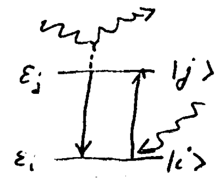
16/10/03

Rate equations and microphysical processes



$(i < j)$

These notes should recapitulate and extend today's class. We'll take a two level atom with states $|i\rangle$ and $|j\rangle$, whatever this means in terms of quantum numbers (the specification of the states doesn't matter here, at least for now). Consider the process of an ~~upward~~ upward transition. We take the cross section and, as we did for the transfer equation, write it as a rate:

$$R^{up} \equiv R^{stim}_{ij} = B_{ij}\, n_i\, I_\nu\, \varphi_{ij} \qquad n_i = \left(\begin{array}{c}\text{fraction of atoms}\\ \text{in state } |i\rangle\end{array}\right)$$

where $I_\nu = I_{\nu_{ij}}$ and $h\nu_{ij} = \varepsilon_j - \varepsilon_i \equiv \Delta\varepsilon_{ij}$. Here B_{ij} is the probability of some upward process provoked by the absorption of a photon. But actually, as I said, this is a very general form for the stimulated rate. We'll explicitly include φ_{ij}, the profile function for this process, the analog of a bandpass. The stimulated downward rate is:

$$R^{stim}_{ji} = B_{ji}\, n_j\, I_\nu\, \varphi_{ji}\,.$$

Now we add the new feature: an atom has a probability A_{ji} of $|j\rangle \to |i\rangle$ with the emission of a photon – a genuine source term. The energy, however, comes from somewhere. Somehow we have prepared this atom with a non-zero n_j. We'll see how in a moment, so:

$$R^{spon}_{ji} = n_j\, A_{ji}\, h\nu\, \varphi_{ji}$$

is the spontaneous rate (always only $|j\rangle \to |i\rangle$). If these are the only rates, that is if we have only radiative processes, then

$$\frac{dn_i}{dt} = -\frac{dn_j}{dt} = R^{stim}_{ji} + R^{spon}_{ji} - R^{stim}_{ij}$$

$$= (B_{ji}\, n_j\, \varphi_{ji} - B_{ij}\, n_i\, \varphi_{ij})\, I_\nu + A_{ji}\, h\nu\, n_j\, \varphi_{ji}$$

In equilibrium, $\frac{dn_i}{dt} = \frac{dn_j}{dt} = 0$ so:

$$I_\nu = \frac{A_{ji}\, n_j\, h\nu\, \varphi_{ji}}{n_i B_{ij}\, \varphi_{ij} - n_j B_{ji}\, \varphi_{ji}}$$

This is also the source function in the absence of transfer, and in thermal equilibrium we know that $I_\nu = B_\nu(T)$. Then,

$$j_\nu \equiv A_{ji}\, n_j\, h\nu\, \varphi_{ji}$$

$$k_\nu \equiv \varphi_{ij}\, n_i\, B_{ij} - n_j\, B_{ji}\, \varphi_{ji},$$

and we'll make – as I did in class – the assumption of complete redistribution by setting $\varphi_{ij} = \varphi_{ji}$. This isn't too strong, quantum mechanically speaking, since for finite width levels the photon can be created or absorbed within the combined bandwidth of the two levels. But you should be aware that it can be different, that this is only an assumption.

Now we couple the matter and radiation. In LTE (I'll use this term – local thermodynamic equilibrium) the population ratio

$$\frac{n_j}{n_i} = \frac{g_j}{g_i}\, e^{-\Delta\varepsilon_{ij}/kT}.$$

But, in fact, we're actually taking another set of rates and balancing them – the collisions – separately from the radiation. In other words, in LTE we make the strong assumption that:

$$n_i C_{ij} = n_j C_{ji} \rightarrow \frac{n_j}{n_i} = \frac{C_{ij}}{C_{ji}}$$

independent of the radiation. The rates balance separately, or put another way,

$$n_j C_{ji} > n_j A_{ji}.$$

Now inserting the Boltzmann population ratio:

$$C_{ij} = \frac{g_j}{g_i} e^{-\Delta\varepsilon_{ij}/kT} C_{ji}$$

because we have a threshold, $\Delta\varepsilon_{ij}$, that must be exceeded to produce an effect. Then:

$$I_\nu = \frac{n_j A_{ji} h\nu}{n_i B_{ij} - n_j B_{ji}} = \frac{h\nu A_{ji}/B_{ji}}{\frac{n_i}{n_j}\frac{B_{ij}}{B_{ji}} - 1} = \frac{2h\nu^3}{c^2}(e^{\Delta\varepsilon_{ij}/kT} - 1).$$

Since we must have I_ν from this in all cases, it holds also for $I_\nu \rightarrow B_\nu$ so:

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

and:

$$\frac{B_{ij}}{B_{ji}} = \frac{g_i}{g_j} \rightarrow B_{ij} g_j = B_{ji} g_i.$$

Thus, from this approximation of LTE, we find that only one rate, A_{ji}, is an empirical constant and (B_{ij}, B_{ji}) are strictly known once we measure A_{ji}. The definition consequently requires knowing (g_i, g_j), the statistical weights for the states, but we know these from the level classifications. Now:

$$\kappa_\nu^{LTE} = n_i B_{ij} - n_j B_{ji} \rightarrow n_i B_{ij} (1 - e^{-h\nu/kT})$$

or, more generally, if we define

$$n_i \equiv b_i n_i^{LTE},$$

with b_i called the departure coefficient, then

$$\kappa_\nu = n_i B_{ij} (1 - \frac{b_j}{b_i} e^{-h\nu/kT})\varphi_{ij}.$$

having restored φ_{ij} for completeness. The correction factor is only important if $h\nu/kT \sim 1$, so we only need to worry about stimulated corrections if we're near the resonant energy with the kinetic energy of the gas or the radiation temperature.

NB We've just written the basis for a laser. If we can ignore (C_{ij}, C_{ji}) then:

$$\frac{n_i}{n_j} = [1 + \frac{h\nu A_{ji}}{I_\nu B_{ji}}] \frac{B_{ji}}{B_{ij}}$$

so in the limit of strong $I_\nu/h\nu$ (notice that this is $n_{\gamma,\nu}$, the number of photons per second at frequency ν) then

$$\frac{n_j}{n_i} \simeq \frac{I_\nu}{h\nu}\frac{B_{ij}}{A_{ji}}$$

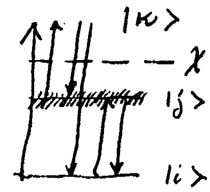
which can easily exceed n_j^{LTE}/n_i^{LTE} if we create a resonant cavity for the light so we have a coherent standing wave in the cavity (done "easily" with mirrors) as under natural conditions for a long enough pathlength. Then once $\kappa_\nu < 0$ we have an amplifier. The width of a level, $\Delta\varepsilon_i$ or $\Delta\varepsilon_j$ is given proportionally by A_{ji} so you can think of $A_{ji}/h\nu$ as a Q^{-1} for this amplifier. The light is taken out of a broad band and compressed into a narrow spectral window. Of course energy is conserved so only the monochromatic power is increased. In interstellar and other low density environments you see this:

Interstellar masers: H_2O, HCO^+, NH_3, SiO, OH,
Circumstellar masers: SiO, OH,
Planetary masers: CO_2;

notice they're all molecular (despite a claimed Fe II laser in the UV in one source, η Car, this being specious – probably wrong – I don't know any others).

Now back to our discussion.

For an addition, let's add one more "level" by allowing for ionization. Now we have a number of new possibilities: take χ to be the ionization energy. Then $|i\rangle \to \chi$, $|j\rangle \to \chi$, $\chi \to |j\rangle, |i\rangle$, $|i\rangle \leftrightarrows |j\rangle$ are all possible. We can take:



$$\beta n_i \equiv R_{ik}^{ion} = n_i \int_{\nu_0}^{\infty} \kappa_\nu^{ion} F_\nu \frac{d\nu}{h\nu}$$

where I've written $\nu_0 = \chi/h$, F_ν replaces I_ν (just integrating over $d\Omega$) and κ_ν^{ion} is the absorption coefficient for any level (so really $\nu_0 = \nu_{0i}$). We'll soon see the exact form for κ_ν^{ion} but, for now, consider that it must fall off with ν (just as any resonance decreases away from ν_0, the resonance frequency) and $\kappa_\nu^{ion} = 0$ for $\nu < \nu_0$. Then for the atom as a whole:

$$\sum_i n_i^r \beta_i = \sum_i n_e n_i^{r+1} \alpha,$$

$\Rightarrow$ now introducing the symbol $\underline{\alpha}$ for the <u>recombination</u> rate. The α is really a sum over all possible routes for the $(r+1)$st ion to go back to the rth ionization state. Now define:

$$Z_r(T) = \sum_j g_j e^{-\varepsilon_j/kT}$$

to be the partition function for the LTE distribution:

$$\frac{n_i}{N} = \frac{n_j}{Z_r(T)} = \frac{g_i e^{-\varepsilon_i/kT}}{\sum_j g_j e^{-\varepsilon_j/kT}}.$$

Then if C_{ij}/C_{ji} is the collision ratio and $C_{ji} \gg A_{ji}$, in LTE:

$$\frac{N_{r+1} n_e}{N_r} = \frac{Z_e Z_{r+1}}{Z_r} e^{-\chi/kT}, \quad N_r = \left(\begin{array}{l}\text{number of atoms}\\ \text{in the } (r+1)\text{st state}\end{array}\right).$$

For LTE, the Z_e is just the electron free particle partition function (nr. of states in the continuum):

$$Z_e(T) = 2(2\pi m_e kT)^{3/2} h^{-3}$$

since the elementary phase space volume is h^3 and there are two (2) spin states. Thus, for LTE:

$$\frac{N_{r+1} n_e}{N_r} = \frac{2(2\pi m_e kT)^{3/2}}{h^3} \frac{Z_{r+1}(T)}{Z_r(T)} e^{-\chi/kT},$$

also known as the <u>Saha equation</u>. Isn't this lovely? Look at it! You now have a way to compute the equation of state for the gas – in LTE – provided you know the level structures of the ions, and this information comes from spectral analysis. It's pure statistical mechanics, senza fotoni e meccanica quantistica. But, alas, it isn't so simple. Consider HI ($\equiv H^0$). Here $g_n = 2n^2$ and $\varepsilon_n = \chi(1-\frac{1}{n^2})$ so for $Z_{H^0}(T)$, as $n\to\infty$, $g_n\to\infty$ but $\varepsilon_n \to \chi < \infty$ so Z_{H^0} diverges for $T\neq 0$!! You must have a way to truncate the sum and this is where the rates we've must defined enter. Again, since the level width is $\sim A_{ji}$ even in the absence of collisions, if $\Delta\varepsilon_{n+1,n} < A_{n+1,n}$, then the levels merge (OK, to be precise if Γ_{n+1} is the width of the upper state then this condition follows ~~precisely~~). Thus there is always an upper bound to $n<\infty$ and Z_{H^0} converges. Now if the collision rate, $n_e C_{ji} > A_{ji}$, then the merger occurs at even lower n so we have a reduction in Z_r and an increase in N_{r+1}/N_r. (The only thing that suppresses this effect, by the way, is degeneracy: as we'll see, - and to be honest, I just realized - since the most probable energy for the ejected electron is $\varepsilon_e = 0$, a degenerate electron gas has a gap between the free electron energy and the bound states! You've seen this before, you know, in "struttura della materia", it's called a semiconductor. There's a gap between the conduction band and the bound states. Non è carina?). (Mi dispiace per queste digressione, è sfortunata di solito).

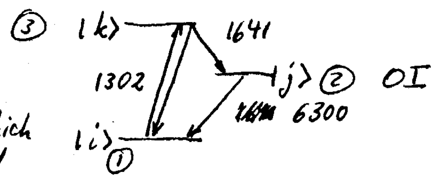
OK, to return to the rates, now add many levels:

$$\frac{dn_i}{dt} = -\sum_{j\neq i} n_i \left(C_{ij} n_e + B_{ij} I_{\nu_{ij}}\right) + \sum_{j\neq i} n_j \left(A_{ji} + n_e C_{ji} + B_{ji} I_{\nu_{ji}}\right)$$

for each level $|i\rangle$ and you see we have a linear system where all of the atomic rates are known, you hope, from laboratory measurements. We can come up with some simple scaling laws for the collision rates by noting that we always average these over some thermal distribution of the particles:

$$C_{ij} = \langle \sigma_{ij}(v) v \rangle .$$

The simplest scaling comes from noting that for constant σ, $C_{ij} \sim T^{1/2}$ while for a quantum mechanical scaling, $r^2 \sim p^{-2}$ (p is now the momentum) so we should expect $C_{ij} \sim T^{-1/2}$. For charged particle collisions, $\sigma \sim v^{-4}$ so we would expect $C_{ij} \sim T^{-3/2}$. These are just quick estimates but you see how they can be useful, since once we know, for instance, $A_{ji}/(C_{ji} n_e)$ at one density, we can scale the collision rates with n_e and T to find when the collisions cease to be important, both for de-excitation and for the broadening of the level. In a dynamical process, remember that anything that shortens the lifetime also broadens a level, hence the line.



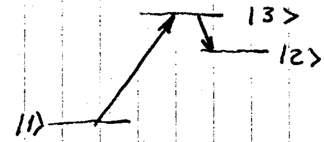
Ex: Hot emitting optically thin gas

I've written the diagram here for OI in which the ground state transition is at 1302 Å followed by a possible de-excitation either directly back (a simple scattering process) or by two much less likely transitions, 1641 Å and 6300 Å.

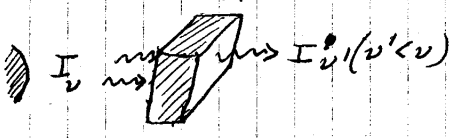
Write out the general 3-level equilibrium solution for $\dot{n}_j = 0$ $\forall j$ and look at the various limits (i.e. $n_e \to 0$, assume $A_{21} > A_{32}$ but $A_{31} \gg (A_{32}, A_{21})$ and $kT \approx \Delta\varepsilon_{21} \ll (\Delta\varepsilon_{13}, \Delta\varepsilon_{23})$.

In this second sense, the process has a non-local character: a photon emitted by one atom can be absorbed by another. I'll return to this soon.

Now let's go back to the 3-level case and look at the process I did at the end of the class today - <u>fluorescence</u>. It is an essentially non-LTE (NLTE) process since it changes populations by <u>radiative</u> processes. As an example, consider an atom in the ground state, or even an excited state, that has a $\Delta\varepsilon_{ij}$ that happens - by chance - to coincide with <u>another</u> atom's transition. We would usually, if just taking a continuum, look at $\int I_\nu d\nu$ over the width of a line and in detailed balance say the brightness of the continuum is decreased locally and then collisions redistribute the absorbed energy into the gas from which it is then re-radiated.



But suppose I_ν is instead from emission in a line of another ion that happens to nearly coincide with an accessible transition in gas at some distance, at a temperature that is lower than the source (at least with a radiation temp. for the source above that of the gas kinetic temp.). Then:



$$R^{up} = B_{ij} n_1 I_\nu$$

is the upward rate (and we can assume $C_{ij} n_e < B_{ij} I_\nu$). For a downward rate, A_{jk}, to some intermediate state $i<k<j$ may occur if $C_{jk} n_e < A_{jk}$, even if the collisions $n_i C_{ik} = C_{ki} n_k$ balance. Then to be specific:

$$n_1 B_{13} I_\nu = A_{32} n_3$$

We then see emission at ν_{32} where collisions could not produce any large population of n_3 and

$$n_2(C_{21} + C_{23}) n_e = n_3 A_{32} + n_1 C_{12} n_e ;$$

so even if $n_1 C_{12} = C_{21} n_2$, we still have $n_2 C_{23} n_e = n_1 B_{13} I_\nu$ and the population of the states clearly departs from LTE.

Some very important near coincides occur: Fe II overlaps with C IV 1550 (the resonance line, formed in $T \sim 3\times10^4$ K gas while Fe II is from $< 10^4$ K); the example I mentioned in class of He II Lyβ coinciding with O III (1036 Å) producing the λ4959, 5007 Å doublet (visible as "down-conversion of a FUV transition"); O VI pumping H_2 ... There's a <u>long</u> list.

An aside on probabilistic methods

I've asserted, at the end of class, that the walk of a photon through a medium is a stochastic process. To be specific, it's a Markov process, defined as one with no memory: at each t, the probability $P(\underset{\sim}{x}, t \mid \underset{\sim}{x}', t')$ of being at any position $\underset{\sim}{x}$ given the previous position $\underset{\sim}{x}'$ at time $t' < t$ is $P(\underset{\sim}{x})$ independent of the history. This can be expressed by:

$$P(\underset{\sim}{x}, t) = P(\Delta \underset{\sim}{x})$$

and then for a path of length $|\underset{\sim}{\ell}|$, $\underset{\sim}{\ell} = \sum^{i} \Delta \underset{\sim}{x}_i$ and $P(\Delta x_i)$ is identically distributed for all i. We have, then, a new way to treat radiative transfer - the Monte Carlo scheme. This method is amazingly simple in principle. The probability of going some step size $\Delta\tau$ is $e^{-\Delta\tau/\mu}$ in any direction μ (really, some distance Δs but we can take a slab and define $\Delta\tau/\mu = \Delta s$). Then at each point, a photon goes a step:

$$\frac{\Delta\tau_i}{\mu_i} = -\ln P_i$$

where P_i is a random number. If we have a phase function $p(\mu', \mu)$, then the photon has a probability $p(|\mu - \mu'|)$ of changing its direction, hence