## Chapter 9

# The structure of hydrogen

One of the many goals of the astronomical spectroscopist is to interpret the details of spectral features in order to deduce the properties of the radiating or absorbing matter. In Chapters 4 and 5, we introduced much of the formalism connecting the atomic absorption features observed in spectra with the all-important atomic absorption coefficient,  $\alpha(\lambda)$ . The mathematical form of absorption coefficients are derived directly from the theoretical model of the atom. As such, it is essential to understand the internal working nature of the atom in order to deduce the physical conditions of the matter giving rise to observed spectral features.

The model of the atom is simple in principle, yet highly complex in detail. Employing only first-order physics, we have been extremely successful at formulating the basic atomic model, including the internal energy structure, transition probabilities, and the spectra of the various atoms and ions. However, first-order physics is not complete enough to precisely describe the internal energy structure of the atom nor the observed spectral features. Enter the complexity of higher-order physics, which are most easily discussed in terms of small corrections to the first-order model.

The simplest atom is hydrogen, which comprises a single proton for the nucleus and a single orbiting electron. The complexity of the physics increases as the number of nuclear protons and orbiting electrons increases. The hydrogen atom serves to clearly illustrate the effects of higher–order corrections while avoiding the complication of multiple interacting electrons.

In this chapter, we focus on the first–order physics, internal energy structure, and resulting spectrum of neutral hydrogen and hydrogen–like ions (those with a single orbiting electron). We begin with the semi–classic Bohr model, including Sommerfeld's relativisitic corrections. We then briefly address the wave nature of matter. After introducing some basic quantum mechanics, including the

Hamiltonian, wave functions, and expectation values, we then discuss the wave model of the atom. The non-relativistic Schrödinger equation and resulting stationary states of hydrogen are presented. This chapter is effectively a highly focused summary of the extensive material available in many standard texts on quantum mechanics.

In Chapters 10 and 11, we will introduce a property of the electron known as spin, discuss the relativistic wave model, including several higher order modifications to the energy states, and apply the principles developed to model the hydrogen atom to more complex atoms, discuss transition probabilities, and provide the expressions for the atomic absorption cross sections.

## 9.1 The semi-classical model

The atomic model proposed by Bohr (1913) is a semi-quantum mechanical approach to what is essentially classical physics. The model applies well to neutral hydrogen atoms and to so-called hydrogen-like ions (those with multiple protons in their nucleus but only a single bound electron). The Bohr model is based upon two postulates:

- 1. The electron moves in circular orbits about the nucleus. The angular momentum of the electron must be an integer number of Planck's constant h. Thus, only certain electron orbits are allowed.
- 2. The orbit of an electron is a stationary state. An atom emits or absorbs electromagnetic radiation (a photon) only when its electron changes orbits. The energy of the photon equals the energy difference of the initial and final electron orbit.

#### 9.1.1 Stationary states

Bohr's first postulate is expressed

$$\oint p_{\phi} d\phi = \oint \left( m_{\rm N} \omega r_{\rm N}^2 + m_e \omega r_e^2 \right) d\phi = nh, \qquad (9.1)$$

where  $p_{\phi}$  is the total azimuthal angular momentum of the atom, assuming the orbit is confined to a plane. The geometric configuration is illustrated in Figure 9.1*a*, where  $r_n = r_N + r_e$  for a nuclues of mass  $m_N$  and electron of mass  $m_e$  orbiting about a common center of mass in state *n* with angular frequency  $\omega$ . Since the orbits are postulated to be circular, and applying  $m_N r_N = m_e r_e$ , we have

$$p_{\phi} = \mu \omega r_n^2 = n\hbar, \qquad (9.2)$$

where  $\hbar = h/2\pi$ , and where  $\mu = m_e/(1 + m_e/m_N)$ , is the reduced mass of the electron. Assuming a Coulomb potential,  $V(r) = -Ze^2/r_n$ , where Ze is the charge of the nucleus, the total energy of the atoms in state n is

$$E_n = -\frac{Ze^2}{2r_n}, \qquad r_n = \frac{\hbar^2}{\mu e^2} \frac{n^2}{Z} = a_0 \frac{n^2}{Z} \frac{m_e}{\mu}, \qquad (9.3)$$



Figure 9.1: (a) The geometric configuration of the Bohr model in state n. (b) A schematic of the Bohr model with the relative sizes of the first five orbits in units of  $a_0$ . The limit  $n = \infty$  is not to scale. When electrons move from one bound orbit to another, photons with energies given by the energy difference of the orbits are absorbed (upward transition) or emitted (downward transition). A transition between n = 4 and n = 2 is shown, for which the photon has energy  $E_4 - E_2$ . Ionization from n = 1 is also shown.

where

$$a_0 = \frac{\hbar^2}{m_e e^2} = 5.29177 \times 10^{-9} \text{ cm}$$
(9.4)

is the Bohr radius for an infinite mass nucleus, and where the ratio  $m_e/\mu$  explicitly accounts for the reduced mass of the electron. For hydrogen  $\mu/m_e = 0.99946$ . For helium  $\mu/m_e = 0.99986$ .

#### 9.1.2 Orbital energy

Substituting  $r_n$  into  $E_n$  (Eq. 9.3), we obtain the binding energy for orbit n,

$$E_n = -\frac{\mu e^4}{2\hbar^2} \frac{Z^2}{n^2} = -\frac{e^2}{2a_0} \frac{Z^2}{n^2} \frac{\mu}{m_e} = -\frac{m_e c^2}{2} \frac{(Z\alpha)^2}{n^2} \frac{\mu}{m_e},$$
(9.5)

where the last form provides the energy in terms of the rest energy of the electron,  $m_ec^2$ , and the fine structure constant  $\alpha = e^2/\hbar c$ . The constant  $\alpha$  will prove to be a fundamental quantity for atomic spectra once relativistic and higher–order effects are taken into account. We define the Rydberg constant,

$$R = \frac{m_e e^4}{2\hbar^2} = \frac{e^2}{2a_0} = \frac{m_e c^2}{2} \alpha^2 = 2.17987 \times 10^{-11} \text{ erg} = 13.60570 \text{ eV}, \quad (9.6)$$

for an infinite mass nucleus, i.e.,  $\mu = m_e$ . In general, for a hydrogen–like atom with nuclear charge Ze,

$$R_z = Z^2 \frac{\mu}{m_e} R. \tag{9.7}$$

We can thus rewrite Eq. 9.5 in the simplified form

$$E_n = -\frac{R_z}{n^2}.$$
(9.8)

For hydrogen, Z = 1 and  $\mu/m_e = 0.99946$ , yielding  $R_{\rm H} = 13.59843$  [eV].

#### 9.1.3 Transitions and spectra

According to Bohr's second postulate, an electron is induced to move from one bound orbit to another via the absorption of a photon (resulting in a gain of energy to a higher n, less bound state) or emission of a photon (loss of energy to a lower n, more bound state). Such a state transition, called a bound-bound transition, is illustrated in Figure 9.1 between n' = 2 and n = 4, where we denote n as the upper level principle quantum number and n' as the lower level quantum number. The photon energy is the difference between the upper level and lower level binding energies,

$$h\nu = \frac{hc}{\lambda} = E_{n'n} = E_n - E_{n'},$$
 (9.9)

where  $\nu$  is the photon frequency, and  $\lambda$  is the photon wavelength. The transition energy is then

$$E_{n'n} = R_z \left[ \frac{1}{n'^2} - \frac{1}{n^2} \right].$$
(9.10)

For each lower state, n', there is a series of allowed energy differences for n > n'. Consider neutral hydrogen (HI); for n' = 1, the series is called the Lyman series, and for n' = 2, it is called the Balmer series. It is customary to denote the first transition in the Lyman series  $(n' = 1 \leftrightarrow n = 2)$  as Ly $\alpha$ , the second transition in the Lyman series  $(n' = 1 \leftrightarrow n = 3)$  as Ly $\beta$ , etc., in order of the Greek alphabet. For larger n, the transitions are simply numbered, i.e., Ly8, etc. The ionization threshold  $(n = \infty)$ , is known as the Lyman limit. The notation is similar for the Balmer series except that "H" is the prefix, i.e., H $\alpha$   $(n' = 2 \leftrightarrow n = 3)$ , H $\beta$   $(n' = 2 \leftrightarrow n = 4)$ , H $\gamma$   $(n' = 2 \leftrightarrow n = 5)$ , etc. The Lyman series gives rise to ultraviolet spectral lines (3646–6563 Å).

The HI Lyman and Balmer series, and the corresponding n' = 1 and n' = 2HeII series, are illustrated in Figure 9.2 as a function of transition wavelength. The n' = 1 and n' = 2 series of HeII lie in the far ultraviolet (228–304 Å for n' = 1; 912–1640 Å for n' = 2). The dotted line provides the series limit. For presentation purposes, only the first 20 transitions are shown; thus there is a an artificial gap between the last shown transition and the series limit. Note that



Figure 9.2: The spectra of the H<sub>I</sub> Balmer (n = 2) and Lyman (n = 1) series (top panels) and the corresponding spectral series for He<sub>II</sub> (bottom panel). The first 20 transitions are shown for each, including the series limits, which are shown as dotted lines. Note that there are some nearly identical transition wavelengths in the H<sub>I</sub> Lyman series and the n = 2 He<sub>II</sub> series.

several of the spectral lines in the HeII n' = 2 series have virtually identical wavelengths to those in the HI Lyman series<sup>1</sup>.

#### 9.1.4 Energy structure

Due to the many possible energy transitions the energy structure is elucidated using various functional quantities. Written in terms of the differences of the orbital energy,  $E_n$ , these terms include the transition energy, the excitation potential, the ionization energy, and the ground state ionization potential. Here, we briefly define each of these energy terms, noting that the transition energy,  $E_{n'n}$ , was defined in Eq. 9.10.

#### **Excitation** potential

The ground state (lowest energy) of hydrogen or hydrogen–like ions is n' = 1, given by  $E_1 = -R_z$ . The excitation energy is the excess stored internal energy of

<sup>&</sup>lt;sup>1</sup>It would seem that this might cause serious confusion for identfying these particular spectral features in astronomical spectra. In practice, this is not a problem; in atrophysical conditions where H<sub>I</sub> persists primarily in the ground state, n' = 1, the same holds for HeII.

the atom when the electron orbits above the ground state. The energy required to excite an atom to level n > 1 from level n' = 1 is called the excitation potential, and is obtained from Eq. 9.10 according to

$$\chi_n = E_n - E_1 = R_z \left[ 1 - \frac{1}{n^2} \right].$$
 (9.11)

The excitation potential of orbit n is often tabulated in units of electron volts [eV]. Note that the excitation potential of the ground state is always  $\chi_1 = 0$  eV, and that  $\chi_n$  increases with increasing n.

#### **Ionization energy**

The minimum photon energy required to liberate, or free, an electron originally bound in orbit n' is called the ionization energy, and is obtained by setting  $n = \infty$  in Eq. 9.10,

$$E_{\text{I}n'} = E_{\infty} - E_{n'} = -E_{n'} = \frac{R_{\text{z}}}{n'^2},$$
(9.12)

where the subscript "In" denotes this is ionization from level n'.

Incident photons with energies,  $E_{\gamma} = h\nu = hc/\lambda$ , equal to or greater than  $E_{in}$  (using *n* generically) are potential ionizing photons, i.e., those with frequencies or wavelengths in the range

$$\nu \ge \frac{R_{\rm z}}{hn^2} \qquad \lambda \le \frac{hcn^2}{R_{\rm z}}.\tag{9.13}$$

Photons with  $E_{\gamma} = E_{\text{In}}$  will liberate the electon from the atom, but with no kinetic energy. For  $E_{\gamma} > E_{\text{In}}$ , the additional energy above and beyond the ionization energy imparts kinetic energy (velocity) to the free electron

$$v = \left[\frac{2(E_{\gamma} - E_{\rm In})}{m_e}\right]^{1/2}.$$
(9.14)

#### **Ionization** potential

The maximum value of the excitation potential is called the ionization potential; it is the minimum energy required to ionizate the atom from the ground state, n' = 1. As such, it is equal to the ionization energy of the ground state. The ionization potential is given by setting n' = 1 and  $n = \infty$  in Eq. 9.10, giving,

$$\chi_{\rm I} = E_{\infty} - E_1 = -E_1 = R_{\rm Z}.\tag{9.15}$$

It is possible to also define the ionization potential from an arbitrary exited state n > 1, which might be represented with the symbol  $\chi_{1n}$ . However, such a quantity is not commonly tabulated as a "potential energy" when discussing the internal energy structure of the atom. Recall that  $E_{1n}$ , given by Eq. 9.12, provides the energy required to ionize an atom from an arbitrary excited state n > 1.

#### Synopsis

In Table 9.1, expressions for the orbital energy,  $E_n$ , transition energy,  $E_{n'n}$ , excitation potential,  $\chi_n$ , ionization energy,  $E_{\text{in}}$ , and the ground state ionization potential,  $\chi_{\text{I}}$ , are listed for convenience. Note that the ionzation energy from level n is simply the negative of the orbital binding energy, and that the ionization potential from the ground state is simply the Rydberg constant.

Table 9.1: Atomic Energies and Potentials

Energy/Potential	Symbol		Expression	Equation
Orbital Energy Transition Energy Excitation Potential Ionization Energy	$E_n \\ E_{n'n} \\ \chi_n \\ E_{\text{In}}$	=	$\frac{-R_{\rm z}/n^2}{R_{\rm z}(1/n'^2 - 1/n^2)} \\ \frac{R_{\rm z}(1 - 1/n^2)}{R_{\rm z}/n^2} \\ \frac{R_{\rm z}}{n^2} \\ $	9.8 9.10 9.11 9.12
Ionization Potential	$\chi_{\mathrm{I}}$	=	$R_{ m z}$	9.15

The expressions for the energies listed in Table 9.1 do not include relativistic and higher-order corrections and thus do not yield precise values. In multi-electron atoms and ions, the ground state configuration is not n = 1; the ionization potential for these atoms and ions is still the negative of the binding energy, but for the least tightly bound electron (though the energies derived from the Bohr model break down due to additional energy terms arising from electron-electron interactions and charge shielding of the nuclear charge).

#### 9.1.5 Energy diagrams

Energy diagrams are a useful visual aid for illucidating the energy structure and transition energies of the atom. Energy diagrams of neutral hydrogen (HI) and the hydrogen–like, singly ionized helium ion (HeII) are shown in Figures 9.3*a* and 9.3*b*. The first ten energy levels are marked with horizontal lines labeled n = 1, etc. The left axes are the excitation potentials (Eq. 9.11) and the right axes are the bound electron energies (Eq. 9.8). Note that the relative structures of the energy levels for the two example ions are in direct proportion by the scaling of  $Z^2(\mu/m_e)$ .

As previously mentioned, the excitation potential,  $\chi_n$ , is 0 [eV] for the ground state, which has electron binding energy  $E_1 = -R_z$ . As *n* increases above the ground state, the excitation potential increases, always has positive value, and reaches a maximum  $\chi_{\infty} = -E_1 = R_z$ . However, the energy of a bound electron is always negative. As *n* increases, the binding energy decreases in magnitude (getting less negative) until it reaches a maximum value (on an absolute sacle) of 0 [eV] at  $n = \infty$ . In this sense, the excitation potential and the orbital energy are complementary.



Figure 9.3: Energy diagrams for neutral hydrogen (HI, panel *a*) and singly ionized helium (HeII, panel *b*). The left axes give the excitation potential,  $\chi_n$  [eV], and the right axes give the electron energy,  $E_n$  [eV]. The horizontal lines represent the respective binding energies for a given *n*. (*a*) For HI, the first four transitions are shown as vertical lines for the n = 1, or Lyman series, as is the Lyman limit. Also shown are the first three transitions of the n = 2, or Balmer series, as is the Balmer limit. The corresponding wavelengths of the photons are provided (in angströms) for each transition. (*b*) For HeII. The same as for HI, except that the energies are all scaled by  $Z^2(\mu/m_e)$ . (The energies in parenthesis are computed from the expressions listed in Table 9.1; they do not include relativistic and higher–order corrections and are thus not precise values.)

#### 9.1.6 Relativistic corrections

The Bohr model provided a self-consistent theoretical vision of the atom and accurately predicted the observed energy structure and resulting resonant frequencies of transitions (as diagramed in Figrue 9.3). However, high resolution spectral observations at the time showed that the Bohr energies were not precisely correct (the observed energies are shifted slightly) and that several of the transitions have finer structure (miniscule energy splittings).

Sommerfeld (1916) generalized the Bohr model to include elliptical orbits and first order classical relativistic effects. The principle quantum number of an elliptical orbits is the sum of a radial and an azimuthal quantum number,

$$n = n_r + k$$
  $(n_r = 0, 1, 2, 3...) (k = 1, 2, 3, 4...).$  (9.16)

Sommerfeld found that the energies,  $E_n$ , and the semi-major axes,  $a_n$ , of elliptical orbits are identical to the circular orbit energies and radii of the Bohr model (see Eq. 9.3), regardless of the combination of  $n_r$  and k. However, the

semi-minor axes of the orbits vary with k according to  $b_{nk} = a_n \sqrt{1 - \epsilon_{nk}^2}$ , where  $\epsilon_{nk}^2 = 1 - k^2/n^2$ . In Figure 9.4, the relative dimensions of several Bohr– Sommerfeld elliptical orbits are shown on the scale applied to the Bohr circular orbits illustrated in Figure 9.1.



Figure 9.4: Schematic of relative shapes (to scale) of elliptical electron orbits for azimuthal quantum numbers k = 1, 2, and 3. The radial quantum number,  $n_r$ , can take on all integer values, including the condition for circular orbits,  $n_r = 0$ . Thus, the total quantum number,  $n = n_r + k$ , has a minimum at n = k (circular orbit). Orbits up to n = 5 are illustrated, for which the length of the semi-major axis is given by the scale on the left. (Figure adapted from Herzberg, 1944)

The degeneracy of the energies,  $E_n$ , for various combinations of  $n_r$  and k arise because the periodicities of the radial degree of freedom and the azimuthal degree of freedom are spatially aligned (i.e., the ellitpical orbits do not precess, so that the sum  $n_r + k$  represents a single quantum condition). A relativistic treatment of the electron breaks the degeneracy; the mass variation in the electron due to its variable velocity along its orbital path results in precessing orbits. From  $p_{\phi} = \mu \omega r_n^2 = n\hbar$ , the electron velocity of the n = 1 circular orbit is  $v_1 = e^2/\hbar$ . The mass correction is  $m'_e = \gamma m_e$ , where  $\gamma = 1/\sqrt{1-v_1^2/c^2} = 1/\sqrt{1-\alpha^2}$ , and where  $\alpha = e^2/\hbar c$  is the fine structure constant mentioned above. This yields a ~ 0.003% increase in  $m_e$ .

For the generalize elliptical orbits shown in Fig 9.4, Sommerfeld showed that the azimuthal angular precessions of the semi-major axes per orbit cycle are given by  $\Delta \phi = 2\pi(\gamma_k - 1)$  where  $\gamma_k = 1/\sqrt{1 - (Z\alpha)^2/k^2}$ . In Figure 9.5*a*, an example of the precession of a Bohr–Sommerfeld elliptical orbit is illustrated. The orbits are rosettes formed by the precession of the semi-major axis, which advances by an angle  $\Delta \phi$  each cycle. For hydrogen, the precession is on the order of 30 seconds of arc for k = 1.

Neglecting terms higher than  $\alpha^2$ , the fractional energy perturbation to the

Bohr energy for bound state nk is

$$\frac{\Delta E_{nk}}{E_n} = -\frac{(Z\alpha)^2}{n^2} \left(\frac{3}{4} - \frac{n}{k}\right),\tag{9.17}$$

so that energy of the state is

$$E_{nk} = E_n \left( 1 + \Delta E_{nk} \right) \tag{9.18}$$

where  $E_n = -R_z/n^2$  is the Bohr energy. In Figure 9.5*b*, the relativistic corrections due to Eq. 9.17 are shown in units of  $\alpha^{-2}\Delta E_{nk}/E_n$  for hydrogen. For all *k*, the fractional energy correction is negative, so that the electron binding energy is increased ( $E_{nk}$  more negative, as illustrated in Figure 9.5*b*). As *k* increases for a given *n*, the energy splittings become progressively less pronounced.



Figure 9.5: (a) The precession of hydrogen elliptical orbits in due to the relativistic corrections (Figure adapted from Semat, 1955) (b) The magnitude and direction of the energy shifts/splits for hydrogen in units of  $\alpha^{-2}\Delta E_{nk}/E_n$ , given by Eq. 9.17, presented for orbits with principle quantum number in the range n = 1 to 5. The quantum number k is incremented upward for each n. The circular Bohr orbits (n = k) have the smallest corrections.

Sommerfeld showed that the full expression for the energy of the electron in an orbit nk, is given by

$$E_{nk} = \mu c^2 \left\{ 1 + \left[ \frac{(Z\alpha)^2}{n - k + [k^2 - (Z\alpha)^2]^{1/2}} \right]^2 \right\}^{-1/2}, \quad (9.19)$$

where we note that  $m_e c^2 = 2R/\alpha^2$ . Note that an energy shift results from the relativistic correction even for circular orbits in which  $n_r = 0$  and k = n (the Bohr orbits).

In order that the number of energy splittings predicted by the model conform to observations, Sommerfeld postulated that transitions must obey

$$\Delta k = \pm 1. \tag{9.20}$$

The allowed transitions based upon this selection rule are illustrated in Figure 9.6. The Ly $\alpha$  transition can only occur between the n = 2, k = 2 orbit and



Figure 9.6: Energy diagram of the Bohr–Sommerfeld model of neutral hydrogen for the first five levels, n = 1, 2, 3, 4, and 5. The energy scales are identical to those on Figure 9.3. For each n, the Bohr energies are labeled for reference, but in fact the energies are slightly offset for each k state, which are presented horizontally. For k = n, the orbits are circular, and for a given n, the orbit eccentricities increase to the left in the diagram. Applying the  $\Delta k = 1$  Sommerfeld selection rule results in the allowed transition illustrated with angled verticle lines. The Lyman and Balmer series are shown with thicker lines.

the n' = 1, k = 1 orbit; there is no predicted fine structure splitting in any of the Lyman series transitions. Note that three splittings are predicted for each Balmer series transition.

Following Bohr's second postulate, the energy of absorbed or emitted photons is equal to the energy difference

$$h\nu = hc/\lambda = E_{nk} - E_{n'k'}.$$
(9.21)

Though the relativistic energy corrections provides improved agreement with the observed spectrum of hydrogen, especially in its accounting of fine energy splittings, the predicted wavelengths are not accurate within experimental precision. For example, the observed wavelength of the Ly $\alpha$  transition is 1215.6701 Å, the Bohr model predicts 1215.684 Å, and the Bohr–Sommerfeld model (Eq. 9.19) predicts 1215.663 Å.

In addition to the inacccuracies in the predicted wavelengths, the model incorrectly predicts the number of observed splittings. As we shall see in Chapter 10, in the full quantum wave mechanics model,  $Ly\alpha$  is observed to have two fine structure splittings and five hyperfine structure splittings. In the final analysis, the observed energy splittings of atomic transitions are not based on classical precessing elliptical orbits.

## 9.2 The wave nature of matter

The Bohr and Bohr–Sommerfeld models have several short comings: (1) the theoretical formalism is not a full quantum mechanical treatment of the atomic physics, but a semi–classical model based upon ad hoc hypotheses, (2) the observed energy splitting of transitions are not in precise agreement with model predictions, (3) there is no theoretical mechanism to account for the observed relative intensities of different transitions, (4) the quantization and dynamics do not account for the wave nature of matter.

The fundamental principle of the wave nature of matter, as proposed by De Broglie, is that the motion of a particle with mass m and velocity v is dynamically equivalent to a propagating wave with velocity v and wavelength

$$\lambda = h/mv. \tag{9.22}$$

De Broglie's hypothesis suggested that the motion of an electron in an atom be investigated using the formalism of wave mechanics as opposed to classical mechanics. One characteristic of waves is that they constructively or destructively interfere with one another. Furthermore, if a single wave is bound, it can interfere with itself.

These considerations lead directly to the Bohr condition for electrons in bound orbits. A wave bound in a circular orbit will destructively interfere with itself unless the circumference of the orbit is an integral number of wavelengths, or  $n\lambda = 2\pi r$ . Given De Broglie's hypothesis, following substitution for  $\lambda$  from Eq. 9.22, we obtain  $mvr = m\omega r^2 = n\hbar$ , the consequence of Bohr's first postulate (Eq. 9.2). Any "orbit" not satisfying this condition will be destroyed by its own wave motion.

#### 9.2.1 The Schrödinger equation

With three degrees of freedom for the electron, the wave model yields a wide variety of orbital configurations that satisfy the condition of constructive intereference. The effect is that the radius and angular momentum of bound electrons are quantized into discrete allowed stationary states. The single assumption of the wave model of the atom is that the particles obey the laws of wave mechanics, i.e., the particles are described by a wave function,  $\Psi(\mathbf{r},t) = \Psi(r,\phi,\theta,t)$ , which is the solution to a governing time-dependent wave equation. The form of the wave equation that replaces the equation of classical mechanics for particles was first derived by Schrödinger, and is called the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r},t) = H\Psi(\mathbf{r},t),$$
(9.23)

where the Hamiltonian is the energy operator

$$H = T + V = -\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r}, t)$$
(9.24)

where T is the kinetic energy operator,  $V(\mathbf{r}, t)$  is the potential specific to the system under consideration, and  $\mu$  is the reduced electon mass. Written out, the Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{L^2}{\hbar^2 r^2} \right] + V(\mathbf{r}, t), \qquad (9.25)$$

where  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  is the angular momentum with  $\mathbf{p}$  being the instantaneous linear momentum, and where  $L^2$  is the angular momentum operator

$$L^{2} = -\hbar^{2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}} \right].$$
(9.26)

Note that  $\mathbf{r}$  is the radial vector position at which  $\Psi(\mathbf{r}, t)$  is evaluated, which in spherical coordinates is given by the position  $\mathbf{r} = (r, \phi, \theta)$ .

The Hamiltonian expressed in Eqs. 9.25 and 9.26 yields the non-relativistic energy and omits other dynamical and/or electromagnetic interaction terms that arise from additional physical processes (such as between magnetic moments, the binding electromagnetic field itself, the non-point charge distribution of the nucleus, etc.). Such "pertubrations" will be discussed in Chapter 10.

The resulting form of the wave function depends on the exact form of the potential,  $V(\mathbf{r}, t)$ . However, under the conditions that the wave function is single valued, piece-wise smooth, and bounded, there are certain behaviors that are key for deriving the stationary states and transition probabilities of the atom.

#### 9.2.2 The wave function

Born postulated that the square of the wave function describing particles provided the probability of finding the particle within the volume element dV centered on a point at  $\mathbf{r}$  at time t, or  $P(\mathbf{r}, t) dV = |\Psi(\mathbf{r}, t)|^2 dV$ , where the volume element is  $dV = r^2 dr d\Omega = r^2 dr \sin \theta \, d\theta \, d\phi$ . Thus, the probability density of the particle position is

$$P(\mathbf{r},t) = \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t), \qquad (9.27)$$

where

$$\int_{0}^{\infty} \oint \Psi^{*}(\mathbf{r}, t) \Psi(\mathbf{r}, t) \, dV = 1.$$
(9.28)

For a time independent potential,  $V(\mathbf{r}, t) = V(\mathbf{r})$ , the Schrödinger equation permits stationary state solutions,  $\psi_n(\mathbf{r})$ , which take the form

$$\Psi_n(\mathbf{r},t) = \psi_n(\mathbf{r}) \exp\left\{-i(E_n/\hbar) t\right\},\tag{9.29}$$

where  $\psi_n(\mathbf{r})$  satisfies the time independent Schrödinger equation

$$H\psi_n(\mathbf{r}) = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\psi_n = E_n\psi_n(\mathbf{r}).$$
(9.30)

The form of Eq. 9.30 reflects the fact that for bound states, i.e., E < 0, only certain value of  $E_n$  are compatible with normalizable solutions. For such cases,

the  $E_n$  are known as energy eigenvalues and the wave functions  $\psi_n(\mathbf{r})$  are the eigenfunctions of the Hamiltonian operator.

The  $E_n$  are real, whereas the  $\psi_n(\mathbf{r})$  can be complex for bound states, since they exhibit spatial periodicity. The complex energy term,

$$\exp\left\{-i\omega_n t\right\} = \cos\omega_n t + i\sin\omega_n t,\tag{9.31}$$

reflects the oscillation of the steady state with frequency  $\omega_n = E_n/h$ . That is,  $\psi_n(\mathbf{r})$  is the wave function amplitude of the stationary state at  $\mathbf{r}$  and this amplitude oscillates at a frequency in proportion to the expectation energy of the state. The spatial amplitudes are orthonormal,

$$\int_{0}^{\infty} \oint \psi_{n}^{*}(\mathbf{r})\psi_{n'}(\mathbf{r}) \, dV = \delta_{nn'}, \qquad (9.32)$$

where  $\delta_{nn'}$  is the Dirac  $\delta$ -function

$$\delta_{nn'} = \begin{cases} 1 & n' = n \\ 0 & n' \neq n. \end{cases}$$
(9.33)

#### 9.2.3 Energies and time dependence

The expectation value,  $\langle a \rangle$  of a given operator, A, is given by the integral over all space  $\langle a \rangle = \int \oint \Psi^*(\mathbf{r}, t) A \Psi(\mathbf{r}, t) dV$ ; thus, the energy for eigenstate n in Eq. 9.29 is obtained using the Hamiltonian operator

$$E_n = \langle H \rangle = \int_0^\infty \oint \psi_n^*(\mathbf{r}) \, H \, \psi_n(\mathbf{r}) \, dV. \tag{9.34}$$

Since the Schödinger equation is linear, the superposition principle applies, so that the full time dependent solution can be written

$$\Psi(\mathbf{r},t) = \sum_{n} c_n(t) \psi_n(\mathbf{r}) \exp\left\{-i(E_n/\hbar) t\right\}, \qquad (9.35)$$

where the  $c_n(t)$  are time dependent coefficients each providing the amplitude of the eigenstate n at time t. The energy at time t is

$$E(t) = \int_0^\infty \oint \Psi^*(\mathbf{r}, t) H \Psi (\mathbf{r}, t) dV.$$
(9.36)

Thus, the state of a system at time t can be interpeted as a superposition of stationary states in proportion to the values of  $c_n(t)$ ; conversely, the state of the system may be a single stationary state in state n' provided  $c_{n'}(t) = 1$  and  $c_n(t) = 0$  for all  $n \neq n'$ . It is also possible that Eq. 9.35 may represent a transitioning between stationary states at some time t. For transitioning to occur, i.e., time changes in the  $c_n(t)$  coefficients, the Hamiltonian must have a time dependence. It is common practice to solve for the  $c_n(t)$  assuming a small amplitude time dependent pertubation to the time independent Hamiltonian. This is known as time–dependent pertubation theory.

### 9.3 Bound stationary states

The simplest atoms are neutral hydrogen and hydrogen–like ions, which have a single orbiting electron. As with the Bohr model, a Coulomb potential,  $V(r) = -Ze^2/r$ , is applied, where Ze is the charge of the nucleus. Substituting into the time independent Schrödinger equation (Eq. 9.30) and manipulating via separation of variables, terms can be combined such that the effective potential is

$$V_{\rm eff}(r) = -V(r) + \frac{l(l+1)\hbar^2}{2\mu r},$$
(9.37)

where l is the angular momentum quantum number (azimuthal degree of freedom).

For  $E \ge 0$ , the effective potential yields a continuum of acceptable eigenfunctions (for which the eigenvalues can take on any value). We will treat the continuum states in § 9.4 For E < 0, only certain acceptable eigenfunctions and eigenvalues solve the Schödinger equation. As such, the wave function is forced to have an integer number of nodes in the radial, and both the azimuthal and polar coordinates. The eigenfunctions are of the form

$$\psi_{nlm}(r,\phi,\theta) = R_{nl}(r) Y_{lm}(\phi,\theta), \qquad (9.38)$$

where  $R_{nl}(r)$  is the radial component, and where  $Y_{lm}(\phi, \theta)$  is the spherical harmonic function, which governs the azimuthal and polar modulations of  $R_{nl}(r)$ . As we shall see, the values of l and m are constrained by the periodic boundary conditions and the requirement of constructive wave interference.

The principle quantum number is

$$n = n_r + l + 1, \tag{9.39}$$

where  $n_r$  is the radial quantum number (recall the Bohr–Sommerfeld model). Since  $n_r = 0, 1, 2, ...$ , we see that the maximum angular momentum quantum number for level n is the integer  $l_{max} = n - 1$ . Thus, the allowed values of l are the integer values

$$l = 0, 1, 2, \dots, n - 1. \tag{9.40}$$

In terms of the elliptical orbits of Bohr–Sommerfeld, we have k = l+1, for which lower values corresponded to higher eccentricity (lower angular momentum) for a given n. The values of m are geometerically limited to the integers -l, -l+1, ..., 0, ..., l-1, l.

#### The radial component

The full general expression for the radial component is,

$$R_{nl}(r) = -\left[\left(\frac{2Z}{a_{\mu}}\right)^{3} \frac{(n-l-1)!}{2n[(n+l)!]^{3}}\right]^{1/2} \rho^{l} \exp\left\{-\frac{\rho}{2}\right\} L_{n+l}^{2l+1}(\rho)$$
(9.41)

where  $L^{2l+1}_{n+l}(\rho)$  is the associated Laguerre polynomial,

$$L_{n+1}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!(2l+1+k)!} \frac{\rho^k}{k!},$$
(9.42)

and where

$$\rho = \frac{2Z}{na_{\mu}}r \qquad a_{\mu} = \frac{\hbar^2}{m_e c^2} \frac{m_e}{\mu} = a_0 \frac{m_e}{\mu}.$$
(9.43)



Figure 9.7: The radial component of the wave functions,  $R_{nl}(r)$  versus  $r/a_{\mu}$  for the first three *n* levels.

The  $L^{2l+1}_{n+l}(\rho)$  are equivalent to the confluent hypergeometric functions times a multiplicative constant

$$L_{n+1}^{2l+1}(\rho) = -\frac{[(n+l)!]^2}{(n-l-1)!(2l+1)!} {}_1F_1(l+1-n,2l+2,\rho),$$
(9.44)

where

$${}_{1}F_{1}(a,c,z) = \sum_{k}^{\infty} \frac{(a)_{k}}{(c)_{k}} \frac{z^{k}}{k!} = 1 + \frac{a}{c} \frac{z}{1!} + \frac{a(a+1)}{c(c+1)} \frac{z^{2}}{2!} + \dots$$
(9.45)

Thus, we also have

$$R_{nl}(r) = \frac{1}{(2l+1)!} \left\{ \left[ 2\mu \frac{Ze^2}{n\hbar^2} \right]^3 \frac{(n+l)!}{2n(n-l-1)!} \right\}^{1/2} \times \rho^l \exp\left\{ -\frac{\rho}{2} \right\} {}_1F_1(l+1-n,2l+2,\rho).$$
(9.46)

The radial component to the wave functions for n = 1, 2, 3 are illustrated in Figure 9.7. Note that the wave functions have an exponential decay for large r (the functions are bounded). There are  $n_r = n - l - 1$  radial nodes, where  $R_{nl}(r) = 0$ .

### The azimuthal and polar components

The  $Y_{lm}(\phi, \theta)$  account for the azimuthal and polar periodicity of the wave properties of the bound electron (the constructive interference). The spherical harmomic functions are written

$$Y_{lm}(\phi,\theta) = \Theta_{lm}(\theta)\Phi_m(\phi), \qquad (9.47)$$

where the azimuthal component is

ć

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp\{im\phi\} = \frac{1}{\sqrt{2\pi}} \left[\cos\phi + i\sin\phi\right].$$
(9.48)



Figure 9.8: The spherical harmonics (based upon the real form) for l = 0 (top panel) and l = 1 for m = -1, 0, +1 (lower panel right to left).

To be single valued, the functions must obey  $\Phi_m(2\pi) = \Phi_m(0)$ , which restricts *m* to integer values,  $m = 0, \pm 1, \pm 2, \pm 3, \dots$  (this is the constructive interference condition following from the De Broglie hypothesis). The polar compo-

nent is

$$\Theta_{lm}(\theta) = \begin{cases} (-1)^m \left[ \frac{(2l+1)(l-m)!}{2(l+m)!} \right]^{1/2} P_l^m(\cos\theta) & m \ge 0\\ (-1)^{|m|} \Theta_{l|m|}(\theta) & m < 0 \end{cases}$$
(9.49)

where  $P_l^m(\cos\theta)$  are the associated Legendre polynomials. Written in full, the spherical harmonics are

$$Y_{lm}(\phi,\theta) = \begin{cases} (-1)^m \left[ \frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{1/2} P_l^m(\cos\theta) \exp\{im\phi\} & m \ge 0\\ (-1)^m Y_{lm}^*(\phi,\theta) & m < 0 \end{cases}$$
(9.50)

which obey the orthonomal property

$$\oint Y_{l'm'}^*(\phi,\theta)Y_{lm}(\phi,\theta)\,d\Omega = \delta_{ll'}\delta_{mm'} \tag{9.51}$$

The azimuthal component,  $\Phi_m(\phi)$ , modulates the amplitude of the wave function in rotation about the z axis. Written in real variables, it is customary to define  $\Phi_m(0) = 1$  for m > 0 and  $\Phi_m(0) = 0$  for m < 0. The polar component,  $\Theta_{lm}(\theta)$ , modulates the amplitude of the wave function in proportion of the angle between the radial vector and the +z axis. In locations where the  $Y_{lm}(\phi, \theta)$  have nodes (zero value), the wave function is vanished. Examples of the l = 0 and the l = 1, m = -1, 0, +1 cases are illustrated in Figure 9.8.

#### 9.3.1 Wave functions

The closed expressions for the wave functions,  $\psi_{nlm}(r,\phi,\theta)$ , for n = 1, 2, 3 are tabulated in Eq 9.52, where we have defined  $\xi = Z/a_{\mu}$ . The radial functions are modulated by the  $Y_{lm}(\phi,\theta)$ , which is to say that the amplitude of the  $R_{nl}(r)$ vary with the azimuthal and polar angle coordinate. For l = 0 the amplitudes are independent of polar coordinate  $\theta$ , and for m = 0 the amplitudes are independent of azimuthal coordinate  $\phi$ . Thus,  $\psi_{n00}(r,\phi,\theta) = R_{n0}(r)$ .

A null angular momentum, l = 0, should not be interpreted as a radial orbit, but as a lack of angular momentum in the wave function itself (no rotation about the origin). With no rotation of the waves, there is no azimuthal interference pattern and therefore no nodes in the azimuthal coordinate. If the wave has angular momentum, then an integer number of azimuthal nodes result from the periodic boundary condition because the wave must constructively interfere with itself to establish a stationary state.

As l increases, the z component to the angular momentum must also obeys the principle of constructive intereference, resulting in nodes along the direction of the polar angle (this is also called space quantization). The polar nodes are constants of rotation about the azimuthal coordinate (if there is a node at

$$\begin{split} \psi_{100}(r,\phi,\theta) &= \frac{1}{\sqrt{\pi}} \xi^{3/2} \exp\{-\xi r\} \\ \psi_{200}(r,\phi,\theta) &= \frac{1}{2\sqrt{2\pi}} \xi^{3/2} (1 - \xi r/2) \exp\{-\xi r/2\} \\ \psi_{210}(r,\phi,\theta) &= \frac{1}{4\sqrt{2\pi}} \xi^{3/2} (\xi r) \exp\{-\xi r/2\} \cos \theta \\ \psi_{21\pm1}(r,\phi,\theta) &= \frac{\pm 1}{8\sqrt{\pi}} \xi^{3/2} (\xi r) \exp\{-\xi r/2\} \sin \theta \exp\{\pm i\phi\} \\ \psi_{300}(r,\phi,\theta) &= \frac{1}{3\sqrt{3\pi}} \xi^{3/2} (1 - 2\xi r/3 + 2\xi^2 r^2/27) \exp\{-\xi r/3\} \\ \psi_{310}(r,\phi,\theta) &= \frac{2\sqrt{2}}{27\sqrt{\pi}} \xi^{3/2} (\xi r) (1 - \xi r/6) \exp\{-\xi r/3\} \cos \theta \\ \psi_{31\pm1}(r,\phi,\theta) &= \frac{\pm 2}{27\sqrt{\pi}} \xi^{3/2} (\xi r) (1 - \xi r/6) \exp\{-\xi r/3\} \sin \theta \exp\{\pm i\phi\} \\ \psi_{320}(r,\phi,\theta) &= \frac{1}{81\sqrt{\pi}} \xi^{3/2} (\xi r)^2 \exp\{-\xi r/3\} (3 \cos^2 \theta - 1) \\ \psi_{32\pm1}(r,\phi,\theta) &= \frac{\pm 1}{81\sqrt{\pi}} \xi^{3/2} (\xi r)^2 \exp\{-\xi r/3\} \sin \theta \cos \theta \exp\{\pm i\phi\} \\ \psi_{32\pm2}(r,\phi,\theta) &= \frac{1}{162\sqrt{\pi}} \xi^{3/2} (\xi r)^2 \exp\{-\xi r/3\} \sin^2 \theta \exp\{\pm 2i\phi\} \end{split}$$

 $\theta = \pi/4$ , for example, the node sweeps out the full  $2\pi$  in the rotation about the z axis).

The total number of nodes (radial + azimuthal + polar) of the wave function is n - 1. We see that the principle quantum number takes on a geometric significance based upon the spatial constraints that govern wave interference patterns.

#### 9.3.2 Angular momentum and wave functions nodes

For the wave model of the atom, we have obtained three integral numbers that characterize the functional form of the quantized stationary states of the electron. These quantum numbers are the principle quantum number n, the angular momentum quantum number, l, and the magnetic quantum number, m. These numbers reflect the three spatial degrees of freedom in which the wave function describing the electron is bound. Recall, the wave function is the solution for which the waves are constructively interfering, and therefore must have integer number of nodes in each degree of freedom. The principle, angular momentum, and magnetic quantum numbers are summarized in Table 9.2.

Table 9.2: Quantum numbers

	Description	Allowed Values	Possibilites
$n \\ l \\ m$	principle angular momentum magnetic	$\begin{array}{l} 1\leq n\leq\infty\\ 0\leq l\leq n-1\\ -l\leq m\leq l \end{array}$	$ \begin{array}{l} \text{infinite} \\ n \\ 2l+1 \end{array} $

Whereas the constant of motion for the Bohr model is the azimuthal orbital angular moment (for the non-relativistic Bohr–Sommerfeld model it is the sum of the azimuthal angular momentum and the radial component), the constants of motion for the Schrödinger wave model are the total angular momentum and the azimuthal (z component) angular momentum. The angular momentum is a vector, **L**, for which the magnitude is

$$|\mathbf{L}| = (L_x^2 + L_y^2 + L_z^2)^{1/2} = \sqrt{l(l+1)}\,\hbar$$
  

$$L_z = m\hbar,$$
(9.53)

where  $L_z$  is the azimuthal or z component in cartesian coordinates. The angular momentum vector and its z projection are illustrated in Figure 9.9a for l = 1and Figure 9.9b for l = 2. The vector processes about the z axis, as shown in Figure 9.9c, has length  $\sqrt{l(l+1)}$  in units of  $\hbar$ . It can reside in any one of 2l+1projections on the z axis with magnitude m in units of  $\hbar$ . For l = 1, the length is  $\sqrt{2}\hbar$  and the possible projections are  $-\hbar, 0, +\hbar$ ; for l = 2, the length is  $\sqrt{6}\hbar$ and the possible projections are  $-2\hbar, -\hbar, 0, +\hbar, +2\hbar$ .

The amplitude of  $\psi_{nlm}(r, \phi, \theta)$  is quantized in the radial direction according to the radial quantum number  $n_r$ , where  $n_r = 0, 1, 2, \ldots$  The relation between nand  $n_r$  is  $n = n_r + l + 1$ , indicating that the principle levels are a coupling of the radial and angular momentum quantization. That is, the radial quantization is a direct result of the angular boundary conditions constraining the angular momentum of the waves. This is why the radial component of the wave function,  $R_{nl}(r)$ , depends upon both n and l.

In principle level n, the number of polar nodes can range from zero (no node) to n-1 nodes; thus, the angular momentum quantum number l can take on the values 0, 1, 2, ..., n-1 (a total of n possibilities). This is a consequence of the angular boundary condition  $0 \le \theta \le \pi$  to the x and y components of the angular momentum. As l increases for a given n, the number of nodes, m, in the azimuthal angular direction are allowed to increase (following the principles of harmonic functions), taking on 2l+1 values ranging over -l, -l+1, ..., 0, ..., l-1, l. The quantum number m is a consequence of the angular boundary condition  $0 \le \phi \le 2\pi$  to the z component of the angular momentum.

The total number of stationary states that an electron can occupy for a given



Figure 9.9: A schematic of the angular momentum vector, **L**, and the z projection,  $L_z$ . These two quantities are the constants of motion for the wave model of the atoms. (a) The confinguration for l = 1, with m = -1, 0, +1. (b) The configuration for l = 2, with m = -2, -1, 0, +1, +2. (c) The precession of **L** around the z axis for l = 1, m = +1/2.

principle level n is represented by  $g_n$ , the multiplicity of states,

$$g_n = \sum_{l=0}^{n-1} (2l+1) = n^2.$$
(9.54)

A schematic of the allowed quantum numbers for n = 1, 2, 3 is presented in Figure 9.10.



Figure 9.10: A schematic chart of the allowed quantum numbers, *nlm*, based upon the spatial boundary conditions and wave interference properties of orbiting electrons.

#### Spectroscopic notation

Each n level is called a shell, and historically, observational spectroscopists named the n = 1 level the K shell, the n = 2 level the L shell, etc. The various angular momentum states, l, were given the spectroscopic notation, "s" for l = 0, "p" for l = 1, "d" for l = 2, and "f" for l = 3. These stand for

"sharp", "principle", "diffuse", and "fundamental". The spectroscopic notation for the various shells and l states are listed in Table 9.3.

Pri	nciple	Angular Moment		ar Momentum	
n	Shell	l	Notation		
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\       6     \end{array} $	K L M N O P	$     \begin{array}{c}       0 \\       1 \\       2 \\       3 \\       4 \\       5     \end{array} $	s p d f g h	sharp principle diffuse fundamental	

Table 9.3: Spectroscopic notation

As an example of the application of the above notation, the stationary state n = 1 with l = 0 resides in the K shell and the wave function and state are denoted "1s". For n = 2 and l = 1, the electron resides in the L shell and the wave function and state are denoted "2p". As an example, there is only a single 1s state (m = 0) and there are three 2p states (m = -1, 0, +1).

#### 9.3.3 Probability density

The interpretation of the wave function rests with Born's postulate, as expressed in Eq. 9.27. Born's postulate is that the meaning of the wave function, as applied to particles, is probabilistic; the amplitude of the wave function squared provides the probability of finding the particle in a volume element centered at  $\mathbf{r} = r, \phi, \theta$ . Thus

$$P(r,\phi,\theta) dV = |\psi_{nlm}(r,\phi,\theta)|^2 dV = \psi_{nlm}^*(r,\phi,\theta)\psi_{nlm}(r,\phi,\theta) r^2 dr d\Omega \quad (9.55)$$

is interpreted as the probability of finding the electon in the stationary state nlm at **r** in the volume element  $dV = r^2 dr d\Omega = r^2 dr \sin\theta \, d\theta \, d\phi$ . The function  $P(r, \phi, \theta) = |\psi_{nlm}(r, \phi, \theta)|^2$  is often called the probability density or the charge density.

Based upon the wave nature of matter, the electron stationary state is not viewed as a mechanical orbit. The stationary state is a wave amplitude for which the spatial probability distribution of the location of a bound electron is the time independent square of this amplitude. Employing a classical view, in a stationary state, the electron can be thought of being a bound kinetic particle moving in a region of space around the atomic nucleus with a stochastic motion such that particle spends greater amounts of time where  $P(r, \phi, \theta)$  is peaked and no time where  $P(r, \phi, \theta) = 0$ . However, this is a very erroneous visualization, for an accelerating charge must radiate and lose energy, whereas the electron, as

a stationary wave pattern (albeit with an amplitude that varies with frequency  $\omega_n = E_n/h$ ) does not.



Figure 9.11: The radial component to the charge density,  $|R_{nl}(r)|^2$ , is plotted as dashed curves for atomic hydrogen for various selected nl states. Plotted as solid curves is the radial distribution function,  $D_{nl}(r)$ , which provides the probability of finding the electron in state nl at radial distance r per unit dr. The vertical scales are arbitrary.

Integrating the probability density over all solid angle (the azimuthal and polar coordinates), we have

$$D_{nl}(r) dr = r^2 |R_{nl}(r)|^2 dr \oint |Y_{lm}|^2(\phi, \theta) d\Omega = r^2 |R_{nl}(r)|^2 dr, \qquad (9.56)$$

where the final step follows from the orthonormal properties of the spherical harmonic functions (Eq. 9.51). The quantity  $D_{nl}(r)$  provides the probability that the electron will be found a distance r from the nucleus per unit dr; it is called the radial distribution function. In Figure 9.11, the radial component to the charge density,  $|R_{nl}(r)|^2$ , and the radial distribution function,  $D_{nl}(r)$ , are plotted for selected nl states for n = 1, 2, and 3.

As discussed in § 9.3 and illustrated in Figure 9.8, the function  $\Theta_{lm}(\theta)$ modulates the amplitude of  $P(r, \phi, \theta)$  with polar angle and the function  $\Phi_m(\phi)$ modulates the amplitude with azimuthal angle about the z axis. For l = 0there is no modulation, but for l = 1, m = 0 the nodes of  $\psi_{nml}(r, \phi, \theta)$  occur at  $\theta = \pi/2$  (the xy plane) and the amplitude maximima occur at  $\theta = 0, \pi$  and are thus aligned with the polar axis (+z and -z). For  $l = 1, m = \pm 1$ , the nodes occur at  $\theta = 0, \pi$  and the maxima at  $\phi = 0, \pi$  (+x, -x) for m = +1 and at  $\phi = \pm \pi/2$  (+y, -y) for m = -1.



Figure 9.12: Intensity diagrams of the probability density functions of the first three principle quantum states are illustrated for the allowed l states and m = 0. The inset provides the geometric viewing angle. The s states are spherically symmetric. The p states have three possible orientations depending upon m. The  $m = \pm 1$  p states are rotated by  $\theta = \pi/2$  with orthogonal x-y orientations for m = -1 and m = +1, The d states have five possible orientations of rotation. (images created by Paul Nylander, http://www.bugman123.com; used by permission)

The probability density functions for the first three principle shells of neutral hydrogen, as viewed from the positive y axis (xz plane), are presented in Figure 9.12. Only m = 0 states for  $mln \ 100 \ (1s)$ , 200 (2s), 300 (3s) 210 (2p), 310 (3p), and 320 (3d) are shown. Based upon the behavior of the spherical harmonic component to the wave function, the  $m = \pm 1$  states for 2p yield probability density functions rotated into the xy plane (nodes in the  $\pm z$  direction) with azimthal rotation (peak amplitude in the  $\pm x$  direction for l = +1 and peak amplitude in the  $\pm y$  direction for l = -1; refer to Figure 9.8). We note that the direction of the axes is an arbitrary construct. Similar rotations apply for the 3p states.

These functions illustrate that the view of an electron as an orbiting particle must be abandoned in favor of the view that the charge density of the electron

is distributed spatially in proportion to the square of the wave function. This is the wave mechanics interpretation of the stationary bound state.

#### 9.3.4 Energy structure and spectra

The eigenenergies of the stationary states,  $\psi_{njm_j}(\mathbf{r})$ , obtained via Eq. 9.34, are identical to those of the Bohr model, namely

$$E_n = -\frac{\mu e^4}{2\hbar^2} \frac{Z^2}{n^2} = -\frac{R_z}{n^2}.$$
(9.57)

for an electron with principle quantum number n bound to a hydrogen–like atom with nuclear charge Ze. For the non–relativistic Schrödinger model, there are  $g_n = n^2$  multiplicity of states for level n with equal energy (when we introduce the electron spin, this multiplicity is doubled).

Consequently, the non-relativistic wave mechanics approach to describing the bound stationary states of electrons in the hydrogen atom yields the same transitions and spectral features (§ 9.1.3) and the same energy structure (§ 9.1.4) as the non-relativistic Bohr model of the atom. However, we note that the physical interpretations of the energy states and transitions are very different for the wave model of the atom as compared to the Bohr model (we will explore this in subsequent discussion).

## 9.4 Continuum states

$$n = -i\frac{Z}{k} \tag{9.58}$$

is imaginary. k can take on any value for  $k \ge 0$ .

$$R_{nl}(r) = \frac{2Z^{1/2}(2kr)^l \exp\{-ikr\}}{(2l+1)! \sqrt{1-\exp\{-2\pi n\}}} F(in+l+1,2l+1,2ikr) \prod_{s=1}^l \sqrt{s^2+l^2}$$
(9.59)

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## Chapter 10

# Finer structure

Relativistic corrections, electron spin, and the Dirac Hamiltonian are then introduced, following which the fine–structure stationary states are presented. Most of what is needed to be known for ultraviolet and optical spectroscopy is a result of the Dirac theory. However, we explore higher–order modifications to the energy states, including the Lamb shift (due to radiative corrections), hyperfine structure, and isotope shifts.

## 10.1 Spin

There is an additional quantized state of the electron, called spin, that is not spatial in nature, but does behave as an additional component to the angular momentum. In 1922, the Stern–Gerlach experiment yielded the unexpected result that silver atoms beamed through a magnetic field were deflected into two discrete beams (they were predicting only a single deflection, if any, in proportion to the magnetic moment of the atom). In 1925, Gouldsmit and Uhlenbeck showed that when atoms are placed in a magnetic field, the spectral lines split in proportion to the field strength (the Zeeman effect).

These results are consistent with the notion that the electron has an intrinisic magnetic moment that is proportional to an intrinisc angular momentum, or spin, of the electron itself. The above experiments are explained if the spin has multiplicity of states  $g_s = 2s + 1$  with s = 1/2. Thus,  $g_s = 2$ ; there are two spin states. The result is that the total magnetic moment of the atom is due to the combined magnetic moment of the electron orbit and the intrinisc magnetic moment of the electron. Thus, we introduce two additional quantum numbers, s = 1/2 and  $m_s = \pm 1/2$ , and the spin wave function, denoted  $\chi_{m_s}$  (which obeys all orthonormal properties).

A schematic of the electron spin vector and its precession is illustrated in

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Figure 10.1: (a) The spin vector has magnitude  $\sqrt{3/4}\hbar$  and precesses about the z axis with projection  $m_s\hbar$ , where  $m_s = \pm 1/2$ . (b) Schematic of the **S** vector precession for the spin "up" state.

Figure 10.1. Similar to the orbital angular momentum,  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , which has magnitude  $L = \sqrt{l(l+1)}\hbar$  with z component  $L_z = m_l\hbar$ , the electron spin, **S**, has magnitude  $S = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$  with z component magnitude  $S_z = m_s\hbar = \pm (1/2)\hbar$ . Spin is mathematically equivalent to an angular momentum of the electron itself.

The wave equation for state  $nlm_lm_s$  is simply given by

$$\psi_{nlm_lm_s}(\mathbf{r}) = R_{nl}(r)Y_{lm_l}(\phi,\theta)\,\chi_{m_s}.$$
(10.1)

When  $m_s = +1/2$ , the function  $\chi_{+1/2}$  is referred to as a spin "up" state, and when  $m_s = -1/2$ , the function  $\chi_{-1/2}$  is referred to as a spin "down" state. For clarification, the quantum number representing the z component of the oribital angular momentum is hereafter written  $m_l$ .

## 10.2 Spin–Orbit coupling

The orbital angular momentum and the spin combine such that the z component of the orbital angular momentum,  $L_z$ , no longer retains its status as a contant of motion. The new constants of motion are the total angular momentum of the electron, **J**, which is the combination of the orbital and intrinisc angular momenta, i.e., the result of spin–orbit coupling,

$$\mathbf{J} = \mathbf{L} + \mathbf{S}.\tag{10.2}$$

and the z component of **J**, i.e.,  $J_z$ . The magnitude of **J** is  $J = \sqrt{j(j+1)\hbar}$ , where the total angular momentum quantum number is given by

$$j = \begin{cases} s & l = 0\\ l \pm s & l \ge 1, \end{cases}$$
(10.3)

where s = 1/2, and where the z component is in multiples  $J_z = m_j \hbar$ , with

$$m_j = m_l + m_s = -j, -j+1, ..., j-1, j.$$
 (10.4)

Since l takes on n possible integer values from l = 0 to n - 1, we see that j takes on n possible values, j = 1/2, 3/2, ..., n - 1/2. Note that for a single electron,  $j \neq l$  and  $m_j$  must always be a half integer.

Because the constants of motion are now the orbitsal angular momentum,  $\mathbf{L}$ , the total angular momentum,  $\mathbf{J}$ , the z axis projection of the total angular momentum,  $J_z$ , and the z, wave functions are stationary states of these quantities, which are represented by the quantum numbers l, j, and  $m_j$ . The wave functions are written  $\psi_{nljm_j}(\mathbf{r})$ . A common method is to compute the wave function as the linear superposition of the Schrödinger stationary states,  $nlm_l$ , and the spin wave functions with stationary state  $m_s$  stationary states,

$$\psi_{nljm_j}(\mathbf{r}) = \sum_{m_lm_s} \alpha_{m_s}^{nljm_j} R_{nl}(r) Y_{lm_l}(\phi, \theta) \chi_{m_s}.$$
 (10.5)

where the sum is over all  $m_l$  and  $m_s$  states for a given nl, and where  $\alpha_{m_s}^{nljm_j}$  are known as the Clebsch–Gordon coefficients, which we do not discuss further.



Figure 10.2: (a) The total angular momentum vector,  $\mathbf{J}$ , as the vector sum of  $\mathbf{L}$  and  $\mathbf{S}$ . For this example, l = 1 leading to j = 3/2 and  $m_j = +3/2$ . The new constant of motion,  $\mathbf{J}$ , precesses azimuthally about the z axis with projection  $m_j$ , whereas  $\mathbf{L}$  precesses about  $\mathbf{J}$ . Note that the projection of  $\mathbf{L}$  on the z axis,  $L_z$ , is no longer a constant of motion; however  $\mathbf{S}$  and  $m_s$  remain constants of motion. (b) Schematic of the vector addition emphasizing the magnitudes of the vectors. The total angular momentum,  $\mathbf{J}$ , is represented by the thick line with the solid arrow and has magnitude  $\sqrt{j(j+1)}\hbar = \sqrt{15/4}\hbar$ . The orbital angular momentum and electron spin are shown as thin lines with open arrows, where the magnitude of the angular momentum is  $\sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$  and the magnitude of the spin is  $\sqrt{3/4}\hbar$ , as always. The possible projections of  $\mathbf{J}$  on the z axis are  $m_j = -3/2, -1/2, +1/2, +3/2$ . Only the  $m_j = +3/2$  case is illustrated.

The spin-orbit coupling (vector addition) rules, given by Eqs. 10.3 and 10.4, are schematically illustrated in Figure 10.2*a* for the state l = 1 and spin states resulting in j = 3/2 and  $m_j = +3/2$ . The vector **J** precesses about the *z* axis in one of 2j+1 = 4 possible projections  $m_j\hbar$ , where  $m_j = -3/2, -1/2, +1/2, +3/2$ .

Only the  $m_j = +3/2$  case is illustrated. The **L** vector precesses about the **J** vector, such that its z component,  $L_z$ , is no longer a constant of motion. The spin, **S**, adds to **L**, but with only two possible z axis projections  $m_s\hbar$ , where  $m_s = -1/2, +1/2$ .

The magnitudes of the **J**, **L**, and **S** vectors are illustrated Figure 10.2b. For l = 1, the magnitude of the orbital angular momentum is  $\sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$ . The magnitude of the total angular momentum (illustrated as thick lines with solid arrow), is  $\sqrt{j(j+1)}\hbar = \sqrt{15/4}\hbar$ . There are four possible z axis projections  $m_j = -3/2, -1/2, +1/2, +3/2$ , though only that latter is shown for clarity. The spin is also represented as a thin line with an open arrow, but originating at the head of the angular momentum vector. Not illustrated is that for l = 1, the state j = 1/2 is also possible.



Figure 10.3: A schematic chart, analogue to Figure 9.10, of the total angular momentum quantum numbers, j, and z projection,  $m_j$ , for the l = 0, 1, 2 states per the coupling of  $m_l$  and  $m_s$ . When spin-orbit coupling is accounted, the number of states for level n are doubled, so that  $g_n = 2n^2$ .

In Figure 10.3, the resulting quantum states for the total angular momentum are illustrated for spin-orbit coupling for l = 1, 2, 3. The two spin states of the electron doubles the number of allowed stationary states for a given principle level n, which doubles the multiplicity of states (see Eq. 9.54) from  $n^2$  to

$$g_n = \sum_{l=0}^{n-1} g_s(2l+1) = 2n^2.$$
(10.6)

## 10.3 Relativistic hydrogen model

In § 9.1.6, it was illustrated that Sommerfeld's inclusion of relativistic effects and various angular momentum states yielded Bohr energies either slightly shifted and/or split by minute amounts depending on the quantum number k, i.e., the angular momentum of allowed elliptical orbits for level n.

In the previous section, we illustrated how, for a radially symmetric time– invariant Coulomb potential, the eigenfunctions to the Schödinger wave equation result from spatial quantization (due to periodic azimuthal and polar boundary conditions), and that these quantized stationary states are identified by the three quantum numbers  $nlm_l$ . Having no counterpart in the Bohr model, spin quantization of the electron yields the additional angular momentum component denoted by s and  $m_s$ . The coupling of spin-orbit angular momenta resulted in a superposition of  $m_s$  and  $m_l$  states for the overall  $nlm_lm_s$  states to form j and  $m_j$  states denoted  $nljm_j$ .

The non-relativistic Hamiltonian (see Eqs. 9.25 and 9.26) does not operate on the spin (or magnetic moment of the electron), and therefore, yields energy expectation values independent of spin-orbit coupling. Including spin, the energies are  $2n^2$  degenerate. If the Hamiltonian is constructed to yield the relativistic energy and provides for electron spin, then the energy degeneracy for several of the states in a given principle level n is broken.

Since the interaction energies due to relativistic and spin-orbit effects are tiny fractions of the  $E_n$ , it is common to use pertubation theory. The approach involves writing the Hamiltonian with small magnitude low-order correction terms. The form of the Hamiltonian with relativistic corrections to order  $v^2/c^2$ is

$$H = \frac{p^2}{2\mu} + V(r) - \frac{p^4}{8\mu^3 c^2} + \frac{1}{2\mu^2 c^2} \frac{1}{r^2} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} + \frac{\hbar^2}{8\mu^2 c^2} \nabla^2 V(r).$$
(10.7)

The first two terms are the classical Hamiltonian. The third term is a relativistic correction to the energy. The fourth term is the spin-orbit interaction energy for  $l \geq 1$  electrons, which includes a relativistic correction to the electromagentic potential. The final term is a correction called the Darwin term for l = 0 electrons (due to a "zwitterbewegung", a jittering precession of the electron spin due to interaction of the angular momentum of the photon field transporting the attractive force of nuclear electromagnetic potential and the electron spin).

## **10.4** Fine structure

For the hydrogen atom, the three energy corrections obtained from the second order correction terms in the Hamiltonian (1) relativistic energy, (2) spin–orbit coupling, and (3) the Darwin term, are of roughly equal magnitude. However, for multi–electron atoms, the spin–orbit term dominates.

The sum results of these corrections terms is that the energy levels have a weak dependence on the j state. This results in small shifts and splittings in the Schrödinger energy states. Fine structure is the term invoked to describe these small energy splittings of otherwise energy degenerate stationary states.

#### 10.4.1 Dirac energies

The resulting energy corrections are obtained employing Eq. 9.34. The relativistic energy correction, for example, is given by

$$\Delta E_1 = \int_0^\infty \oint \psi_{nljm_j}^*(\mathbf{r}) \left[ -\frac{p^4}{8\mu^3 c^2} \right] \psi_{nljm_j}(\mathbf{r}) \, dV \tag{10.8}$$

The correction is applied by adding  $\Delta E$  to  $E_n$  (Eq. 9.57). The other correction terms to the energy are similarly computed and added. We note that the mean value of the spin–orbit term  $\mathbf{L} \cdot \mathbf{S}$  is

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \langle \mathbf{J} \cdot \mathbf{J} - \mathbf{L} \cdot \mathbf{L} - \mathbf{S} \cdot \mathbf{S} \rangle = \frac{\hbar}{2} \left[ j(j+1) - l(l+1) - s(s+1) \right], \quad (10.9)$$

which is instrumental in computing the spin-orbit contribution,  $\Delta E_2$ , to the energy correction following insertion into Eq. 9.34. We have

$$\frac{\Delta E_1}{E_n} = -\frac{(Z\alpha)^2}{n^2} \left[ \frac{3}{4} - \frac{n}{l+1/2} \right],$$

$$\frac{\Delta E_2}{E_n} = -\frac{(Z\alpha)^2}{n} \left[ \frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+1/2)(l+1)} \right] \quad l \neq 0, \quad (10.10)$$

$$\frac{\Delta E_3}{E_n} = -\frac{(Z\alpha)^2}{n} \qquad l = 0,$$

where the total energy correction is  $\Delta E/E_n = (\Delta E_1 + \Delta E_2 + \Delta E_3)/E_n$ .

Following the addition of the three correction terms, the energy for an electron in state nj can be expressed

$$E_{nj} = E_n \left( 1 + \Delta E_{nj} \right) = E_n \left[ 1 + \frac{(Z\alpha)^2}{n^2} \left( \frac{n}{j + 1/2} - \frac{3}{4} \right) \right], \quad (10.11)$$

where  $E_n$  is given by Eq. 9.57, and  $\alpha = e^2/\hbar c$  is the fine structure constant. Since there are 2j + 1 possible projections for  $m_j$ , the  $E_{nj}$  are 2j + 1 degenerate. The form of Eq. 10.11 clearly shows that the energy shifts and splittings scale in direct proportion to  $\alpha^2$  and inversely proportional to  $n^2$ . The resulting energy splittings are very small relative to  $E_n$  (thus the name fine structure).

The exact solution was obtained by Dirac using the so-called Dirac equation based upon full treatment of relativistic energies, electron spin, and interaction of the electron and nuclear magnetic moments as applied to the wave equation. The treatment is well beyond the scope of this text. Dirac's result is

$$E_{nj} = \mu c^2 \left\{ \left[ 1 + \left[ \frac{Z\alpha}{n - (j - 1/2) + [(j + 1/2)^2 - (Z\alpha)^2]^{1/2}} \right]^2 \right]^{-1/2} - 1 \right\},$$
(10.12)

which is equivalent to Eq. 10.11 to order  $(Z\alpha)^2$ . For an infinite mass nucleus, the reduced mass of the electron is replaced with the rest mass,  $m_e$ .

#### 10.4.2 Energy splittings

Since j takes on n possible values, the Dirac theory predicts n energy splittings for level n. Each set of splittings at level n form what is known as a fine structure

multiplet. The fine structure constant,  $\alpha$ , provides the scale of the multiplet energy splitting.

In Figure 10.4, the quantity  $\alpha^{-2}\Delta E_{nj}/E_n$  from Eq. 10.11 is schematically illustrated for n = 1, 2, 3 for the hydrogen atom. We have invoked the spectroscopic notation listed in Table 9.3, i.e., the n = 2, l = 1 state is written 2p, etc., with the added convention of including the subscript j to denote the spin–orbit coupling, or total angular momentum state. Thus, the n = 2, l = 0, j = 1/2state is written  $2p_{1/2}$ , etc.



Figure 10.4: The hydrogen fine structure energy shifts,  $\alpha^{-2}\Delta E_{nj}/E_n$ , for the first three principle levels n = 1, 2, 3. The quantum states are identified using spectroscopic notation. The energy differences between fine structure states are illustrated in the center schematic, whereas the absolute shifts relative to the Shrödinger energies are illustrated on the left.

The result of relativistic spin-orbit coupling is that binding energy of the electron is increased (the energy is more negative) relative to the non-relativistic Shrödinger treatment. Because several of the stationary states remain energy degenerate, there are only n fine structure multiplets for level n. In reality, these energies are not degenerate when higher-order physics is taken into account (see § 10.5). The fine structure splitting is a completely different physical phenomenon than the splittings proposed by Sommerfeld in the Bohr model (which are not in agreement with observations, see Figure 9.5).

#### 10.4.3 Spectral multiplets

Spectral features are due to the emission or absorption of electromagnetic energy accompanied by the electron transitioning from one stationary state to another.

The photon wavelength is

$$\frac{hc}{\lambda} = E_{nj} - E_{n'j'},\tag{10.13}$$

where the energies are given by Eq. 10.11 or 10.12 for states n'j' and nj. Given the fine structure multiplets dictated by Eq. 10.12, it is clear that the transition energies will cluster in multiplets as well. The spectral lines that result from transitions between fine structure multiplets associated with states nl and n'l'are simply called "a multiplet" (of spectral lines).

The strongest transitions (those with the highest probability of taking place), obey the selection rule

$$\Delta l = \pm 1. \tag{10.14}$$

If a spin flip does not occur, we have  $\Delta j = \pm 1$ . If a spin flip occurs we obtain  $\Delta j = 0$ . Thus, the additional selection rule is

$$\Delta j = 0, \pm 1. \tag{10.15}$$

These selection rules are derived from the so-called dipole approximation (we will be discussing this in subsequent sections). Transitions obeying these selection rules are called "permitted" transitions. Less probable transitions, for which  $\Delta l \neq \pm 1$  are understood in terms of the quadrapole approximation; they are known as "forbidden" transitions. There are no restriction on the principle qauntum number, so that  $\Delta n$  can take on any value, including  $\Delta n = 0$ .

In Figure 10.5, the permitted transitions for hydrogen Ly $\alpha$  and H $\alpha$  are illustrated. As also illustrated in Figure 10.4, there is only a single 1s state with j = 1/2 (though its energy is shifted relative to the Schrödinger energy). There are three fine structure states for n = 2, but the  $2s_{1/2}$  and  $2p_{1/2}$  states are energy degenerate (we will see that this degeneracy is broken when we introduce an additional energy correction called the Lamb shift). According to the selection rules, a  $2s_{1/2}-1s_{1/2}$  transition is forbidden, since it would require  $\Delta l = 0$ . Since the path for an electron in the  $2s_{1/2}$  state to transition to the  $1s_{1/2}$  state is forbidden, and  $1s_{1/2}$  is the only n = 1 state, the  $2s_{1/2}$  state is "metastable". Both the  $2p_{3/2}-1s_{1/2}$  and the  $2p_{1/2}-1s_{1/2}$  transitions are permitted with  $\Delta l = \pm 1$  and  $\Delta j = \pm 1$  and 0, respectively. Thus, the fine structure Ly $\alpha$  spectral feature is a doublet.

Similar discussion applies to the H $\alpha$  transition, which can occur as any one of seven transitions. Note that the transition  $3d_{5/2}-2p_{1/2}$  is forbidden, because it would require  $\Delta j = \pm 2$ , even though  $\Delta l = \pm 1$  would otherwise be allowed. Also note that the two transitions  $3p_{3/2}-2s_{1/2}$  and  $3d_{3/2}-1p_{1/2}$  have equal energy. Thus, the Dirac theory predicts that observed spectra will show only five unque features in the H $\alpha$  multiplet.

Applying the selection rules, in the Dirac theory the Lyman series spectral features are all doublets due to the transitions  $np_{1/2}-1s_{1/2}$  and  $np_{3/2}-1s_{1/2}$ , where n = 2 is Ly $\alpha$ , n = 3 is Ly $\beta$ , etc. Each Balmer series spectral feature is a five fold multiplet based upon a seven fold branching of the multiplets at



Figure 10.5: The Ly $\alpha$  doublet  $(2p_{3/2}-1s_{1/2} \text{ and } 2p_{1/2}-1s_{1/2})$  and H $\alpha$  multiplet. These fine structure multiplets arise from the relativistic treatment and spin-orbit coupling. The selection rules are  $\Delta l = \pm 1$  and  $\Delta j = 0, \pm 1$  for permitted transitions. The downward arrows would indicate emission, though the corresponding absorption transitions are also a possibility in the presence of a photon field. Not illustrated is the permitted Ly $\beta$  doublet  $(3p_{3/2}-1s_{1/2})$ and  $3p_{1/2}-1s_{1/2}$ ) Also not illustrated is the allowed  $2p_{3/2}-2s_{1/2}$ , for which  $\Delta n = 0$ .

general level n and the n = 2 multiplets,

$$\begin{array}{rrrr} np_{3/2}-2s_{1/2} & nd_{3/2}-2p_{1/2} & nd_{5/2}-2p_{3/2} \\ np_{1/2}-2s_{1/2} & ns_{1/2}-2p_{1/2} & nd_{3/2}-2p_{3/2} \\ & & ns_{1/2}-2p_{3/2}. \end{array}$$

Note that fine structure energy splittings decrease with increasing n such that spectral feature multiplets from a high n to a much lower n (except to n = 1) are dominated by the low n fine structure. The transitions between fine structure multiplets do not have equal probability of occuring. Thus, the observed spectral multiplets have different intensities. Transition rates and probabilities will be considered in detail in Chapter 11.

## 10.5 Higher order corrections

For astronomical ultraviolet and optical atomic spectroscopy, as with all observational sciences, the level at which the atomic physics must be considered is

a function of the application (the science goals). For a large majority of astronomical applications, fine structure provides a sufficient accuracy to the energy corrections. Fine structure is the theoretical formalism by which the very commonly observed doublet and multiplet spectral features can be exploited for the astronomical sciences. For most applications discussed in this book, knowledge of higher order energy corrections is not required. However, for completeness, we briefly discuss a few additional physical effects. The main higher order corrections are

- The Lamb shift, also known as radiative corrections
- Hyperfine shifts and splittings, also known as hyperfine structure
- Isotope shifts, also known as the mass polarization correction

#### **10.5.1** Radiative corrections

Based upon the treatment of Dirac, in cases where l = 0, the energy levels are shifted with respect to the Schrödinger energies, and in the cases where  $l \ge 1$ , both shifts and fine structure energy splittings result. However, in cases where l' - 1/2 = l + 1/2, where l' = l + 1, the energy shifts away from the Schrödinger levels are identical; Dirac theory predicts that the two states have equal energy. Historically important examples are the  $2s_{1/2}$  and the  $2p_{1/2}$  states, which are energy degererate in the Dirac theory (as illustrated in Figures 10.4 and 10.5).

Early experimental tests of the Dirac energies suggested (inconclusively) that the  $2s_{1/2}$  state has slightly higher energy (is less bound) than the  $2p_{1/2}$  state. Since the selection rules for permitted transitions place no limits on  $\Delta n$ , transitions for which  $\Delta n = 0$  are not dissallowed. In 1947, Lamb and Retherford devised a well–designed experiment in which they conclusively demonstrated that transition frequency between the  $2s_{1/2}$  and  $2p_{1/2}$  state is roughly 1000 [MHz]. The currently accepted value is  $4.3 \times 10^{-6}$  [eV] corresponding to a photon wavelength of 28.34 [cm] and a frequency of 1057.77 [MHz]. This energy difference corresponds to roughly 10% of the fine structure shift in the  $2s_{1/2}$  state, and has been named the Lamb shift.

The quest to explain the Lamb shift facilitated the development of the theory of quantum electrodynamics, which takes into account the quantized nature of the electromagentic field binding the electron in the atom. The mathematical formalism of the theory is beyond the scope of this book. Conceptually, the quantum electrodynamic treatment of the binding force acting on the electron is that the force is carried by virtual photons and that this quantized radiation field can fluctuate in energy so that it has a non-zero lowest energy state. Consistent with the Heisenberg uncertainty principle, this fluctuating energy within the virtual field can change forms as long as energy and momentum are conserved.

Schematics of the quantized radiative interactions (known as Feynman diagrams) are illustrated in Figure 10.6. Time moves forward to the right in the diagrams. The lines represent the motion of particles in space and time and the vertices represent their interactions. Photons are represented with wavey lines.

![](_page_36_Figure_1.jpeg)

Figure 10.6: Feynman diagrams of the interaction of electrons with the electromagnetic field. (a) Photon–electron scattering. (b) Electron–electron scattering. (c) Electron–electron scattering with first order vacuum polarization loop.

Lines that are connected at two vertices are virtual particles. The virtual particles are the carriers of the "force" by which particles interact with one another. Energy and momentum, or the four vector quantity energy–momentum is conserved at each vertice and as time passes (thus resulting in deflected particle paths).

The interaction represented in Figure 10.6*a* is the scattering between an electron and a photon. Note that following the electron-photon interaction, a virtual electron temporarily conserves and carries the energy-momentum of the system through time, following which an electron and photon are released, also conserving energy-momentum. In Figure 10.6*b*, a zeroth order electron-electron scattering is represented. The reaction takes place by the passage of a virtual photon that transports energy-momentum between the electrons.

Perturbation theory accounts for higher order interactions between virtual particles (the carriers of force) during the interactions. In Figure 10.6c, a first order perturbation to the virtual photon is illustrated. The virtual photon converts into a virtual electron-positron pair, which annihilate and convert back into a virtual photon. This first order pheonomenon is known as a vacuum polarization loop. In the atom, where the interaction is between protons and electrons, the electron attracts the virtual positrons and repulses the virtual electron results in these polarization loops (of which there can be an infinite number of possibilities). This polarization in the immediate vicinity of the electron results in a "screeing" of the bare electron charge. The effect of this screening increases with distance from the electron, that is e = e(r). Vacuum polarization also results in a change in  $\alpha$  as a function of proximity of the interacting particles.

These modifications to the forces between particles are known as radiative corrections and, as mentioned above, they are handled through the formalism of quantum electrodynamics. Full treatment requires that all possible combinations of higher order polarization loops be accounted. The energy corrections, based upon the lowest order radiative corrections (see Bethe & Salpeter, 1957), are

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$$\frac{\Delta E_{n0}}{E_n} = -\frac{8\alpha}{3\pi} \frac{(Z\alpha)^2}{n} \left[\frac{19}{13} + K_{n0}\right]$$
(10.16)

for the s (l = 0) states, and are

$$\frac{\Delta E_{nl}}{E_n} = -\frac{8\alpha}{3\pi} \frac{(Z\alpha)^2}{n} \left[ \frac{3}{8} \frac{1}{C_{lj}(2l+1)} + 2\log Z\alpha + K_{nl} \right]$$
(10.17)

or all  $l \neq 0$  states, where

$$C_{lj} = \begin{cases} l+1 & j = l+1/2 \\ -l & j = l-1/2. \end{cases}$$
(10.18)

The terms  $K_{n0}$  and  $K_{nl}$  can be expressed most simply as

$$K_{nl} = \frac{3n^3}{16} \sum_{n} \langle f_{1n} \rangle \left[ (E_n - E_1)/h \right]^2 \log \left| (E_n - E_1)/h \right|, \qquad (10.19)$$

where  $\langle f_{1n} \rangle$  is the mean oscillator strength (see § 11.6.3) for transitions from level 1 to level *n*. The sum is over all levels, including the continuum states<sup>1</sup>. The numeric value of  $K_{n0}$  is on the order of unity to 1.3, and the value of  $K_{nl}$ is on the order of a few × 10<sup>-2</sup> for the l = 1 states and a few × 10<sup>-3</sup> for the l = 2 states.

In Figure 10.7, the energy shifts following radiative corrections, or the Lamb shifts, are illustrated for levels n = 1, 2, 3. The left most levels are the non-relativistic energies from the Schrödinger treatment, whereas the central levels are the fine structure splittings from the Dirac treatment. The Lamb shifts are shown on the right, though the scale is exaggerated relative to the fine structure separations. The selection rules for fine structure transitions apply identically for the Lamb shifted transitions. Thus, the number of spectral multiplets for  $\Delta n \geq 1$  transitions are unchanged by the Lamb shifts which serve only to shift the Dirac energies (and therefore the observed wavelengths of the spectral multiplets).

Since  $\Delta n = 0$  is allowed by the selection rules for transitions, we see that additional radio wavelength spectral features are predicted above and beyond those resulting from fine structure alone; for example, the famous  $2s_{1/2}-2p_{1/2}$  transition, and both the  $3s_{1/2}-3p_{1/2}$  and  $3p_{3/2}-3d_{3/2}$  transitions that are energy degenerate in the Dirac theory.

The fine structure splitting is on the order  $(Z\alpha)^2$ , whereas the magnitude of the Lamb shifts are on the order  $\alpha(Z\alpha)^2$ , placing them on the order of less than a percent of the fine structure separations. For  $j \geq 3/2$  the energy splitting of the levels due to the Lamb shift is  $\sim 0.2\%$  of the fine structure separation. Though we have not yet discussed the natural widths of the states (which are due to Heisenberg's uncertainty principle and the finite lifetime of the states), we point out that the widths of the states can be on the order of the Lamb shifts. For j = 1/2 the natural energy width of the state is narrower than the Lamb shift; but for  $j \geq 3/2$  the natural width is greater than the Lamb shift.

<sup>&</sup>lt;sup>1</sup>For clarity, we have substantially simplified discussion of the treatment. Further details may be sought in standard texts on quantum mechanics of atomic states.

![](_page_38_Figure_1.jpeg)

Figure 10.7: The energy shifts in the n = 1, 2, and 3 levels due to the Dirac fine structure splitting and the radiative corrections (also called the Lamb shift). The energy splittings are not to scale in that the Lamb shifts are expanded relative to the fine structure splittings.

#### 10.5.2 Hyperfine structure

Additional energy splittings, known as hyperfine splittings, were deduced based upon the spectrum of hydrogen. Such detail in the spectrum was noted prior to 1900 by Michelson and by Fabry and Perot. As postulated by Pauli in 1924, there should be a weak interaction between the magnetic moment of the nucleus and that of the electron. Recall that electron spin was hypothesized to explain the magnetic moment of that particle and to explain fine structure spittings. We thus introduce the nuclear spin state, **I**, which follows the quantum rules

$$\begin{split} I &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots \\ |\mathbf{I}| &= \sqrt{I(I+1)} \,\hbar \end{split} \tag{10.20} \\ M_I &= -I, -I\!+\!1, \dots I\!-\!1, I, \end{split}$$

where  $M_I$  provides the magnitude  $I_z = M_I \hbar$ . The nuclear spin is treated similarly as with the electron spin, behaving as an angular momentum of sorts. This spin results in electromagnetic multipoles, of which the magentic dipole moment and electric quadrapole moment dominate in strength. We discuss the dominant of the two, namely the magnetic dipole moment  $\mathbf{M}_{\rm N} = g_I \mu_{\rm N} \mathbf{I}/\hbar$ , where  $g_I$  is the nuclear Lande' factor (of order unity), and  $\mu_{\rm N}$  is the nuclear

magneton,

$$\mu_{\rm N} = \frac{m_e}{m_p} \mu_{\rm B} = \frac{e\hbar}{2m_p c} \tag{10.21}$$

where  $\mu_{\rm B} = e\hbar/2m_ec$  is the Bohr magneton for the electron.

The nuclear and electron magnetic dipole moments interact through both the angular momentum  $\mathbf{L}$  and the spin  $\mathbf{S}$ . The lowest order correction term for the interaction to be added to the Hamiltonian is

$$H = \frac{2}{\hbar^2} \frac{g_I \mu_{\rm N} \mu_{\rm B}}{r^3} \left[ \mathbf{L} \cdot \mathbf{I} - \mathbf{S} \cdot \mathbf{I} + 3 \frac{(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})}{r^2} \right], \qquad (10.22)$$

for  $r \neq 0$ . We simplify the model by writing the total angular momentum as the vector sum of the nuclear and electron components,

$$\mathbf{F} = \mathbf{I} + \mathbf{J} \tag{10.23}$$

where the addition rules are

$$F = |I-j|, |I-j|+1, ..., I+j-1, I+j$$

$$|\mathbf{F}| = \sqrt{F(F+1)} \hbar$$

$$M_F = -F, -F+1, ...F-1, F,$$
(10.24)

and where  $M_F$  provides the magnitude  $F_z = M_F \hbar$ . The vector summation  $\mathbf{F} = \mathbf{I} + \mathbf{J}$  and  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  are illustrated in Figure 10.8. The total angular momentum precesses about the *z* axis with projection  $M_F$ , whereas the electron angular momentum precesses about  $\mathbf{F}$  with *z* projection  $m_j$ .

![](_page_39_Figure_11.jpeg)

Figure 10.8: A schematic of the vector summation of  $\mathbf{I} + \mathbf{J}$  to obtain the total angular momentum. The vector  $\mathbf{S}$  adds with  $\mathbf{L}$  to form  $\mathbf{J}$ , where  $\mathbf{S}$  and  $\mathbf{L}$  precess about the resulting  $\mathbf{J}$ . The vector  $\mathbf{I}$  adds with  $\mathbf{J}$  to form  $\mathbf{F}$ , where  $\mathbf{I}$  and  $\mathbf{J}$  precess about the resulting  $\mathbf{F}$ .

The resulting wave functions are now described by the stationary states  $nljm_jFM_F$ , which can be expressed as linear combinations of the stationary

states  $nljm_jIM_i$ . The resulting energy corrections are

$$\Delta E = 2 \frac{g_I \mu_{\rm N} \mu_{\rm B}}{n^3} \left(\frac{Z}{a_\mu}\right)^3 \left[\frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)}\right].$$
 (10.25)

Substitution of the fundamental constants for the magnetons and reduced Bohr radius,  $a_{\mu}$ , in Eq. 10.25 yields

$$\frac{\Delta E}{E_n} = 2g_I \frac{m_e}{m_p} \left(\frac{\mu}{m_e}\right)^2 \frac{Z\alpha^2}{n} \left[\frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)}\right].$$
 (10.26)

Note that because  $M_{\scriptscriptstyle F}$  can take on 2F+1 values, each hyperfine level is 2F+1 degenerate.

The hyperfine energy levels of hydrogen for n = 1 and 2 are illustrated in Figure 10.9, which shows the states for the combinations of ljF. The number of resulting hyperfine multiplets is always the lesser of the multiplicity of j states or the the multiplicity of I states,

hyperfine multiplets = min 
$$(2I + 1, 2j + 1)$$
. (10.27)

Because I = 1/2 for the hydrogen nucleus, the hyperfine splittings are all doublets. For deuterium, for example, I = 1, so that the hyperfine multiplets are doublets for j = 1/2 and are triplets for all  $j \ge 3/2$ .

![](_page_40_Figure_9.jpeg)

Figure 10.9: The hyperfine energy splits in the n = 1 and 2 levels due to the magnetic dipole interaction approximation as derived from the formalism of the nuclear spin interaction. The energy levels are presented similarly as in Figure 10.7. The scales are exaggerated from left to right, with the hyperfine splitting at the far right labeled as the F states. The permitted transitions, based upon the selection rules of the dipole approximation, are shown as the solid downward arrows. The forbidden ground-state F = 1 to F = 0 transition giving rise to the famous 21-cm emission and absorption is illustrated by the dashed open arrow.

The dipole selection rules for hyperfine transitions are  $\Delta l = \pm 1$ ,  $\Delta j = 0, \pm 1$ , and  $\Delta F = 0, \pm 1$ , with the stipulation that F = 0 to F = 0 is forbidden. There is no restriction on  $\Delta n$ , the principle quantum number. The permitted hyperfine transitions for n = 1, and 2 are illustrated in Figure 10.9 as the solid arrows. For

transitions with  $\Delta n \geq 1$ , the energy differences of permitted transitions, and therefore the ultraviolet and optical spectrum of hydrogen, remain dominated by the fine structure levels. This is because radiative corrections and hyperfine structure are refinements on the order of a tenth of a percent and a hundredth of a percent of fine structure, respectively.

Transitions between F states with  $\Delta n = 0$  comprise the infrared and microwave region of the hydrogen spectrum; the features are often very weak. We note that the famous radio 21–cm radiation is the F = 1 to F = 0 hyperfine transition of the ground state, for which  $\Delta l = 0$ , which is not permitted by the dipole selection rules. This forbidden transition is illustrated in Figure 10.9 as the dashed open arrow.

#### 10.5.3 Isotope shifts

Isotope shifts do not result in energy splittings, but in energy shifts. There are two types of isotope shifts; the first is a mass effect and the second is a volume effect. The mass effect is simply an energy correction due to the dependence of the center of mass of the atom on the finite mass of the nucleus. The second is a correction due to the fact that the nucleus is not a point charge, but has a charge distribution, the form of which depends upon the volume of the nucleus, which in turn depends upon the number of nucleons. Here, we continue our focus on single electron atoms and ions.

#### **Reduced** mass

For hydrogen atoms and hydrogen–like ions, the finite mass of the nucleus is accounted using the reduced mass of the single bound electron,

$$\mu = \frac{m_e}{1 + m_e/m_{\rm N}},\tag{10.28}$$

which is derived from the relations  $r_{\rm N} + r_e = r_n$  and  $m_e r_e = m_{\rm N} r_{\rm N}$ , where the terms are defined and illustrated in Figure 9.1*a*. The Bohr and Schrodinger energies are directly proportional to  $\mu$ . The relativistic and higher–order corrections to these energies are also directly proportional to  $\mu$  (though the hyperfine splittings are proportional to  $\mu^3$ ). The larger  $m_{\rm N}$ , the larger  $\mu$  becomes, asymptotically approaching  $\mu = m_e$ , the value for an infinite mass nucleus. As such, the lightest elements have the greatest energy shifts due to the mass effect.

An important astrophysical quantity is the cosmological deuterium to hydrogen abundance ratio. This ratio can be estimated from absorption systems using the relative strengths of the Lyman series absorption features from hydrogen and dueterium, the latter of which includes and additional neutron of mass,  $m_n$ , in the nucleus. Since transition energies have proportionality  $\Delta E \propto \mu \propto 1/\lambda$ , the fractional wavelength shift between hydrogen and deuterium for any given transition is

$$\frac{\lambda_{\rm D} - \lambda_{\rm H}}{\lambda_{\rm H}} = \frac{1/\mu_{\rm D} - 1/\mu_{\rm H}}{1/\mu_{\rm H}} = \frac{m_{\rm H}/m_{\rm D} - 1}{1 + m_{\rm H}/m_e}$$
(10.29)

where  $m_{\rm H} = m_p$ , yielding  $m_{\rm H}/m_e = 1836.15$ , and where  $m_{\rm D} = m_p + m_n$ , yielding  $m_{\rm H}/m_{\rm D} = 0.500384$ . Thus, the fractional wavelength shift between deuterium and hydrogen spectral features is 0.027%. For the Ly $\alpha$  transition at  $\lambda_{\rm H} = 1216.6701$  Å, this corresponds to an observed wavelength shift of -0.33 Å in the rest-frame.

#### Mass polarization correction

The ratio of the radius of the nucleus to the size of the Bohr orbit is on the order of  $10^{-5}$ . As such, the zeroth order approximation is to treat the nucleus as a point mass and point charge distribution. As early as 1931, it was realized that the different proton distributions of the isotopes for a given atom or ion will produce unique energy shifts. For multi-electron atoms, the interaction term is known as the mass polarization correction.

Electrons in stationary states that have non-zero charge density at the origin will be most strongly affected by the charge distribution of the nucleus. Assuming the volume of the nucleus can be approximated as  $(4\pi/3)R^3 = (4\pi/3)Ar_0^3$ , were  $r_0 \simeq 10^{-13}$  [cm] is roughly the radius of a single nucleon and A is the atomic mass number (the number of nucleons in the nucleus). Within this volume, the charge density will be slightly modified, since the electrostatic potential will depart from  $V(r) = -Ze^2/r$ . We have

$$V(r) = \begin{cases} \frac{Ze^2}{2R} \left(\frac{r^2}{R^2} - 3\right) & r \le R\\ -\frac{Ze^2}{r} & r > R \end{cases}$$
(10.30)

The correction term of the Hamiltonian is the difference between Eq. 10.30 and  $-Ze^2/r$ , yielding

$$H = \frac{Ze^2}{2R} \left( \frac{r^2}{R^2} + 2\frac{R}{r} - 3 \right), \qquad (10.31)$$

for  $r \leq R$  and H = 0 for r > R. The energy correction term<sup>2</sup> is (see Eq. 9.34),

$$\Delta E = \int_0^R \int_0^{2\pi} \int_0^{\pi} \psi_{nlm}^*(\mathbf{r}) H \psi_{nlm}(\mathbf{r}) \, dV$$

$$= \frac{Ze^2}{2R} \int_0^R |R_{nl}(r)|^2 \left(\frac{r^2}{R^2} + 2\frac{R}{r} - 3\right) r^2 dr.$$
(10.32)

Making the approximation  $R_{nl}(r) \simeq R_{n0}(0)$ , and substituting  $|R_{n0}(0)|^2 = (1/\pi)(Z/na_{\mu})^3$  as obtained from Eq. 9.52, we obtain

$$\Delta E = \frac{2}{5} e^2 R^2 \frac{Z^4}{n^3 a_{\mu}^3} = \frac{2}{5} e^2 r_0^2 A^{2/3} \frac{Z^4}{n^3 a_{\mu}^3} \qquad l = 0.$$
(10.33)

 $<sup>^2 \</sup>rm We$  use the states nlm in Eq. 10.32 because we are determining the perturbation correction to the Schrödinger stationary states.

From Eq. 9.5,  $E_n = -(\mu c^2/2)(Z\alpha/n)^2 = (e^2/2a_\mu)(Z/n)^2$ , we the fractional correction is

$$\frac{\Delta E}{E_n} = -\frac{4}{5}A^{2/3}\frac{r_0^2}{a_\mu^2}\frac{Z^2}{n} = -\frac{4}{5}A^{2/3}\frac{r_0^2\mu^2c^2}{\hbar^2}\frac{(Z\alpha)^2}{n} \qquad l = 0,$$
(10.34)

where the ratio  $(r_0/a_\mu)^2 \simeq 5 \times 10^{-10}$ . Note that the nature of the energy correction is that l = 0 electrons are less bound in proportion to the volume of the nucleus. For hydrogen and deuterium, the energy shift is a minimum, on the order of  $\Delta E/E_n \simeq 10^{-10}$  and with  $\Delta E/E_n$  for deuterium a factor of  $2^{2/3} = 1.6$  larger than for hydrogen. The correction is largest for the 1s states of large Z hydrogen–like ions.

#### 10.5.4 Energy scales of corrections

In Table 10.1, the fractional energy corrections to the Schrödinger energies are listed in multiples of the the scaling factor,  $\alpha$ , the fine structure constant. Also included are the dependence to the nuclear charge, Z, and the principle quantum level, n. In the case of hyperfine structure, the ratio  $m_e/m_p$  is an additional proportionality of order  $5 \times 10^{-4}$ . The magnitudes of the fractional corrections to the energies,  $\Delta E/E_n$ , are listed in the last column, where  $E_n$  is the Schrödinger energy,  $(\mu c^2/2)(Z\alpha/n)^2$ . Since  $\Delta E/E = \Delta \lambda/\lambda$ , the third column also provides the order of magnitude of the fractional correction to the transitions wavelength.

Table 10.1: Magnitude of energy corrections

Interaction Energy	Fractional Correction	$\Delta E/E_n$
Fine structure	$Z^2 \alpha^2/n^2$	$5  imes 10^{-5} Z^2/n^2$
Lamb shift	$Z^2 \alpha^3/n$	$4\times 10^{-7}Z^2/n$
Hyperfine structure	$(m_e/m_p)(\mu/m_e)^2 Z \alpha^2/n$	$3\times 10^{-8}(\mu/m_e)^2 Z/n$
Mass polarization	$A^{2/3}(r_0^2\mu^2c^2/\hbar^2)Z^2\alpha^2/n$	$5\times 10^{-10}A^{2/3}Z^2/n$

In the ultraviolet region of the spectrum, for  $\lambda \sim 1000$  [Å] and Z/n = 1, the fractional wavelength corrections are  $\Delta \lambda \simeq \text{few} \times 10^{-2}$ ,  $10^{-4}$ , and  $10^{-5}$  [Å], respectively. For transitions in large Z elements, the fine structure splitting can be as large as a few to several angetoms. The lamb shifts for such transitions are on the order of a few  $\times 10^{-2}$  [Å].

The resolving power of modern astronomical spectrographs are characterized by the quantity  $R_s = \lambda/\Delta\lambda_s$ , where  $\Delta\lambda_s$  is the FWHM of an unresolved feature. The precision of centroiding an absorption feature is typically  $0.1\Delta\lambda_s =$  $0.1\lambda/R_s$ . As such, resolutions on the order of 100 are marginally capable of resolving fine structure multiplets and resolutions on the order of 10,000 are marginally capable of centroiding to the accuracy of the Lamb shift energy corrections. In order to resolve hyperfine multiplets in ultraviolet violet and optical spectra, resolutions greater than 100,000 are required.

Note that the *fractional* energy corrections leading to the fine structure and Lamb shift are independent of the mass shift, i.e., the reduced mass  $\mu$ , whereas the fractional correction leading to hyperfine structure is proportional to  $(\mu/m_e)^2$ . Since  $E_n \propto \mu$ , we see that the resulting energies shifts and/or splittings will in fact be unique to each isotope. As the mass of the nucleus increases, the difference between isotopes dimishes for the mass shift; however, the mass polarization shift increases (for l = 0 states).

## References

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## Chapter 11

# **Atomic Transitions**

The Bohr model was based upon two postulates, and the second of these postulates was in defiance of well established classical laws of physics. In fact, Bohr's model of hydrogen was a dipole configuration with accelerating charges. It was a major shortcoming of the model that the orbiting (and therefore accelerating) electron did not radiate and lose energy. A second shortcoming of the model is that the relative intensities of the emission and absorption transitions in the spectra could not even be addressed. The wave model of the atom naturally resolved both these issues.

A transition occurs over a very short time period in which the electron charge densities oscillate between two stationary states, with a frequency  $\omega_{n'n} = (E_n - E_{n'})/\hbar$ , which is the Bohr frequency corresponding to a photon with wavelength  $\lambda = 2\pi c/\omega_{n'n}$ . In the case of emission, that atom radiates a photon of wavelength  $\lambda$ . In the case of incident photons on the atom, those of wavelength  $\lambda$  will induce the oscillation between stationary states. Because the time dependence of the wave function for the atom is understood as a superposition of all stationary states (Eq. 9.35),

$$\Psi(\mathbf{r},t) = \sum_{n} c_n(t) \psi_n(\mathbf{r}) \exp\left\{-i(E_n/\hbar) t\right\},$$
(11.1)

where the  $c_n(t)$  are time dependent coefficients each providing the amplitide of the eigenstate n at time t, the oscillation can occur simultaneously between multiple states of differen n' and n. The time depedence for stationary states was originally stated in Eq. 9.29, where interpretation is that the stationary state has an amplitude of  $\psi_n(r, \phi, \theta)$  at  $\mathbf{r}$  that oscillates with angular frequency  $\omega_n = E_n/\hbar$ . Recall that although the state is stationary, i.e., spatially bounded, it behaves as standing wave "packets" with oscillation energy  $E_n$ .

The two states between which a completed transition finally takes place is a matter of the time dependence of the  $c_n(t)$ , for which the probability of a given

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state transitioning to another state is  $|c_{n'n}(t)|^2$ , where

where V(r,t) is the time varying potential. The integration of Eq. 11.2 for all n'n yields a matrix of transition probabilities (see Eq. 11.4). A transition process within an atom transpires over a short period of time and is viewed as a multitude of stationary states oscillating between one another at different frequencies, but for which the amplitudes (probabilities) are different; the final transition will occur to one of these states based upon its relative probability (where the resonance mode dominates).

## 11.1 Transition probabilities

Calculating transition probabilities requires time–dependent perturbation theory, the treatment of which is beyond the scope of this book. Essentially, a time dependent "correction term" to the Hamiltonian is introduced that includes the interaction of the electron with the electromagentic field. As with any time varying electromagnetic system, the spatial distribution of emitted radiation, or the sensitivity to absorption, depends strongly upon the orientation of the electric field polarization,  $\hat{\boldsymbol{\epsilon}}$ , with respect to the geometry of the system if the system is not spherically symmetric. As such, we will need to consider various polarization directions, from which averages over all polarization directions can be determined.

Following insertion of the Hamiltonian into the time dependent Schrödinger equation (Eq. 9.23), we obtain that the probability per unit time for a spontaneous transition between state n and state n' (where we adopt the convention n > n') at wavelength  $\lambda$  for a photon with electric field polarization  $\hat{\boldsymbol{\epsilon}}$  and wavenumber  $\boldsymbol{k} = k \,\hat{\mathbf{s}} = (2\pi/\lambda) \,\hat{\mathbf{s}}$ , where  $\hat{\mathbf{s}}$  is the propagation direction into solid angle  $d\Omega$  is (Bethe & Salpeter, 1957)

$$W_{n'n}^{\boldsymbol{k},\hat{\boldsymbol{\epsilon}}} d\Omega = \frac{e^2 \hbar \,\omega_{n'n}}{2\pi m_e^2 c^3} \left| M_{n'n}^{\boldsymbol{k},\hat{\boldsymbol{\epsilon}}} \right|^2 d\Omega,$$
(11.3)

where

$$M_{n'n}^{\boldsymbol{k},\hat{\boldsymbol{\epsilon}}} = \int_0^\infty \oint \psi_{n'}^*(\mathbf{r}) \; [\exp\{i(\boldsymbol{k}\cdot\mathbf{r})\}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{\nabla}] \; \psi_n(\mathbf{r}) \, dV, \tag{11.4}$$

is known as the matrix element, and where

$$\omega_{n'n} = 2\pi\nu = ck = \frac{1}{\hbar}(E_n - E_{n'})$$
(11.5)

is proportional to the energy difference of the unpretrubed two stationary states. The exponential term in Eq. 11.4 arises from the assumption of the weak field approximation to the electromagnetic vector potential, usually denoted  $\mathbf{A}(\mathbf{r}, t)$ .

We have used the shorthand n' to represent the stationary state  $n'l'm'_l$  and n to represent the stationary state  $nlm_l$ , i.e., the non-relativistic Schrödinger states ignoring fine-structure, radiative corrections (Lamb shifts), and hyperfine structure. We will discuss fine structure transitions in § 11.6.

#### Importance of wave functions

The form of the matrix element highlights the critical importance of knowing the wave functions for the stationary states. The calculation of the relative strengths of transitions are related to their transition probabilities; transitions between different stationary states will have different transition probabilities and therefore different intensities. The spontaneous emission intensities are obtained by multiplying the transition probabilities by the photon energy,  $\hbar\omega_{n'n}$ .

As we shall see below, similar principles apply for absorption. Thus, in the context of spectral analysis, we shall see that the measure of the column density from an absorption line has a proportionality to the matrix element, which essentially is the volume integral over the moment of the charge density,  $(\psi_{n'}^*\psi_n)$  between the two stationary states n and n' corresponding to the transition.

## 11.2 The dipole approximation

The weak field assumption can further be simplified invoking the expansion series

$$\exp\{i(\boldsymbol{k}\cdot\boldsymbol{\mathbf{r}})\} = 1 + (i\boldsymbol{k}\cdot\boldsymbol{\mathbf{r}}) + \frac{1}{2!}(i\boldsymbol{k}\cdot\boldsymbol{\mathbf{r}})^2 + \cdots, \qquad (11.6)$$

for small  $\mathbf{k} \cdot \mathbf{r}$ . For transitions on the order of  $10^3$  [Å],  $k \simeq 10^5$  [cm<sup>-1</sup>], whereas the radial distance at where the electromagnetic potential acts on the electron is  $r \simeq a_{\mu} \simeq 10^{-8}$  [cm]. Thus,  $|\mathbf{k} \cdot \mathbf{r}| \ll 1$ , and we have  $\exp\{i(\mathbf{k} \cdot \mathbf{r})\} \simeq 1$ . This is known as the dipole approximation; in this approximation all moments of the magnetic field are vanished.

Substituting the dipole approximation for Eq. 11.6 into Eq. 11.4, and by recognizing that the gradiant in Eq. 11.4 is related to the momentum operator,

$$\mathbf{p} = -i\hbar\boldsymbol{\nabla},\tag{11.7}$$

we make the substitution

$$M_{n'n}^{\boldsymbol{k},\hat{\boldsymbol{\epsilon}}} = \hat{\boldsymbol{\epsilon}} \cdot \frac{i}{\hbar} \int_{0}^{\infty} \oint \psi_{n'}^{*}(\mathbf{r}) \mathbf{p} \psi_{n}(\mathbf{r}) dV$$
  
$$= \hat{\boldsymbol{\epsilon}} \cdot \frac{m_{e}(E_{n} - E_{n'})}{\hbar^{2}} \int_{0}^{\infty} \oint \psi_{n'}^{*}(\mathbf{r}) \mathbf{r} \psi_{n}(\mathbf{r}) dV$$
(11.8)

where the last step invokes the Heisenberg relation,  $\mathbf{p} = (-im_e/\hbar)(\mathbf{r}H - H\mathbf{r})$ . Invoking Eq. 11.5 and rewriting, we have

$$M_{n'n}^{\hat{\boldsymbol{\epsilon}}} = \frac{m_e}{\hbar} \,\omega_{n'n} \left( \hat{\boldsymbol{\epsilon}} \cdot \mathbf{r}_{n'n} \right), \tag{11.9}$$

where

$$\mathbf{r}_{n'n} = \int_0^\infty \oint \psi_{n'}^*(\mathbf{r}) \, \mathbf{r} \, \psi_n(\mathbf{r}) \, dV.$$
(11.10)

An interpretation of Eq. 11.10 is that it is the spatial moment of the charge density between two stationary states. We will work out the evaluation of  $\mathbf{r}_{n'n}$  in § 11.3. Multiplying by the electron charge, one obtains the electric dipole moment between the states

$$\boldsymbol{P}_{n'n} = e\,\mathbf{r}_{n'n}.\tag{11.11}$$

For the approximation applied, the conditions are the  $\mathbf{k} \cdot \mathbf{r} = 2\pi r/\lambda \ll 1$ . Thus, the approximation holds best for small r and longer  $\lambda$ . The approximation breaks down for large n and in the X-ray region. In a semi-classical view, when  $\mathbf{P}_{n'n} \neq 0$ , there exists a dipole moment between the two stationary states n' and n; if this moment is time varying, then radiation is emitted (or can be either emitted via stimulation or absorbed in the presence of incident photons).

#### 11.2.1 Revisiting Bohr's postulates

Bohr's first postulate that the electron does not radiate in its stationary state can now be demonstrated as a consequence of the orthonomal properties of wave functions for bound stationary states (even though they oscillate with frequency  $\omega_n = E_n/\hbar$ ). Following Dirac, we find that there is no electric dipole moment for a stationary state itself,

$$\boldsymbol{P}_{nn} = e \, \mathbf{r}_{nn} = e \int_0^\infty \oint \psi_n^*(\mathbf{r}) \, \mathbf{r} \, \psi_n(\mathbf{r}) \, dV = 0, \qquad (11.12)$$

because  $\mathbf{r}_{nn} = 0$  (recall that the term *n* represent the full state,  $nlm_l$ ). The integral over all solid angle results in a contribution of unity because of the orthonomal properties of the spherical harmonic functions (Eq. 9.51). It is the integral over radius that vanishes,

$$\int_{0}^{\infty} R_{nl}(r) R_{nl}(r) r^{3} dr = 0, \qquad (11.13)$$

which occurs because there is no spatial moment to the radial distribution function. As such, there is no electric dipole moment for a given stationary state, and therefore the bound electron does not radiate. Dirac further showed that the dipole moment between two different stationary states can be a non-vanishing and time varying quantity,

$$\mathbf{P}_{n'n}(t) = e \int_0^\infty \oint \Psi_{n'}^*(\mathbf{r}, t) \, \mathbf{r} \, \Psi_n(\mathbf{r}, t) \, dV$$
  
=  $e \left[ \int_0^\infty \oint \psi_{n'}^*(\mathbf{r}) \, \mathbf{r} \, \psi_n(\mathbf{r}) \, dV \right] \exp \left\{ -(i/\hbar)(E_n - E_{n'}) \, t \right\}$  (11.14)  
=  $e \, \mathbf{r}_{n'n} \exp \left\{ -(i/\hbar)(E_n - E_{n'}) \, t \right\},$ 

as long as  $\mathbf{r}_{n'n}$  does not vanish. As we will show below,  $\mathbf{r}_{n'n}$  will vanishes except for only certain combinations of  $n'l'm' \leftrightarrow nlm$ . We thus see that a dipole moment between certain states allows for the electron charge densities to oscillate between these two states, with a frequency  $\omega_{n'n} = (E_n - E_{n'})/\hbar$ , which is the Bohr frequency (2nd postulate) of the transition corresponding to a photon with wavelength  $\lambda = 2\pi c/\omega_{n'n}$ . This oscillation will be short lived and will, in the case of emission, radiate a photon of wavelength  $\lambda$ . In the case of absorption, photons of wavelength  $\lambda$  will induce the oscillation between states.

#### 11.2.2 Dipole emission transition rates

In the context of the dipole approximation, the spontaneous transition rate that emits a photon of polarization  $\epsilon$  propagating into solid angle  $d\Omega$  can now be written

$$W_{n'n}^{\hat{\boldsymbol{\epsilon}}} d\Omega = \frac{e^2 \,\omega_{n'n}^3}{2\pi\hbar c^3} \left| \hat{\boldsymbol{\epsilon}} \cdot \mathbf{r}_{n'n} \right|^2 d\Omega, \qquad (11.15)$$

If the angle between the electric vector polarization  $\hat{\boldsymbol{\epsilon}}$  and the dipole axis  $\mathbf{r}_{n'n}$  is  $\cos \theta$ , then the total transition probability over all solid angle (independent of viewing direction) from state n' to n is

$$A_{n'n} = \frac{e^2 \,\omega_{n'n}^3}{2\pi\hbar c^3} \left| \mathbf{r}_{n'n} \right|^2 \oint \cos^2\theta \, d\Omega = \frac{4}{3} \frac{e^2 \,\omega_{n'n}^3}{\hbar c^3} \left| \mathbf{r}_{n'n} \right|^2. \tag{11.16}$$

## 11.3 The oscillator strength

Further examination of the transition probabilities is made convenient via introduction of the oscillator strength,

$$f_{n'n} = \frac{2m_e}{3\hbar} \,\omega_{n'n} \,|\mathbf{r}_{n'n}|^2 \,. \tag{11.17}$$

The transition probability (Eq. 11.16) from state n to n' can then be expressed

$$A_{n'n} = \frac{2e^2 \,\omega_{n'n}^2}{m_e c^3} f_{n'n}.\tag{11.18}$$

To account for linear polarization states of the radiation (from a dipole), and eventually the average over these polarization directions,  $\mathbf{r}_{n'n}$  is computed using the x, y, and z projections of the dipole moment for radiation with electric field polarization parallel to the x, y, and z axes. The oscillator strength is then written,

$$f_{n'n} = f_{nlm}^{n'l'm'}(\uparrow) = \frac{2m_e}{3\hbar} \omega_{n'n} \left( \left| x_{nlm}^{n'l'm'} \right|^2 + \left| y_{nlm}^{n'l'm'} \right|^2 + \left| z_{nlm}^{n'l'm'} \right|^2 \right) \quad (11.19)$$

where the explicit notation  $f_{nlm}^{n'l'm'}(\uparrow)$  denotes a transition from upper state nlm to lower state n'l'm', with the arrow providing the direction of the transition

with respect to the indices. We will ultilize the simpler version of the notation, i.e.,  $f_{n'n}$  when such simplification is possible without loss of precision in meaning. From the spherical relations  $x = r \cos \phi \sin \theta$ ,  $y = r \sin \phi \sin \theta$ , and  $z = r \cos \theta$ , the components to the dipole moment are

$$\begin{aligned} x_{nlm}^{n'l'm'} &= \int_0^\infty R_{n'l'}(r) R_{nl}(r) \, r^3 dr \oint Y_{l'm'}^*(\phi,\theta) Y_{lm}(\phi,\theta) \, \cos\phi \sin^2\theta \, d\theta \, d\phi \\ y_{nlm}^{n'l'm'} &= \int_0^\infty R_{n'l'}(r) R_{nl}(r) \, r^3 dr \oint Y_{l'm'}^*(\phi,\theta) Y_{lm}(\phi,\theta) \, \sin\phi \sin^2\theta \, d\theta \, d\phi \\ z_{nlm}^{n'l'm'} &= \int_0^\infty R_{n'l'}(r) R_{nl}(r) \, r^3 dr \oint Y_{l'm'}^*(\phi,\theta) Y_{lm}(\phi,\theta) \, \cos\theta \sin\theta \, d\theta \, d\phi, \end{aligned}$$
(11.20)

Using this formalism, determination of the transition probabilities involves computing the  $x_{nlm}^{n'l'm'}$ ,  $y_{nlm}^{n'l'm'}$ , and  $z_{nlm}^{n'l'm'}$ . As alluded to above, not all  $\mathbf{r}_{n'n}$  are non-zero for  $n' \neq n$ ; there are defi-

As alluded to above, not all  $\mathbf{r}_{n'n}$  are non-zero for  $n' \neq n$ ; there are definite selection rules that apply and they are specific to the polarization direction of the photon electric field. Consider photons polarized with  $\hat{\epsilon}$  in the z direction. We find that integration of  $z_{nlm}^{n'l'm'}$  over  $\phi$  vanishes unless m = m', since  $\Phi_{m'}^*(\phi)\Phi_m(\phi) = (2\pi)^{-1}\exp\{i(m-m')\phi\} = 1$ , so that the integral over the azimuthal angle,  $\phi \to 2\pi$  is unity. For all  $m \neq m'$ , the integral averages to zero. We also find that integration over  $\theta$  vanishes unless  $l' = l \pm 1$  (though this is a more involved calculation). We thus find the general result

$$z_{nlm}^{n'l'm'} = 0$$
  $(l' \neq l \pm 1, m' \neq m),$  (11.21)

For all cases in which  $l' = l \pm 1$  and  $\Delta m = 0$ , the results for photons with z axis polarization are

$$z_{nlm}^{n'\,l+1\,m} = \sqrt{\frac{(l+1)^2 - m^2}{(2l+3)(2l+1)}} R_{nl}^{n'\,l+1}$$

$$z_{nlm}^{n'\,l-1\,m} = \sqrt{\frac{l^2 - m^2}{(2l+1)(2l-1)}} R_{nl}^{n'\,l-1}$$
(11.22)

where  $R_{nl}^{n'l'}$  is the spatial magnitude of the dipole moment,

$$R_{nl}^{n'l'} = \int_0^\infty R_{n'l'}(r) R_{nl}(r) r^3 dr, \qquad (11.23)$$

which is commonly called the radial overlap integral. Obtaining the x and y components to the dipole moment is more complicated, but is simplified by combining the components such that the polarization is in general perpendicular to the z axis. Stating the result directly, we find

$$\left|x_{nlm}^{n'l'm'}\right|^{2} + \left|y_{nlm}^{n'l'm'}\right|^{2} = 0 \qquad (l' \neq l \pm 1, m' \neq m \pm 1), \tag{11.24}$$

for all integrals except when  $\Delta l = \pm 1$  and  $\Delta m = \pm 1$ . Thus, radiation with polarization perpendicular to the z axis (in the dipole approximation) can only occur if the electron angular momentum and the z projection of the electron angular momentum change by a single integer in the constants of motion. For these permitted transitions, we have

$$\begin{aligned} \left| x_{nlm}^{n'\,l+1\,m+1} \right|^{2} + \left| y_{nlm}^{n'\,l+1\,m+1} \right|^{2} &= \frac{(l+m+2)(l+m+1)}{(2l+3)(2l+1)} \left( R_{nl}^{n'\,l+1} \right)^{2} \\ \left| x_{nlm}^{n'\,l+1\,m-1} \right|^{2} + \left| y_{nlm}^{n'\,l+1\,m-1} \right|^{2} &= \frac{(l-m+2)(l-m+1)}{(2l+3)(2l+1)} \left( R_{nl}^{n'\,l+1} \right)^{2} \\ \left| x_{nlm}^{n'\,l-1\,m+1} \right|^{2} + \left| y_{nlm}^{n'\,l-1\,m+1} \right|^{2} &= \frac{(l-m)(l-m-1)}{(2l+1)(2l-1)} \left( R_{nl}^{n'\,l-1} \right)^{2} \\ \left| x_{nlm}^{n'\,l-1\,m-1} \right|^{2} + \left| y_{nlm}^{n'\,l-1\,m-1} \right|^{2} &= \frac{(l+m)(l+m-1)}{(2l+1)(2l-1)} \left( R_{nl}^{n'\,l-1} \right)^{2} \end{aligned}$$
(11.25)

#### 11.3.1 Selection and sum rules

The non-vanishing terms of the dipole moment between stationary states provide the selection rules for transitions. Employing  $\Delta m = m' - m$ , and  $\Delta l = l' - l$ , we have

$$\epsilon \parallel \text{to } z \quad \epsilon \perp \text{ to } z$$

$$\Delta l \quad \pm 1 \qquad \pm 1 \qquad (11.26)$$

$$\Delta m \quad 0 \qquad 0, \pm 1.$$

Thus, accounting for all orientations of polarization, we have the selection rules  $\Delta m = 0, \pm 1$ , and  $\Delta l = \pm 1$ . Transitions that obey these rules are called "permitted". Below, we will discuss "forbidden" transitions, which are governed by the electric quadrapole and magnetic dipole approximations.

The oscillator strength obeys various useful sum laws, the most often quoted being the Thomas–Reiche–Kuhn rule,

$$\sum_{n'=1}^{\infty} f_{nlm}^{n'l'm'}(\uparrow\downarrow) = \mathcal{N}_e \qquad (n' \neq n)$$
(11.27)

where  $\mathcal{N}_e$  is the number of bound electrons ( $\mathcal{N}_e = 1$  for hydrogen), and where the sum is taken over all transitions that originate in state nlm. This rule holds regardless of the ionization stage of the atom and for any polarization direction. For hydrogen, the oscillator strengths decrease in proportion to  $n^{-3}$  for large values.

#### 11.3.2 The average oscillator strength

The emission line intensities and absorption line strengths observed in spectra arise from  $nl \rightarrow n'l'$  transitions between the 2l+1 possible m' states. We thus introduce the average oscillator strength, which is the oscillator strength summed

over all m' states for the n'l' state. Accounting for all possible orientations of the polarization direction and all allowed transitions, we define the average oscillator strength,

$$\bar{f}_{n'n} = \bar{f}_{nl}^{n'l'}(\uparrow) = \frac{2m_e}{3\hbar} \omega_{n'n} \left| \mathbf{r}_{nl}^{n'l'} \right|^2 
= \frac{1}{3} \frac{h\nu_{n'n}}{R_z} \frac{1}{a_\mu^2} \left| \mathbf{r}_{nl}^{n'l'} \right|^2 
= \frac{1}{3} \frac{(n+n')(n-n')}{n'^2 n^2} \frac{1}{a_\mu^2} \left| \mathbf{r}_{nl}^{n'l'} \right|^2,$$
(11.28)

where

$$\left|\mathbf{r}_{nl}^{n'l'}\right|^{2} = \sum_{m'=-l'}^{l'} \left|\mathbf{r}_{nlm}^{n'l'm'}\right|^{2}, \qquad (11.29)$$

and where we have invoked the energy relationships between Eqs. 11.5, 9.9 and 9.10 and have invoked the reduced Bohr radius,  $a_{\mu} = (\mu/m_e) a_0$  (see Eq. 9.4) and Rydberg's constant (Eqs. 9.6 and 9.7). Note that  $\bar{f}_{n'n}$  depends only upon the change in total orbital angular momentum and the change in principle level. For l' = l + 1, we have

$$\sum_{m'=-(l+1)}^{l+1} \left| \mathbf{r}_{nlm}^{n'\,l+1\,m'} \right|^2 = \left| x_{nlm}^{n'\,l+1\,m+1} \right|^2 + \left| y_{nlm}^{n'\,l+1\,m+1} \right|^2 + \left| x_{nlm}^{n'\,l+1\,m-1} \right|^2 + \left| x_{nlm}^{n'\,l+1\,m-1} \right|^2 + \left| z_{nlm}^{n'\,l+1\,m-1} \right|^2 = \frac{l+1}{2l+1} \left( R_{nl}^{n'\,l+1} \right)^2.$$
(11.30)

Similarly, for l' = l - 1, we have

$$\sum_{m'=-(l-1)}^{l-1} \left| \mathbf{r}_{nlm}^{n'\,l-1\,m'} \right|^2 = \frac{l}{2l+1} \left( R_{nl}^{n'\,l-1} \right)^2.$$
(11.31)

Combining Eqs. 11.30 and 11.31 into a single expression,

$$\left|\mathbf{r}_{nl}^{n'l'}\right|^{2} = \sum_{m'=-l'}^{l'} \left|\mathbf{r}_{nlm}^{n'l'm'}\right|^{2} = \frac{\max(l,l')}{2l+1} \left(R_{nl}^{n'l'}\right)^{2}, \quad (11.32)$$

where l' = l + 1 or l' = l - 1, and the term 2l + 1 is the multiplicity of states,  $g_n$ , reflecting the energy degeneracy for the initial state, n. Substituting into Eq. 11.28, the average oscillator strength is

$$\bar{f}_{n'n} = \bar{f}_{nl}^{n'l'}(\uparrow) = \frac{1}{3} \frac{\max(l,l')}{2l+1} \frac{(n+n')(n-n')}{n'^2 n^2} \left(\frac{R_{nm}^{n'l'}}{a_{\mu}}\right)^2.$$
(11.33)

Because the multiplicity of initial state,  $g_n = 2l + 1$ , is the factor that effectively averages the sum, the average oscillator strength for the opposite sense of the transition,  $\bar{f}_{nn'}$ , is not equal to  $\bar{f}_{n'n}$ . Explicitly, we have

$$\bar{f}_{n'l'}^{nl}(\uparrow) = \frac{2l+1}{2l'+1} \bar{f}_{nl}^{n'l'}(\uparrow) = \frac{g_n}{g'_n} \bar{f}_{nl}^{n'l'}(\uparrow), \qquad (11.34)$$

which provides the well known relation

$$g_{n'}\bar{f}_{nn'} = g_n\bar{f}_{n'n},\tag{11.35}$$

where the statistical weights represent the initial state of the inverse transitions.

## 11.4 Total average transition probabilities

From Eq. 11.18, the average total transition probability  $[\sec^{-1}]$  over all solid angle and accounting for all polarizations of the emitted radiation for spontaneous emission is

$$\bar{A}_{n'n} = \bar{A}_{nl}^{n'l'}(\uparrow) = \frac{2e^2 \,\omega_{n'n}^2}{m_e c^3} \bar{f}_{nl}^{n'l'}(\uparrow), \qquad (11.36)$$

from initial state nl to final state n'l', where n > n'. Often, the expression is written

$$\bar{A}_{n'n} = 8.0325 \times 10^9 \left(\frac{h\nu_{n'n}}{R}\right)^2 \bar{f}_{nl}^{n'l'}(\uparrow) \quad \text{sec}^{-1}, \tag{11.37}$$

where the constant is  $(8\pi^2 e^2/m_e c^3)(R/h)^2$ , where R is Rydberg's constant (for  $\mu = m_e$  and Z = 1 for hydrogen). The total probability (per unit time) that state n will spontaneously transition to a lower state is obtained by summing the  $\bar{A}_{n'n}$  over all lower states n',

$$\beta_n = \sum_{n' < n} \bar{A}_{n'n}, \tag{11.38}$$

where  $\beta_n$  is called the decay constant for level *n*. The mean life time of state *n* is the inverse of the decay constant

$$\langle t_n \rangle = \frac{1}{\beta_n} = \left(\sum_{n' < n} \bar{A}_{n'n}\right)^{-1}.$$
(11.39)

For absorption, the direction of the transition is reversed and one must multiply by the power (energy per unit time) of the incoming radiation beam,

$$P = \int_0^\infty P_\nu(\nu) \, d\nu = \int_0^\infty \frac{c^3}{4h\nu^3} \, \rho_\nu(\nu) \, d\nu = \frac{1}{2} \int_0^\infty \frac{2\pi^2 c^2}{\hbar\omega^3} F_\omega(\omega) \, d\omega, \qquad (11.40)$$

where  $\rho_{\nu}(\nu)$  is the energy density per unit frequency, and where  $\rho_{\omega}(\omega) = F_{\omega}(\omega)/c$  is the energy density per unit angular frequency with  $F_{\omega}(\omega)$  being the

flux [erg sec<sup>-1</sup> cm<sup>-2</sup> (rad sec<sup>-1</sup>)<sup>-1</sup>], the integral of the specific intensity,  $\mathcal{I}_{\omega}$  (see Eq. 4.8), integrated over  $2\pi$  steradians (see Eq. 4.9). In Eq. 11.40, we have invoked the conservation per unit frequency interval, namely  $\rho_{\nu}(\nu) d\nu = \rho_{\omega}(\omega) d\omega$ . Though there is a very narrow frequency range over which transitions can occur (we will discuss this in § 11.7), we can approximate the integral as a  $\delta$  function evaluated at  $\omega = \omega_{n'n}$ , the transition frequency, which gives  $P = (\pi^2 c^2 / \hbar \omega_{n'n}^3) F(\omega_{n'n})$ .

Thus, the corresponding absorption transition probability  $[\sec^{-1}]$  over all solid angle and accounting for all polarizations of the absorbed radiation is

$$\bar{A}_{nn'} = \bar{A}_{n'l'}^{nl}(\uparrow) = \frac{2\pi^2 e^2}{m_e \hbar c} \frac{F(\omega_{n'n})}{\omega_{n'n}} \bar{f}_{n'l'}^{nl}(\uparrow) = \frac{2\pi^2 e^2}{m_e \hbar c} \frac{F(\omega_{n'n})}{\omega_{n'n}} \frac{g_n}{g'_n} \bar{f}_{nl}^{n'l'}(\uparrow)$$
(11.41)
$$= \frac{4\pi^2 e^2}{3\hbar^2 c} F(\omega_{n'n}) \left| \mathbf{r}_{nl}^{n'l'} \right|^2,$$

where we have invoked Eq. 11.34, and the definition of the average oscillator strength Eq. 11.28. We note that  $e^2/\hbar c = \alpha$ , which provides an alternate expression for the constants.

#### 11.4.1 Total line intensities

To obtain total average emission line intensities, we multiply the total spontaneous transition rate (Eq. 11.36) by the transition energy,  $\hbar\omega_{n'n}$ ,

$$\bar{J}_{n'n} = \hbar \omega_{n'n} \bar{A}_{nl}^{n'l'}(\uparrow) = \frac{2e^2 \hbar \,\omega_{n'n}^3}{m_e c^3} \bar{f}_{nl}^{n'l'}(\uparrow).$$
(11.42)

#### 11.4.2 Total absorption cross sections

The quantity known as intenisity is not commonly applied for absorption. It is more common to describe the line strength in terms of the integrated absorption cross section,  $\alpha$ , in units [cm<sup>2</sup> absorber<sup>-1</sup>]. The term "integrated" denotes that the cross section is the total over the frequency width of the absorption (not per unit frequency or wavelength). The total absorption cross section is obtained by multiply the total transition rate for absorption (Eq. 11.41) by the transition energy,  $\hbar \omega_{n'n}$ , and dividing by the incident flux,  $F(\omega_{n'n})$ . This latter step derives from the definition of cross sections defined in Eq. 4.28 of § 4.3.2. We have

$$\alpha_{nn'} = \int_0^\infty \alpha_{nn'}(\omega) \, d\omega = \frac{\hbar \omega_{n'n}}{F(\omega_{n'n})} \bar{A}_{n'l'}^{nl}(\uparrow) = \frac{2\pi^2 e^2}{m_e c} \frac{g_n}{g'_n} \bar{f}_{nl}^{n'l'}(\uparrow).$$
(11.43)

## 11.5 Evaluating radial overlap interals

In order to obtain the final expressions for the average oscillator strength, and therefore the transition probabilities, the overlap integral

$$R_{nl}^{n'l'} = \int_0^\infty R_{n'l'}(r) R_{nl}(r) r^3 dr, \qquad (11.44)$$

must be evaluated. Accounting for the selection rule  $l' = l \pm 1$ , we note that the overlap integral is symmetric with respect to the change in n and l,

$$R_{nl}^{n'l-1} = \int_0^\infty R_{n'l-1'}(r) R_{nl}(r) r^3 dr = \int_0^\infty R_{n1}(r) R_{n'l-1}(r) r^3 dr \qquad (11.45)$$

since the choice of nl as the upper state and n'l' as the lower state is arbitrary (the subscripts can be interchanged)

$$R_{nl}^{n'\,l-1} = R_{n'\,l-1}^{nl} \tag{11.46}$$

Evaluating  $R_{nl}^{n'l-1}$  is very difficult, but was worked out in closed from by Gordon (1929) using the hypergeometric functions that appear in the radial component of the wave function (see Eqs. 9.45 and 9.46). A more recent derivation has also been presented by Malik, Malik, & Varnim (1991), who developed an expression more suitable for numerical computation. The classic expression for  $n' \neq n$  is

$$\frac{R_{nl}^{n'l-1}}{a_{\mu}} = \frac{(-1)^{n'-l}}{4(2l-1)!} \sqrt{\frac{(n+l)!(n'+l-1)!}{(n-l-1)!(n'-l)!}} \frac{(4n'n)^{l+1}(n-n')^{n+n'-2l-2}}{(n+n')^{n+n'}} \Upsilon_{nm}^{n'l-1}$$
(11.47)

where

$$\Upsilon_{nm}^{n'l-1} = F(-n_r, -n'_r, 2l, -u) - \left[\frac{n-n'}{n+n'}\right]^2 F(-n_r - 2, -n'_r, 2l, -u)$$
(11.48)

where  $u = 4n'n/(n-n')^2$ , and where  $n_r = n - l - 1$ , and  $n'_r = n' - l$  (recall l = l' - 1). The F are the generalized hypergeometric functions

$$F(\alpha,\beta,\gamma,\zeta) = \sum_{j=0}^{\infty} \frac{(\alpha)_j(\beta)_j}{(\gamma)_j} \frac{\zeta^j}{j!} = 1 + \frac{\alpha\beta}{1!\gamma}\zeta + \frac{\alpha(\alpha+1)\beta(\beta+1)}{2!\gamma(\gamma+1)}\zeta^2 + \cdots$$
(11.49)

where  $(\alpha)_i$  is the Pochhammer symbol for the quantity

$$(\alpha)_j = \alpha(\alpha+1)(\alpha+2)\cdots(\alpha+j-1), \qquad (11.50)$$

where j is a positive integer. By definition,  $(\alpha)_0 = 1$ . Note that if either  $\alpha$  or  $\beta$  are null or negative integers then the hypergeometric series terminates.

The expression for n' = n is much simpler,

$$\frac{R_{nl}^{n\,l-1}}{a_{\mu}} = \frac{R_{n\,l-1}^{nl}}{a_{\mu}} = \frac{3}{2}\sqrt{n^2 - l^2}.$$
(11.51)

In the Schrödinger theory, the energies are degenerate so that there would be no corresponding spectral features, though the transitions are permitted. Accounting for higher–order interactions terms in the Hamiltonian, transitions between fines structure states and between Lamb shift corrected energy states result in microwave and radio spectral features, for which Eq. 11.51 applies.

#### 11.5.1 Computing oscillator strengths

Consider the Lyman series transitions between the 1s - np states, for which n' = 1, l' = 0 and l = 1 for various n > n'. From Eq. 11.47, we have

$$\left(\frac{R_{10}^{n1}}{a_{\mu}}\right)^2 = \left(\frac{R_{n1}^{10}}{a_{\mu}}\right)^2 = 2^8 n^7 \frac{(n-1)^{2n-5}}{(n+1)^{2n-5}},\tag{11.52}$$

For absorption, we compute (Eq. 11.33 and Eq. 11.34)

$$\bar{f}_{10}^{n1}(\uparrow) = \frac{1}{3} \frac{(n+1)(n-1)}{n^2} \left(\frac{R_{10}^{n1}}{a_{\mu}}\right)^2 = \frac{2^8 n^5 (n-1)^{2n-4}}{3(n+1)^{2n+4}}.$$
(11.53)

For the Ly $\alpha$  transition, n = 2, we obtain  $\bar{f}_{10}^{21}(\uparrow) = 0.4162$ . To obtain the mean oscillator strength for emission, we apply Eq. 11.34. Multiplying by the ratio of the multiplicity of states, (2l'+1)/(2l+1),

$$\bar{f}_{n1}^{10}(\uparrow) = \frac{1}{3} \bar{f}_{10}^{n1}(\uparrow) = \frac{2^8 n^5 (n-1)^{2n-4}}{9(n+1)^{2n+4}},$$
(11.54)

which yields  $\bar{f}_{21}^{10}(\uparrow) = 0.1387$  for Ly $\alpha$  emission.

In Table 11.1, we list the average absorption oscillator strengths for the Lyman and Balmer series transitions of hydrogen, computed directly from Eq 11.33 and Eq. 11.34. For each transitions, the ratio  $(R_{n'1}^{nl}/a_{\mu})^2$  is given in the square brackets. More extensive tables of these formulas can be found in Menzel & Pekeris (1935) and Condon & Shortley (1964). Numeric values up to n = 8 out the 4d and 4g states (the partial Lyman, Balmer, Paschen, and Brackett series) are tabulated in Bethe & Salpeter (1957).

The average emission oscillator strengths for the Lyman and Balmer series are obtained using, Eq. 11.34, from which we obtain

Lyman series 
$$1s - np$$
  $\bar{f}_{n1}^{10}(\uparrow) = \frac{1}{3}\bar{f}_{10}^{n1}(\uparrow)$   
Balmer series  $2s - np$   $\bar{f}_{n1}^{20}(\uparrow) = \frac{1}{2}\bar{f}_{20}^{n1}(\uparrow)$   
 $2p - nd$   $\bar{f}_{n2}^{21}(\uparrow) = \frac{3}{5}\bar{f}_{21}^{n2}(\uparrow)$   
 $2p - ns$   $\bar{f}_{n0}^{21}(\uparrow) = \frac{3}{1}\bar{f}_{21}^{n0}(\uparrow).$ 
(11.55)

## **11.6** Fine structure transition rates

The above formalism for treating transition proabailities, emission intensities, and absorption cross section neglects spin and realtivistic effects; Schrödinger

Lyman
$\frac{1 \mathrm{s} - n \mathrm{p}}{\bar{f}_{10}^{n1}}(\uparrow) = \frac{(n+1)(n-1)}{3n^2} \left[ \frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}} \right] = \frac{2^8 n^5 (n-1)^{2n-4}}{3(n+1)^{2n+4}}$
Balmer
$\frac{2s-np}{\bar{f}_{20}^{n1}(\uparrow)} = \frac{(n+2)(n-2)}{3\cdot 4n^2} \left[ \frac{2^{17}n^7(n^2-1)(n-2)^{2n-6}}{(n+2)^{2n+6}} \right] = \frac{2^{17}n^7(n^2-1)(n-2)^{2n-5}}{3\cdot 4(n+2)^{2n+5}}$
$ \begin{array}{l} 2\mathbf{p}-n\mathbf{d} \\ \bar{f}_{21}^{\ n2}(\uparrow) = \frac{2(n+2)(n-2)}{3^2 \cdot 4n^2} \left[ \frac{2^{19}n^9(n^2-1)(n-2)^{2n-7}}{3(n+2)^{2n+7}} \right] = \frac{2^{20}n^9(n^2-1)(n-2)^{2n-6}}{3^3 \cdot 4(n+2)^{2n+6}} \end{array} $
$\frac{2p-ns}{\bar{f}_{21}^{n0}(\uparrow)} = \frac{(n+2)(n-2)}{3^2 \cdot 4n^2} \left[ \frac{2^{15}n^9(n-2)^{2n-6}}{3(n+2)^{2n+6}} \right] = \frac{2^{15}n^9(n-1)^{2n-5}}{3^3 \cdot 4(n+1)^{2n+5}}$

Table 11.1: Lyman and Balmer series average oscillator strengths

theory applies only for the two constants of motion (1) the electron angular momentum and (2) its z axis projection, as described by the quantum numbers l and  $m_l$ , respectively.

The inclusion of spin resulted in a spin-orbit coupling interaction (via the electron magnetic moment) and yielded new constants of motion, the total electron angular momentum and its z axis projects, as described by the quantum numbers j and  $m_j$ , respectively. As we described above (§ 10.2) for the inclusions of relativistic and spin-orbit effects, the eigenfunctions for stationary state  $nlm_l$  no longer described a stationary state, primarily because  $m_l$  is no longer a constant of motion (**L** precesses about **J**, see Figure 10.2). Spin orbit coupling resulted in small energy splittings between different j states with the same l (given by  $\Delta E_2$  in Eq. 10.10), which are 2j + 1 degenerate for the various  $J_z$ . The stationary state accounting for spin-orbit coupling is denoted by the quantum numbers  $nljm_j$  (see Eq. 10.5).

The second most significant modification to the Schrödinger sationary states are energy shift (given by  $\Delta E_1$  in Eq. 10.10) due to relativistic momentum of the electron, which we described in § 10.3. The third modification was the Darwin term for l = 0 electrons (given by  $\Delta E_3$  in Eq. 10.10). The correction terms  $\Delta E_1$ ,  $\Delta E_2$ , and  $\Delta E_3$  are based upon approximation methods (pertubation theory) that will have errors on the order of  $(Z\alpha)^2$ . We have not described the full relativistic treatment by Dirac (see e.g., Bethe & Salpeter, 1957, for a full

treatment).

#### 11.6.1 Pauli and Dipole Approximations

If one applies what is known as the Pauli approximation to the Dirac theory, and then applies the dipole approximation, the final result is that the transition probabilities between states  $nljm_j$  and  $n'l'j'm'_j$ , summed over all  $jm_j$  states, are directly proportional to the Schrödinger theory transition nl to n'l'. A new set of selection rules result that are similar to those for the Schrödinger stationary states. The proportionality between the Schrödinger transition rates and those for fine structure multiplets are derived via consideration of the multiplicity of states. We briefly outline these results in the next few sections.

In the relativistic Dirac theory, the operator  $\mathbf{p} = -i\hbar \nabla$  is replaced with  $m_e c \alpha$ , which is a 2 × 2 matrix operator whose elements are the 2 × 2 Pauli spin matrices,  $\boldsymbol{\sigma}$ . The wave functions themselves are also matrices known as four component spinors. The result is that the operator of the matrix element (see Eq. 11.4) is replaced accordingly,

$$\exp\left\{i(\boldsymbol{k}\cdot\boldsymbol{\mathbf{r}})\right\}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{\nabla}\to\frac{im_ec}{\hbar}\exp\left\{i(\boldsymbol{k}\cdot\boldsymbol{\mathbf{r}})\right\}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{\alpha}.$$
(11.56)

We emphasize that this is a matrix operation on four component wave functions, known as spinors (see below). The Pauli approximation consists of expanding  $\alpha$  in powers of the quantity  $p/m_ec$ , which results in the matrix element being expressed to the first power of the Pauli spin matrices,

$$\boldsymbol{\alpha} = \frac{1}{m_e c} \left\{ \boldsymbol{p} + \frac{1}{2} \left[ \boldsymbol{k} + i \left( \boldsymbol{k} \times \boldsymbol{\sigma} \right) \right] \right\}.$$
(11.57)

Dropping the higher order terms has an associated error on the order of  $(Z\alpha)^2$ .

Applying the electric dipole approximation (§ 11.2) is mathematically equivalent to setting  $\mathbf{k} = 0$  in Eqs. 11.56 and 11.57, which yields  $\boldsymbol{\alpha} = \mathbf{p}/m_e c$  and recovers the matrix element for the Schrödinger theory (Eq. 11.9)

$$M_{n'n}^{\hat{\boldsymbol{\epsilon}}} = \hat{\boldsymbol{\epsilon}} \cdot \frac{i}{\hbar} \int_0^\infty \oint u_{n'}^*(\mathbf{r}) \, \mathbf{p} \, u_n(\mathbf{r}) \, dV = \frac{m_e}{\hbar} \, \omega_{n'n} \left( \hat{\boldsymbol{\epsilon}} \cdot \mathbf{r}_{n'n} \right), \tag{11.58}$$

where  $u_n(\mathbf{r}) = u_{nljm_j}^{j-lm_j-m_l}(r,\phi,\theta)$  are the four component Pauli spinors,

$$\begin{bmatrix} u_{nljm_{j}}^{+\frac{1}{2}+\frac{1}{2}} \\ u_{nljm_{j}}^{+\frac{1}{2}-\frac{1}{2}} \end{bmatrix} = \frac{l}{\sqrt{2l+1}} R_{nl}(r) \begin{bmatrix} -\sqrt{l-m_{l}+\frac{1}{2}} Y_{l\,m_{l}+\frac{1}{2}}(\phi,\theta) \\ \sqrt{l+m_{l}+\frac{1}{2}} Y_{l\,m_{l}-\frac{1}{2}}(\phi,\theta) \end{bmatrix}$$

$$\begin{bmatrix} u_{nljm_{j}}^{-\frac{1}{2}+\frac{1}{2}} \\ u_{nljm_{j}}^{-\frac{1}{2}-\frac{1}{2}} \end{bmatrix} = \frac{l}{\sqrt{2l+1}} R_{nl}(r) \begin{bmatrix} \sqrt{l+m_{l}+\frac{1}{2}} Y_{l\,m_{l}+\frac{1}{2}}(\phi,\theta) \\ \sqrt{l-m_{l}+\frac{1}{2}} Y_{l\,m_{l}-\frac{1}{2}}(\phi,\theta) \end{bmatrix},$$
(11.59)

written in terms of l and  $m_l$  for direct comparison with the Schrödinger wave functions with

$$\mathbf{r}_{n'n} = \mathbf{r}_{nljm_j}^{n'l'j'm_j'} = \int_0^\infty \oint u_{n'}^*(\mathbf{r}) \,\mathbf{r} \,u_n(\mathbf{r}) \,dV.$$
(11.60)

We remind the reader these wave functions were derived based upon the Pauli approximation and are not the complete Driac wave functions. The z projection of the electron spin is not constant of motion (S precesses around  $\mathbf{J}$ ), thus  $m_s$  does not appear in the  $u_n(\mathbf{r})$ . Applying the dipole approximation has an associated error on the order of  $Z\alpha$ .

#### 11.6.2Selection rules

Determining the transition probabilities and selection rules of fine structure transitions requires evaluation of Eq. 11.60. Following the Schrödinger theory, it is convenient to employ the oscillator strength (see  $\S$  11.3). Using the superposition principle, it is also instructive to write the spinors in terms of the Schrödinger wave functions  $\psi_{nlm_l}(\mathbf{r})$  and the spin components of the two orthonomal functions  $\chi_{m_s}$ , from which sums rules are derived that allow the fine structure oscillator strengths to be written in terms of the Schrödinger theory oscillator strengths. From superposition, we have

$$u_{nljm_{j}}^{j-l\,m_{j}-m_{l}}(\mathbf{r}) = \begin{cases} \sum_{m_{j}} \alpha_{m_{s}}^{ljm_{j}} \psi_{nlm_{l}}(\mathbf{r}) \,\chi_{+\frac{1}{2}} \\ \\ \sum_{m_{j}} \alpha_{m_{s}}^{ljm_{j}} \psi_{nlm_{l}}(\mathbf{r}) \,\chi_{-\frac{1}{2}}, \end{cases}$$
(11.61)

where  $m_i = m_l + m_s$ . The coefficients form a complete orthonomoral set

$$\sum_{m_s} = \left| \alpha_{m_s}^{ljm_j} \right|^2 = 1, \qquad \sum_j \left( \alpha_{m'_s}^{ljm_j} \right)^* \alpha_{m_s}^{ljm_j} = \delta_{m_s m'_s}, \tag{11.62}$$

from which the dipole moment for the relativistic wave functions (the spinors) can be computed

$$\mathbf{r}_{nljm_{j}}^{n'l'j'm_{j}'} = \sum_{m_{s}} \alpha_{m_{s}}^{ljm_{j}} \left(\alpha_{m_{s}}^{l'j'm_{j}'}\right)^{*} \mathbf{r}_{nlm_{l}}^{n'l'm_{l}'}, \qquad (11.63)$$

where  $m_j = m_l + m_s$ , and where  $\mathbf{r}_{nlm_l}^{n'l'm'_l}$  is given by Eq. 11.10. As before, the non–vanishing terms of the components of the dipole moment between stationary states provide the selection rules for transitions. From examination of Eq. 11.63, and the results given by Eqs. 11.21 and 11.24, the dipole moment vanishes for all transitions except for  $\Delta l = \pm 1$  and  $\Delta m_l = 0, \pm 1$ ; these selection rules immediatly apply. Since  $j = l \pm 1/2$ , it also immediately follows that  $\Delta i = \pm 1$  is a selection rule (below, we will see there are additional selection rules).

Employing Eqs. 11.30, 11.31, and 11.32, and summing Eq. 11.63 over all final j' and  $m'_j$  states, we have

$$\sum_{j'm'_{j}} \mathbf{r}_{nljm_{j}}^{n'l'j'm'_{j}} = \sum_{j'm'_{j}} \left[ \sum_{m_{s}} \alpha_{m_{s}}^{ljm_{j}} \left( \alpha_{m_{s}}^{l'j'm'_{j}} \right)^{*} \mathbf{r}_{nlm_{l}}^{n'l'm'_{l}} \right] = \left| \mathbf{r}_{nl}^{n'l'} \right|^{2}.$$
(11.64)

This sum rule demonstrates that the average oscillator strength (subject to the Pauli and dipole approximations) is independent of the initial j and  $m_j$  states and the electron spin. Further, the sum rule expressed in Eq. 11.64 shows that the average dipole moment over all j and  $m_j$  fine structure states is proportional to the dipole moment of the Schrödinger states (Eq. 11.29).

A full derivation of the oscillator strengths for transitions between individual fine structure states (subject to the Pauli and electric dipole moment assumptions) results in expressions identical to Eqs. 11.22 and 11.25 but with lreplaced with j and m (=  $m_l$ ) replaced with  $m_j$ . The subscripts  $nlm_l$  on the x, y, and z polarization components of the dipole moment are replaced with  $nljm_j$ . Full evaluation of Eq. 11.63 similarly vanishes for all transitions<sup>1</sup> except for  $\Delta j = 0, \pm 1$  and  $\Delta m_j = 0, \pm 1$ . In Eqs. 11.22 and 11.25, there is no analog for  $\Delta j = 0$ . For  $\Delta j = 0$ , in which  $\Delta l = \pm 1$  and  $m_j = 0, \pm 1$ , the dipole components are

$$\left|z_{nljm_{j}}^{n'l'jm_{j}}\right|^{2} = \frac{m_{j}^{2}}{4j^{2}(j+1)^{2}} \left(R_{nl}^{n'l'}\right)^{2}$$

$$\left|z_{nljm_{j}}^{n'l'jm_{j}+1}\right|^{2} + \left|y_{nljm_{j}}^{n'l'jm_{j}+1}\right|^{2} = \frac{(j+m+1)(j-m)}{4j^{2}(j+1)^{2}} \left(R_{nl}^{n'l'}\right)^{2} \qquad (11.65)$$

$$\left|z_{nljm_{j}}^{n'l'jm_{j}-1}\right|^{2} + \left|y_{nljm_{j}}^{n'l'jm_{j}-1}\right|^{2} = \frac{(j+m-1)(j-m+2)}{4j^{2}(j+1)^{2}} \left(R_{nl}^{n'l'}\right)^{2}$$

An additional rule of transitions is that there must be a parity change in the stationary states; this is known as Laporte's rule. Parity change due to a transition follows  $(-1)^{\Delta l}$ . The spin wave functions obey  $\chi_{+1/2} = -\chi_{-1/2}$ . Since  $\Delta l = \pm 1$  it follows that  $m'_s = m_s$ , (no spin flip for dipole transitions). Employing  $\Delta l = l' - l$ ,  $\Delta s = s' - s$ ,  $\Delta j' - j$ ,  $\Delta m_j = m'_j - m_j$ , we have the fine structure transition rules:

$$\hat{\boldsymbol{\epsilon}} \parallel \text{to } \boldsymbol{z} \quad \hat{\boldsymbol{\epsilon}} \perp \text{to } \boldsymbol{z}$$

$$\Delta l \qquad \pm 1 \qquad \pm 1$$

$$\Delta s \qquad 0 \qquad 0$$

$$\Delta j \qquad 0, \pm 1 \qquad 0, \pm 1$$

$$\Delta m_j \qquad 0, \pm 1 \qquad 0, \pm 1$$
(11.66)

<sup>1</sup>For multi-electron atoms, J = L + S, where  $L = \sum l$  and  $S = \sum s$ , where the sums are over all electrons. The additional rule is that  $J = 0 \rightarrow J' = 0$  is not allowed.

#### 11.6.3 Oscillator strengths

Though full calculation of the oscillator strengths for fine structure transitions is relatively straight forward, the final results are more easily obtained by the use of sum rules. From the sum rule given by Eq. 11.64, we obtain a second sum rule, namely

$$\sum_{j'm'_j} f_{nljm_j}^{n'l'j'm'_j}(\uparrow) = (2j+1) \,\bar{f}_{nl}^{n'l'}(\uparrow), \tag{11.67}$$

where the unprimed state represents the initial upper (higher n or higher energy) level. This is a very important relationship, which states that the average oscillator strength over all j and  $m_j$  states can be simply expressed as the oscillator strength for the Schrödinger states times a single factor of proportionality, which is the multiplicity of the initial state, 2j + 1.

The average oscillator strengths over all  $m_j$  states, i.e., the oscillator strength for transitions from nlj to n'l'j' (the 2j + 1 energy degenerate fine structure states), is given by 11.67 multiplied by the fractional normalized statistical weight between the initial state and final state,  $C_{lj}^{l'j'}$ ,

$$\bar{f}_{nlj}^{n'l'j'}(\uparrow) = \sum_{m'_j} f_{nljm_j}^{n'l'j'm'_j} = C_{lj}^{l'j'} \sum_{j'm'_j} f_{nljm_j}^{n'l'j'm'_j} = C_{lj}^{l'j'}(2j+1) \,\bar{f}_{nl}^{n'l'}(\uparrow), \quad (11.68)$$

where

$$C_{jl}^{j'l'} = \frac{g(lj|l'j')}{\sum_{j'} g(lj|l'j')}$$
(11.69)

and where g(lj|l'j') is the relative statistical weight of the initial state lj to final state l'j' and the sum is taken over j' for transitions sharing the same j state. The convention is that the umprimed state is the upper state. To determine the g(lj|l'j'), consider the fine structure multiplet for a single electron atom, as schematically illustrated in Figure 11.1.

#### The s-p doublet

The  $s_{1/2}-p_{3/2}$  and  $s_{1/2}-p_{1/2}$  doublet is shown in Figure 11.1*a*, as transitions  $\alpha$  and  $\beta$ , respectively. These two transitions share the  $s_{1/2}$  state and transition to or from the split  $p_{1/2}/p_{3/2}$  state. The relative statistical weights for transitions sharing a given state are determined from the split state multiplicities, the 2j+1 z projections of **J** denoted by  $m_j$ . Again, the convention is that the unprimed state is the upper state. For  $\alpha$ , the statistical weight of the split  $p_{3/2}$  state is

$$g(\alpha) = 2j + 1 = 2(l + 1/2) + 1 = 2l + 2.$$
(11.70)

For  $\beta$ , the  $p_{1/2}$  state multiplicity is

$$g(\beta) = 2(l-1/2) + 1 = 2l. \tag{11.71}$$

The ratio is  $g(\alpha):g(\beta) = (l+1):l$ . Since l = 1 for the unprimed state, we have  $g(\alpha):g(\beta) = 2:1$ . We see that fine structure doublets between the  $s_{1/2}$  and  $p_{1/2}$  and  $p_{3/2}$  states have intensity ratios and absorption cross section ratios of 2:1, where the  $s_{1/2}-p_{3/2}$  transition has twice the strength of the  $s_{1/2}-p_{1/2}$  transition. Note, since  $E_{n,p_{3/2}} > E_{n,p_{1/2}}$ , the shorter wavelength component of a doublet has twice the intensity as the longer wavelength component. Amost all doublets in spectra follow this intensity ratio behavior; the "blue" component is twice the strength of the "red" component.

#### The p–d and d–f multiplets

For upper states with l > 1, there are always three components to the multiplet (for single electron atoms). This scenario is illustrated in Figure 11.1*b*, where the transitions  $d_{5/2} - p_{3/2}$  or  $f_{7/2} - d_{5/2}$  (denoted  $\gamma$ ),  $d_{3/2} - p_{3/2}$  or  $f_{5/2} - d_{5/2}$  (denoted  $\delta$ ), and  $d_{3/2} - p_{1/2}$  or  $f_{5/2} - d_{3/2}$  (denoted  $\epsilon$ ), are illustrated.

![](_page_63_Figure_4.jpeg)

Figure 11.1: (a) Schematic of fine structure transitions between s(l'=0) and p(l=1) states, which result in a doublet. The doublet ratio is  $g(\alpha):g(\beta) = 2:1$ . (b) Fine structure transition between higher l states. Illustrated in this figure is a transition between p(l'=1) and d(l=2) or a transition between d(l'=2) and f(l=3), but the configuration is appropriate for  $\Delta l = \pm 1$  for which none of the states are the s state. The multiplet has three components with ratio  $g(\gamma):g(\delta):g(\epsilon) = 9:1:5$  for p-d and 20:1:14 for d-f.

In principle, these triple multiplets can be taken to higher angular momentum states, l, since the spin-orbit coupling for any l results in a single splitting,  $j = l \pm 1/2$  (this is not the case in general for multi-electron atoms, as we will elaborate upon below). Note that, under the electric dipole approximation, the transitions  $d_{5/2} - p_{1/2}$  and  $f_{7/2} - d_{3/2}$  do not occur, since they would require  $\Delta j = 2$ , which is not allowed by the selection rules.

Consider the upper levels (unprimed states) for  $d_j - p_{j'}$  transitions. As illustrated in Figure 11.1*b*, both  $\delta$  and  $\epsilon$  share at the same  $d_{1/2}$  state. As such, it is the sum of statistical weights of  $\delta + \epsilon$  that are in proportion to the statistical

weight for  $\gamma$ , which transitions from the  $d_{3/2}$  state. We have

$$g(\gamma) = 2j + 1 = 2(l+1/2) + 1 = 2l + 2,$$
  

$$g(\delta) + g(\epsilon) = 2j + 1 = 2(l-1/2) + 1 = 2l.$$
(11.72)

Similarly, for the lower levels (primed states) of the  $d_j - p_{j'}$  transitions,  $\delta$  shares the  $d_{3/2}$  state with  $\gamma$ , and we see that the sum of statistical weights for  $\delta + \gamma$  are in proportion to the statistical weight for  $\epsilon$ . From examination of Figure 11.1*b*, we have

$$g(\epsilon) = 2j' + 1 = 2(l' - 1/2) + 1 = 2(l - 3/2) + 1 = 2l - 2,$$
  

$$g(\delta) + g(\gamma) = 2j' + 1 = 2(l' + 1/2) + 1 = 2(l - -1/2) + 1 = 2l.$$
(11.73)

We obtain the two ratios (two equations and three unknowns),

$$\frac{g(\gamma)}{g(\delta) + g(\epsilon)} = \frac{2l+2}{2l}, \qquad \frac{g(\epsilon)}{g(\delta) + g(\gamma)} = \frac{2l-2}{2l}.$$
(11.74)

Setting  $g(\delta) = 1$  and solving the two equations for two unknowns, we obtain the relative statistical weight ratios

$$g(\gamma):g(\delta):g(\epsilon) = [(l+1)(2l-1)]:1:[(l-1)(2l+1)],$$
(11.75)

which shows that  $\gamma$  is the strongest transition,  $\epsilon$  is the second strongest, and  $\delta$  is the weakest.

#### Computing oscillator strengths

From the above, the relative statistical weight ratios for the s, p, and d fine structure multiples of hydrogen and hydrogen–like ions are

$$s \leftrightarrow p \quad (l=1) \quad g(p_{3/2}|s_{1/2}):g(p_{1/2}|s_{1/2}) = 2:1$$
  

$$p \leftrightarrow d \quad (l=2) \quad g(d_{5/2}|p_{3/2}):g(d_{3/2}|p_{3/2}):g(d_{3/2}|p_{1/2}) = 9:1:5 \quad (11.76)$$
  

$$d \leftrightarrow f \quad (l=3) \quad g(f_{7/2}|d_{5/2}):g(f_{5/2}|d_{5/2}):g(f_{5/2}|d_{3/2}) = 20:1:14.$$

Note that Eq. 11.76 can be extended by incrementing l and j.

To determine the fine structure oscillator strengths for transitions between states nlj and n'l'j', we require the  $C_{lj}^{l'j'}$  (Eq. 11.69) for evaluation of Eq. 11.68. Consider the fine structure of the H $\alpha$  transition, as illustrated in Figure 11.2. The sums in Eq. 11.69 apply for transitions with shared upper states. Since  $\alpha$ ,  $\beta$ , and  $\gamma$  do not share upper states with any other transitions, we have

$$C(\alpha) = C_{1\frac{3}{2}}^{0\frac{1}{2}} = 1, \qquad C(\beta) = C_{1\frac{1}{2}}^{0\frac{1}{2}} = 1, \qquad C(\gamma) = C_{2\frac{5}{2}}^{1\frac{3}{2}} = 1.$$
 (11.77)

![](_page_65_Figure_1.jpeg)

Figure 11.2: Schematic of the seven-fold spectral multiplet of the H $\alpha$  fine structure transitions. The slight energy offsets due to the Lamb shifts are illustrated, otherwise the identical j states for each principle level n are degenerate in the Dirac theory.

Since  $\eta$  and  $\zeta$  share the upper  $3s_{1/2}$  state and  $\delta$  and  $\epsilon$  share the upper  $3d_{3/2}$  state, we have

$$C(\eta) = C_{0\frac{1}{2}}^{1\frac{1}{2}} = \frac{g(\eta)}{g(\eta) + g(\zeta)} = \frac{1}{1+2} = \frac{1}{3}$$

$$C(\zeta) = C_{0\frac{1}{2}}^{1\frac{3}{2}} = \frac{g(\zeta)}{g(\eta) + g(\zeta)} = \frac{2}{1+2} = \frac{2}{3}$$

$$C(\delta) = C_{2\frac{3}{2}}^{1\frac{3}{2}} = \frac{g(\delta)}{g(\delta) + g(\epsilon)} = \frac{1}{1+5} = \frac{1}{6}$$

$$C(\epsilon) = C_{2\frac{3}{2}}^{1\frac{1}{2}} = \frac{g(\epsilon)}{g(\delta) + g(\epsilon)} = \frac{5}{1+5} = \frac{5}{6}.$$
(11.78)

The ingredients to compute the  $\bar{f}_{nlj}^{n'l'j'}(\uparrow)$  for H $\alpha$  fine structure transitions are listed in Table 11.2. The tabulated values applies to emission. The multiplicity 2j + 1 (column 3) is that of the upper state. The average oscillator strengths for the Schrödinger states are computed from the Balmer series formulae listed in Table 11.1 and Eq. 11.55.

#### 11.6.4 Fine structure line intensities and cross sections

One of the modifications that are required is that the multiplicity of states for fine structure multiplets is 2j + 1. Thus,

We see that, to order  $Z\alpha$ , the dipole moments between initial and final states of transitions, and therfore, the transition probabilities, depend only upon their initial and final l and  $m_l$  states, a condition identical to the Schrödinger theory. Thus, to a first order approximation, a transition rate between states nlj and n'l'j' is identical to a transition between the Schrödinger states nl and n'l',

$$\bar{A}_{nlj}^{n'l'j'}(\uparrow) = \bar{A}_{nl}^{n'l'}(\uparrow), \qquad \bar{A}_{n'lj'}^{nlj}(\uparrow) = \bar{A}_{n'l'}^{nl}(\uparrow), \qquad (11.79)$$

	Transition	$C_{lj}^{l^\prime j^\prime}$	$2j\!+\!1$	$\bar{f}_{nl}^{n'l'}(\uparrow)$	$\bar{f}_{nlj}^{n'l'j'}(\uparrow)$
$(\alpha)$	$2s_{1/2}\!-\!3p_{3/2}$	1	4	0.142	0.57
$(\beta)$	$2s_{1/2} - 3p_{1/2}$	1	2	0.142	0.28
$(\gamma)$	$2p_{3/2}\!-\!3d_{5/2}$	1	6	0.417	2.50
$(\delta)$	$2p_{3/2}\!-\!3d_{3/2}$	1/6	4	0.417	0.28
$(\epsilon)$	$2p_{1/2}\!-\!3d_{3/2}$	5/6	4	0.417	1.39
$(\eta)$	$2p_{1/2}\!-\!3s_{1/2}$	1/3	2	0.041	0.03
$(\zeta)$	$2p_{3/2}\!-\!3s_{1/2}$	2/3	2	0.041	0.05

Table 11.2: Fine structure oscillator strengths for  $H\alpha$ 

where  $\bar{A}_{nl}^{n'l'}(\uparrow)$  is given by Eq. 11.36 for emission and Eq. 11.41 for absorption. On average, the initial j and  $m_j$  state of the electron is irrelevant. This treatment is tantamount to stating that  $m_l$  is still a "good quantum number", which is equivalent to stating that the precession of L about J can be neglected to order  $Z\alpha$ .

## 11.7 Lifetimes and the radiation width

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 $\Delta E_n = \hbar / \langle t_n \rangle = \hbar \beta_n = \Gamma_n$ Define  $\Gamma_n$  as the radiation width of an energy level.

$$\exp\left\{-\frac{i}{\hbar}\left(E_n - \frac{1}{2}i\Gamma\right)t\right\}$$
(11.80)

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