Chapter 7

Line transfer

In contrast to dust, the opacities of gas are usually dominated by lines. These are often called *bound-bound transitions* and they are ruled by quantum mechanics. The gas atoms or molecules have discrete energy states. Collisions between the molecules or atoms allow them to jump from one state to another. These are called *collisional transitions*. Another kind of transition is by sending out a photon or by absorbing one. These are called *radiative transitions*, and these are the main ingredient in line radiative transfer. In this chapter we will start with the basics of line radiative transfer. Then we will discuss several well-known atoms and molecules and their energy level diagrams, their quantummechanical selection rules for radiative transitions etc. We will then discuss method for solving line transfer problems. And finally we will discuss some example problems.

7.1 Quantum states of atoms & molecules

7.1.1 Levels and their occupations

Consider an atom or molecule with N_{levels} discrete quantummechanical energy states. In radiative transfer jargon they are called *levels*. Let us write their energies as E_i with $i = 1 \cdots N_{\mathrm{levels}}$, and order then in ascending order in energy: $E_{i+1} \geq E_i$.

Suppose now that we have one cubic cm of the atom/molecule gas somewhere, and we count how many of these molecules are in each state. This gives us the *occupation number density* N_i belonging to each state (note that also this symbol is an N-symbol, like N_{levels}, but it is customary to write occupation numbers with the symbol N_i). The total number of atom/smolecules per cubic cm is written as N and we have $N = \sum_i N_i$. We can now define the *fractional occupation number* n_i as

$$n_i = \frac{N_i}{N} \tag{7.1}$$

such that $\sum_i n_i = 1$. One of the tasks of line radiative transfer is to compute the n_i (or equivalently N_i).

Collisions between atoms or molecules can cause the atom/molecule to transit from any state i to any other state j. In dense environments these collisions take place so often that it is safe to assume that the occupation numbers are thermally distributed:

$$\frac{n_j}{n_i} = \frac{N_j}{N_i} = e^{-(E_j - E_i)/k_B T} \tag{7.2}$$

where k_B is Boltzmann's constant and T is the temperature of the gas. If this can be assumed at some location, we say that the system is locally in thermodynamic equilibrium, or in radiative transfer jargon: in *local thermodynamic equilibrium (LTE)*.

If, however, the density is very low, the radiative transitions can become more frequent than collisional transitions, and this may lead to a *non-LTE* situation: the level populations will then no longer follow Eq. (7.2). The computation of the level populations n_i can then become quite complicated and we will discuss various methods to tackle this problem in this chapter.

7.1.2 Degenerate states, statistical weights

Usually atoms and molecules have many states with exactly the same energy, i.e. $E_{i+1} = E_i$ for some i. This is related to rotational symmetry. Consider, for example, a hydrogen atom. As we learned from our quantum mechanics courses, we can expand the wave functions of the electron position relative to the nucleus into states that are a product of a radial and an angular part. The angular part can be expanded into spherical harmonics Ψ_{lm}, where l and m are integers. The index l has values from $l = 0$ and upward and is the index for the total angular momentum. For a given l, the values of m range from $m = -l, \cdots, +l$. There are $2l + 1$ values of m. For a given l, the values of m denote the different *angular orientations* of the wave function. The classical analog is a spinning wheel that has angular momentum l along its rotational axis. The m then gives the direction in which the axis points. Classically this would have to be *two* angles; quantummechanically it is *one* integer m.

If there is no external influence that could "break the rotational symmetry" (such as an electric or a magnetic field), the various states $m = -l, \cdots, +l$ *cannot* have different energies, because the different orientations of the electron wave function should not matter. One can then say that these states are actually the same state, but that the state is *degenerate*. In other words: rather than treating all orientations of that state as individual states, we treat it as a single state i with a *statistical weight* g_i. For electronic transitions of atoms we have $g_i = 2l + 1$, where l is the orbital angular momentum of the electron in state i.

Sometimes one is not interested in very small energy differences between levels. One can then merge levels of nearly equal energy into one. The statistical weight of such a combined state is then the total number of "real" states that are packaged into this combined one.

If we include the statistical weights, Eq. (7.2) becomes

$$\frac{n_j}{n_i} = \frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/k_B T} \tag{7.3}$$

7.1.3 Partition function

Equation (7.3) gives the ratios of the fractional occupation numbers n_j/n_i, but not the fractional occupation numbers n_i themselves. To find these we have to compute the *partition function* $Z(T)$

$$Z(T) = \sum_i g_i e^{-E_i/k_B T} \tag{7.4}$$

which is a function of the temperature T. It is important to sum over *all* states. The fractional occupation number can then be written as

$$n_i = \frac{1}{Z(T)} g_i e^{-E_i/k_B T} \tag{7.5}$$

Eq. (7.5) gives the fractional occupations of the various levels of atoms or molecules that are in LTE. The $Z(T)$ is the "normalization constant" of this equation.

7.1.4 Collisional transitions between levels

A given atom or molecule typically does not stay in a given state forever. Atoms or molecules regularly collide with each other, which can cause transitions from any state i to any other state j. The rate (= events per second) by which an atom in state i is collisionally changed to state j can be written as

$$C_{i\rightarrow j} = NK_{i\rightarrow j}(T) \tag{7.6}$$

where N is the number density (atoms per cubic cm) of possibly colliding particles, and $K_{i\rightarrow j}(T)$ is the collision coefficient. The computation of $K_{i\rightarrow j}(T)$ is often very complicated, but thankfully: for many atom/molecule species these calculations have already been done by specialists and we can use their results.

If $E_j < E_i$, the collision coefficient is only weakly dependent on temperature, and its values can sometimes be found in tables. The upward coefficient can then be computed from the downward coefficient by demanding that the collisional upward/downward rates keep the LTE populations intact:

$$n_j C_{j\rightarrow i} = n_i C_{i\rightarrow j} \tag{7.7}$$

With Eq. (7.3) this leads to

$$C_{j\rightarrow i} = C_{i\rightarrow j}\frac{g_i}{g_j}e^{-(E_i-E_j)/k_BT} \tag{7.8}$$

In general, however, molecules or atoms may have different collision partners. For instance, a CO molecule in the interstellar medium is typically much more often hit by H_2 molecules than with other CO molecules. And in hot atomic gas, atoms are typically most often hit by free electrons. For each type of collision partner one would thus have a separate set of collision rates. If you are lucky, there is one type of particle that clearly dominates, but sometimes two or more types of collision partners could be important (for instance H_2 and He for CO molecules).

7.2 Line emission and absorption

7.2.1 Einstein coefficients

A transition from one level to another can also be facilitated by the emission or absorption of a photon. This is called a *radiative transition*, or a *spectral line transition*. It means that we have to solve the radiative transfer equation:

$$\frac{dI_\nu}{ds} = j_\nu - \alpha_\nu I_\nu \tag{7.9}$$

where the j_ν and α_ν are due to this radiative transition. Typically these are only appreciably non-zero very close to the frequency corresponding to the energy difference between the levels:

$$h\nu_{ij} = E_i - E_j \tag{7.10}$$

for $E_i > E_j$. Due to various *line broadening effects* the photon that is absorbed or emitted does not have to be *exactly* at the frequency ν_{ij}. Instead we define a *line profile* $\phi(\nu)$ that describes the susceptibility of the transition to photons of frequency ν. The function is normalized ($\int_0^\infty \phi(\nu) = 1$), and has its maximum at $\nu = \nu_{ij}$, and quickly drops off for $\nu < \nu_{ij}$ and $\nu > \nu_{ij}$. We will discuss the details of this line profile function in Section 7.5.

Given the line profile $\phi(\nu)$ the emissivity due to *spontaneous radiative decay* is given by

$$j_{ij,\nu} = \frac{h\nu_{ij}}{4\pi}N_i A_{ij}\phi_{ij}(\nu) \tag{7.11}$$

where, like before, $N_i = Nn_i$, and A_{ij} is the *Einstein A-coefficient*, or *radiative decay rate* for this transition, which has the dimension of s^{-1}. In other words, $1/A_{ij}$ gives the average time, in seconds, that an atom/molecule can stay in state i before radiatively decaying to state j, assuming no collisional (de-)excitations take place.

In a similar fashion one could attempt to write the extinction coefficient, which can radiatively excite an atom/molecule from the lower to the higher level:

$$\alpha^0_{ij,\nu} = \frac{h\nu_{ij}}{4\pi} N_j B_{ji} \phi_{ij}(\nu) \tag{7.12}$$

where B_{ji} is the *Einstein B-coefficient for extinction*. I write here deliberately a ^{0}, because we will slightly modify the expression for $\alpha_{ij,\nu}$ in a minute.

In addition to spontaneous emission and extinction there is also *stimulated emission*, a process that we know as *laser emission*. It turns out that the best way to describe this kind of emission is not by adding a term to the emissivity Eq. (7.11), but instead add a *negative opacity* contribution to the extinction. This results in the following modification of Eq. (7.12):

$$\alpha_{ij,\nu} = \frac{h\nu_{ij}}{4\pi} (N_j B_{ji} - N_i B_{ij}) \phi_{ij}(\nu) \tag{7.13}$$

where B_{ji} is the *Einstein B-coefficient for stimulated emission*. Whenever we have $N_j B_{ji} < N_i B_{ij}$, we obtain a negative opacity and we get laser emission (for microwaves this is called maser emission).

The Einstein coefficients are all related to one-another:

$$A_{ij} = \frac{2h\nu^3_{ij}}{c^2} B_{ij} \qquad\qquad B_{ji} g_j = B_{ij} g_i \tag{7.14}$$

These are called the *Einstein relations*. They must apply in order to conserve a thermal Boltzmann distribution (Eq. 7.3) in the presence of a Planckian radiation field at the same temperature. It means that we only need to know A_{ij}, and from that we can calculate B_{ji} and B_{ij}.

The values of A_{ij} for permissible combinations of i and j for most atoms and molecules of interest have been measured in laboratories. In Sections 7.3 and 7.4 we will discuss these for various atoms and molecules, and where you can find the values of A_{ij} on the internet.

7.2.2 Alternative notation: The oscillator strength

Instead of the spontaneous radiative decay rate A_{ij} (for $E_i > E_j$), some papers and databases instead quote the *oscillator strength* f_{ij}. The two are related via the following formulae:

$$f_{ij} = -\frac{1}{3} A_{ij}/\gamma_{\mathrm{cl}} \tag{7.15}$$

where $\gamma_{\mathrm{cl},ij}$ is the classical decay rate of the single-electron oscillator at frequency $\omega_{ij} = 2\pi\nu_{ij}$ given by

$$\gamma_{\mathrm{cl},ij} = \frac{2e^2\omega^2_{ij}}{3mc^3} \tag{7.16}$$

with e the electron charge, m the electron mass and c the light speed. This gives

$$f_{ij} = -\frac{mc^3}{2e^2\omega^2_{ij}} A_{ij} \tag{7.17}$$

Now the *absorption oscillator strength* f_{ji} obeys

$$g_j f_{ji} = -g_i f_{ij} \tag{7.18}$$

So we get

$$g_i A_{ij} = -\frac{2e^2\omega_{ij}^2}{mc^3} g_i f_{ij} = \frac{2e^2\omega_{ij}^2}{mc^3} g_j f_{ji} \tag{7.19}$$

which is identical to Eq. (10.34) of Rybicki & Lightman. Typically the $g_j f_{ji}$ (i.e. the down-up) values are given in the typical line lists you find on the web. The corresponding decay rate A_{ij} can then be found using Eq. (7.19). The paper by Hilborn (1982, American Journal of Physics, 50, 982) gives an overview of the sometimes confusing and conflicting definitions used in the literature. Note, however, that Hilborn uses SI units, while we use CGS here.

7.2.3 Doppler shift

If we have a moving gas with velocity $\mathbf{v}$, then the lines will be doppler shifted with respect to an observer at rest in the laboratory frame. The Doppler shift will depend on the direction in which the observer is looking. Most radiative transfer codes use the laboratory frame for the definition of the frequencies (and so will we in this lecture), and so we must include the Doppler shift in the line profile. So, depending on the direction of the radiation $\mathbf{n}$, the line profile will be:

$$\phi_{ij}(\nu, \mathbf{v}) = \phi_{ij}\left(\nu\left[1 - \frac{1}{c}\mathbf{n}\cdot\mathbf{v}\right]\right) \tag{7.20}$$

The velocity $\mathbf{v}$ is allowed to be dependent on location: $\mathbf{v}(\mathbf{x})$. This means that for a given ray with given direction $\mathbf{n}$ the Doppler shift (and thus the value of $\phi_{ij}(\nu, \mathbf{v})$) can change along the ray. This is a very important fact to keep in mind, because it means that light at some frequency ν may pass through gas for long stretches unattenuated, and then rather suddenly (at a location where the line-center frequency ν_{ij} doppler shifts close to the frequency ν) the opacity rapidly increases and then (once the line-center frequency passes ν) decreases again. This may thus lead to a limited region along the ray where the gas becomes opaque. Likewise, a photon that is emitted at the comoving line-center frequency ν_{ij}, corresponding to laboratory frame frequency ν, if it is lucky enough to not get absorbed for some distance, may suddenly find itself "free" because the gas velocity gradient has shifted the line profile away from its own frequency ν.

7.2.4 Selection rules

Radiative transitions are typically only possible between a select set of pairs of states ($i \rightarrow j$). The quantummechanical "rules" that tell you which radiative transitions are possible and which are not are called *selection rules* and they are usually described in textbooks that describe the quantummechanical properties of the atoms/molecules at hand. These rules are related to angular momentum conservation and symmetry considerations in the atom+$\gamma \rightarrow$ atom* or atom$^* \rightarrow$ atom+γ "reactions" (where "atom" could also mean "molecule" and the * denotes a higher-energy state).

In practice we do not really have to worry ourselves about these rules, because we will use atomic/molecular data files in which the possible radiative transitions are listed in *line lists* (see below).

7.2.5 Which atomic/molecular data we need to know

If we assume that the level populations of the molecules and atoms are *always in LTE*, then we can do radiative transfer using only the following data:

- *A line list*. This is a list (usually in ascii format) in which for each line the A_{ij}, E_i, ν_{ij}, g_i, g_j are given. From E_i and ν_{ij} the lower energy level can be found from $E_j = E_i - h\nu_{ij}$. Some line lists also provide information about the shape of the line profile (see Section 7.5). In the sections below we will explain where to find such lists.

- *A tabulated partition function*. From the line list alone we cannot yet compute the level populations. As you can see from Eq. (7.5) we need the partition function as well. Often these are given in tabulated form as a function of temperature. A simple linear interpolation in the table for the temperature of interest is usually sufficient, since the partition function is usually a very smooth well-behaved function.

For *non-LTE* radiative transfer we need more information:

- *A level list*, in which for each level the E_i and g_i is given.
- *A table (or formula) for the collisional transition rates*. The collisional rates C_{ij} between each pair of levels. This can be a rather large table, since it also has to be listed for a set of temperatures. Since often the downward rates are not so strongly temperature dependent, usually the downward rates are listed for a few temperatures, requiring you to interpolate. The upward rates can then be found using Eq. (7.8). Sometimes, instead of a table, a formula is given.
- *A line list*, but this time containing, for each line, the index i of the upper and j of the lower level, where these indices refer to the level list mentioned above. An addition to this it should of course also list the A_{ij} and possible information about the line profile. In principle the line frequency ν_{ij} can now be calculated using $h\nu_{ij} = E_i - E_j$, but this is often not accurate enough, so usually this list also contains ν_{ij}.

Since collisional rates are notoriously difficult to measure in the lab, for many atomic/molecular species only the line lists (for LTE radiative transfer) are available. And for those species for which the collisional data *is* available, those data are sometimes not 100% reliable. Therefore, non-LTE line transfer is not only difficult from a technical perspective, but also from the perspective of the uncertain collisional rates (the A_{ij} rates, in contrast, can be relatively easily measured and are thus much more secure).

7.3 Some examples of atomic species

For atomic species the lines are electronic transitions. The electron(s) in the outermost shell can be excited and deexcited, leading to the lines we see. It is virtually always a good assumption to assume that all other electrons in the atom are in their respective ground state, so that we only have to worry about the electron in the outer shell that is in an excited state. The level diagram of the atom thus corresponds to the energy levels of that electron. For atoms which have only a single electron (H, He^+, Li^{2+}, Be^{3+} etc), often called *hydrogen-like*, the level diagram are all nearly identical to that of hydrogen, just scaled by Z^2, where Z is the proton-number of the nucleus. Likewise, atoms that have two electrons (He, Li^+, Be^{2+}, B^{3+} etc), called *helium-like*, the level diagrams are those of Helium, scaled by $(Z/2)^2$, etc.

Note: It is customary to write lines from neutral atoms as e.g. HI, or HeI, or OI-lines etc., while for singly ionized species the lines are HeII, OII-lines. This is a historic custom. Unfortunately this custom is often not entirely correctly applied, for instance by talking about an HII atom (i.e. proton). Strictly speaking the notation should apply to the lines (or other spectral features), while the atoms are better identified as H^+ or He^+ or O^{2+} etc.

7.3.1 The hydrogen atom and hydrogen-like atoms

The hydrogen atom is the fundamental atomic example by which the atomic models for the higher-mass atoms are inspired. Hence its particular importance.

The electron in hydrogen atom has a ground-state energy equal to the *Rydberg constant*:

$$E_1 \equiv -\mathrm{Ry} = -\frac{m_e e^4}{2\hbar^2} = -\frac{m_e c^2 \alpha^2}{2} = -13.6\ \mathrm{eV} \tag{7.21}$$

where m_e is the electron mass, e the electron charge and $\hbar = h/2\pi$, and $\alpha = e^2/\hbar c \simeq 1/137$ is the fine-structure constant. For hydrogen-like atoms with nuclear charge Z this formula becomes

$$E_1 = -Z^2 \frac{m_e e^4}{2\hbar^2} = -Z^2 \mathrm{Ry} \tag{7.22}$$

The higher quantum levels are marked with the *principal quantum number* $n = 1, 2, 3, \cdots, \infty$, the electron orbital angular momentum quantum number $l = 0, 1, \cdots, n-1$ and the corresponding angular orientation quantum number $m = -l, \cdots, +l$, as well as the electron spin state $s = \pm\frac{1}{2}$. To first order the energies of the quantum states only depend on n:

$$E_{nlms} = E_n = -Z^2 \frac{\mathrm{Ry}}{n^2} \tag{7.23}$$

This means that the states with principal quantum number n are $2n^2$-fold degenerate, because there are n^2 orbital states and 2 spin states for each n, all having the same energy. In principle this means that we might want to bundle all these degenerate states into one "super-level" of the hydrogen atom. This is not entirely correct, because even though all these levels have the same energy, the selection rules do not allow transitions between orbital states of the same l. This means that if an electron is stuck in the $n = 2$, $l = 0$, $m = 0$, $s = +\frac{1}{2}$ state, it cannot radiatively decay down to the ground state of hydrogen ($n = 1$, $l = 0$, $m = 0$, $s = \pm\frac{1}{2}$). In the very low density environments of the interstellar medium the collisional downward rate (which is not bound by selection rules) may be so rare, that the atom can stay in that $n = 2$ state for a very long time. Only a two-photon emission can then bring the hydrogen atom back to the ground state, but (a) such two-photon processes have a very low rate and (b) they produce a *continuum* rather than a line, because for a two-photon deexcitation only the sum of the two photon energies has to fit to the energy difference of the two levels. Therefore, in spite of the fact that the levels have the same energy, we still cannot bundle them all together. We *can* bundle all levels of the same n and l, but different m and s together into a "super-level", since they behave identically.

When we include the effects of special relativity (because, close to the nucleus the electron moves at a speed not too far from the light speed) and spin-orbit coupling (because the electron spin and the electron orbit can interact) the energy levels at a given n will acquire small adjustments, giving the different quantum states slightly different energies:

$$E_{nlms} = E_{nl} = -Z^2 \frac{\mathrm{Ry}}{n^2} \left(1 + \frac{(Z\alpha)^2}{n^2} \left[\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] \right) \tag{7.24}$$

where j is the total angular momentum quantum number.

The total angular momentum quantum number is a combination of the orbital and spin angular momenta. For a given orbital angular momentum l and given spin s the total angular momentum is:

$$j = |l + s| \tag{7.25}$$

In other words: if the electron spins oppositely to its orbit, it lowers the total angular momentum quantum number j, while if it spins in the same direction, it increases it.

For $l = 0$ we have $j = \frac{1}{2}$ as the only possibility. For $l = 1$ we have $j = \frac{1}{2}$ and $j = \frac{3}{2}$ as the two possibilities.

Now, where does m come in? One might be tempted to say that for each combination of l and s we have $2l + 1$ possible values of m, which would lead to $2l + 1$ states with $j = l - \frac{1}{2}$ and $2l + 1$ states with $j = l + \frac{1}{2}$. However this does not work this way. Suppose we measure s along the z-axis, then for $m \neq 0$ we cannot speak of "opposite to orbit" or "same direction as orbit" because $m \neq 0$ means that the orbital spin is not aligned in z-direction. Instead we have to start with a combination of l and j, each having $2j + 1$ states, i.e. the statistical weight is

$$g = 2j + 1 \tag{7.26}$$

Together, the $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$ states are $2(2l + 1)$ states.

Example: Let us look at all the possible $l = 1$ states. For $j = \frac{1}{2}$ will have 2 states and $j = \frac{3}{2}$ will have 4 states. Together they have 6 states, which is indeed equal to $2(2l + 1)$.

For this reason it is more useful to use the n, l and j quantum numbers instead of n, l and s.

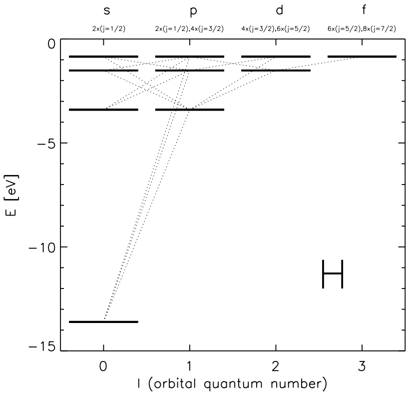
The splitting of the principal levels according to Eq. (7.24) is called *fine-structure splitting*. It clearly is the strongest for small n (because then the electron is the closest to the nucleus, and thus moves the fastest) and for large Z (because then the electron is even closer to the nucleus).

If we would also include the coupling between the electron and the nuclear spin, we would split the levels even further, according to the *hyperfine splitting*. For hydrogen this leads to the famous 21 cm radio line, which plays a fundamental role in the observation of neutral hydrogen in our Milky Way and the Universe. However, for most other astrophysical applications hyperfine splitting is not so important, so we will not dig into this any further.

The only levels that have *exactly* the same energy are those with the same n, l, j, but different m. The reason is simple: the quantum number m has to do with the *orientation* of the orbitals in space. If there are no external influences which introduce a preferred direction, the energies *cannot possibly* be different. Only if we impose an external electric or magnetic field we can break this rotational symmetry, and only then can the different orientations m possibly have different energies. Breaking the rotational symmetry with a magnetic field is called *Zeeman splitting* and with an electric field it is called *Stark splitting*.

Traditionally the quantum states are written with the following notation: States with orbital angular momentum $l = 0$ are written with the symbol s, those with $l = 1$ with the symbol p, those with $l = 2$ with d, those with $l = 3$ with f and continuing with g, h etc. A state with $n = 3$ and $l = 1$ is then written as 3p. The ground state is 1s. For $n = 2$ we have 2s and 2p, for $n = 3$ we have 3s, 3p and 3d, etc.

Typically the levels and their possible transitions are shown in a *Grotrian diagram*, in which the energy is on the y-axis and the orbital quantum number l on the x-axis. The reason why on the x-axis the l quantum number is given is because the most rigorous selection rule states that $\Delta l = \pm 1$. In the Grotrian diagram the transitions always have to connect levels in neighboring columns, not in levels in the same column (same l).



7.3.2 Multi-electron atoms

When an atom contains more than just 1 electron, things become more complicated, but we can still use much of what we know from the hydrogen atom: electrons still occupy levels with principal quantum number n, orbital quantum number l and spin s, just like in the hydrogen atom. The differences are: (a) if one of the electrons occupies a level, that level is no longer available to the other electrons (apart from the statistical weight of the level), (b) the presence of other electrons changes the overall charge distribution in the atom, and thus changes the energy levels of the electronic states, (c) it now becomes important to consider how the electron's spin and orbital states relate to each other.

The state of an atom is given by the *occupations of the orbitals* and the *term symbol*.

The way we write the occupation of the orbitals is by denoting the number of electrons in each configuration as a superscript. For instance, the ground state of Helium would be $1s^2$ while the group state of He^+ or H is $1s^1$. For Lithium ($Z = 3$) the ground state is $1s^22s^1$, the oxygen ($Z = 8$) ground state it is $1s^22s^22p^4$, etc.

For a given occupation of the orbitals, there can be different configurations of the electrons among each other, leading to different total spin S, total orbital angular momentum L and total angular momentum J of the multi-electron system. We will not go into any detail on how these come about, but merely introduce the *Russell-Saunders term symbol* as a way of writing this configuration:

$$^{2S+1}L_J \tag{7.27}$$

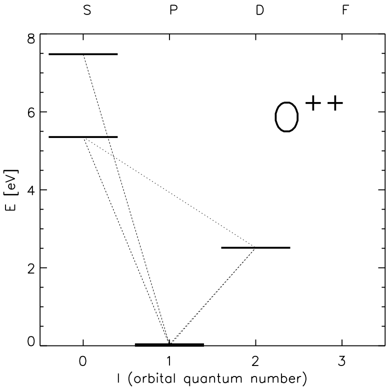
where L is to be replaced with S for $L = 0$, P for $L = 1$, D for $L = 2$ etc (the symbols being the capital-letter versions of the orbital notation of the hydrogen atom). The symbol S can be integer or half-integer, and so can J. The statistical weight for each state (due to rotational symmetry, see the hydrogen atom) is:

$$g = 2J + 1 \tag{7.28}$$

Typical excitations are of electrons in the outer shell (i.e. largest principal quantum number). That means that usually all the inner shells are fully occupied, and we need to concentrate only on the outer shell.

Example: the doubly-ionized oxygen atom (O++, sometimes written as OIII) has the following lower 6 levels:

i	E (eV)	g	L	J	S	configuration
1	0.0000000	1	1	0	1	$1s^22s^22p^2\ {}^3P_0$
2	0.0140323	3	1	1	1	$1s^22s^22p^2\ {}^3P_1$
3	0.0379609	5	1	2	1	$1s^22s^22p^2\ {}^3P_2$
4	2.5135777	5	2	2	0	$1s^22s^22p^2\ {}^1D_2$
5	5.3543760	1	0	0	0	$1s^22s^22p^2\ {}^1S_0$
6	7.4793581	5	0	2	2	$1s^22s^12p^3\ {}^5S_2$



The first column is just a counter. Note that the energy offset is chosen such that the ground state is $E = 0$. Its grotrian diagram is shown in the margin figure. The spin values are integers, because we have an even number (6) of electrons of half-spin.

The list of possible radiative transitions between these lowest 6 levels of O^{++} is:

i	j	λ [μm]	A_{ij} [s^{-1}]
2	1	88.356397	2.597×10^{-5}
4	1	0.49326031	2.322×10^{-6}
3	2	51.814541	9.632×10^{-5}
4	2	0.49602952	6.791×10^{-3}
5	2	0.23216635	2.255×10^{-1}
6	2	0.16608090	$1.450 \times 10^{+2}$
4	3	0.50082404	2.046×10^{-2}
5	3	0.23321132	6.998×10^{-4}
6	3	0.16661496	$4.260 \times 10^{+2}$
5	4	0.43644361	$1.685 \times 10^{+0}$

The transition from the $1s^22s^22p^2\ {}^1D_2$ state ($i = 4$) to the $1s^22s^22p^2\ {}^3P_2$ state ($j = 3$) is the famous [OIII] $\lambda = 0.5007\,\mu$m "forbidden line" often observed in hot ionized nebulae such as planetary nebulae. The difference between the $\lambda = 0.5007\,\mu$m and the $\lambda = 0.5008\,\mu$m listed in the table is due to the wavelength in air being shorter than the wavelength in vacuum.

The term "forbidden line" is a bit misleading. It suggests that selection rules do not allow this radiative transition, while in fact it only means that there is no *dipole* transition possible. Instead a *quadrupole* transition *is* possible, but the A_{ij} for such quadrupole transitions are extremely small compared to "normal" radiative transitions.

7.3.3 Databases for atomic lines, levels and rates

The atomic levels and radiative transitions, as well as the collisional transition rates, have been measured and reported in countless scientific papers. If you are interested in a very specific case and you know exactly which levels and lines you are looking for, you can look up these data in the respective papers. But often this is rather impractical, in particular if you want to include many lines. Fortunately there are websites where these data have been bundled in databases that you can query. Many atomic lines are listed in The Opacity Project[1] (TOP) and The Iron Project[2] (TIP). Analytic formulae for the collisional rates with free electrons were derived, for instance, by Van Regemorter (1962, Astrophysical Journal 136, 906) and Allen (1973, Astrophysical Quantities, 3rd edition, Athlone Press London). Tabulated collisional excitation coefficients can be found for instance at the website of Dima Verner[3]. But a more complete set of atomic data, including collisional rates, can be obtained from the CHIANTI database[4]. The data in the tables above (for O^{++}) were taken from the CHIANTI database.

7.4 Some examples of molecular species

The lines from molecules are usually not due to electronic transitions in the atoms, but due to vibrations within the molecule as well as rotations of the molecule. These energy levels are typically at much lower energy than electronic ones, and hence molecular lines are usually at longer wavelengths than atomic lines.

7.4.1 Rotational lines

Let us first look at the rotational levels of molecules, and let us focus on a simple molecule such as CO. Since CO is a linearly shaped molecule (in contrast to, e.g. H_2O which is banana-shaped) the rotational quantum levels are very simple. There is only one quantum number, J, which is the rotational quantum number, and at the same time gives the total angular momentum of the molecule. The statistical weight is then, as in the atomic case,

$$g = 2J + 1 \tag{7.29}$$

The energies of the levels are:

$$E = \frac{\hbar^2}{2I} J(J+1) \tag{7.30}$$

where I is the moment of intertia of the molecule. For CO this is $I = 1.46 \times 10^{-39}$. The first few levels are thus:

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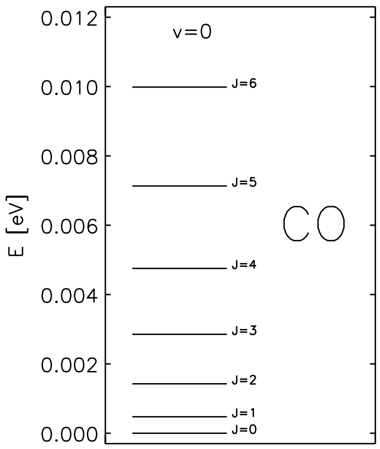
[1] http://cdsweb.u-strasbg.fr/topbase/topbase.html

[2] http://cdsweb.u-strasbg.fr/tipbase/home.html

[3] http://www.pa.uky.edu/~verner/exc.html

[4] http://www.chiantidatabase.org/

i	E (eV)	g	J
1	0.0000000000	1	0
2	0.0004767258	3	1
3	0.0014301549	5	2
4	0.0028602695	7	3
5	0.0047669889	9	4



where slight variation from Eq. (7.30) are due to the fact that the centrifugal forces of the rotation may stretch the CO molecule a bit, and thus change its moment of intertia.

Radiative transitions can only take place between levels $J \rightarrow J-1$, because a photon has spin 1, and thus angular momentum conservation requires the angular momentum change to be ± 1. This means that the frequencies of these transitions from $J \rightarrow J-1$ obey:

$$h\nu = \frac{\hbar^2}{2I}[J(J+1)-(J-1)J] = \frac{\hbar^2}{I}J \tag{7.31}$$

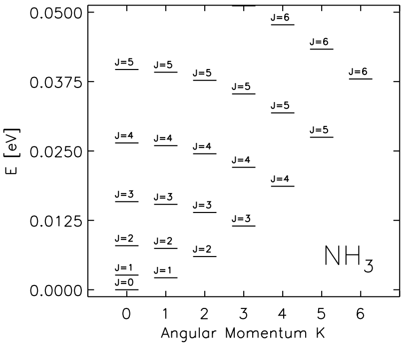
The frequencies of the lines are therefore increasing linearly with J. A very simple spectrum indeed. This is called a *rotational ladder*. In numbers: for the CO molecule the first four rotational lines are

i	j	Name	λ [μm]	A_{ij} [s^{-1}]
2	1	J=1→0	2600.7576	7.203×10^{-8}
3	2	J=2→1	1300.4037	6.910×10^{-7}
4	3	J=3→2	866.96337	2.497×10^{-6}
5	4	J=4→3	650.25151	6.126×10^{-6}

These are lines in the millimeter wavelength range, and they are the typically the strongest lines emerging from cold molecular interstellar and circumstellar material in this wavelength domain.

One might wonder: why aren't rotational lines of molecular hydrogen (H_2) more prominent than CO lines? After all, there is a lot more molecular hydrogen in such clouds than CO (by roughly a factor of 10^4). The answer is that H_2 is a symmetric molecule, and therefore does not have a permanent electric dipole moment. This means that if such a molecule rotates, it does not produce dipole radiation. It can only produce quadrupole radiation, which have much smaller A_{ij} rates. Molecular hydrogen lines are therefore very weak. Another issue is that H_2 is a much lower-mass molecule with a much smaller moment of inertia ($I = 4.7 \times 10^{-41}$). According to Eq. (7.30) this implies that the quantum levels are at much higher energies. Moreover, because the lines are quadrupole lines, they require $\Delta J = \pm 2$ (instead of $\Delta J = \pm 1$ for asymmetric linear molecules). The longest-wavelength rotational line of H_2 is $\lambda = 28.24\,\mu$m, i.e. the mid-infrared.

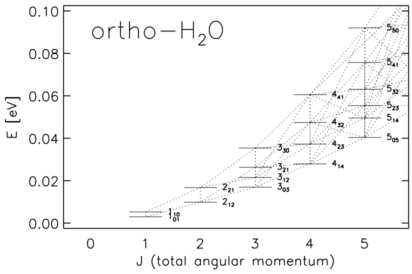
In the interstellar medium CO is by far the strongest emitter of millimeter and sub-millimeter emission lines, simply because it is, after molecular hydrogen, the most abundant molecule. Also in the far-infrared CO lines are often the most prominent lines. But there are many other commonly observed molecules in this wavelength range, too, for instance CS, OH, as well as triatomic linear molecules such as HCO^+, HCN etc.

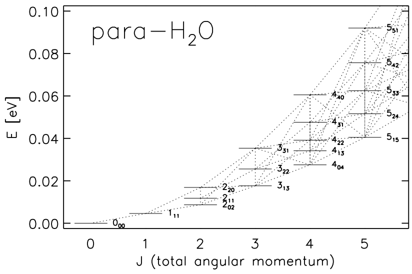


But not all molecules are linear. The NH_3 molecule, for instance, consists of an N atom surrounded by three H atoms in a "symmetric top" configuration: The N atom is above the plane spanned by the three H atoms. This introduces, in addition to J, another quantum number, which we write as K. This K tells you whether the axis of rotation is perpendicular to the plane spanned by the three H atoms, or at another axis. The level diagram is shown in the margin figure.

The selection rules say that dipole radiation is only possible for $\Delta K = 0$. In the level diagram this means that you can radiatively decay only vertically downward. If you start in a state with $K > 0$, radiative decay will cascade down to the "backbone" state for that value of K: the lowest-energy state for given K. The molecule will get "stuck" there for a while. Eventually through collisional deexcitation it can reach the true ground state. It can also decay radiatively through quadrupole radiation, though the rates for that process are very low.

Molecules that are "asymmetric top", such as H_2O, are even more complex. H_2O has three rotational quantum numbers: J, K_+, K_-. The J is the total angular momentum while K_+ and K_- are the angular momenta around the axes of largest and smallest moment of inertia. Water exists in two forms: *ortho-water* and *para-water*, depending on whether the two hydrogen nuclei have their spin aligned (ortho, magnetic moment $m = \frac{1}{2} + \frac{1}{2} = 1$) or opposite (para, magnetic moment $m = \frac{1}{2} - \frac{1}{2} = 0$). The ortho version of water is a triplet (because of $m = 1$ giving $g = 2m + 1 = 3$ statistical weight) while the para version of water is a singlet (because of $m = 0$ giving $g = 2m + 1 = 1$ statistical weight). Under thermodynamic equilibrium conditions at not too low temperatures one therefore would expect that Nature has a ratio of ortho/para water of 3/1. There are conditions, however, where a different ratio is expected. There are no radiative transitions between ortho and para versions of water, and even collisions are very inefficient at flipping the nuclear spin of one of the two hydrogen atoms. In liquid water on earth it takes about an hour to equilibrate the ortho/para ratio through collisions, while in the gas in interstellar space it can take many millions of years. It is believed that in ice form (icy mantels on interstellar dust grains or the ice in comets) it can be preserved nearly forever.





The ortho and para versions of H_2O have different rotational level diagrams. For ortho-water we have only levels with $K_- + K_+$ being odd, while for para-water we have only levels with $K_- + K_+$ being even. The rotational diagrams for both versions of water are shown in the margin figure (data taken from the LAMDA database in Leiden, see below). You see that only para-water has a $J = 0$ ground state, while the ground state of ortho-water has $J = 1$.

7.4.2 Ro-vibrational lines

In addition to rotating, molecules can also vibrate. Let us take again the example of CO. The vibrational quantum number is v. The ground state is $v = 0$, $J = 0$. The first vibrational state is $v = 1$, and the second $v = 2$ etc. Because molecules are quite sturdy, the energy levels for these vibrational modes are much higher than for rotational modes. For CO they are:

$$E_i = h\nu_0 v \tag{7.32}$$

where ν_0 is the vibrational frequency, which for CO is $\nu_0 = 6.4 \times 10^{13}$ Hz. This leads to the first three energy levels to be 0 eV, 0.26 eV and 0.53 eV respectively. The line frequency for the transition from $v_i \rightarrow v_j$ is

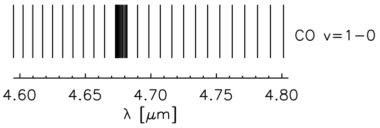
$$h\nu_{ij} = h\nu_0(v_i - v_j) \tag{7.33}$$

This means that all transitions with $\Delta v = v_i - v_j$ have the same frequency. The transitions $v = 1 \rightarrow 0$, $v = 2 \rightarrow 1$, $v = 3 \rightarrow 2$ etc. are near $\lambda = 4.7\mu$m and are collectively called the *fundamental transition*. The transitions $v = 2 \rightarrow 0$, $v = 3 \rightarrow 1$, $v = 4 \rightarrow 2$ etc. are near $\lambda = 2.3\mu$m and are collectively called the *overtone transition*.

It is important to understand that, in addition to vibrating, a molecule can also still rotate. These two things do not exclude each other. The selection rules say that any Δv is possible. In addition to that, in the same transition, the rotational quantum number may change by $\Delta J = -1, 0$ or $+1$. For this reason these transitions are called *ro-vibrational lines*. Example: Suppose your CO molecule starts from $v = 1$, $J = 4$, then it can radiatively decay to $v = 0$, $J = 3$, or to $v = 0$, $J = 4$ or to $v = 0$, $J = 5$. Rovibrational lines with $\Delta J = +1$ are called *P-branch* lines, those with $\Delta J = 0$ are called *Q-branch* lines and those with $\Delta J = -1$ are called *R-branch* lines. Since the energy of the rotation (see Eq. 7.30) is added to that of the vibration (Eq. 7.32):

$$E_{vJ} = h\nu_0 v + \frac{\hbar^2}{2I} J(J+1) \tag{7.34}$$

we see that the ΔE for the P-branch and R-branch are not exactly $h\nu_0(v_i - v_j)$, but they get slightly modified by the second term in Eq. (7.34). I say "slightly", because the second term in Eq. (7.34) is typically very small compared to the first term. Yet, this slight shift of the line due to the ΔJ is clearly discernable in the spectrum: instead of just a single fundamental line, there will be the fundamental line for the *Q*-branch, a rotational ladder toward short wavelength for the *R*-branch and an inverse rotational ladder for the *P*-branch. The idea with the *R* branch is that in addition to the energy gained from the $\Delta v = -1$, also a bit of energy is gained from $\Delta J = -1$, leading to a slightly more energetic photon. In contrast, for the P-branch, a small fraction of the energy gained from the $\Delta v = -1$, is invested (and thus lost) in spinning up the molecule ($\Delta J = +1$), leading to a slightly less energetic photon.



A very peculiar phenomenon happens for the *R*-branch for large *J*: A vibrating CO molecule has a *slightly* larger moment of inertia than a non-vibrating one, because due the vibration the atoms are, on average, slightly further apart. This means that the rotational energy levels for $v = 1$ are slightly smaller than those for $v = 0$. For large *J* this has the effect that the ladder of the *R* branch reaches some minimum wavelength and then turns back toward longer wavelength. This leads to a strong clustering of rovibrational lines near this turn-back point. This is called a *bandhead*.

7.4.3 Databases for molecular lines, levels and rates

Like with the atomic data, you can find information about the lines, levels and rates in papers. But also in this case there are databases on the web that you can make use of. For rotational lines in the (sub-)millimeter regime the LAMDA database[5] in Leiden is very useful as it contains easy-formatted ascii files with levels, lines, rates as well as collision rates in tabulated form. However, that database is focussed on rotational lines only, and of 32 of the most common molecules. The Cologne Database for Molecular Spectroscopy (CDMS)[6] has line lists for 641 molecules, including rovibrational lines, but no collisional rates. The JPL molecular spectroscopy database[7] is also based on line lists. The HITRAN database[8] provides accurate line lists for atmospheric research, but these data are also often used in astrophysics.

The variety of molecules and the variety of conditions under which they are studied is so large that these databases cannot be fully complete. You may sometimes need to dig out the data for your molecule of interest yourself from the relevant papers.

Note that sometimes in these databases the energy is written in the unit cm^{-1}. To convert to erg just multiply by hc.

7.5 The line profile function

7.5.1 Doppler broadening: Thermal case

The simplest form of line broadening is broadening caused by the thermal motion of the gas particles. If a molecule has a line at frequency ν_i in the rest frame of the molecule, then it will experience a little doppler shift if the particle moves with respect to the observer. For thermally moving particles the velocity distribution projected

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[5] `http://www.strw.leidenuniv.nl/~moldata/`
[6] `http://www.astro.uni-koeln.de/cdms`
[7] `http://spec.jpl.nasa.gov/`
[8] `http://www.cfa.harvard.edu/hitran/`

along the line of sight toward the observer is

$$P(v_x) = \frac{1}{\sigma_x\sqrt{2\pi}}\exp\left(-\frac{v_x^2}{2\sigma_x^2}\right) \tag{7.35}$$

where σ_x^2 is the single-directional variance of the velocity distribution given by

$$\sigma_x^2 = \sqrt{\langle v_x^2\rangle} = \sqrt{\frac{kT}{m}} \tag{7.36}$$

where k is the Boltzmann constant and m is the mass of the molecule. Note that this is a factor of $\sqrt{3}$ smaller than the perhaps more familiar $\sqrt{\langle v^2\rangle} = \sqrt{3kT/m}$ formula. This is because we focus on just one of the three spatial directions. With this distribution of velocities the line profile becomes

$$\phi(\nu) = \frac{1}{\gamma_{i,\mathrm{th}}\sqrt{\pi}}\exp\left(-\frac{(\nu-\nu_i)^2}{\gamma_{i,\mathrm{th}}^2}\right) \tag{7.37}$$

where $\gamma_{i,\mathrm{th}}$ is the thermal line width given by

$$\gamma_{i,\mathrm{th}} = \sqrt{2}\nu_i\frac{\sigma_x}{c} = \frac{\nu_i}{c}\sqrt{\frac{2kT}{m}} \tag{7.38}$$

In the radiative transfer community this is often written, equivalently, as

$$\phi(\nu) = \frac{c}{a\nu_i\sqrt{\pi}}\exp\left(-\frac{c^2(\nu-\nu_i)^2}{a^2\nu_i^2}\right) \tag{7.39}$$

with

$$a = \sqrt{\frac{2kT}{m}} = \frac{c}{\nu_i}\gamma_{i,\mathrm{th}} \tag{7.40}$$

where a is the line width in cm/s.

It is important to keep in mind that the doppler broadening depends on the mass of the molecule that is emitting the line. For heavy molecules this broadening is less than for lightweight molecules.

7.5.2 Doppler broadening: Microturbulence

Another source of randomized doppler shift could be microturbulence. The term "microturbulence" is a bit vaguely defined. Turbulence is the phenomenon of pseudo-randomly moving parcels of gas or fluid on top of some average large scale flow pattern. The word "microturbulence" can also be called "subgrid turbulence": it is the turbulence on spatial scales smaller than the smallest grid cell size. This small-scale turbulence can not be treated numerically as moving fluid elements. Instead we must treat it as a velocity dispersion. A reasonable approximation for the probability distribution of velocities is a Gaussian distribution as given in Eq. (7.35). The variance of the particles σ_x^2 is now, however, *independent* of the molecular mass, and is also not related to temperature. One must have knowledge of the strength of the micro-turbulence to know what this σ_x^2 is. In other words: one must have a good model for the turbulent velocity dispersion. Typically in the radiative transfer community people write this in terms of a contribution to the a in Eq. (7.39):

$$a = \sqrt{a_{\mathrm{th}}^2 + a_{\mathrm{turb}}^2} \tag{7.41}$$

with

$$a_{\mathrm{th}} = \sqrt{\frac{2kT}{m}} \qquad \text{and} \qquad a_{\mathrm{turb}} = \sqrt{2}\langle v_{x,\mathrm{turb}}^2\rangle = \sqrt{\frac{2}{3}}\langle v_{\mathrm{turb}}^2\rangle \tag{7.42}$$

7.5.3 Collisional broadening

Collisional broadening, also called impact pressure broadening, can be best understood with an example. Suppose we have a CO molecule that is vibrating with its fundamental frequency ν_i in the rotational ground state. The vibration is then described by a positional offset of the O atom that is proportional to $\cos(2\pi\nu_i t)$. If the vibrating molecule is left alone for a very long time compared to a single oscillation cycle, and assuming that it does not experience a transition to another quantum state, then the oscillation can be described well by this cosine function, and the Fourier transform in time produces a delta function around the frequency ν_i to very high approximation. However, if collision events at random times disturb the phase of the oscillation, the Fourier transform will broaden, as the oscillation no longer describes a perfectly phase-stable cosine.

When such an imperfectly oscillating molecule interacts with radiation, it will be susceptible not only to photons with the exact frequency $h\nu_0$, but also photons at slightly offset frequencies, according to the broadning of the timelike Fourier transform of the oscillation. The corresponding line profile is called the *Lorentz profile* (or Cauchy profile or Breit-Wigner profile). It is given by

$$\phi(\nu) = \frac{1}{\pi}\frac{\gamma_{i,\mathrm{coll}}}{(\nu-\nu_i)^2+\gamma_{i,\mathrm{coll}}^2} \tag{7.43}$$

where $\gamma_{i,\mathrm{coll}}$ is the collisional broadening parameter, which has the same units as the frequency. This parameter is not easy to calculate from first principles, in contrast to the doppler broadening. This is because the precise way by which the collision perturbs the vibration or rotation of a molecule depends very much on the details of the collision process, including which type of molecule is the collision partner. We typically rely on tabulated values. In the HITRAN database (Section 7.4.3), for instance, the $\gamma_{i,\mathrm{coll}}$ value for each line is given, for a pressure of 1 atm and a temperature of 296 K. We can scale this to another pressure and temperature using the following scaling relation:

$$\gamma_{i,\mathrm{coll}}(p,T) = \gamma_{i,\mathrm{coll}}(p_0,T_0)\frac{p}{p_0}\left(\frac{T_0}{T}\right)^{n_i} \tag{7.44}$$

with $p_0 = 1$ atm and $T_0 = 296$ Kelvin.

The linear dependence on p can be understood if we assume that collisions are infinitely short duration events. If we keep the temperature constant, then the number of collisions each molecule will experience per second increases linearly with the density.

The exponent n_i gives the temperature-dependence, and it is also listed in the HITRAN database. Typically the value of n_i is somewhere between 0.5 and 1.0. A value of $n_i = 0.5$ would mean that, if we assume an ideal gas law of $p = nkT$ and we keep the number density n constant but vary the temperature T, we get $\gamma_{i,\mathrm{coll}} \propto \sqrt{T}$. This makes sense because the velocity of the molecules scales as $\sqrt{T}$, meaning that $\gamma_{i,\mathrm{coll}}$ scales simply with the collision rate. In reality, however, the speed at which the collisions occur also affects $\gamma_{i,\mathrm{coll}}$, which is why n_i typically deviates from 0.5.

Note that the HITRAN database gives *two* values of the collisional broadning parameter: $\gamma_{i,\mathrm{self}}$ and $\gamma_{i,\mathrm{air}}$. The first one is for collisions of the molecule with molecules of the same kind, while the second one is for collisions of the molecule with a standard mixture of air in the Earth's atmosphere. The formula for broadening for a mixture of air and molecule is then:

$$\gamma_{i,\mathrm{coll}}(p,T) = \left\{\gamma_{i,\mathrm{air}}(p_0,T_0)\frac{p-p_s}{p_0} + \gamma_{i,\mathrm{self}}(p_0,T_0)\frac{p_s}{p_0}\right\}\left(\frac{T_0}{T}\right)^{n_i} \tag{7.45}$$

where p_s is the partial pressure of the molecule itself.

Collisional broadening occurs mainly in rather dense environments such as planetary and stellar atmospheres. In planetary atmospheres it dominates usually by a considerably amount over doppler broadening. In interstellar and circumstellar gases such as molecular clouds or protostellar/protoplanetary disks, collisional broadening rarely plays a role.

7.5.4 Natural broadening

Natural broadening can be understood in much the same way as collisional broadening, even though its origin is very different. Consider again the oscillating molecule. Now, instead of perturbing it with a collision, we perturb it by the emission or absorption of a photon, i.e. the transition to another quantum state. The finite duration of the oscillation between two successive radiative or collisional (de-)excitations means that its Fourier transform is not a perfect delta-function, but instead broadened. It is essentially the Heisenberg uncertainty principle, in which the finite duration in time Δt and the uncertainty in energy ΔE are related via $\Delta E \Delta t \simeq h/2\pi$. The resulting line profile is, again, a Lorentz profile (Eq. 7.43). This time, however, the width $\gamma_{i,\mathrm{nat}}$ is easy to calculate from the uncertainty principle:

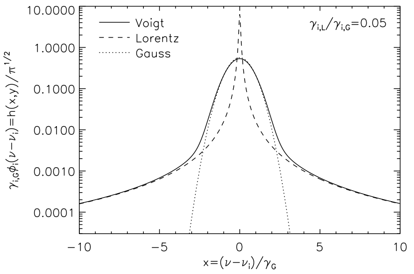
$$\gamma_{i,\mathrm{nat}} = \frac{1}{2\pi\Delta t} \tag{7.46}$$

where Δt is the average life time of the state. If we have predominantly spontaneous decay, given by the Einstein coefficient A_i, then $\Delta t = 1/A_i$.

Natural broadening rarely plays a role in molecular lines. But for atomic lines, in particular in UV and X-ray, it can play a role.

7.5.5 Combining Lorentz and Gauß: The Voigt profile

If we have multiple sources of broadening, then the combined effect is the convolution of them. Combining the thermal and microturbulent broadening yields a Gaussian profile with width:



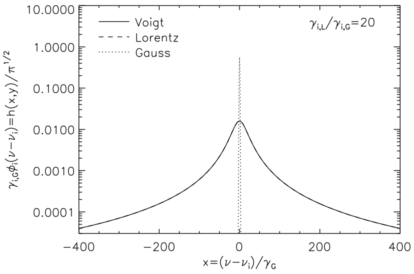
$$\phi_{i,\mathrm{G}}(\nu) = \frac{1}{\sqrt{\pi}\,\gamma_{i,\mathrm{G}}} \exp\left(-\frac{(\nu-\nu_i)^2}{\gamma_{i,\mathrm{G}}}\right) \qquad \text{with} \qquad \gamma_{i,\mathrm{G}} = \sqrt{\gamma_{i,\mathrm{th}}^2 + \gamma_{i,\mathrm{turb}}^2} \tag{7.47}$$

which is equivalent to Eq. (7.41). Combining natural and collisional broadening yields again a Lorentz profile with

$$\phi_{i,\mathrm{L}}(\nu) = \frac{1}{\pi}\frac{\gamma_{i,\mathrm{L}}}{(\nu-\nu_i)^2 + \gamma_{i,\mathrm{L}}^2} \qquad \text{with} \qquad \gamma_{i,\mathrm{L}} = \gamma_{i,\mathrm{coll}} + \gamma_{i,\mathrm{nat}} \tag{7.48}$$

But combining this Lorentz profile with a Gaussian profile requires us to actually carry out the convolution of the two profiles, which is not trivial:

$$\phi_i(\nu) = \int_0^\infty \phi_{i,\mathrm{G}}(\nu')\phi_{i,\mathrm{L}}(\nu_i + \nu - \nu')d\nu' \tag{7.49}$$



This is called the Voigt profile. In a radiative transfer code it is rather numerically expensive to carry out such an integral each time the codes needs to evaluate the line profile. Humlicek (1982, J. Quant. Spectros. Radiat. Transfer 27, 437) developed a fast numerical procedure to approximate the Voigt profile very accurately. This procedure was refined by Schreier (1992, J. Quant. Spectros. Radiat. Transfer 48, 743-762). A fortran code for this procedure is publically available[9]. In this Fortran-77 function, called `HUMLICEK`, the function $h(x,y)$ is evaluated, where

$$x = \frac{\nu - \nu_i}{\gamma_{i,\mathrm{G}}} \qquad \text{and} \qquad y = \frac{\gamma_{i,\mathrm{L}}}{\gamma_{i,\mathrm{G}}} \tag{7.50}$$

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[9] http://www.op.dlr.de/oe/ir/voigt.html

The full Voigt line profile $\phi_i(\nu)$ can be found from $h(x, y)$ through:

$$\phi_i(\nu) = \frac{h(x, y)}{\sqrt{\pi}\,\gamma_{i,\mathrm{G}}} \tag{7.51}$$

The figures in the margin show that if the thermal and microturbulent broadening are weak compared to the collisional and/or natural broadening ($\gamma_{i,\mathrm{G}}/\gamma_{i,\mathrm{L}} \ll 1$), we have a profile that is virtually identical to the Lorentz profile. But if the thermal and microturbulent broadening are strong compared to the collisional and/or natural broadening ($\gamma_{i,\mathrm{G}}/\gamma_{i,\mathrm{L}} \gg 1$), the Gaussian line profile dominates near the line center, but sufficiently far from the line center the wings of the Lorentz profile will always re-appear.

In very rarified media, such as the interstellar medium or circumstellar disks, the distance from the center of the line where this happens *may*, however, be so far that we can safely ignore this effect. It is, however, important to check this on a case-by-case basis. For very dense media, such as stellar or planetary atmospheres, the Gaussian component is usually too small to be important.

7.6 Some features of line formal transfer: Case of LTE

If we have a medium that is dense enough, most atoms and/or molecules will experience so many collisions per second, that their level populations are thermal. We speak of Local Thermodynamic Equilibrium (LTE). In this case the radiative transfer is relatively straightforward, *if* the gas temperature (and of course also the number density of the molecule in question) is known everywhere. The formal transfer equation is Eq. (7.9) and the extinction and emissivity are given by Eq. (7.13) and Eq. (7.11), respectively. Taking into account the velocity-dependence of the line profile due to the Doppler-shift (see Eq. 7.20) the formal radiative transfer equation becomes

$$\mathbf{n}\cdot\nabla I_\nu(\mathbf{x},\mathbf{n}) = j_\nu(\mathbf{x},\mathbf{n}) - \alpha_\nu(\mathbf{x},\mathbf{n})I_\nu(\mathbf{x},\mathbf{n}) \tag{7.52}$$

If we make a spectrum of some object with this equation, the line shape that we compute will have a certain width $\Delta\nu$ which is partly due to the intrinsic width of the line (Section 7.5) and partly due to contributions to the line from gas parcels moving at various line-of-sight velocities (let us call this the "dynamic line width"). The larger our field of view that we use to compute the spectrum, the larger is the chance of picking up emission from different velocity parcels. But even if we have a very narrow beam, then parcels with different velocities that are behind each other (along the same line of sight) will contribute to the spectral line width, or create complex-shaped lines.

Because of this relation between frequency and velocity, observed (or predicted) line spectra are often plotted with velocity v on the x-axis instead of frequency ν.

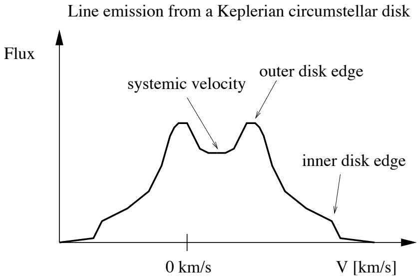
The intrinsic thermal line width depends on the mass m of the molecule (Eq. 7.40), but the dynamic line width does not. This means that if one could measure line width of lines from different molecular or atomic species, one could conceivably distinguish between the thermal and dynamic contributions. We can relate this to the isothermal sound speed $c_s = \sqrt{kT/\mu}$ of the gas, where μ is the mean molecular weight:

$$a = \sqrt{\frac{2k_BT}{m}} = \sqrt{2\frac{\mu}{m}}\,c_s \tag{7.53}$$

If the molecule has a mass $m \simeq 2\mu$ the thermal line broadning is equal to the isothermal sound speed. For $m \gg 2\mu$ the thermal line width of that molecule is substantially smaller than the sound speed of the gas. So if you want to measure the line-of-sight velocity of some parcel of gas with a tolerance much smaller than the gas sound speed (typically when you wish to measure speeds of subsonic flows), then it is useful to take a heavy molecule to do so. Example: CO has mass $m = 28m_p$ (with m_p the proton mass), while the mean molecular weight of a typical hydrogen-helium mixture is $\mu = 2.3 m_p$. This means that, for CO, the thermal line width is $a = 0.4\, c_s$, while for H_2 quadrupole lines it is $a = 1.5\, c_s$. This means that, for measuring velocities, CO is better than H_2.

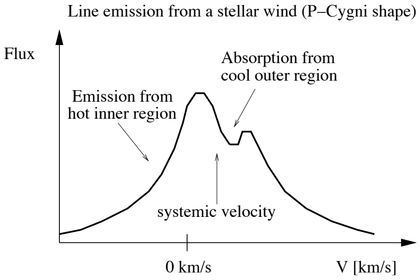
7.6.1 Integrated line spectrum from an accretion disk

Many object are surrounded by gaseous disks. For instance: the dust+gas disks surrounding many young stars. These disks are differentially rotating according to the Kepler profile. The gas close to the star rotates at higher speeds and has a higher temperature than the gas on outer orbits. If we see the disk face-on, the orbital velocities cannot be observed using doppler shift measurement. But if the disk is at some inclination, then the line shape is a typical "double peaked line profile". The emission from the inner disk produces much of the line wings while the emission from the outer disk produces the line center. Since most disks have an outer edge at some reasonable distance from the star, there will be gas missing at very low doppler shift. This gives the slight dip at the line center of the spectrum (which creates the double-peaked shape). Tilting the disk to ever more edge-on orientations makes the entire line shape broader. Until, of course, the inclination is so large, that the outer regions of the disk start to obscure the view to the star and the inner disk regions.


Line emission from a Keplerian circumstellar disk

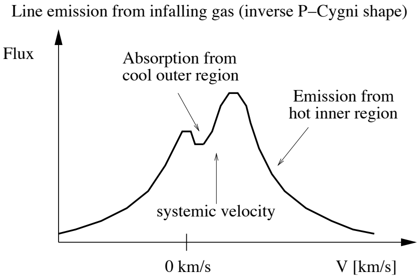
7.6.2 P-Cygni line shape from a stellar wind

With doppler shifts, the resulting observed line shapes can become pretty complex. Consider a star with a spherically symmetric stellar wind. Let us assume that the wind accelerates away from the star ($dv_r(r)/dr > 0$) and that the temperature drops with radius ($dT(r)/dr < 0$). The gas near to the star is hot and moves subsonic. It produces a bright and broad emission line. But the outer regions of the wind are cooler and they move at a blue-shifted velocity along the line of sight toward the observer. This means that the outer regions of the wind produce a blue-shifted narrow absorption line on the wide emission line. This leads to an asymmetric double-peaked line shape, with the blue shoulder weaker than the red shoulder. This is called a *P-Cygni line shape*.


Line emission from a stellar wind (P–Cygni shape)

7.6.3 Inverse P-Cygni line shape from an infalling envelope

A very similar line shape can be obtained from an infalling envelope. If matter falls toward a star, it accelerates as it comes closer to the star, and it might also become hotter. This produces a very broad (thermal + dynamic) line emission feature, but the cool outer non-accelerated regions of the infalling envelope produce a narrow absorption dip in the line. This also leads to a non-symmetric double-peaked line shape, but this time the red shoulder is weaker while the blue shoulder is stronger. This is called an *inverse P-Cygni line shape*.


Line emission from infalling gas (inverse P–Cygni shape)

7.7 Non-LTE line transfer: The optically thin case

In the very tenuous environment of interstellar space, collisions between atoms or molecules are often not frequent enough to keep the level populations thermal. Spontaneous radiative decay can then be strong compared to the collisional re-population, so that the population of the higher levels may drop below the LTE value, while those of the lower levels may exceed the LTE value. In other words, the problem has become *non-LTE*. The simplest non-LTE line transfer problem is one in which the medium is assumed to be optically thin at all wavelength, so that any photons emitted by a gas parcel at one point do not re-excite a level somewhere else in the cloud. This eliminates the radiative coupling between different regions of the cloud, so that the level populations can be calculated at every point in the cloud independently, i.e. locally.