = \hbar\omega_{ij}$  from the electromagnetic field, where here, unlike Eq. (I-18),  $E_i$  and  $E_j$  correspond to the energy of the two bound levels  $i$  and  $j$  (note that  $E_j > E_i$ )  $\implies$  the atom absorbs a **photon** and the atom becomes *excited*. This process is known as **absorption**.

- c) Photon perturbations also can cause electrons to *de-excite* in an atom (called **stimulated emission**).
- d) From the HUP ( $\Delta E \Delta t \geq \hbar/2$ ), electrons also can *de-excite* spontaneously (*i.e.*, **spontaneous emission**).
  - i)  $\Delta t$  represents the half-life of the time an electron stays excited before spontaneously decaying back to a lower energy state.
  - ii)  $\Delta E$  in HUP represents the “half-width” of the thickness of the energy probability distribution of a given state. For this *natural broadening*, this is typically nothing more than a Gaussian (*i.e.*, normal) distribution. Note that  $\Delta E = 0$  for the ground state of an atom (or molecule) since an electron stays there indefinitely until perturbed by a passing photon.
- e) In all, there are 5 distinct physical processes involving **bound-bound** (b-b) transitions, which is often referred to as *line opacity* in the study of radiative transfer (see Figure I-3):
  - i) *Radiative excitation*:  $e^-$  jumps from a lower state “*i*” to an upper state “*j*” with an energy difference  $\Delta E_{ij}$  via a photon absorption of energy  $h\nu_{ij}$  such that  $\Delta E_{ij} = h\nu_{ij}$ . Note that here, unlike the HUP,  $\Delta E_{ij} = E_j - E_i$  is the energy difference between states *i* and *j*.
  - ii) *Spontaneous de-excitation* (or *emission*): a bound  $e^-$  in an upper state has a finite lifetime in such state and can spontaneously (*i.e.*, without external stimuli) decay to a lower state. This decay leads

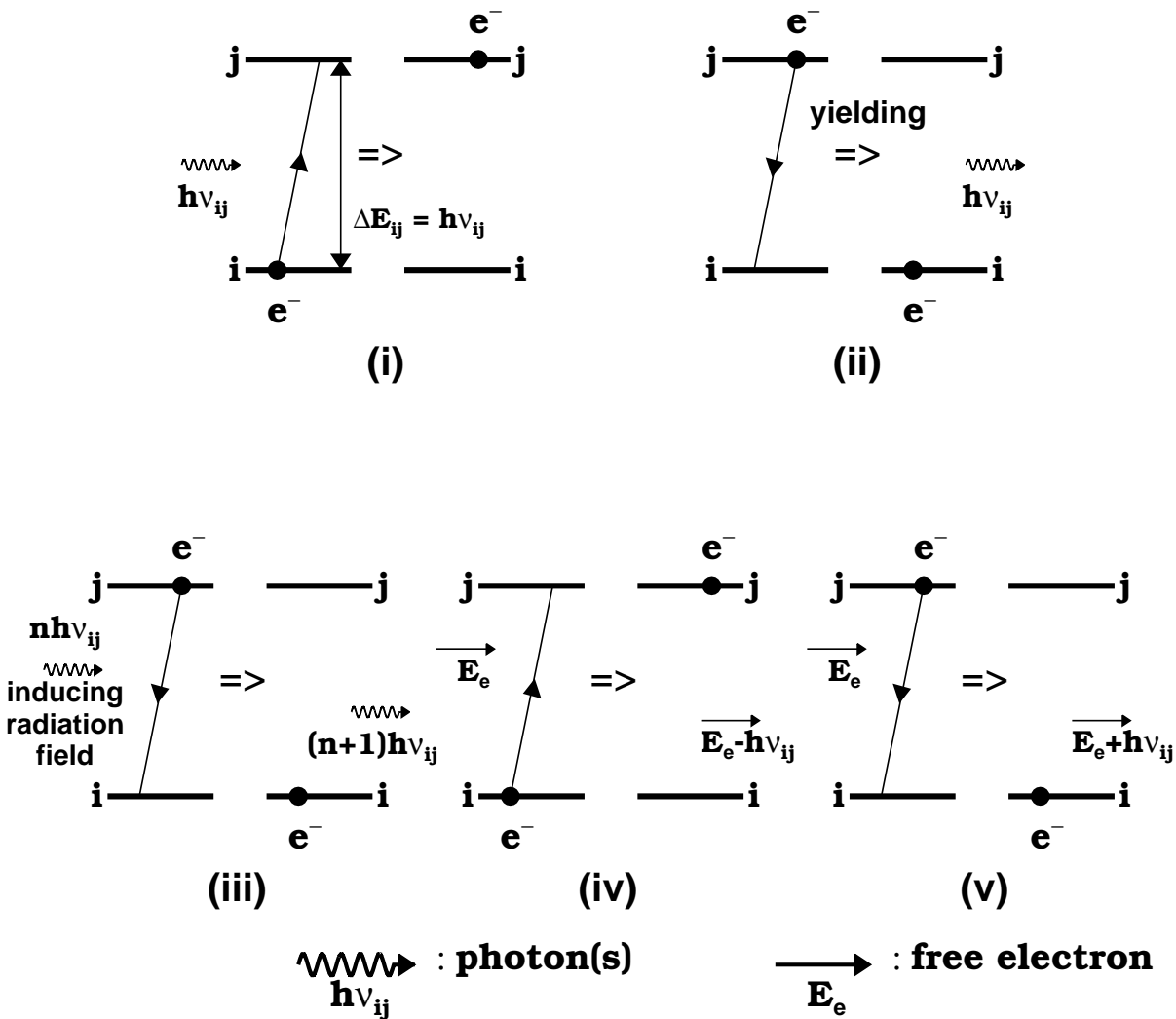


Figure I-3: The 5 processes involving bound-bound transitions. For each subframe, the left side represents “before” the interaction, and the right side, “after” the interaction.

to a lower energy state of the  $e^-$ , which must be conserved by the emission of a photon — again  $\Delta E_{ij} = h\nu_{ij}$ .

- iii) *Stimulated de-excitation (or emission)*: a bound  $e^-$  in an upper state can decay to a lower state if the atom/ion is bombarded by radiation of frequency  $h\nu_{ij} \implies nh\nu_{ij} + E_j = E_i + (n + 1)h\nu_{ij}$ .
- iv) *Collision excitation*:  $e^-$  jumps from a lower to upper state via a free  $e^-$  collision  $E_e + E_i = E_j + E'_e$  ( $E'_e = E_e - \Delta E_{ij}$ ).
- v) *Collisional de-excitation*: free  $e^-$  collision induces an excited bound  $e^-$  to decay to a lower state, which adds to the free  $e^-$  energy  $\implies E_e + E_j = E_i + E'_e$  ( $E'_e = E_e + \Delta E_{ij}$ ).

## F. Radiative Transfer.

1. In a radiation field, the radiant energy flowing per unit time through a surface element  $d\sigma$  within a small solid angle  $d\Omega$  about a direction defined by the polar angles  $\theta, \phi$  (see Figure I-4) within the frequency interval  $\nu$  to  $\nu + d\nu$  is

$$dE = I_\nu(\theta, \phi) d\nu \cos \theta d\sigma d\Omega. \quad (\text{I-22})$$

2. The **intensity**  $I_\nu(\theta, \phi)$  denotes the energy flow per unit time per unit frequency interval per unit solid angle about the direction  $\theta, \phi$  across the unit area  $\perp$  to this direction [ $\text{W/m}^2/\text{Hz}/\text{sr}$  in SI units and  $\text{erg/s/cm}^2/\text{Hz}/\text{sr}$  in cgs units, where  $\text{sr} \equiv \text{steradian}$ ].

- a)  $I_\lambda$  as a function of wavelength is related to  $I_\nu$  via

$$I_\lambda d\lambda = I_\nu d\nu \quad (\text{I-23})$$

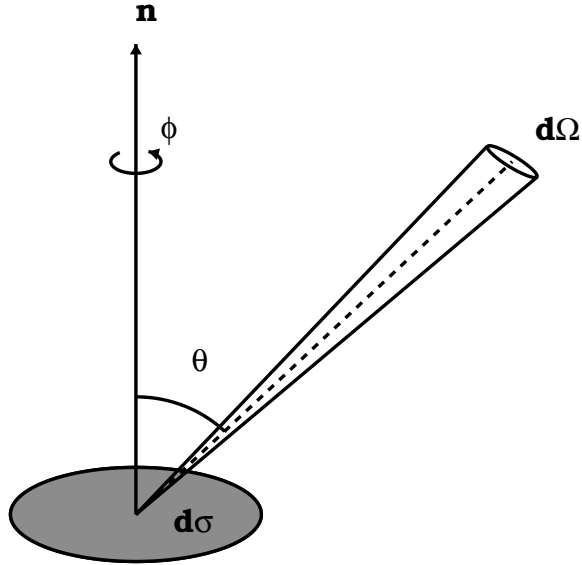


Figure I-4: Definition of the intensity of the radiation.

or

$$I_{\lambda} = (c/\lambda^2) I_{\nu} , \quad (\text{I-24})$$

since  $\nu = c/\lambda$ .

- b)** The total intensity is

$$I = \int_0^{\infty} I_{\nu} d\nu = \int_0^{\infty} I_{\lambda} d\lambda. \quad (\text{I-25})$$

- c)** It is related to the electric field of the EM wave by the equation

$$I_{\nu}(z) = \epsilon_0 c |E_{\nu}(z)|^2 , \quad (\text{I-26})$$

where  $\epsilon_0$  is the permittivity of free space,  $c$  is the speed of light, and  $I$  is the intensity of the electric field at point  $z$  in space along the “path” of the EM wave.

- d)** Once a photon is emitted into a vacuum (say from a star’s surface), that is, it does not interact with matter during flight, its intensity remains the same at all points along its flight path  $\rightarrow I_{\nu}$  independent of distance  $r$  (or  $d$ ).

3. The *brightness* or *strength* of light corresponds to the **radiation flux**:

$$\mathcal{F}_\nu = \pi F_\nu = \int_0^{2\pi} \int_{-1}^1 I_\nu(\mu, \phi) \mu d\mu d\phi. \quad (\text{I-27})$$

- a)  $\mu = \cos \theta$  and  $d\Omega = \sin \theta d\theta d\phi = d\mu d\phi$ .
- b)  $F_\nu$  is called the **astrophysical flux**.
- c) In an **isotropic** (*i.e.*, same in all directions),  $I_\nu$  is independent of  $\theta$  and  $\phi \implies F_\nu = 0$ .
- d) It is often useful to separate  $F_\nu$  [W/m<sup>2</sup>/Hz in SI units and erg/s/cm<sup>2</sup>/Hz in cgs units] into an outward and an inward component in an atmosphere of gas:

$$\pi F_\nu^+ = \int_0^{2\pi} \int_0^1 I_\nu \mu d\mu d\phi \quad (\text{I-28})$$

( $0 \leq \mu \leq 1$ ) outward flux

$$\pi F_\nu^- = \int_0^{2\pi} \int_{-1}^0 I_\nu \mu d\mu d\phi \quad (\text{I-29})$$

( $-1 \leq \mu \leq 0$ ) inward flux,

from which we can write

$$F_\nu = F_\nu^+ + F_\nu^-. \quad (\text{I-30})$$

- e) If  $I_\nu$  is axisymmetric (*i.e.*, independent of  $\phi$ ), then the flux equation becomes:

$$\mathcal{F}_\nu = 2\pi \int_{-1}^1 I_\nu \mu d\mu. \quad (\text{I-31})$$

- f) The total radiation flux is then given by

$$\mathcal{F} = \int_0^\infty \mathcal{F}_\nu d\nu = \int_0^\infty \mathcal{F}_\lambda d\lambda. \quad (\text{I-32})$$

- g) Note that  $4\pi R^2 \mathcal{F}_\nu = L_\nu$  is the monochromatic luminosity, where  $R$  is the radius of a spherical object (*e.g.*, a star) emitting the light.

h)  $\mathcal{F}_\nu = \pi I_\nu$  if  $I_\nu$  is isotropic outward and zero inward.

4. Unlike intensity, flux does scale with distance  $\implies$  an object gets fainter the farther away it is:

$$f_\nu = \left(\frac{R_\star}{d}\right)^2 \mathcal{F}_\nu = \frac{1}{4} \alpha_\star^2 \mathcal{F}_\nu . \quad (\text{I-33})$$

- a)  $f_\nu$  is the observed flux of a star of radius  $R_\star$  at a distance  $d$ .
- b)  $\alpha_\star$  is the angular diameter (in radians) of the star as seen at distance  $d$ .

## 5. The Radiative Transfer Equation.

- a) If a photon is traveling within a medium (*i.e.*, non-vacuum), its intensity does change as it propagates through the gas depending on the opacity of the gas.
- i) The **opacity**,  $\chi$  [ $\text{cm}^{-1}$ ], of a gas measures how opaque the gas is. The opacity of a transition (or continuum) depends primarily on the probability that a transition can occur, which, of course, depends upon the wave functions of the transition.
- ii) It is the inverse of the *mean-free-path*,  $L$  [cm], of the photon  $\implies$  the distance a photon travels before it interacts with another particle.
- iii) The opacity dictates how *deep* we can see into a gas. As such, the **optical depth** along depth  $s$  ( $s$  increasing outward) of a gas is defined by

$$d\tau_\nu = -\chi_\nu ds , \quad (\text{I-34})$$

$\tau_\nu$  increases in the opposite direction to  $s$ ,  $\tau_\nu = 0$  at the top and getting larger as you go inward.

iv) One typically does not see deeper into a gas than  $\tau_\nu \approx 1$ .

v) Typically, opacity is broken up into two components:

$$\chi_\nu = \kappa_\nu + \sigma_\nu , \quad (\text{I-35})$$

where  $\kappa_\nu$  is the **absorption opacity** (*i.e.*, once the photon is absorbed, its energy is given up to the thermal pool of the gas via subsequent particle collisions) and  $\sigma_\nu$  is the **scattering opacity** (*i.e.*, the photon is re-emitted by the absorbing atom before giving its energy up to the surrounding medium).

b) Consider a rectangular “slab” of gas. As a photon travels through a gas along a small length  $ds$  in direction  $\theta$  ( $\mu = \cos \theta$ ) with respect to a normal line of a rectangular surface,  $I_\nu$  is attenuated by the following expression:

$$\mu \frac{dI_\nu}{ds} = -\chi_\nu I_\nu . \quad (\text{I-36})$$

c) As previously mentioned, besides this absorption process, particles in the gas can also emit photons (*i.e.*, emission). Hence,  $I_\nu$  can increase along this path by

$$\mu \frac{dI_\nu}{ds} = \eta_\nu , \quad (\text{I-37})$$

where  $\eta_\nu$  [W/m<sup>3</sup>/Hz/sr in SI units and erg/s/cm<sup>3</sup>/Hz/sr in cgs units] is the **emissivity** of the gas.

d) Summing these 2 equations gives the manner in which photons travel through a gas  $\implies$  the **Equation of Radiative Transfer**:

$$\mu \frac{dI_\nu}{ds} = \eta_\nu - \chi_\nu I_\nu . \quad (\text{I-38})$$

e) We can divide each term by  $\chi_\nu$  and get

$$\mu \frac{dI_\nu}{d\tau_\nu} = I_\nu - S_\nu . \quad (\text{I-39})$$

i)  $S_\nu$  is called the **source function** and is the ratio of the number of photon creation events divided by the number of photon destruction events ( $S_\nu = \eta_\nu/\chi_\nu$ ) for a given region of gas.

ii) As such, you can view the transfer equation as the change in intensity of a photon equals the incident intensity on a volume of gas plus any photons created by the gas minus any photons destroyed by the gas.

iii) Often  $S_\nu$  will be separated into a *continuum* component and a *line* component:  $S_\nu \propto S_\nu^\ell + S_\nu^c$ .

f) For gas in thermodynamic equilibrium, collisional rates exceed radiative (*i.e.*, scattering) rates by large amounts. Hence  $\kappa_\nu \gg \sigma_\nu$  in Eq. (I-35) and  $\chi_\nu \approx \kappa_\nu$ . When this occurs, the emissivity of the gas is given by

$$\eta_\nu = \kappa_\nu B_\nu(T) , \quad (\text{I-40})$$

hence the source function becomes the Planck function for this gas and the transfer equation is somewhat easy to solve:

$$I_\nu = I_{\nu,\circ} e^{-\tau_\nu/\mu} + \frac{1}{\mu} \int_{\tau_\nu} B_\nu(\tau_\nu) dt . \quad (\text{I-41})$$

g) For non-thermodynamic equilibrium gas, however,  $S_\nu$  is much more difficult to ascertain, since it will depend upon both the mean intensity ( $J_\nu = \frac{1}{2} \int I_\nu d\mu$ ) of the photons and the thermal nature of the gas in the volume of interest

$\implies$  the equation of transfer becomes a *integral-differential equation* in  $I_\nu$ !

- i) The differential portion of the radiative transfer is obvious from Eq. (I-38). The integral portion comes from the expression of the source function in these cases:

$$S_\nu = \frac{r_\nu}{\phi_\nu + r_\nu} S_\nu^c + \frac{\phi_\nu}{\phi_\nu + r_\nu} S_\nu^\ell, \quad (\text{I-42})$$

where  $S_\nu^c$  is the continuum source function,  $S_\nu^\ell$  is the line source function,

$$r_\nu = \frac{\chi_\nu^c}{\chi_{\nu_0}^\ell} \quad (\text{I-43})$$

is the fraction of the continuous opacity,  $\chi_\nu^c$ , over the line center opacity,  $\chi_{\nu_0}^\ell$ ,

$$\phi_\nu = \frac{\chi_\nu^\ell}{\chi_{\nu_0}^\ell} \quad (\text{I-44})$$

is the profile function (usually a Gaussian, Lorentzian, or Voigt [combination of the first two] profile) of the line which is the fraction of the line opacity at some portion of the profile,  $\chi_\nu^\ell$ , over the line center opacity,  $\chi_{\nu_0}^\ell$ .

- ii) The *continuum* source function is determined by

$$S_\nu^c = \frac{\kappa_\nu B_\nu + \sigma_\nu J_\nu}{\kappa_\nu + \sigma_\nu} = \epsilon_\nu^c B_\nu + (1 - \epsilon_\nu^c) J_\nu, \quad (\text{I-45})$$

where  $J_\nu$  is the angle-averaged mean intensity (*i.e.*, an integral over angle  $\theta$  — see previous page), and  $\epsilon_\nu^c = \kappa_\nu / (\kappa_\nu + \sigma_\nu)$  is the thermal fraction of the continuum emission.

- iii) The *line* source function is somewhat more difficult to determine in non-equilibrium cases:

$$\begin{aligned} S_\nu^\ell &= (1 - \epsilon_\nu^\ell) \int \phi_\nu J_\nu d\nu + \epsilon_\nu^\ell B_\nu \\ &= (1 - \epsilon_\nu^\ell) \bar{J} + \epsilon_\nu^\ell B_\nu, \end{aligned} \quad (\text{I-46})$$

where  $\bar{J}$  is the profile-integrated mean intensity, and  $\epsilon_\nu^\ell$  is the thermal fraction of the line emission.

- iv) The line source function also can be determined from

$$S_\nu^\ell = \frac{2h\nu^3}{c^2} \left( \frac{n_i g_j}{n_j g_i} - 1 \right)^{-1}, \quad (\text{I-47})$$

where  $n_i$  and  $n_j$  are the particle number densities of the lower ('*i*') and upper ('*j*') energy states, respectively, and  $g_i$  and  $g_j$  are their corresponding *statistical weights* which are calculated from quantum numbers and discussed at the end of this section of the notes (see Table I-2). In this equation, the number density ratio is determined from the radiative and collisional rate equations and the solution to radiative rates equation require integrals to be solved (see below). Note that Eq. (I-47) reduces to the Planck function is the particle density ratio achieves its equilibrium value.

## G. Radiative Rates.

### 1. Einstein's Coefficients.

- a) Let  $N_i$  be the number of atoms in a sample of gas who have electrons in a lower-energy state and let  $N_j$  be the number in the upper-energy state. If we ignore matter

particle collisions, the rate in which the upper level either gains or loses an electron to the lower level is given by

$$\frac{dN_j}{dt} = -N_j A_{ji} - N_j B_{ji} \rho(\nu_{ij}) + N_i B_{ij} \rho(\nu_{ij}) . \quad (\text{I-48})$$

**i)**  $A_{ji}$  represents the spontaneous emission rate. The number of particles leaving this state, per unit time, by this mechanism is  $N_j A_{ji}$ .

**ii)** The transition rate for stimulated emission is proportional to the energy density of the EM field,  $\rho$ , whose energy corresponds to the energy difference of the two states,  $h\nu_{ij}$ . The number of particles leaving this state, per unit time, by this mechanism is  $N_j B_{ji} \rho(\nu_{ij})$ .

**iii)** The transition rate for absorption from the lower level to the upper level also is proportional to the energy density of the electromagnetic field of energy  $h\nu_{ij}$ . The number of particles entering the upper state from the lower state, per unit time, is  $N_i B_{ij} \rho(\nu_{ij})$ .

**b)** If these atoms are in thermal equilibrium with the ambient field, the level densities remain *constant*, hence  $dN_j/dt = 0$ , then

$$\rho(\nu_{ij}) = \frac{A_{ji}}{(N_i/N_j) B_{ij} - B_{ji}} . \quad (\text{I-49})$$

Another way of saying this is when a gas is in equilibrium, statistically the number of transitions each second into a given energy level should equal the number of transitions out of that energy level, so that the number of atoms in any energy level does not change with time.

- c) Let us continue this analysis of radiative rates using the intensity of light instead of the energy density of the EM field. By doing this, we need to incorporate the volume information into the particle number variable, such that  $n = N/V$  is the number density of particles in a given state. Then, the number of transitions per unit volume from the lower level  $i$  to the upper level  $j$  due to the absorption of a photon is given by

$$R_{ij} = n_i J(\nu_{ij}) B_{ij} , \quad (\text{I-50})$$

where  $n_i$  is the number of atoms per volume in level  $i$ ,  $J(\nu_{ij})$  is the mean intensity of the photons at frequency  $\nu$  corresponding to the energy difference between the two levels  $\Delta E_{ij} = h\nu_{ij}$  interacting with the atoms, and  $B_{ij}$  is the **Einstein absorption probability** for the transition  $i \rightarrow j$  to occur.

- d) In the reverse direction, an electron can cascade back down to a lower level through either **spontaneous emission**, which results from the HUP, or **stimulated emission**, in which a passing photon stimulates the transition to occur. Einstein wrote down this de-excitation rate as

$$R_{ji} = n_j A_{ji} + n_j J(\nu_{ij}) B_{ji} = n_j (A_{ji} + J(\nu_{ij}) B_{ji}) , \quad (\text{I-51})$$

where  $n_j$  is the number of atoms in upper level  $j$  per  $\text{cm}^3$ ,  $B_{ji}$ , the **Einstein stimulated-emission probability**, and  $A_{ji}$  is called the **Einstein spontaneous-emission probability** (called the *Einstein A-value* for short).

- e) In thermal equilibrium, *detailed balance* occurs, so  $R_{ij} = R_{ji}$ , and Boltzmann's equation describes the statistics of the level populations:

$$\frac{n_j}{n_i} = \frac{n_j^*}{n_i^*} = \frac{g_j}{g_i} e^{-h\nu_{ij}/kT} , \quad (\text{I-52})$$

where the  $g$ 's are the statistical weights of the levels (see below),  $k = 1.38062 \times 10^{-16}$  erg/K =  $1.38062 \times 10^{-23}$  J/K, is Boltzmann's constant,  $T$  the temperature of the gas composed of the atoms, and the \* indicates that the level densities are at equilibrium values. As well, the radiation field is *thermalized* in equilibrium, and as such, the mean intensity is given by the **Planck function**,

$$J(\nu_{ij}) = B_\nu(T) = \frac{2h\nu_{ij}^3/c^2}{e^{h\nu_{ij}/kT} - 1} . \quad (\text{I-53})$$

- f) With these relations, the detailed balance equation becomes

$$n_j [A_{ji} + B_{ji} J(\nu_{ij})] = n_i B_{ij} J(\nu_{ij}) \quad (\text{I-54})$$

$$n_j^* [A_{ji} + B_{ji} B(\nu_{ij}, T)] = n_i^* B_{ij} B(\nu_{ij}, T) . \quad (\text{I-55})$$

- g) Solving for  $B(\nu_{ij}, T)$  gives

$$\begin{aligned} B(\nu_{ij}, T) &= \frac{A_{ji}}{(n_i^*/n_j^*)B_{ij} - B_{ji}} \\ &= \frac{A_{ji}/B_{ji}}{e^{h\nu_{ij}/kT} \left( \frac{g_i B_{ij}}{g_j B_{ji}} \right) - 1} . \end{aligned} \quad (\text{I-56})$$

- h) Since the Einstein coefficients and statistical weights are independent of  $T$ , it follows that

$$\frac{A_{ji}}{B_{ji}} = \frac{2h\nu_{ij}^3}{c^2} \quad (\text{I-57})$$

$$g_i B_{ij} = g_j B_{ji} . \quad (\text{I-58})$$

## 2. The Lifetime of an Excited State.

- a) In absence of EM fields from photons, we can solve Eq. (I-48) to determine the length of time that an electron will stay excited.

- i) Ignoring the absorption and stimulated emission terms in Eq. (I-48), we get the following differential equation:

$$dN_j = -A_{ji}N_j dt . \quad (\text{I-59})$$

- ii) The solution to this DE is trivial giving

$$N_j(t) = N_j(0) e^{-A_{ji}t} , \quad (\text{I-60})$$

where  $N_j(0)$  is the number of atoms with electrons in excite state  $j$  at some initial time (set to zero here).

- iii) From Eq. (I-60) we see that the number of atoms in the excited state decreases exponentially over time with a time constant of

$$\tau_j = \frac{1}{A_{ji}} . \quad (\text{I-61})$$

We call  $\tau$  the lifetime of the ( $j$ ) state (don't confuse this with the optical depth variable  $\tau_\nu$ ). Technically, it is the time it takes for  $N_j(t)$  to reach  $1/e \approx 0.368$  of its initial value.

- b) From this analysis, the Einstein  $A$ -value is essentially the reciprocal of the probable time span an  $e^-$  stays in an excited state before spontaneously decaying to a lower level. This is what we are referring to in the energy-time description of the HUP (*i.e.*,  $\Delta E \Delta t \geq \hbar/2$ ), where  $\tau = \Delta t$  from the HUP equation.
- c) **Note that Eq. (I-61) is valid only for an idealized two-level atom, or for the two lowest energy levels in an atom.** Most of time, an excited atom has many different **decay modes** to states that lie at lower energies.

In that case the transition rates *add*, and the net lifetime is

$$\tau_j = \frac{1}{A_{j1} + A_{j2} + A_{j3} + \dots} = \left( \sum_{i=1}^{j-1} A_{ji} \right)^{-1}, \quad (\text{I-62})$$

where in this sum, the  $j$  state always has a higher energy than the various  $i$  states it *talks* to.

- d) The value of the Einstein- $A$  value is sensitive to **selection rules** of a transition occurring (see §I.I on Quantum Numbers).

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**Example I–5.** Electrons will stay in the ground state of any atoms for an infinite amount of time unless a photon or a collision with another particle knocks it to a higher level. However as mentioned above, electrons will stay in an excited state for only a short period of time. The Mg II  $k$  transition at 2795 Å has an Einstein  $A$ -value of  $2.67 \times 10^8 \text{ s}^{-1}$ . Since the lower level of this transition is the ground state, that means an  $e^-$  will stay in the Mg II  $k$ -line excited state for an average of 3.7 nanoseconds before spontaneously cascading back down to the ground state — as you can see,  $e^-$  don't stay excited very long!

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## H. Opacity

1. The opacity of gas is a measure of the resistance to photon flow.
2. The concept of opacity is what links radiative transfer to quantum mechanics. The opacity of the gas is a function of atomic transition rates, which are related to transition cross sections.

3. As mentioned above, there are 2 basic types of opacity in gas:
  - (1) **continuous opacity** and (2) **line opacity**.
  
4. We have already discussed the *bound-bound* or line transition types. There are 4 basic continuum processes involving the interaction of radiation and matter.
  - a) **Bound-free** (ionization or b-f) transitions  $\implies e^-$  liberated from atom, ion, or molecule. The inverse process (free-bound) is called recombination.
    - i) *Photoionizations*  $\implies$  photon absorption liberates  $e^-$ . The reverse process is called *radiative recombination*.
  
    - ii) *Collisional ionizations*  $\implies$  atom, ion, or molecule collides with an electron (typically) or some other particle (*i.e.*, H I, H<sub>2</sub>, He I, etc.). The reverse process is called *collisional recombination*.
  
  - b) **Free-free** (f-f) transitions.
    - i) *f-f absorption*  $\equiv$  free  $e^-$  absorbs photon in vicinity of an ion  $\implies$  KE of  $e^-$  is altered.
  
    - ii) *Bremsstrahlung*  $\equiv$  free  $e^-$  altered by E-field of an ion giving up a photon (inverse f-f).
  
  - c) **3-body ionizations and recombinations**  $\implies$  photoexcitation (*i.e.*,  $e^-$  jumps from a lower to upper bound state through photon absorption) followed immediately by a collisional ionization (3 particles = atom, photon, colliding particle) and the inverse process is called 3-body recombination.

- d) **Scattering**  $\implies$  photon redirected in its flight path and not absorbed by the gas.
- i) *Thomson* or *electron scattering* results from a free  $e^-$  (or ion) oscillating in an EM field.
  - ii) *Compton scattering* results from an actual collision between a photon and electron (or some type of charged particle)  $\rightarrow$  requires high energy (*i.e.*, X-ray or higher energy) photons.
  - iii) *Rayleigh scattering* results when the oscillating EM field of a photon perturbs, in an oscillating manner, the bound  $e^-$  in the atom or molecule as the photon passes. This in turn affects the EM field of the photon. This process causes the Earth's sky to be blue since the shorter the wavelength, the more efficient (*i.e.*, higher probability) Rayleigh scattering becomes.
  - iv) *Mie scattering* results from photons scattering off of dust particles.

5. Figure I-3 has already shown the 5 distinct physical processes involving **bound-bound** (b-b) transitions.

- a) A b-b transition will typically occur if certain **selection rules** are satisfied (see the end of this section of the notes).
- b) The **line opacity** has the following functional form (neglecting stimulated emission):

$$\kappa_\nu = n_i \alpha_\nu = n_i \frac{\pi e^2}{mc} f_{ij} \phi_\nu, \quad (\text{I-63})$$

or in wavelength units (note that  $\phi(\nu) d\nu = -\phi(\lambda) d\lambda$ )

$$\kappa_\lambda = n_i \alpha_\lambda = n_i \frac{\pi e^2 \lambda_o^2}{m c^2} f_{ij} \phi_\lambda, \quad (\text{I-64})$$

where  $n_i$  is the number density in the lower state,  $\alpha$  is the cross section of the transition,  $\pi e^2/mc$  is the *classical oscillator cross section*,  $f_{ij}$  is the **oscillator strength**, a quantum correction to the classical cross section,  $\lambda_o = \lambda_{ij}$  is the line-center wavelength, and  $\phi$  is the line profile.

- c) Eqs. I-63 & I-64 result from a semi-classical treatment of the matter-radiation interaction (classical EM  $\longrightarrow$  harmonic oscillator & quantum mechanics of matter  $\longleftarrow f_{ij}$ ).
- d)  $f_{ij}$ , the **absorption oscillator strength**, is inversely proportional to the probable amount of time an  $e^-$  will reside in the  $j$ th level. Allowed transitions:  $f_{ij} > 10^{-2}$  (strongest:  $f_{ij} \sim 1$ ). Forbidden transitions:  $f_{ij} < 10^{-8}$  (with semi-forbidden transitions in between the two).
- e) The oscillator strength is related to the Einstein- $A$  value with the following equation:

$$g_j A_{ji} = \frac{8\pi^2 e^2 \nu_o^2}{m c^3} g_i f_{ij} . \quad (\text{I-65})$$

- f) This natural-broadening absorption profile effectively describes the probability of finding an electron at a specific energy in a given energy level — actually, the profile is a convolution of the probability of electrons in both the upper and lower levels of the transition.

## 6. Level Thickness.

- a) The functional form of the energy-level thickness is described by the line profile function. This function,  $\phi_\nu$ , in the opacity equation (Eq. I-63 or I-64) attempts to detail the manner in which a photon is absorbed by the gas  $\implies \phi_\nu$  is called the absorption profile.
- b) We must include not just one atom but the entire ensemble of atoms  $\implies$  we define  $n_i\phi_\nu$  to be the probability of a photon of frequency  $\nu$  traveling in the direction (*i.e.*, solid angle)  $\Omega$  being absorbed by an ensemble  $n_i$  atoms with an bound electron in the lower level.
- c) Correspondingly we define  $n_j\psi_\nu$  to be the probability of an ensemble of  $n_j$  atoms in the excited state emitting a photon of frequency  $\nu$  and direction  $\Omega$  as result of spontaneous and stimulated de-excitation (note that the  $\psi_\nu$  profile is the same for stimulated and spontaneous emission).
- d) Often it is assumed that  $\psi_\nu = \phi_\nu$  (*i.e.*, the emission profile = the absorption profile)  $\implies$  *complete redistribution* of the photons in the line.
- e) As described above, each excited energy state has a natural finite width associated with it in accordance to the HUP (*i.e.*,  $\Delta E \Delta t \geq \hbar/2$ ).
  - i)  $\Delta t = \tau$  (see Eqs. I-61 and I-62) is the probable time that an  $e^-$  stays in an excited state.
  - ii) The thickness of the level (in energy space) can then be described by the HUP:

$$\Delta E \approx \frac{\hbar}{2\tau} . \quad (\text{I-66})$$

iii) Note that the ground state has an infinite lifetime and as such is infinitely sharp in energy space (*i.e.*,  $\Delta E = 0$ ).

f) Besides this *natural broadening*, states can be broadened further by interactions with other particles  $\implies$  *collisional broadening*. These additional broadening mechanisms are described in detail in the Astrophysics (ASTR-3415) course and will not be addressed further here.

## I. Quantum Numbers: Electronic Configurations, Spectroscopic Notation, and Selection Rules.

1. Here we will describe a mechanism for both identifying electronic states and the selection rules which govern the probability that a transition between two states will occur. At the end of the course, we will re-examine what is described here via the techniques learned in this course.

2. Each element/ion has an **electronic configuration** associated with it, which is based on the periodic table. Each  $e^-$  in that configuration has a characteristic set of quantum numbers.

a)  $n \equiv$  *principal quantum number*  $\implies$  shell ID

$$\begin{array}{rcccccccc} n & = & 1 & 2 & 3 & 4 & 5 & 6 & \dots \\ \text{shell} & : & \text{K} & \text{L} & \text{M} & \text{N} & \text{O} & \text{P} & \dots \end{array}$$

Each shell can contain a maximum of  $2n^2 e^-$ s.

b)  $\ell \equiv$  *orbital angular momentum quantum number*  $\implies$  sub-shell ID.

$$\begin{array}{rcccccccc} \ell & = & 0 & 1 & 2 & 3 & 4 & 5 & \dots & (n-1) \\ \text{subshell} & : & \text{s} & \text{p} & \text{d} & \text{f} & \text{g} & \text{h} & \dots & \end{array}$$

- i) These designations correspond to *sharp* for ‘s’, *principle* for ‘p’, *diffuse* for ‘d’, and *fundamental* for ‘f’. Then each levels above is labeled with the next English letter in alphabetic sequence, except for those previously used.
- ii) This resulted primarily from the appearance of spectral lines that originate out of these levels.
- iii) Each subshell can contain a max of  $2(2\ell + 1) e^-$ s.
- iv) The orbital angular momentum vector can have  $2\ell + 1$  orientations in a magnetic field from  $-\ell$  to  $+\ell$ :

$$-\ell \leq m_\ell \leq \ell .$$

- c)  $s \equiv$  *spin angular momentum quantum number*  $\implies$  spin direction (*i.e.*, up or down).

$$s = \frac{1}{2}$$

The spin angular momentum vector can have  $2s + 1$  ( $=2$ ) orientations in a B-field.

$$m_s = \pm \frac{1}{2} .$$

- d)  $j \equiv$  *total angular momentum quantum number*.

$$j = \ell \pm s .$$

The total angular momentum vector can have  $2j + 1$  orientations ( $-j \leq m_j \leq j$ ) in a B-field.

e) *Examples:*

i) An  $e^-$  with  $n = 2$ ,  $\ell = 1$ , and  $j = 3/2$  is denoted by  $2p_{3/2}$ .

ii) The lowest energy state of neutral sodium, Na I, has an  $e^-$  configuration of  $1s^2 2s^2 2p^6 3s$ . (NOTE: the exponents indicate the number of  $e^-$ s in that subshell, no number  $\equiv 1$ .) Here, the K- and L-shells are completely filled — the  $3s e^-$  is called a **valence  $e^-$** .

3. For one  $e^-$  atoms (*i.e.*, hydrogen-like: H I, He II, C VI, Fe XXVI, etc.  $\implies$  in astrophysics, ionization stages are labeled with Roman numerals: I = neutral, II = singly ionized, etc.), the principal ( $n$ ) levels have energies of

$$E_n = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2}, \quad (\text{I-67})$$

where  $Z$  = charge of the nucleus.

a) Negative energies  $\implies$  bound states

Positive energies  $\implies$  free states

Ionization limit ( $n \rightarrow \infty$ ) in Eq. (I-67) has  $E = 0$ .

b) In astronomical spectroscopy, the ground state is defined as zero potential (*i.e.*,  $E_1 = 0$ ) and atomic states are displayed in terms of *energy level diagrams* (see Figure I-5), where the energy levels are determined by

$$E_n = 13.6 Z^2 \left(1 - \frac{1}{n^2}\right) \text{ eV}. \quad (\text{I-68})$$

$n \rightarrow \infty$  defines the **ionization potential** (IP) of the atom (or ion), so that for H: IP = 13.6 eV, for He II: IP = 54.4 eV, etc.

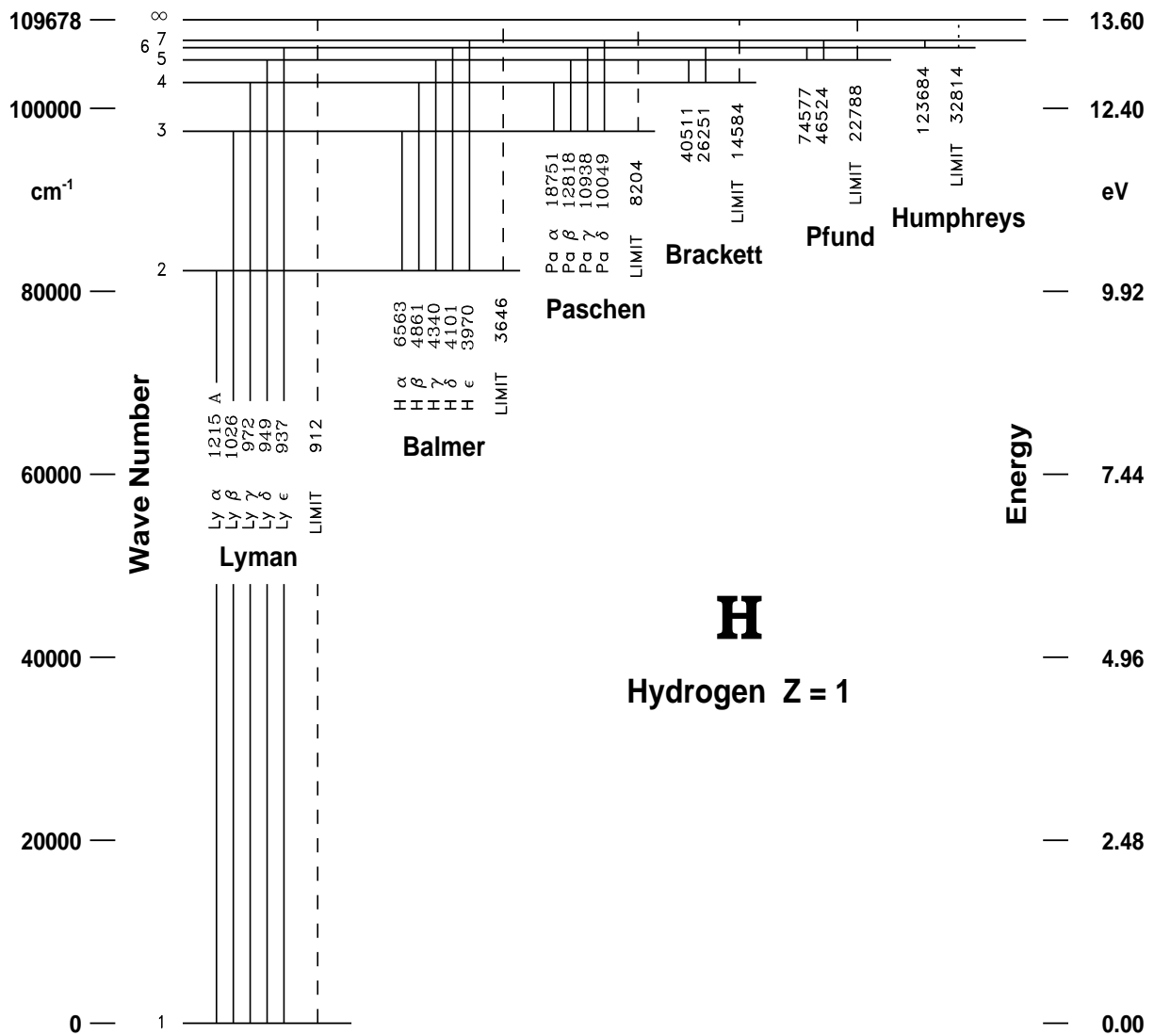


Figure I-5: A partial Grotrian diagram of neutral hydrogen. The lowest 7 levels are shown with various transitions labeled.

c) NOTE:  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 1.602 \times 10^{-12} \text{ erg} = 8066 \text{ cm}^{-1} = 12,398 \text{ \AA} = 11,605 \text{ K}$ .

d) The lowest energy state ( $E = 0$ ) is called the **ground state**. States above the ground are said to be **excited**.

4. For atoms or ions with several  $e^-$ s, the angular momentum vectors are described as follows:

a) Orbital angular momenta  $\vec{\ell}$  are added vectorally:  $L = \Sigma \vec{\ell}$ .

- b) Ditto for spin:  $S = \Sigma \vec{s}$ .
- c) L and S combine vectorally to give the total angular momentum J:  $|L - S| \leq J \leq L + S$ .
- d) A particular pair of values for S and L constitutes a **term**.
  - i) A level or state is designated by its **spectroscopic notation**:  $(^{2S+1})L_J$

$L$	=	0	1	2	3	4	5	...
state	:	S	P	D	F	G	H	...

- ii)  $2S + 1 \equiv$  **multiplicity** of the state  $\implies$  number of  $J$ -levels if  $L \geq S$ . If  $L < S$ ,  $2L + 1 \implies$  number of  $J$ -levels in the state.
- iii)  $S = 0 \implies 2S + 1 = 1 \implies$  singlet state  
 $S = 1/2 \implies 2S + 1 = 2 \implies$  doublet  
 $S = 1 \implies 2S + 1 = 3 \implies$  triplet, etc.
- iv) A level can have *odd* or *even* **parity** depending upon whether the arithmetic sum of the  $\ell$ -values of the participating  $e^-$ s is odd or even.
- e) Another rule that must be followed is the **Pauli Exclusion Principle**: No two electrons can exist in the same quantum state at the same time. All electrons must have a combination of unique quantum numbers.

**5. Hund's Rules** (see Figure I-6): For any given electron configuration,

- a) Higher  $S \implies$  lower energy.

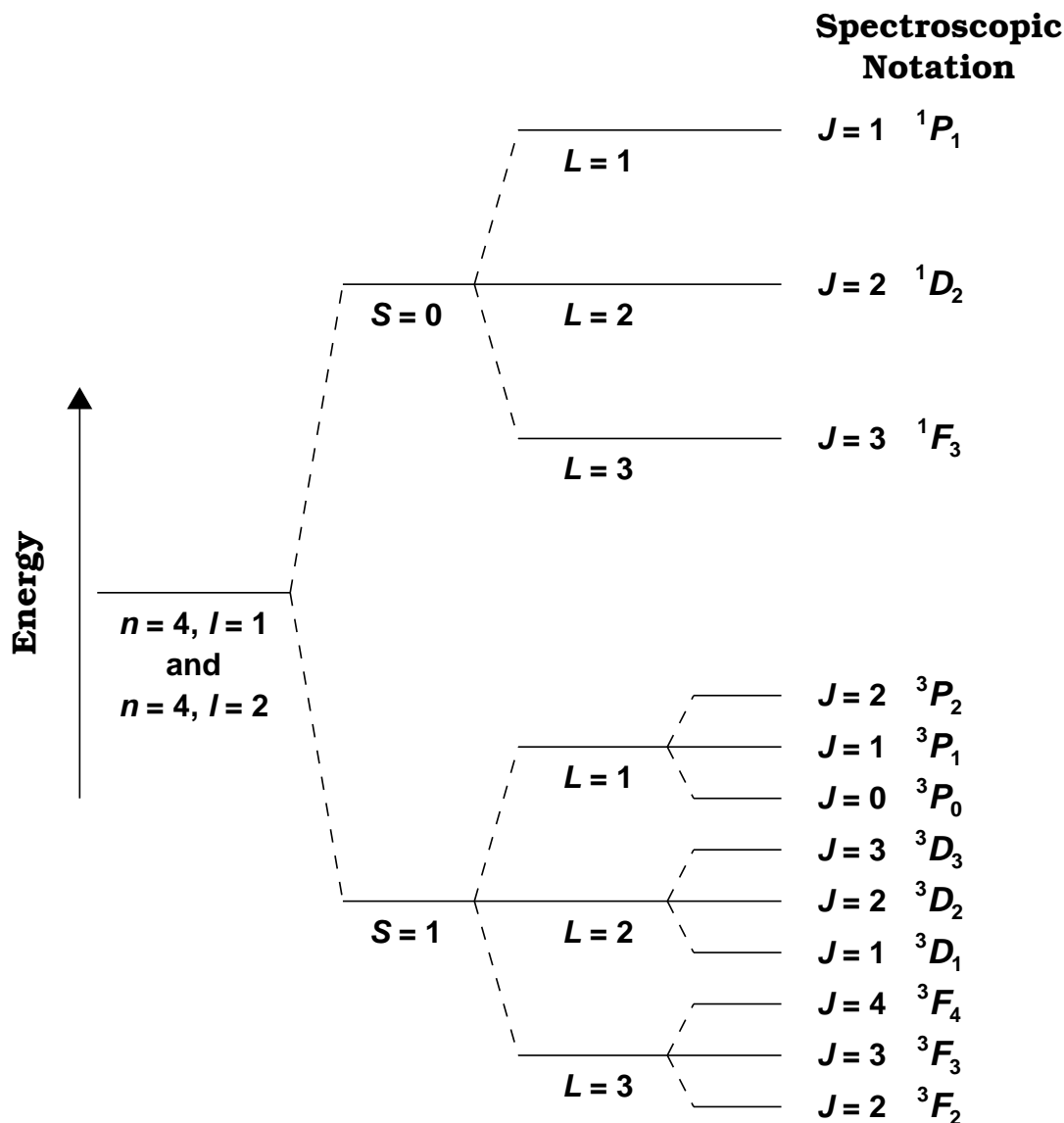


Figure I-6: Hund's rules demonstration: Example of energy splitting in the LS coupling scheme.

- b) Higher  $L$  (for this  $S$  value)  $\implies$  lower energy.
  - c) Higher  $J$   $\implies$  higher energy if subshell is less than half-filled, lower energy if more than half-filled.
6. Various terminology is used to describe transitions in spectroscopy. Table I-2 defines and relates some of these terms (from Allen 1976, *Astrophys. Quant.*, 3rd Ed., p.53).

Table I-2: Atomic Terminology

Atomic Division	Specification	Statistical Weight $g$	Transition
State	Specified by $L, S, J, M$ , or $L, S, M_L, M_S$	1	Component of line
Level	Specified by $L, S, J$ , e.g., $^3P_{1/2}$	$2J + 1$	Spectrum line
Term	Group of levels specified by $L, S$	$(2S + 1)(2L + 1)$	Multiplet
Polyad	Group of terms from one parent term with same multiplicity or $S$		Super-multiplet
Configuration	Specified by $n$ and $\ell$ of all electrons		Transition array

**7. LS or Russell-Saunders coupling:** For lighter atoms with several  $e^-$ s outside closed shells, a spin-orbit interaction exists between the  $e^-$ s which is small compared to the nuclear Coulomb (*i.e.*, electrostatic) interaction. The LS coupling technique (*i.e.*, the spin-orbit interaction is treated as a perturbation) is used in these cases to describe the electronic states and transition probabilities. The following are LS selection rules governing **dipole radiative** transitions:

- a) Only one  $e^-$  jumps.
- b)  $\Delta\ell = \pm 1$  (parity rule).
- c) For terms:
  - i)  $\Delta S = 0$ .
  - ii)  $\Delta L = 0, \pm 1$ .
  - iii)  $\Delta J = 0, \pm 1$  (but  $J = 0 \not\rightarrow J = 0$ ).

**8.** A transition is **allowed** if none of the selection rules are violated. Allowed transitions from the  $E = 0$  (*i.e.*, ground) state are called

**resonance lines** (*i.e.*, the Ca II K line is a resonance line from the  $4s^2S_{1/2}$  state to the  $4p^2P_{3/2}^{\circ}$  state, note that the LS dipole selection rules are not violated). Allowed transitions, for example, are labeled as “Ca II K” or “Ca II 3934 Å” or “Ca II  $\lambda$ 3934.”

9. A transition is said to be **semi-forbidden** if the  $\Delta S$  rule (spin forbidden) or the  $\Delta L$  rule (orbit forbidden) are violated. Semi-forbidden transitions are labeled with one right-side square bracket  $\implies$  “C II]  $\lambda$ 2325.”
10. A transition is said to be **forbidden** (or completely forbidden) if both the  $\Delta S$  and  $\Delta L$  rules are violated and/or the transition involves no change in parity and/or  $|\Delta J| > 1$  and/or  $J = 0 \rightarrow J = 0$ . Forbidden transitions are labeled with both square brackets  $\implies$  “[O III]  $\lambda$ 5006.”
11. Radiative transitions can occur if one or more of the selection rules are violated via a magnetic dipole interaction or electric quadrupole interaction.
12. Transitions between spectroscopic terms in the same subshell are called **intersystem** (or **intercombination**) **lines** and are always semi-forbidden or completely forbidden (note that the transitions among the  $^3P$ ,  $^1S$ , and  $^1D$  terms in the  $2p^2$  subshell of N II and O III are intersystem lines (see the figure passed out in class) — the 5006 Å line between  $(2p^2)^3P$  and  $(2p^2)^1D$  is the famed nebular line, which give nebulae that greenish tint to the naked eye).
13. Transitions within the *ground state* multiplet are called **fine-structure lines** and are always forbidden ( $\Delta\ell = 0, \Delta J = 1$ ). They are almost always in the IR or far-IR (*e.g.*, C II 158  $\mu\text{m}$ ,

${}^2P_{3/2} \rightarrow {}^2P_{1/2}$ ). These lines are efficient in cooling low-temperature (30-300 K) gas.

14. **Hyperfine lines** are transitions resulting from an electron spin flip in the ground state (*e.g.*, H I 21 cm line).
15. When an excited state is not directly coupled via dipole transitions to the ground state, it is called a **metastable state** since it behaves as an  $e^-$  reservoir like the ground state (*i.e.*, the lower level of the He I 10,830 Å line).
16. When elements and ions have the same total number of electrons, they are said to be **isoelectronic sequences** of each other. For instance, the **Grotrian diagram** passed out in class of the N II and O III ions have the same  $e^-$  configurations as C I. Hence C I, N II, and O III are all isoelectronic sequences of each other.

## J. Matter and Energy: Particles or Waves?

1. In 1905, Einstein proposed that the energy in an EM field is not spread out over a spherical wavefront, as Maxwell had assumed, but instead is localized in indivisible clumps — in *quanta*.
  - a) Each quantum of frequency  $\nu$  travels through space at the speed of light  $c$ , carrying a discrete amount of energy  $h\nu$  and momentum  $h\nu/c$ .
  - b) Thus Einstein formulated the *particle* view of light.
  - c) G.N. Lewis subsequently dubbed Einstein's and Planck's quantum of radiation energy a **photon**, the name we use today.
  - d) In Einstein's view, not only is the radiation found in clumps, but *the radiation field itself is quantized!*

- e) Einstein went on to use this photon model to describe the photoelectric effect — the ejection of electrons from a metal, such as sodium, when light impinges on it. Einstein won a Nobel Prize for his theory of the photoelectric effect.
  - f) Millikan reported a precise verification of Einstein's equation of Planck's quantized energy idea,  $E = h\nu$ , and the first measurement of the Planck constant, hence further showing the validity of the particle-like nature of light.
  - g) In 1923, Compton published results of his X-ray scattering experiments, and drove the last nail in the coffin of the wave theory of light. Wavelength shifts were observed as the X-rays scattered off a thin carbon film which were inconsistent with Maxwell's theory. However, the scattering was easily explained in the particle theory of light.
2. However, classical physics is filled with experiments that show light as a wave phenomenon: diffraction and interference are two such experiments.
- a) **Light takes on whatever characteristic for which the experiment is testing.** The observation gives the photon its identity!
  - b) We won't get into the details of this wave-like phenomena in this course since it is covered in detail in optics.
3. As this wave-particle debate continued for photons, a set of experimentalists set out to run known *particles* (*e.g.*, electrons) through the same experiments that produce wave-like characteristics for light.
- a) Surprisingly, electrons also showed wave-like characteristics!

b) When electrons are passed through a double slit, interference patterns arose on the detector that mimics the results for photons — the slits *defracted* the electrons.

c) Electrons were found to have a wavelength of

$$\lambda = \frac{h}{\sqrt{2mE}} , \quad (\text{I-69})$$

where  $m$  and  $E$  are the mass and energy of the electron, respectively.

d) de Broglie came up with the answer — *all microscopic material particles are characterized by a wavelength and a frequency, just like photons*  $\implies$  **matter waves**. This idea led de Broglie, with the help of Einstein, to equations relating to the equality of matter and radiant energy.

i) The photon is a relativistic particle of rest mass  $m_o = 0$  and its momentum is defined by

$$p = \frac{E}{c} . \quad (\text{I-70})$$

ii) The energy of a photon is

$$E = h\nu , \quad (\text{I-71})$$

and using this in Eq. (I-70) gives

$$p = \frac{h\nu}{c} . \quad (\text{I-72})$$

iii) For a wave in free space, the wavelength is  $\lambda = c/\nu$ , so Eq. (I-72) becomes

$$p = \frac{h}{\lambda} . \quad (\text{I-73})$$

iv) For a particle with mass traveling at relativistic velocities (in a zero potential energy field), its total

energy is

$$E^2 = p^2c^2 + m_0^2c^4 . \quad (\text{I-74})$$

- v) If its velocity is non-relativistic ( $v \ll c$ ), then its kinetic energy is simply

$$T = \frac{p^2}{2m_0} , \quad (\text{I-75})$$

where  $T$  is the kinetic energy, or

$$T = E - m_0c^2 . \quad (\text{I-76})$$

- vi) de Broglie proposed that Eqs. (I-71) and (I-73) be used for material particles as well as photons. Thus, for electrons, atoms, photons and all other quantum particles, the energy and momentum are related to the frequency and wavelength by

$\begin{aligned} p &= h/\lambda \\ E &= h\nu \end{aligned}$	de Broglie-Einstein equations. (I-77)
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- vii) Notice that the *de Broglie wavelength* equation  $\lambda = h/p$  implies an *inverse* relationship between the total energy  $E$  of a particle and its wavelength, *viz.*,

$$\lambda = \frac{hc/E}{\sqrt{1 - \left(\frac{m_0c^2}{E}\right)^2}} . \quad (\text{I-78})$$

If applied to a photon (by setting the rest mass to zero), this equation reduces to Eq. (I-71). Hence the larger the energy of a particle, the smaller is its wavelength, and *visé versa*.

- e) Trying to understand the meaning of these *matter waves* led Schrödinger and Heisenberg to create the physics of quantum mechanics.