Line Radiation From Atoms and Ions

1. Permitted and Forbidden Transitions

First, let's review the selection rules for $L - S$ coupling:
$\Delta L = \pm 1$ (or 0)
$\Delta S = 0$
$\Delta J = 0, \pm 1$ except $J = 0 \rightarrow 0$

Rule 1: Photons carry angular momentum.
Rule 2: Transitions only occur between terms of the same multiplicity.

Spectroscopic notation is: $n^{(2S+1)}L_J$ where n is the principal quantum number, S is the electron spin quantum number, L is the orbital angular momentum quantum number and J is the total angular momentum quantum number.

Using this notation, let's look at the transition from the lowest energy state of the triplet He (2^3S_1) to the ground state of singlet He (1^1S_0). We see that $\Delta n = 1$, $\Delta S = 1$, $\Delta L = 0$ and $\Delta J = 1$. Because the first two rules of $L - S$ coupling are broken, this is a (semi)forbidden transition and has a long lifetime (> 2 hours).

Now let's look at the transition to the ground state of Na I from ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$. In this case $\Delta S = 0$, $\Delta L = 1$ and $\Delta J = 1$. This transition follows the rules of $L - S$ coupling and is a strongly allowed (*resonance*) line.

These electronic transitions can often be observed in the UV for light elements or in X-rays for highly ionized heavier elements (due to the higher potentials). They are seen both in emission (e.g. emission nebulae) and absorption against UV continuum sources. In the case of absorption, the H Lyman series (transitions to/from the ground state) is widely observed due to the high abundance of H.

Observations of ions such as C^{+2}, N^{+3} and O^{+4} that are produced by collisional ionization can be used to reveal the presence of hot (1-3$\times 10^5$ K) gas in the ISM due to their high ionization potentials (47.9, 77.5 and 113.9 eV, respectively).

Note that in the ISM, because of its low density, forbidden line emission is still possible because the timescales for collisional de-excitation can be quite long. In fact, observations show that forbidden lines of the most common elements (e.g. C, N, O) are often some of the strongest in the ISM. One example is the ${}^2D_{5/2} \rightarrow {}^4S_{3/2}$ transition of O^+ at λ3729.

2. Fine-Structure Lines

Fine structure lines are those that occur between levels with the L and S values but different J. These levels are a result of spin-orbit interactions.

Consider a p^2 electron configuration there are two electrons each with spin angular momentum of 1/2. In the case that $S = 0$ we are in the antiparallel state and if $S = 1$ then we are in the parallel state, corresponding to multiplicity values of 1 (singlet) and 3 (triplets).

For $L = 1$ the possible values of J are 0, 1 and 2. Possible values for the sum of the electron spins is 0 and 1. If $S = 1$ then the state ${}^3P_{0,1,2}$ each have slightly different energies due to spin-orbit coupling.

Fine-structure lines are much lower energy than the transitions between different levels of n, L and S that have been previously discussed, and are typically observed in the IR and radio. For instance, the ground state of CI has an electronic configuration of $1s^22s^22p^2$ and has fine-structure lines from the ${}^3P_2 \rightarrow^3 P_1$ and ${}^3P_1 \rightarrow^3 P_0$ transitions at 370 μm and 609 μm.

These fine-structure lines come from transitions within the same multiplet, and violate the rules of $L - S$ coupling, and so are forbidden transitions. However, they are still strong lines (compared to common mm-wave rotational lines because of the ν^3 dependence on the Einstein A coefficient. The A value of the 609 μm transition of CI (7.8×10^{-9} s^{-1}) is small compared to that for the CII $2p^2P^o_{3/2} \rightarrow 2p^{22}S_{1/2}$ A value (1.5×10^9 s^{-1}) at 1037 Å but is roughly comparable to that for the permitted rotational line of CO (1–0) at 2.6 mm.

The IR lines of C are especially useful because the are not affected by dust, which strongly extinguishes optical and UV light. It is therefore a good tracer of diffuse and molecular clouds throughout the galaxy and is important in interstellar cooling.

In the diffuse ISM ($A_V < 5$) the absorption of UV light by CI creates CII because it has a lower ionization potential than HI (11.25 vs. 13.6 eV). The 158 μm line of CII (${}^2P_{3/2} \rightarrow^2 P_{1/2}$) is therefore widely present in the ISM and in the Milky Way the total luminosity in this CII line is $\sim 5 \times 10^7$ L$_\odot$. As a reference, the total dust luminosity of the Milky Way is $\sim 2 \times 10^{10}$ L$_\odot$. CII is often the brightest emission line in the spectrum of external galaxies and is used as a tracer of star formation.

3. Hyperfine Lines

Until now we have only considered transitions involving L, S and J. However, there is a class of line splittings called *hyperfine lines* arising from the interaction of electron angular momentum with the *nuclear* spin (I). Although I is referred to as the total nuclear spin, it is actually a measure of the total nuclear angular momentum, and not just its spin.

Nucleons of the same type tend (but are not required) to combine to form zero angular momentum, if possible, so even numbers of one type of nucleons have zero angular momentum and an odd number of nucleons will have $I = 1/2$. For instance, ^{13}C has 6 protons and 7 neutrons, and will have angular momentum of $I = 1/2$.

The total angular momentum vector is now defined as the vector sum of $\mathbf{F} = \mathbf{L} + \mathbf{S} + \mathbf{I}$. F can take values ranging from the smallest positive integer or half integer that can be formed from L, S and I and $L + S + I$.

The selection rules for electric-dipole or magnetic-dipole transitions between hyperfine states are:

$\Delta F = 0, \pm 1$
$F = 0 \rightarrow 0$ is forbidden.

Perhaps the most famous hyperfine line is the 21 cm line of neutral atomic H in the ground state ($1^2S_{1/2}$). If the electron and proton spins are parallel then $F = I + S = 1$ and if they are antiparallel then $F = 0$. Note that $\Delta L = 0$ so the hyperfine transition is forbidden. The energy involved in the transition from parallel to antiparallel states is low ($\nu = 1420$ MHz, $\lambda = 21$ cm) and the magnetic-dipole probability is also small, so the spontaneous emission rate is also very small (2.869×10^{-15} s^{-1}).

Despite the low transition rate, the 21 cm line is widely seen in the Milky Way and external galaxies and is one of the most important tracers of diffuse gas the galactic rotation rates.

4. Absorption and Emission

We will discuss the types of radiative processes that can take an electron from one state to another in an atom. For now we will call the higher energy state i and the lower energy state j. For more complete derivations of the following formulas, see Kwok chaper 5.5.

Spontaneous decay from a higher to a lower state is accompanied by the emission of a photon with energy $h\nu$ equal to the energy E_{ij} separating the two states. The Einstein spontaneous emission coefficient (A_{ij}) is the transition probability such that the change in the number density of the upper state $\Delta n_i = -n_i A_{ij} \Delta t$ over all solid angles and frequencies.

An electron can be brought from energy state j to i through the absorption of a photon with energy $h\nu_{ij}$. The transition rate is dependent on the local radiation density. The Einstein induced absorption coefficient (B_{ji}) is given by $\Delta n_j = -n_j B_{ji} \overline{J} \Delta t$, where $\overline{J}$ is the local radiation field averaged over all angles and frequencies.

The local radiation field can also cause a downward transition, called stimulated emission. The Einstein stimulated coefficient B_{ij} is defined as $\Delta n_i = -n_i B_{ij} \overline{J} \Delta t$.

Assuming that the level populations and the radiation field is in detailed balance, and under thermodynamic equilibrium, we get the following equations:

$$n_i(A_{ij} + B_{ij}\overline{J}) = n_j B_{ji} \overline{J}$$

$$\overline{J} = I_\nu = B_\nu = \frac{2h\nu^3}{c^2} \frac{1}{exp(h\nu/kT) - 1}$$

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-h\nu/kT}$$

where the last identity assumes that the population distribution is given by the Boltzman equation. Combining these equations we get two identities:

$$\frac{g_j}{g_i} \frac{B_{ji}}{B_{ij}} = 1$$

$$\frac{A_{ij}}{B_{ij}} = \frac{2h\nu^3}{c^2}$$

We can use the Einstein A and B coefficients to describe the absorption (κ_ν) and emission (j_ν) coefficients for bound-bound transitions. Here we will assume that the emission and absorption profiles (ψ_ν and ϕ_ν) are the same (Doppler) profile.

$$\kappa_\nu = \frac{h\nu}{4\pi}(n_j B_{ji} - n_i B_{ij})\phi_\nu$$

$$j_\nu = \frac{h\nu}{4\pi} n_i A_{ij} \phi_\nu$$

The source function is given by:

$$S_\nu = j_\nu / \kappa_\nu$$

$$S_\nu = \frac{A_{ij}/B_{ij}}{\frac{n_j B_{ji}}{n_i B_{ij}} - 1}$$

$$S_\nu = \frac{2h\nu^3/c^2}{\frac{g_i n_j}{g_j n_i} - 1}$$

The absorption by atom is given by:

$$a_\nu = \frac{\kappa_\nu}{n_j}$$

$$a_\nu = \left(1 - \frac{n_i}{n_j}\frac{g_j}{g_i}\right)\frac{h\nu}{4\pi} B_{ji} \phi_\nu$$

$$a_\nu = (1 - e^{-h\nu/kT})\frac{h\nu}{4\pi} B_{ji} \phi_\nu$$

5. Spectral Line Formation and Scattering

Here I will just touch on Kwok chapters 5.6 and 5.7. Please see the text for a full derivation of the absorption index, refractive index, Lorentz profile and oscillator strength.

One important equation from this chapter is the formula for the Lorentz profile, which is given by:

$$\kappa_\nu = N\frac{\pi e^2}{m_e c}\frac{\gamma/(4\pi^2)}{(\Delta\nu)^2 + (\gamma/4\pi)^2}$$

where $\Delta\nu = (\omega_o - \omega)/2\pi$ and $\gamma = \frac{2}{3}\frac{e^2\omega_o^2}{m_e c^3}$ and ω_o is the natural frequency of the harmonic oscillator used to approximate the electronic transition.

The atomic absorption coefficient (a_ν) is defined by $a_\nu = \kappa_\nu/N$. In the case that $(\omega - \omega_o) \gg \gamma$,

$$a_\nu = \frac{8\pi e^4}{3m_e^2c^4}\frac{1}{\left(\frac{\omega_o^2}{\omega^2} - 1\right)^2}$$

At low frequencies where $\omega \ll \omega_o$,

$$a_\nu = \frac{8\pi e^4}{3m_e^2c^4}\frac{\omega^4}{\omega_o^4} \propto \lambda^{-4}$$

This is known as Rayleigh scattering and is responsible for making the sky blue during the day and making sunsets appear red.

At high frequencies where $\omega \gg \omega_o$,

$$a_\nu = \frac{8\pi}{3}\left(\frac{e^2}{m_e c^2}\right)^2$$

The frequency independence of the scattering is referred to as the Thompson cross section.

Finally, when an incident photon encounters an atom the cross section is enhanced as resonance wavelengths corresponding to electronic transitions. If the photon has energy $h\nu_o$ and a transition has energy E_o that is less than that of photon, then the scattered photon of energy $h\nu_o - E_o$ can be produced. This process is known as Raman scattering, and the shift in frequency of the photon is called the Raman shift.

6. Line Broadening

6.1. Natural Broadening

The minimum width of any spectral line is given by the Heisenberg uncertainty principle $\Delta E \Delta t \sim h/2\pi$. Because the lifetime of a state (Δt) is finite, the energy of a transition has a finite spread. If the line profile is given by the Lorentz profile, then the frequency at which the intensity is half of the maximum occurs when:

$$\Delta\nu_{1/2} = \frac{\gamma}{4\pi}$$

$$\Delta\nu_{1/2} = \frac{1}{4\pi}\left(\frac{2}{3}\frac{e^2\omega_o^2}{m_e c^3}\right)$$

In wavelength units, the half width is given by,

$$\Delta\lambda_{1/2} = \frac{c}{\nu^2}\Delta\nu_{1/2}$$

$$\Delta\lambda_{1/2} = \frac{2}{3}\frac{\pi e^2}{m_e c^2}$$

This value (5.9×10^{-5} Å) is called the natural width.

6.2. Doppler Broadening

The natural line width is much lower than any observed line width in the ISM. In interstellar clouds the broadening of spectral lines is dominated by random motions of the gas particles. These motions produce Doppler shifts and create line wings on both sides of ν_o. According to the Doppler formula, line-of-sight motion v_z will cause a frequency shift,

$$\frac{\Delta\lambda}{\lambda_0} = \frac{\Delta\nu}{\nu_0} = \frac{v_z}{c}$$

If the motions of the gas particles is purely thermal, then the distribution in v_z is given by the Maxwellian distribution,

$$\frac{N(v_z)dv_z}{N} = \frac{1}{\sqrt{\pi}}\exp\left(-\frac{v_z^2}{\alpha^2}\right)\frac{dv_z}{\alpha}$$

where N is the total number population, m is the mass of each atom, and α is defined by $\alpha^2 \equiv 2kT/m$.

After some algebra (see Kwok chapter 5.8) one finds that the full-width-half-maximum of the line is given by,

$$2\Delta\nu_{1/2} = \frac{2}{c}\sqrt{\alpha \ln(2)}\nu_0$$

In terms of velocity,

$$\frac{\Delta v}{c} = \frac{\Delta\nu}{\nu_0}$$

$$v_{FWHM} = 2\sqrt{\frac{2kT}{m}\ln(2)}$$

The linewidth from Doppler motions of CO $J = 1 \rightarrow 0$ at $\nu_0 = 115$ GHz and kinetic temperature 50 K the Doppler broadening is $\sim 10^5$ times larger than the natural width.

Not all Doppler broadening comes from thermal motions. Turbulent motions will also create a Doppler broadening, but with no dependency on T or m. In the presence of turbulence, the total Doppler line width is given by

$$v^2_{FWHM,total} = v^2_{FWHM,thermal} + v^2_{FWHM,turbulent}$$

In general, measurement of the width of a single line gives the total line width but is unable to distringuish between the thermal and turbulent components. However, measurement of multiple line widths of atoms, ions or molecules with different masses can break this degeneracy.

7. The Voigt Profile

The Voigt profile is the convolution of the Lorentz and Doppler profiles. The derivation of the profile is in Kwok chapter 5.9. The most important aspects of the Voigt profile is that near the line center the line profile has a Gaussian shape, and away from the line center the line wings are dominated by radiative and collisional damping.

Near the line center,

$$a_\nu = a_1 e^{-\left(\frac{\nu-\nu_0}{\Delta\nu_D}\right)^2}$$

where a_1 is a constant given by Eq. (5.79) in Kwok.

In the line wings,

$$a_\nu = \frac{\pi e^2}{m_e c} f \frac{\Gamma}{4\pi^2} \frac{1}{(\nu-\nu_0)^2}$$

where Γ is the damping constant and f is the oscillator strength.

8. Equivalent Width and the Curve of Growth

The equivalent width is a measure of the total strength of an absorption line, and is defined by,

$$W_\nu = \frac{\int_{line}(F_c - F_\nu)d\nu}{F_c}$$

$$W_\nu = \int_{line} \left(1 - \frac{F_\nu}{F_c}\right) d\nu$$

where F_ν is the flux of the line at wavelength ν and F_c is the flux of the continuum. The continuum can be considered to be constant over the narrow width of a line.

For an optically thin line ($\tau \ll 1$), one can derive that,

$$W_\nu = \left(\frac{\pi e^2}{m_e c}\right) fN$$

where N is the column density.

For an optically thick line ($\tau \gg 1$), one can derive that,

$$W_\nu \propto \sqrt{Nf\Gamma}$$

In the optically thick case, adding additional column density along the line of sight does not affect the absorption from the line center because it is already saturated. Instead, all of the addition absorption comes from the line wings of the Voigt (Lorentz) profile. This change in behavior from linear to square-root dependence on column density is called the curve of growth.

9. Recombination Lines

In typical interstellar conditions the H atom cannot be excited by collisional means and there is very little background interstellar radiation in the visible region available for excitation by absorption. The only way that an H atom can be found in an excited state is by recombination. After each recombination, the atom will cascade to lower states by a series of spontaneous emissions, creating recombination lines along the way.

The spontaneous transition probability $A_{nl,n'l'}$ for electric-dipole transitions in hydrogenic ions is given by,

$$A_{nl,n'l'} = \frac{64\pi^4\nu^3}{3Z^2hc^3}\frac{\max(l,l')}{2l+1}e^2a_0^2\left[\int_0^\infty R_{n'l'}\left(\frac{r}{a_0}\right)R_{nl}dr\right]^2$$

where

$$\nu = R_z Z^2\left(\frac{1}{n^2}-\frac{1}{n'^2}\right)$$

and R_{nl} and $R_{n'l'}$ are the normalized radial wavefunctions of the intial (i) and final (j) states, respectively, Z is the nuclear charge, R_z is the Rydberg constant, and a_0 is the Bohr radius. For electric-dipole transitions the select rule is $l-l' = \pm 1$. See Kwok chapter 5.11 for specific solutions for the H atom.

9.1. Optical Depth of Lyman α

The Lyman transition decay rates are much higher than the recombination rates, so any recombination will quickly decay to the ground state. In this case all H atoms in the ISM can be assumed to be in the ground state. For gas at a temperature of $\sim 10^4$ K, the absorption coefficient $a_\nu \sim 10^{-13}$ cm^2 for the Lyman α line. The mean free path for a Lyα photon is $1/n_h a_\nu$, which is extremely short compared to the typical size of a molecular cloud. The optical depth in the line is

$$\tau = \int_0^L n_1 a_\nu ds$$

$$\tau \sim 3\times 10^5\left(\frac{n_H}{\text{cm}^{-3}}\right)\left(\frac{L}{\text{pc}}\right)$$

This high optical depth implies that Lyα photons will be scattered many times before escaping a nebula. Since the H atoms have a spread in velocities, some of the Lyα photons will be scattered into the line wings, making it easier for them to escape.

9.2. Population Distribution of the H atom

In general, deriving the level population distribution of H atoms requires a full radiative transfer calculation because of optical depth and self-absorption effects. However, there are two cases in which the population distribution can be calculated analytically.

In Case A, one assumes that all of the H transitions are optically thin. In Case B, one assumes that the entire Lyman series is optically thick, with the net effect that every Lyman series photon is eventually converted to photons of lower H series plus a Lyα photon.

For Case B every Lyα photon will be scattered from atom to atom until it escapes from the nebula or is absorbed by dust, but either way it will have no effect on the population distribution of the remaining states, with the net effect that the $n = 1$ is totally absent from the calculation of states.

In either Case, the absorption and stimulated emission terms can be omitted and the statistical equilibrium equation is:

$$\sum_{i=n+1}^{\infty} \sum_{l'} n_{il'} A_{il',nl} + n_p n_e \alpha_{nl}(T_e) = n_{nl} \sum_{j=1\mathrm{or}2}^{n-1} \sum_{l''} A_{nl,jl''}$$

where the first term on the left represents cascade from levels above, the second term on the left represents direct capture of a free electron, and term on the right represents cascade to levels below. For Case A the sum on the right-hand side begins with $j = 1$ and for Case B with $j = 2$. $\alpha_{nl}(T_e)$ is the recombination coefficient defined in Eq. (4.41) in Kwok.

10. Collisionally Excited Lines

Although the abundances of metals are much lower than that of H, collisionally excited atomic lines in galactic nebulaue are often as strong as the H recombination lines because collisionsal processes are several orders of magnitude faster than the recombination process. The collisional cross section for transition from level j to level i is inversely proportional to ν^2 above the energy treshold E_{ij} and zero below.

10.1. The 21-cm HI line

Neutral H has two hyperfine states, so it can be approximated by a two-level atom. The relative populations of these states is determined by collisions due to the long radiative lifetime ($\sim 10^6$ years) of the upper state.

The absorption coefficient is given by,

$$a_\nu = \left(1 - e^{-h\nu/kT}\right) \frac{\pi e^2}{m_e c} f_{ji} \phi_\nu$$

Since $h\nu \ll kT$,

$$a_\nu = \left(\frac{h\nu}{kT}\right) \left(\frac{\pi e^2}{m_e c}\right) f_{ji} \phi_\nu$$

$$a_\nu = [1.05 \times 10^{-15} \mathrm{cm}^2 \mathrm{s}^{-1}] \left(\frac{10\mathrm{K}}{T}\right) \phi_\nu$$

One can see that the optical depth of 21-cm line is generally small, and that HI absorption is dominated by cold gas. The column density of atomic hydrogen can be derived from the integrated strength of the 21-cm line, which also gives the velocity and velocity dispersion of the gas. When seen in absorption, the 21-cm line reals the presence of cold diffuse clouds.

10.2. Forbidden Lines of Metals

Due to the low metal abundances and small transition rates, the collisionally excited lines are generally optically thin and the line intensity is directly proportional to the line emissivity.

The emissivity is given by,

$$j_\nu = \frac{h\nu}{4\pi} n_i A_{ij} \psi_\nu$$

We can consider the [OII] doublet as a pair of two-level atom systems due to the small energy difference of the upper states (3726 and 3728 Å) of $^2D_{3/2}$ and $^2D_{5/2}$. If we approximate that $E_2 = E_3$ and $\nu_{31} = \nu_{21}$ and no transitions between levels 3 and 2 then the intensity ratio is given by:

$$\frac{I(3726\mathring{A})}{I(3728\mathring{A})} = \frac{n_3 A_{31}}{n_2 A_{21}}$$

$$\frac{I(3726\mathring{A})}{I(3728\mathring{A})} = \frac{C_{13}}{C_{12}} \frac{1 + \frac{n_e C_{21}}{A_{21}}}{1 + \frac{n_e C_{31}}{A_{31}}}$$

At low densities this line ratio gives $I_{31}/I_{21} = 2/3$. At high densities the line ratio $I_{31}/I_{21} = 3.3$. Because the line ratios are so different at low and high density, observations of the [OII] doublet and other similar ions can be used as density probes of a nebula.

Measurement of other line ratios can be used to study the electron temperature (see Kwok chapter 5.12.2). For instance, let's consider the set of forbidden lines of [OIII] from ${}^1S_0 -{}^1 D_2 -{}^3 P_{0,1,2}$. In the low density limit, every collisional excitation will result in the emission of a photon, and the upper states can be populated by collisional excitation from the ground state. In this case the equations for statistical equilibrium are

$$n_2 A_{21} = n_1 n_e C_{12}$$

$$n_3(A_{31} + A_{32}) = n_1 n_e C_{13}$$

$$\frac{n_3}{n_2} = \frac{C_{13}}{C_{12}} \frac{A_{21}}{A_{31} + A_{32}}$$

The intensity ratio of the ${}^1S_0 -{}^1 D_2$ line to the sum of the ${}^1D_2 -{}^3 P_2$ and ${}^1D_2 -{}^3 P_1$ lines is

$$\frac{I(4363\mathring{A})}{I(5007\mathring{A} + 4959\mathring{A})} = \frac{n_3 \nu_{32} A_{32}}{n_2 \nu_{21} A_{21}}$$

after some algebra one finds that

$$\frac{I(4363\mathring{A})}{I(5007\mathring{A} + 4959\mathring{A})} = 0.132 \times e^{-32990/T_e}$$