Part VI Radiative Transitions

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1 Atomic/molecular coupling with radiation

1.1 Interaction with electromagnetic radiation

The coupling term between charged particles and the electromagnetic field, $\vec{p_i} \cdot \vec{A}(\vec{k}\cdot\vec{x}-wt)^1$, can be expressed through an expansion in $\vec{k}\cdot\vec{x}$ as $H_{\rm int} = H_{\rm d} + H_{\rm M} + H_{\rm Q}$ (see Shu I,24), for which

$$H_{\rm d} = -\vec{E} \cdot \vec{d} \,(\text{zeroth order})$$

where, for a molecule, $\vec{d} = \vec{d}_{\rm el} + \vec{d}_{\rm nuc}$.

$$H_{\rm M} = -\vec{B} \cdot \vec{M}$$
 (first order)

where the magnetic dipole moment $\vec{M} \propto \vec{L}$, and

$$H_{\rm Q} = -\frac{e}{6} \vec{\nabla} \vec{E} : (3\vec{x}\vec{x} - |\vec{x}|^2 \mathbb{I}) \text{ (also order one)}.$$

In general $H_{\rm M} > H_{\rm Q}$.

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¹when substituting $\vec{p} \rightarrow \vec{p} - \frac{q}{c}\vec{A}$, and neglecting terms in A^2 (OK for the ISM) see Shu I, 21

1.2 Bound-bound transition probabilities and cross-sections

In time-dependent perturbation theory, the rate of radiative excitations $i \rightarrow f$ is:

$$\frac{dP_{if}}{dt} \propto \mathfrak{N}(\omega_{if}) \left| \langle \phi_f | H_{\text{int}}(\omega) | \phi_i \rangle \right|^2.$$

In a cubic box where the ocupation number of state \vec{n} is \mathfrak{N} , the density of states is $d^3\vec{n} = V d^3\omega/(2\pi c)^3$, with a volume $V \to \infty$.

The absorption cross-section σ_{if} derives from $P_{if} = N_f/N_i \propto \#$ of absorbed photons ²:

$$P_{if} = \int d^3 \vec{n} \, \frac{\mathfrak{N}(\vec{n})}{V} c \, t \, \sigma_{if} \, \Rightarrow \, \frac{dP_{if}}{dt} = \int_0^\infty \sigma_{if} \, c \, \mathfrak{N}(\omega) \, \frac{4\pi\omega^2}{(2\pi)^3 c^2} d\omega$$

Identifying (see Shu I, 22, 23), we obtain

$$\sigma_{if} \propto |\langle \phi_f | H_{\text{int}}(w) | \phi_i \rangle|^2 \, \delta(\omega - \omega_{if}).$$

1.3 Oscilator strength

For the electric dipole Hamiltonian, one gets

$$\sigma_{if} = \frac{4\pi^2}{3\hbar c} \left| \langle \phi_f | \vec{d} | \phi_i \rangle \right|^2 \delta(\omega - \omega_{if}),$$

which is usually expressed in terms of the oscilator strength f_{if} ,

$$\sigma_{if} = \frac{\pi e^2}{m_e c} f_{if} \delta(\nu - \nu_{if}), \quad \text{con} \quad f_{if} \equiv \frac{4\pi m_e}{3e^2\hbar} \nu_{if} \left| \langle \phi_f | \vec{d} | \phi_i \rangle \right|^2.$$

For a single electron with position \vec{x} ,

$$f_{if} = \frac{2m_e(\omega_{if}\langle f|\vec{x}|i\rangle)^2}{3\hbar w_{if}},$$

which is roughly the ratio between the vibrational potential energy of the electron and that of the radiated photon.

1.4 Relationship with Einstein coeficients

The equation of detailed balance,

$$n_i B_{if} J_{\nu_{if}} = n_f A_{fi} + n_f B_{fi} J_{\nu_{fi}},$$

and the LTE relationships,

$$\frac{n_f}{n_i} = \frac{g_f}{g_i} \exp(-\frac{h\nu_{if}}{kT}), \text{ and } J_{\nu} = B_{\nu}(T), \text{ lead to}$$
$$A_{fi} = \frac{g_i}{g_f} (2h\nu^3/c^2) B_{if}, \qquad B_{fi} = \frac{c^2}{2h\nu^3} A_{fi} = (g_i/g_f) B_{if}.$$

²note optically thin case: $dN_f = -\Gamma N_f dt + \frac{dP_{if}}{dt} N_i dt$.

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• The rate of stimulated excitations is related to the oscilator strength using the requirement

$$n_i B_{if} J_{\nu_{if}} = \int d\nu \int d\Omega \sigma_{if} n_i \frac{J_{\nu}}{h\nu} = \int d\nu 4\pi \sigma_{if} n_i \frac{J_{\nu}}{h\nu} \tag{1}$$

• Therefore,

$$B_{if} = \frac{4\pi^2}{h\nu} \frac{e^2}{m_e c} f_{if}.$$
 (2)

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1.5 Natural line width

- We consider an atom in state *i*, subjected to radiation with frequency ω_{ji} , corresponding to the energy interval with a final state *f*.
- The wave function of the target can be expanded as

$$|\phi\rangle = \sum_{j} c_{j} |\phi_{j}\rangle.$$
(3)

• Denoting $\Gamma = A_{ji}$, then the probably amplitude for state f satisfies

$$\frac{d|c_f|^2}{dt} = -\Gamma|c_f|^2. \tag{4}$$

• In terms of the amplitude coefficients, Fermi's golden rule should be modified to account for spontaneous decay:

$$\dot{c}_f = -i\hbar^{-1} \langle \phi_f | H_\alpha^{\rm abs} | \phi_i \rangle e^{(\omega_{fi} - \omega)t} - \frac{\Gamma}{2} c_f.$$
(5)

- We can solve Eq. 5 recognizing $e^{\Gamma t/2}$ as an integrating factor.
- After taking the modulus, in the limit $t \to \infty$,

$$|c_f(\infty)|^2 = \hbar^{-2} \frac{\left| \langle \phi_f | H_\alpha^{\rm abs} | \phi_i \rangle \right|^2}{(\omega_{fi} - \omega)^2 + (\Gamma/2)^2}.$$
 (6)

1.6 Selection rules

- Electric dipole
 - atoms: $\Delta l = 1$, $\Delta m = 0$.
 - molecules:

- * vibrational-rotational transitions, or rovibrational, $\Delta J = \pm 1$, $\Delta m = 0$, $\Delta v = \pm 1$, allowed when $\Lambda \neq 0$, $\Delta J = 0^{-3}$.
- * electronic transitions, $\Delta \Lambda = 0, \pm 1, \Delta S = 0$
- * electronic-vibrational-rotational transitions (i.e. *vibronic* transitions): $\Delta J = 0, \pm 1, \ \Delta m = 0, \pm 1 \text{ and } \Delta J \neq 0 \text{ si } \Lambda = \Delta \Lambda = 0 \text{ and if } J = 0.$

$$\Delta J = \begin{cases} +1 \rightarrow \text{R branch} \\ 0 \rightarrow \text{Q branch} \\ -1 \rightarrow \text{P branch} \end{cases}$$

- magnetic dipole, atoms: $\Delta l = 0, \Delta m = 0, \pm 1$.
- electric quadrupole, atoms: Δl = 0, ±2, Δm = 0, ±1, ±2, rotational transitions in molecules ΔJ = 0, ±1, ±2.

CO

Subaru - IRCS + echelle & X-disperser (Goto et al. 2003, ApJ, 598, 1038)



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³*Lambda doubling*, two states $\pm \Lambda$ for each *J*. Example: hyperfine structure of the OH Λ doublet at ~1.7 GHz.

1.7 Selection rules – H₂

- In the case of H_2 we have $\vec{d} = 0$. Moreover the fundamental state is $\vec{L} = 0$, and $\vec{S} = 0$, so that $\vec{M} = 0$ and all low-energy transitions for H_2 are quadrupolar.
- Note that the antisymmetry of the nuclear wave function implies that the state J = 1 (J odd) is triplet (**Ortho** H₂, $I = S_{nuclear} = 1$), while J = 0 (J even) is singlet (**Para** H₂, I = 0).
- In H₂ the exclusion principle ⁴ forbids $\Delta J = 1$, unless the transition involves a change in spin state. The spin transitions can only occur through the exchange of protons in collisions. Radiative transitions between spin states can occur, but at a rate corresponding to the quadrupolar transitions in the Hamiltonian of the deviations to the Born-Oppenheimer approximations.
- In the ISM, **Ortho** and **Para** H_2 are effectively different molecules. The distinction extends to all molecules that contain H_2 radicals.
- Rovibrational transitions between an upper level ¹ and a lower level ² are written $(v_1 v_2)O(J_2)$ when $J_2 J_1 = -2$, $(v_1 v_2)Q(J_2)$ when $J_2 J_1 = 0$, $(v_1 v_2)S(J_2)$ when $J_2 J_1 = +2$.

2 Photoionization and radiative recombination

2.1 Photoionization

In time-dependent perturbation theory, the rate of transition between two states, $i \rightarrow f$, is:

$$\frac{dP_{if}}{dt} = \frac{e^2}{hc^3m_e^2} \sum_{\alpha=1}^2 \int \omega_{fi} \,\mathcal{N}_{\alpha}(\vec{k}) \,|\langle \phi_f| e^{i\vec{k}\cdot\vec{x}} \vec{e}_{\alpha}\cdot\vec{p} |\phi_i\rangle|^2 \,d\Omega,$$

where $\mathcal{N}(\vec{k})$ is the occupation number of photons in the state corresponding to \vec{k} , with frequency ν_{fi} .

In a photoionization process the final states f belong to the continuum. The Born approximation neglects the influence of the ion on $|\phi_f\rangle$, and for a description of the continuum we adopt a hard box normalization, with a size $L \to \infty$. With icorresponding to the fundamental state of the hydrogen atom, we obtain (Shu I, 23),

$$\frac{dP_{if}}{dt} \propto \omega_{fi}^{-3} \mathcal{N}(\omega), \text{ where } \mathcal{N}(\omega) = \int d\Omega \mathcal{N}(\vec{\omega}).$$

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⁴the requirement that the wave function be antisymmetric

The rate of absorption of ionizing photons with frequencies in the range $[\nu, \nu + \nu]$ is $dN_f \frac{dP_{if}}{dt}$, where dN_f is the number of free states in the corresponding range of energies,

$$dN_f = \frac{V}{2\pi^3} 4\pi \ k_e^2 \ dk_e,$$

where $\vec{k_e}$ refers to the free electron.

The cross-section of ionization is defined through

$$P_{if}dN_f = t \ \sigma_{if}(\omega)c \ \frac{\mathcal{N}(\vec{n})}{V} \ 4\pi n^2 dn, \text{ with } \frac{d^3\vec{n}}{V} = \frac{d^3\omega}{(2\pi)^3c^3}$$

Identifying for $\sigma(\nu)$ we get

 $\sigma(\nu) \propto \nu^{-3} g(\nu),$

where $g(\nu)$ is a gaunt factor, $g(\nu) \propto \nu^{-1/2}$, in the Born approximation, which is valid far from the ionization edge ν_{\circ} . $g_{\nu} \approx 1$ in the vicinity of ν_{\circ} , where the free-particle approximation breaks down.

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2.2 Radiative recombination

Photoionization and its inverse process, radiative recombination, are related by the Einstein - Milne relations (e.g. Osterbrock, A1; Shu I,75; Spitzer p104)). The

detailed balance between photon absorptions with frequency ν and electron-ion recombinations with relative velocity v is

$$n_{\mathcal{X}} a_{\nu} 4\pi \frac{B_{\nu}}{h\nu} d\nu = n_{\mathcal{X}^+} n_e v \sigma(v) f(v) dv + n_{\mathcal{X}^+} n_e \sigma_2(v) B_{\nu} v f(v) dv,$$

where $\frac{1}{2}mv^2 + h\nu_T = h\nu$, and where f(v) is the Maxwellian integrated over angles. We get (tarea) that $\sigma_2 = \sigma/(2h\nu^3/c^2)$, and

$$\sigma(v) = \frac{g}{g_+} \frac{h^2 \nu^2}{m^2 c^2 v^2} a_\nu,$$

where g and g_+ are the degeneracies of X and X^+ in their fundamental levels.