Bound – Bound Transitions

Einstein Relation for Bound-Bound Transitions

- Lower State i : g_i = statistical weight
- Upper State j : g_j = statistical weight
- For a bound-bound transition there are three direct processes to consider:
- #1: Direct absorption: upward $i \rightarrow j$
- #2: Return Possibility 1: Spontaneous transition with emission of a photon
- #3: Return Possibility 2: Emission induced by the radiation field

The Absorption Process

Possibility 1: Upward i → j

- $N_i(\nu)\, R_{ij}\, d\omega/4\pi = N_i(\nu)\, B_{ij}\, I_\nu\, d\omega/4\pi$
- R_{ij} is the rate at which the transition occurs
- $N_i(\nu)$ is the number of absorbers cm^{-3} in state i which can absorb in the range $(\nu, \nu + d\nu)$
- The equation defines the coefficient B_{ij}
- Transitions are not infinitely sharp so there is a spread of frequencies φ_ν (the absorption profile)

$$\int_0^\infty \phi_\nu d\nu = 1$$

Let Us Absorb Some More

- If the total number of atoms is N_i then the number of atoms capable of absorbing at frequency ν is $N_i(\nu) = N_i\varphi_\nu$
- In going from i to j the atom absorbs photon of energy $h\nu_{ij} = E_j - E_i$
- The rate that energy is removed from the beam is:

$$\rho a_\nu I_\nu = N_i B_{ij} \frac{h\nu_{ij}}{4\pi} \phi_\nu I_\nu$$

- a_ν is a macroscopic absorption coefficient such as K_ν

The Return Process: j → i

Going Down Once

- Spontaneous transition with the emission of a photon
- Probability of a spontaneous emission per unit time $\equiv A_{ij}$
- Emission energy rate:
- ρj_ν (spontaneous) $= N_j\, A_{ji}\, (h\nu_{ij}/4\pi)\, \psi_\nu$
- The emission profile is normalized:

$$\int \psi_\nu d\nu = 1$$

The Return Process: j → i

Going Down Twice

- Emission induced by the radiation field
- $\rho j_\nu(\text{induced}) = N_j \, B_{ji} \, \psi_\nu \, I_\nu \, (h\nu_{ij}/4\pi)$
- Note that the induced emission profile has the same form as the spontaneous emission profile.
- Spontaneous emission takes place isotropically.
- Induced emission has the same angular distribution as I_ν

Assume TE

This gives us $I_\nu = B_\nu$ and the ratio of the state populations!

- $I_\nu = B_\nu$ and the Boltzman Equation

$$\frac{N_j^*}{N_i^*} = \frac{g_j}{g_i} e^{\frac{-h\nu_{ij}}{kT}}$$

- $N_i^* B_{ij} B_\nu = N_j^* A_{ji} + N_j^* B_{ji} B_\nu$ (♓)
  - Upward = Downward
- What did we do to get (♓)?
  - Integrate over ν and assume that $B_\nu \neq f(\nu)$ over a line width. The two pieces that depend on ν are B_ν (assumed a constant) and (φ_ν, ψ_ν) but the latter two integrate to 1!

Now we do Some Math

Solution of (♓) for B_ν

$$B_\nu = \frac{N_j^* A_{ji}}{N_i^* B_{ij} - N_j^* B_{ji}}$$

Boltzman Equation

$$N_j^* = \frac{g_j}{g_i} N_i^* e^{\frac{-h\nu_{ij}}{kT}}$$

Substitute for N_j* and
note that N_i* falls out!

$$B_\nu = \frac{\frac{g_j}{g_i} N_i^* e^{\frac{-h\nu_{ij}}{kT}} A_{ji}}{N_i^* B_{ij} - \frac{g_j}{g_i} N_i^* e^{\frac{-h\nu_{ij}}{kT}} B_{ji}}$$

Onward!

Use this to multiply the top and bottom of the previous equation

$$\frac{g_i}{g_j}\frac{1}{B_{ji}}e^{\frac{h\nu_{ij}}{kT}}$$

But this is just the Planck function so

$$B_\nu = \frac{\dfrac{A_{ji}}{B_{ji}}}{\left(\dfrac{g_i}{g_j}\dfrac{B_{ij}}{B_{ji}}e^{\frac{h\nu_{ij}}{kT}} - 1\right)}$$

A Revelation!

The Intersection of Thermodynamics and QM

$$B_\nu = \frac{\dfrac{A_{ji}}{B_{ji}}}{\left(\dfrac{g_i}{g_j}\dfrac{B_{ij}}{B_{ji}} e^{\frac{h\nu_{ij}}{kT}} - 1\right)} = \frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

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

$$\left(\frac{g_j}{g_i}\frac{B_{ij}}{B_{ji}}\right) = 1$$

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

$$g_j B_{ij} = g_i B_{ji}$$

What Does this Mean?

- We have used thermodynamic arguments but these equations must be related *only* to the properties of the atoms and be independent of the radiation field
- ==> These are perfectly general equations
- ==> These arguments predicted the existence of stimulated emission.
- NB: Stimulated (induced) emission is not intuitively obvious. However, it is now an observed fact.

The Equation of Transfer

Note the Following:

$$\frac{\mu dI_\nu}{\rho dz} = j_\nu - \mathrm{K}_\nu I_\nu$$

$$\rho a_\nu I_\nu = N_i B_{ij} \frac{h\nu_{ij}}{4\pi} \phi_\nu I_\nu$$

$$\rho j_\nu = N_j A_{ji} \frac{h\nu_{ij}}{4\pi} \psi_\nu$$

$$\rho j_\nu = N_j B_{ji} \frac{h\nu_{ij}}{4\pi} \psi_\nu I_\nu$$

$$\frac{\mu dI_\nu}{dz} = N_j A_{ji} \frac{h\nu_{ij}}{4\pi} \psi_\nu + N_j B_{ji} \frac{h\nu_{ij}}{4\pi} \psi_\nu I_\nu - N_i B_{ij} \frac{h\nu_{ij}}{4\pi} \phi_\nu I_\nu$$

$$\frac{\mu dI_\nu}{dz} = \frac{h\nu_{ij}}{4\pi} \left[N_j A_{ji} \psi_\nu - (N_i B_{ij} \phi_\nu - N_j B_{ji} \psi_\nu) I_\nu \right]$$

The Coefficients Are:

Line Absorption Coefficient usually denoted l_v

$$b_i \equiv \frac{N_i(T,N_e,J_\nu)}{N_i^*(T,N_e)}$$

Departure Coefficient

$$l_\nu = \frac{h\nu_{ij}}{4\pi} N_i B_{ij}\phi_\nu \left[1 - \frac{N_j B_{ji}\psi_\nu}{N_i B_{ij}\phi_\nu}\right]$$

Gather the terms on I

$$\frac{N_j}{Ni} = \frac{b_j N_j^*}{b_i N_i^*} = \frac{b_j g_j}{b_i g_i} e^{\frac{-h\nu_{ij}}{kT}}$$

Boltzmann Equation

$$l_\nu = \frac{h\nu_{ij}}{4\pi} N_i B_{ij}\phi_\nu \left[1 - \frac{g_j B_{ji}\psi_\nu}{g_i B_{ij}\phi_\nu}\frac{b_j}{b_i} e^{\frac{-h\nu_{ij}}{kT}}\right]$$

g_iB_{ij} = gjB_{ji}

$$l_\nu = \frac{h\nu_{ij}}{4\pi} N_i B_{ij}\phi_\nu \left[1 - \frac{\psi_\nu b_j}{\phi_\nu b_i} e^{\frac{-h\nu_{ij}}{kT}}\right]$$

The Line Source Function

Source Function = j/

$$S_\nu = \frac{N_j A_{ji} \psi_\nu}{N_i B_{ij} \phi_\nu - N_j B_{ji} \psi_\nu}$$

Divide by $N_j B_{ji} \psi_\nu$

$$= \frac{\dfrac{A_{ji}}{B_{ji}}}{\dfrac{N_i B_{ij} \phi_\nu}{N_j B_{ji} \psi_\nu} - 1}$$

$$= \frac{2h\nu^3}{c^2} \frac{1}{\dfrac{b_i \phi_\nu}{b_j \psi_\nu} e^{\frac{h\nu_{ij}}{kT}} - 1}$$

Use relations between A & B’s

$$\frac{\mu}{\ell_\nu} \frac{dI_\nu}{dz} = I_\nu - S_\nu$$

The equation of transfer for a line!

Let Us Simplify Some

- Assume $\varphi_\nu = \psi_\nu$ (Not unreasonable)
- If we assume LTE then $b_i = b_j = 1$
- Then $I_\nu = N_i B_{ij} \varphi_\nu (1-e^{-h\nu/kT})$
  - The term $(1-e^{-h\nu/kT})$ is the correction for stimulated emission
- $S_\nu = B_\nu$

An Alternate Definition

With Respect to the Energy Density

- Define $B_{i,j}$ as
- $u_\nu B_{ij} = B_{ij}\ 8\pi/c^3\ (h\nu^3/(e^{h\nu/kT}-1))$
  - Bi,j is the probability that an atom in lower level i will be excited to upper level j by absorption of a photon of frequency $\nu = (E_j - E_i) / h$
  - This B is defined with respect to the energy density U of the radiation field, not I_ν ($=B_\nu$) as previously.
- For this definition
  - $A_{ji} = (8\pi h\nu^3/c^3)\ B_{ji}$
  - $g_i B_{ij} = g_j B_{ji}$

Now Let Us Try To Determine A_{ji}, B_{ij}, and B_{ji}

- Classical Oscillator and EM Field
  - Dimensionally correct but can be off by orders of magnitude
- QM Atom and Classical EM Field
  - Correct Expression for B_{ij}
- QM Atom and a Quantized EM Field
  - Gives B_{ij}, B_{ji}, and A_{ji}
- However, note that B_{ij}, B_{ji}, and A_{ji} are interrelated and if you know one you know them all!

A Classical Approach

- The probability of an event generally depends on the number of ways that it can happen. Suppose photons in the range $(\nu, \nu + d\nu)$ are involved. The statistical weight of a free particle: Position $(x, x+dx)$ and momentum $(p, p+dp)$ is $dN/h^3 = dxdydzdp_xdp_ydp_z/h^3$
- Then the statistical weight per unit volume of a particle with total angular momentum p, in direction $d\Omega$, is $p^2dpd\Omega/h^3$.

Free Particles

- Momentum of a photon is $p = h\nu/c$ so the statistical weight per unit volume of photons in $(\nu, \nu+d\nu)$ is $\nu^2 d\nu d\Omega/hc^2$.
- This means high frequency transitions have higher transition probabilities than low frequency transitions.

Semiclassical Treatment of an Excited Atom

- Oscillating Dipole (electric) in which the electron oscillates about the nucleus.
- For the case of no energy loss the equation of motion is:
  - ν_0 is the frequency of the oscillation
- The electric dipole radiates (classically) and energy is lost due to the radiation

$$m\frac{d^2r}{dt^2} = -4\pi^2\nu_0^2 r$$

$$I = \frac{2}{3}\frac{e^2}{c^3}\left|\frac{d^2r}{dt^2}\right|^2$$

A Damped Oscillator

- The energy loss leads to a further term in the equation of motion which slows the electron
- The damping force is $F = \frac{2}{3}\frac{e^2}{c^3}\frac{d^3r}{dt^3}$
- If F is small then the motion can be considered to be near a simple harmonic r = r_0 cos ($2\pi\nu_0 t$)

$$\dddot{r} = -4\pi\nu_0^2 r^2 \dot{r}$$

$$m\ddot{r} = -4\pi\nu_0^2 r^2 \dot{r} - 4\pi^2\nu_0^2 \frac{2}{3}\frac{e^2}{c^3}\dot{r}$$

The Solution is

Damped Harmonic Oscillator

$$r = r_0 e^{\frac{-\gamma t}{2}} \cos(2\pi \nu_0 t)$$

$$\gamma = \frac{8\pi^2 e^2}{3 m_e c^2} \nu_0^2 = 2.47(10^{-22}) \nu_0^2$$

- γ is called the classical damping constant

Electric Field

- The field set up by the electron is proportional to the electron displacement

$$E(t) = E_0 e^{\frac{-\gamma t}{2}} \cos(2\pi\nu_0 t)$$

- At time t = $(\gamma/2)^{-1}$ we get E(t) = E_0/e which characterizes the time scale of the decay

A Result!

- The decay time must be proportional to A_{ji} -the probability of a spontaneous transition downwards
- $A_{\text{classical}} = \gamma$
  - For Hα, $= 6563\text{Å}$; $\nu_0 = c/\lambda$ so $\gamma \simeq 5(10^7)\ \text{s}^{-1}$
- The field decays exponentially so the frequency is not monochromatic. To get the frequency dependence do a Fourier analysis
- The square of the spectrum is the intensity of the field!

The Broadening Profile

Lorentz Profile

$$I(\nu) = I_0 \frac{\gamma}{4\pi^2(\nu-\nu_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$= I_0 \frac{\frac{\gamma}{4\pi^2}}{(\nu-\nu_0)^2 + \left(\frac{\gamma}{4\pi}\right)^2}$$

$$I = \frac{I_0}{2} = I_0 \frac{\frac{\gamma}{4\pi^2}}{(\nu-\nu_0)^2 + \left(\frac{\gamma}{4\pi}\right)^2}$$

$$(\nu-\nu_0)^2 + \left(\frac{\gamma}{4\pi}\right)^2 = \frac{2\gamma}{4\pi^2}$$

$$(\nu-\nu_0)^2 = \left|\frac{2\gamma}{4\pi^2} - \left(\frac{\gamma}{4\pi}\right)^2\right|$$

$$2\gamma << \gamma^2$$

$$\therefore$$

$$(\nu-\nu_0)^2 = \left(\frac{\gamma}{4\pi}\right)^2$$

$$(\nu-\nu_0) = \frac{\gamma}{4\pi}$$

$$FWHM = \frac{\gamma}{2\pi}$$

More On Broadening

- In QM the natural broadening arises due to the uncertainty principle
- The uncertainty in the time in which an atom is in a state is its lifetime in that state.
- Average lifetime A^{-1}
- Thus the uncertainty OE = hOt ≈ Ah
- This means that Oν 🕘 A 🕘 γ

Oscillator Strengths

- Since γ is of the same order as A we usually express exact values of A in terms of the classical value of γ.
- Oscillator Strength $n_{upper} \rightarrow m_{lower}$
- $A_{nm} \equiv 3\,(g_m/g_n)\,f_{nm}\,\gamma$
- $= (g_m/g_n)\,(8\pi^2 e^2 \nu^2/m_e c^3)\,f_{nm}$
- $= (g_m/g_n)\,7.42(10^{-22})\,\nu^2\,f_{nm}$
- $B_{mn} = (\pi e^2/m_e h\nu)\,f_{nm}$

Oscillator Strengths

Balmer Series of H

$$f_{nm} = \frac{2^6}{3\sqrt{3}\pi} \frac{1}{g_m} \left(\frac{1}{m^2} - \frac{1}{n^2} \right)^{-3} \frac{G_I}{n^3 m^3}$$

$$g_m = 2m^2$$

$$f_{nm} = \frac{32}{3\sqrt{3}\pi} \left(\frac{1}{m^2} - \frac{1}{n^2} \right)^{-3} \frac{G_I}{n^3 m^5}$$

This is known as Kramer's Formula. G_I is the Gaunt Factor which is order 0.1 - 10

Line	U-L	f
Hα	3-2	0.641
Hβ	4-2	0.119
Hγ	5-2	0.044
Hδ	6-2	0.021
Hε	7-2	0.012

The Absorption Coefficient

- We are now ready to determine the absorption coefficient a_ν per atom of an absorption line centered at ν_0.
- It is defined so that the probability of absorption per unit path length of a photon is Na_ν where N is the number density of atoms capable of absorption.
- Consider a beam of intensity I_ν traveling across a unit cross-sectional area. In time dt the photons have traveled cdt.

Energy Considerations

- The energy removed from the beam in (ν, ν + dν) is I_ν na_ν cdt. Alternately, the number of transitions is I_ν na_ν cdt / hν. The volume occupied by the photons is cdt (unit cross sectional area).
- The number of transitions per unit volume per unit time per unit frequency due to the beam is I_ν na_ν / hν.
- Integrating over solid angle and assuming thermal equilibrium ($4\pi I_\nu = cU_\nu$) the number of absorptions is cU_ν na_ν / hν.

Onward

- We now integrate over frequency over the line profile only to obtain the number of transitions from lower state to upper state per unit volume per unit time

$$Transition\ Rate = cN\int_0^\infty \frac{U_\nu}{h\nu} a_\nu d\nu$$

- But this is equal to $U_\nu B_{nm} N$ so

$$U_\nu B_{nm} N = cN\int_0^\infty \frac{U_\nu}{h\nu} a_\nu d\nu$$

Line Absorption

The nature of line absorption

- U_ν does not vary across the line
- a_ν is small except near ν_0: $\nu_0 = (E_n - E_m) / h$
- $U_\nu/h\nu$ varies slowly across the line

$$cN\int_0^\infty \frac{U_\nu}{h\nu} a_\nu d\nu \cong cN\frac{U_{\nu_0}}{h\nu_0}\int_0^\infty a_\nu d\nu$$

$$U_\nu B_{nm} N \cong cN\frac{U_{\nu_0}}{h\nu_0}\int_0^\infty a_\nu d\nu$$

For $\nu = \nu_0$

$$\frac{\pi e^2}{m_e h\nu} f_{nm} = \frac{c}{h\nu_0}\int_0^\infty a_\nu d\nu$$

$$\int_0^\infty a_\nu d\nu = \frac{\pi e^2}{m_e c} f_{nm}$$

cm^2 Hz

We are about done

$$\int_0^\infty a_\nu d\nu = \frac{\pi e^2}{m_e c} f_{nm}$$

- The integral of a_ν over ν can be thought of as the total absorption cross section per atom initially in the lower state. We rewrite a_ν as

$$a_\nu = \frac{\pi e^2}{m_e c} f_{nm} \phi_\nu$$

- φ_ν is the absorption profile and we expect it to follow the Lorentz profile

Combine the Profile

$$a_\nu = a_0 \frac{\frac{\gamma}{4\pi^2}}{(\nu-\nu_0)^2 + \left(\frac{\gamma}{4\pi}\right)^2}$$

So

$$a_\nu = \frac{\pi e^2}{m_e c} f_{nm} \frac{\frac{\gamma}{4\pi^2}}{(\nu-\nu_0)^2 + \left(\frac{\gamma}{4\pi}\right)^2}$$

- In principal $f_{nm} \sim \gamma$ but there are other broadening mechanisms.
  - – Natural width (γ) is small compared to other mechanisms (Stark, Doppler, van der Waals, etc)
- For $\nu = \nu_0$: $a_0 = (\pi e^2/m_e c)\,(f_{nm}/\gamma)$

Stimulated Emission

- We have yet to account for stimulated emission
- We usually assume emission is isotropic but if it goes as $B_{mn}I_\nu$ then it correlates with I_ν
- We treat this as a negative absorption and reduce the value of a_ν by the appropriate factor.
- In our discussion of the Einstein coefficients we found the factor to be $(1 - e^{-(h\nu/kT)})$ so the corrected a_ν is

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