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Part V

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 $H_{\text{int}} = H_{\text{d}} + H_{\text{M}} + H_{\text{Q}}$ (see Shu I,24), for which

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

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

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

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

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

In general $H_{\text{M}} > H_{\text{Q}}$. .3

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[1] when substituting $\vec{p} \to \vec{p} - \frac{q}{c}\vec{A}$, 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 $i \to f$ is (Fermi's golden rule):

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

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

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

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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 oscillator strength f_{if},

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

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. .5

1.4 Relationship with Einstein coeficients

The equation of detailed balance,

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

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

and the LTE relationships,

$$\frac{n_f}{n_i} = \frac{g_f}{g_i}\exp(-\frac{h\nu_{if}}{kT}), \quad \text{and} \quad J_\nu = B_\nu(T), \quad \text{lead to}$$

$$A_{fi} = \frac{g_i}{g_f}(2h\nu^3/c^2)B_{if}, \qquad B_{fi} = \frac{c^2}{2h\nu^3}A_{fi} = (g_i/g_f)B_{if}.$$

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- The rate of stimulated excitations is related to the oscillator 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,

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

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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

$$|\phi\rangle = \sum_j c_j |\phi_j\rangle. \tag{3}$$

- Denoting $\Gamma = A_{ji}$, 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:

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

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

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

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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): $\Delta J = 0, \pm 1$, $\Delta m = 0, \pm 1$ and $\Delta J \neq 0$ if $\Lambda = \Delta\Lambda = 0$ 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: $\Delta l = 0, \pm 2$, $\Delta m = 0, \pm 1, \pm 2$, rotational transitions in molecules $\Delta J = 0, \pm 1, \pm 2$.

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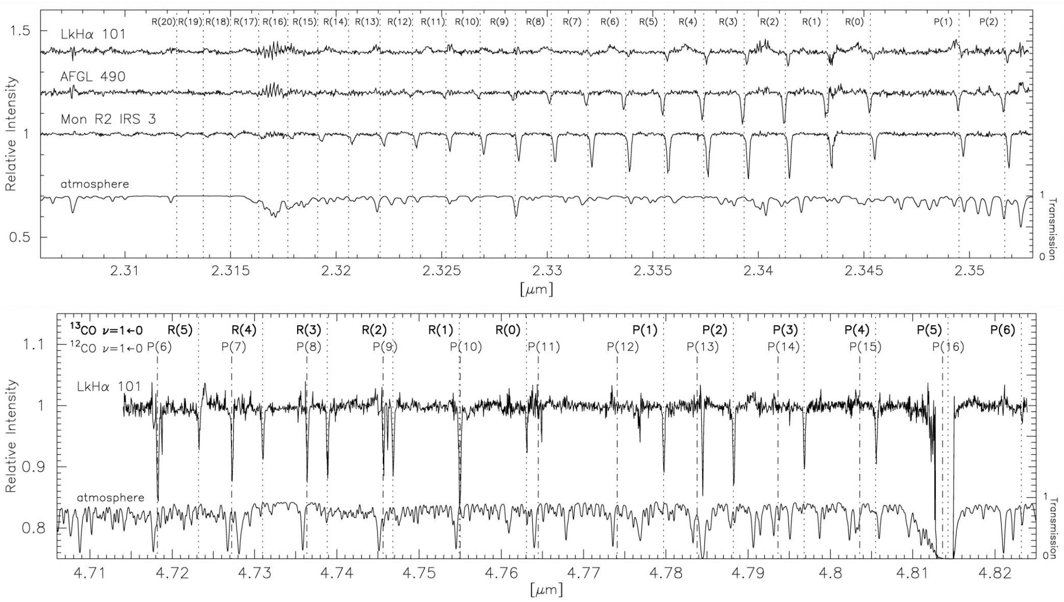
Subaru - IRCS + echelle & X-disperser (Goto et al. 2003, ApJ, 598, 1038)



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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 – H_2

- 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** H_2, $I = S_{\mathrm{nuclear}} = 1$), while $J = 0$ (J even) is singlet (**Para** H_2, $I = 0$).
- In H_2 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.

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- 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 $J_2 - J_1 = +2$.

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2 Photoionization and radiative recombination

2.1 Photoionization

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

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

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 $L \rightarrow \infty$. With i corresponding to the fundamental state of the hydrogen atom, direct integration yields (Shu I, 23):

$$\frac{dP_{if}}{dt} = \frac{8\pi e^2 a_Z^3}{3V\hbar m_e^2 c^3} \mathcal{N}(\omega)(\hbar k_e)^2 \left(\frac{\hbar}{m_e a_Z^2}\right)^4, . \qquad (7)$$

where$\mathcal{N}(\omega) = \int d\Omega \mathcal{N}(\vec{\omega})$. .14

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[4] the 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. Conservation of energy, $E_f = \hbar\omega - E_i$, and $\hbar k_e = \sqrt{2M_eE_f}$, yield $k_e dk_e = \frac{m_e}{\hbar}d\omega$.

The cross-section of ionization is defined through

$$P_{if}dN_f = t\, \sigma_{if}(\omega) c\, \frac{\mathcal{N}(\vec{n})}{V}\, 4\pi n^2 dn, \text{ with } \frac{d^3\vec{n}}{V} = \frac{d^3\omega}{(2\pi)^3c^3}. \tag{8}$$

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Comparing Eq. 8 and Eq. 7 allows the identification of $\sigma(\nu)$:

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

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 $\nu_\circ$. $g_\nu \approx 1$ in the vicinity of $\nu_\circ$, where the free-particle approximation breaks down.

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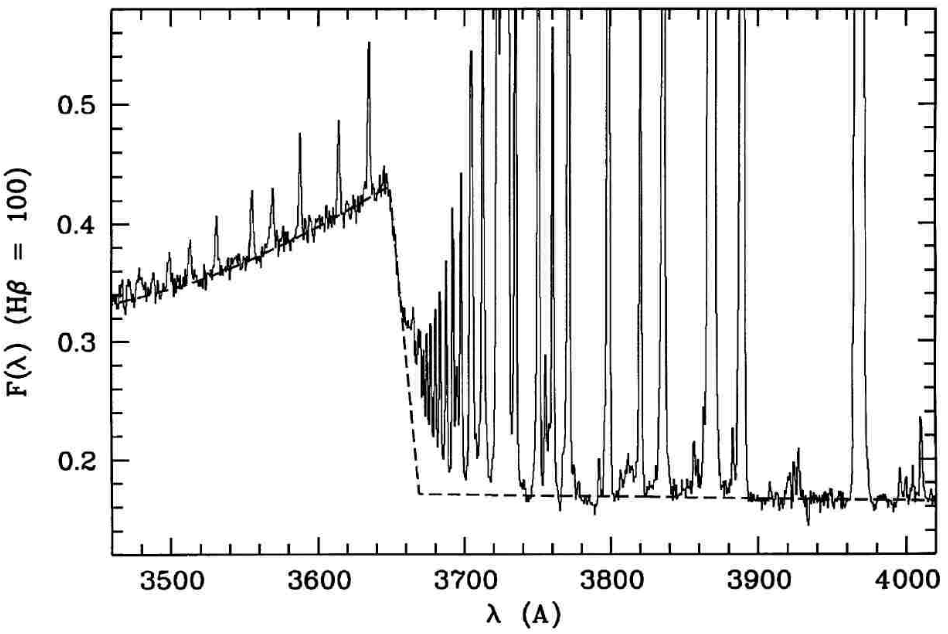

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2.2 Radiative recombination

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

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

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

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

where g and g_+ are the degeneracies of X and X^+ in their fundamental levels. .18