

Astrophysics

Lecture 14

December 04 (Mon.), 2023

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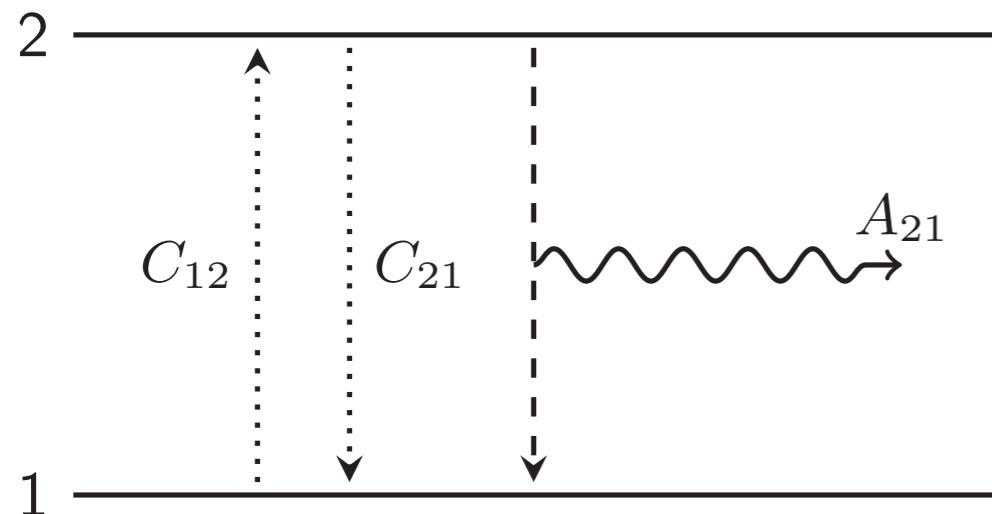
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[Atomic Emission Line Mechanisms in ISM]

- **Collisional Line**

(collisional excitation + spontaneous emission)

Collisions with electrons can excite ions (or atoms), moving it from level 1 to 2, or de-excite it, moving it from level 2 to 1, with rate C_{21} and C_{12} , respectively.



Note that collisional de-excitation yields no photons

An excited ion can also spontaneously emit radiation at the Einstein A_{21} .

In low density ISM, collisions are rare, so when the occasional collisional excitation happens, the ion(atom) is much more likely to return to level 1 through the emission of a photon than through collisional de-excitation.

- **Recombination Line (photoionization + recombination)**

Hot stars produce ultraviolet radiation that can ionize hydrogen and other atoms. Once ionized, recombination back to the neutral state produces recombination continuum and lines. Of course, the recombination requires that the ion encounter an electron, which is a slow process in diffuse gas.

The recombination of a free electron with a proton can occur to any of the energy levels n . For instant, if $n > 1$, the excited hydrogen atom will then decay to lower levels until it reaches the ground state, $n = 1$. This cascade produces a set of photons, the first with an energy corresponding to the potential of the previously unbound electron-proton pair and then the others at fixed values corresponding to the discrete energy jumps between different n .

In most cases, the Lyman alpha and Balmer lines are recombination lines.

[Collisional Excitation]

- Under the conditions of very low density and weak radiation fields,
 - **The vast majority of the atoms reside in the ground state.**
collisional excitation timescale \gg radiative decay time scale
This condition will remain true even if the excited state has a radiative lifetime of several second, which is frequently the case for the forbidden transitions observed in ionized astrophysical plasmas.
 - ***Flux of an emission line \propto number of collisions \propto product of the number densities of the two colliding species by the probability that a collision will produce a collisional excitation.***
 - If the energy gap between the ground state and the excited state E_{12} is much larger than the mean energy of the colliding species ($\sim T$), then, because there are few very energetic collisions, relatively few collisional excitations can occur. Therefore, the resulting emission line will be very much weaker than when $E_{12} < kT$.
This gives us the possibility of measuring temperature from the relative strengths of lines coming from excited levels at different energies above the ground state.

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- At high enough densities,
 - The collisional timescales are short.
 - The population in any upper level is set by the balance between collisional excitation, and the collisional de-excitation out of these levels, and are governed by the Boltzmann equilibrium.

Boltzmann equilibrium:
$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left(-\frac{E_{12}}{k_B T}\right)$$

- At intermediate densities,
 - The collisional rates and the radiative decay rates are compatible.
 - The intensity of an emission line is determined by both the temperature and the density.
 - If the temperature is known, the density can be determined from the intensity ratio of two such lines.

[Collisional Excitation & De-excitation]

- **Collisional Rate (Two Level Atom)**

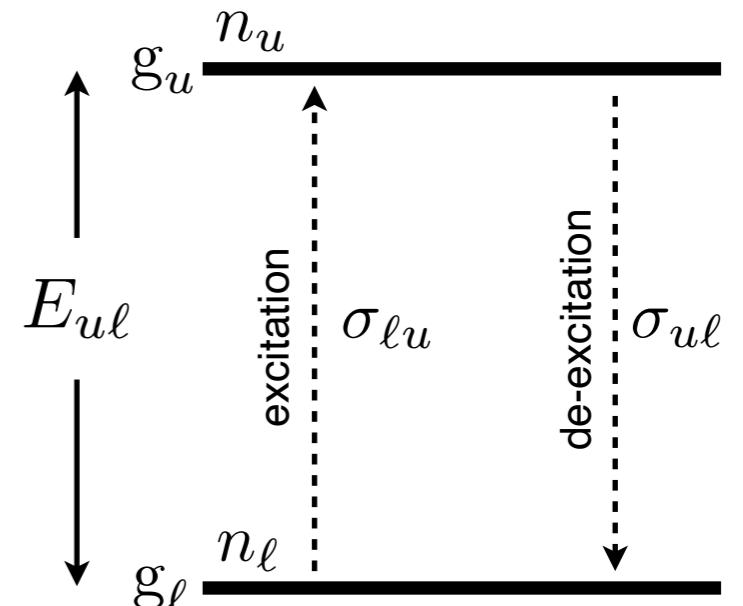
- The cross section $\sigma_{\ell u}$ for collisional excitation from a lower level ℓ to an upper level u is, in general, inversely proportional to the impact energy (or v^2) above the energy threshold $E_{u\ell}$ and is zero below.
- The collisional cross section can be expressed in the following form using a dimensionless quantity called the ***collision strength*** $\Omega_{\ell u}$:

$$\begin{aligned}\sigma_{\ell u}(v) &= (\pi a_0^2) \left(\frac{hR_H}{\frac{1}{2}m_e v^2} \right) \frac{\Omega_{\ell u}}{g_\ell} \text{ cm}^2 \quad \text{for } \frac{1}{2}m_e v^2 > E_{u\ell} \\ &= \frac{h^2}{4\pi m_e^2 v^2} \frac{\Omega_{\ell u}}{g_\ell}\end{aligned}$$

or $\sigma_{\ell u}(E) = \frac{h^2}{8\pi m_e E} \frac{\Omega_{\ell u}}{g_\ell} \quad \left(E = \frac{1}{2}m_e v^2 \right)$

where, $a_0 = \frac{\hbar^2}{m_e e^2} = 5.12 \times 10^{13}$ cm, Bohr radius

$$R_H = \frac{m_e e^4}{4\pi \hbar^3} = 109,737 \text{ cm}^{-1}, \text{ Rydberg constant} \quad \left(\hbar = \frac{h}{2\pi} \right)$$



- The collision strength $\Omega_{\ell u}$ is a function of electron velocity (or energy) but is often approximately constant near the threshold. Here, g_ℓ and g_u are the statistical weights of the lower and upper levels, respectively.

- Advantage of using the collision strength is that (1) it removes the primary energy dependence for most atomic transitions and (2) they have the symmetry between the upper and the lower states.

The principle of detailed balance states that ***in thermodynamic equilibrium each microscopic process is balanced by its inverse. Hence, The collisional excitation and de-excitation are balanced in TE.***

$$n_e n_\ell v_\ell \sigma_{\ell u}(v_\ell) f(v_\ell) dv_\ell = n_e n_u v_u \sigma_{u\ell}(v_u) f(v_u) dv_u$$

Here, v_ℓ and v_u are electron velocities before and after the collision, related by $\frac{1}{2}m_e v_\ell^2 = \frac{1}{2}m_e v_u^2 + E_{u\ell}$, and $f(v)$ is a Maxwell velocity distribution of electrons. Using the Boltzmann equation of thermodynamic equilibrium,

$$\frac{n_u}{n_\ell} = \frac{g_u}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

and the Maxwell distribution function in 3D velocity space

$$f(\mathbf{v}) d^3\mathbf{v} = \left(\frac{m_e}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_e v^2}{2kT}\right) d^3\mathbf{v}$$

or the distribution function of speed

$$f(v) dv = \left(\frac{m_e}{2\pi kT}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{m_e v^2}{2kT}\right) dv$$

we can derive the relation between the cross-sections for excitation and de-excitation

$$\frac{1}{2}m_e v_\ell^2 = \frac{1}{2}m_e v_u^2 + E_{u\ell} \quad \rightarrow \quad v_\ell dv_\ell = v_u dv_u$$

(energy conservation)

$$n_e n_\ell v_\ell \sigma_{\ell u}(v_\ell) f(v_\ell) dv_\ell = n_e n_u v_u \sigma_{u\ell}(v_u) f(v_u) dv_u$$

$$\rightarrow \sigma_{\ell u}(v_\ell) v_\ell^2 \exp\left(-\frac{m_e v_\ell^2/2}{kT}\right) = \sigma_{u\ell}(v_u) v_u^2 \exp\left(-\frac{m_e v_u^2/2}{kT}\right) \frac{g_u}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

Relation between the cross-section for excitation and de-excitation

$$g_\ell v_\ell^2 \sigma_{\ell u}(v_\ell) = g_u v_u^2 \sigma_{u\ell}(v_u) \quad \rightarrow \quad g_\ell \cdot (E + E_{u\ell}) \cdot \sigma_{\ell u}(E + E_{u\ell}) = g_u \cdot E \cdot \sigma_{u\ell}(E)$$

where $E = \frac{1}{2}m_e v_u^2$

We also obtain the symmetry of the collision strength between levels are

$$\sigma_{\ell u}(v_\ell) = \frac{h^2}{4\pi m_e^2 v_\ell^2} \frac{\Omega_{\ell u}}{g_\ell}$$

$$\sigma_{u\ell}(v_u) = \frac{h^2}{4\pi m_e^2 v_u^2} \frac{\Omega_{u\ell}}{g_u} \quad \rightarrow \quad \Omega_{\ell u} = \Omega_{u\ell} \quad \text{more precisely } \Omega_{\ell u}(E + E_{u\ell}) = \Omega_{u\ell}(E)$$

These two relations were derived in the TE condition. However, ***the cross-sections are independent on the assumptions, and thus the above relations should be always satisfied.***

- Collisional excitation and de-excitation rates

The ***collisional de-excitation rate per unit volume per unit time, which is thermally averaged,*** is given by

$$\left(\frac{dn_\ell}{dt} \right)_{u \rightarrow \ell} = n_e n_u \int_0^\infty v \sigma_{u\ell}(v) f(v) dv \rightarrow k_{u\ell} \equiv \langle \sigma v \rangle_{u \rightarrow \ell}$$

$[cm^{-3} s^{-1}]$

The collisional de-excitation rate coefficient can be written as follows:

$$\begin{aligned} k_{u\ell} &= \int_0^\infty v \sigma_{u\ell}(v) f(v) dv \\ &= \left(\frac{2\pi\hbar^4}{k_B m_e^3} \right)^{1/2} T^{-1/2} \frac{\langle \Omega_{u\ell} \rangle}{g_u} \\ &= \frac{\beta}{T^{1/2}} \frac{\langle \Omega_{u\ell} \rangle}{g_u} [cm^3 s^{-1}], \end{aligned}$$

$$\beta \equiv \left(\frac{2\pi\hbar^4}{k m_e^2} \right)^{1/2} = 8.62942 \times 10^{-6}$$

Here, the effective collision strength, averaged over the energy, is given by

effective collision strength: $\langle \Omega_{u\ell} \rangle \equiv \int_0^\infty \Omega_{u\ell}(E) e^{-E/k_B T} d(E/k_B T)$

From $\Omega_{\ell u}(E + E_{u\ell}) = \Omega_{u\ell}(E) \rightarrow \langle \Omega_{\ell u} \rangle = \langle \Omega_{u\ell} \rangle$

Here, $k_{u\ell}$ is the **collisional rate coefficient for de-excitation** in units of $cm^3 s^{-1}$.

Its typical values are
 $10^{-2} < \langle \Omega_{u\ell} \rangle < 10$

The T dependence of the effective collision strength is very weak.

Similarly, the ***collisional excitation rate per unit volume per unit time, which is thermally averaged,*** is

$$\begin{aligned} \left(\frac{dn_u}{dt} \right)_{\ell \rightarrow u} &= n_e n_\ell \int_{v_{\min}}^{\infty} v \sigma_{\ell u}(v) f(v) dv \\ &= n_e n_\ell k_{\ell u} \quad [\text{cm}^{-3} \text{ s}^{-1}] \end{aligned}$$

Here, $\frac{1}{2} m_e v_{\min}^2 = E_{u\ell}$

$$k_{\ell u} \equiv \langle \sigma v \rangle_{\ell \rightarrow u}$$

Here, $k_{\ell u}$ is the **collisional rate coefficient for excitation** in units of $\text{cm}^3 \text{ s}^{-1}$.

$$\begin{aligned} k_{\ell u} &= \int_{v_{\min}}^{\infty} v \sigma_{\ell u}(v) f(v) dv \\ &= \left(\frac{2\pi\hbar^4}{k_B m_e^3} \right)^{1/2} T^{-1/2} \frac{\langle \Omega_{u\ell} \rangle}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right) \\ &= \frac{\beta}{T^{1/2}} \frac{\langle \Omega_{u\ell} \rangle}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right) \quad [\text{cm}^3 \text{ s}^{-1}], \end{aligned}$$

$$\beta \equiv \left(\frac{2\pi\hbar^4}{km_e^2} \right)^{1/2} = 8.62942 \times 10^{-6}$$

We note that ***the rate coefficients for collisional excitation and de-excitation are related by***

$$k_{\ell u} = \frac{g_u}{g_\ell} k_{u\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

$$\langle \sigma v \rangle_{\ell \rightarrow u} = \frac{g_u}{g_\ell} \langle \sigma v \rangle_{u \rightarrow \ell} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

Collisionally-Excited Emission Line

- Emission line flux
 - In the low density limit, the collisional rate between atoms and electrons is much slower than the (spontaneous) radiative de-excitation rate of the excited level. Thus, we can balance the collisional feeding into level u by the rate of radiative transition back down to level ℓ . The level population is determined by

$$n_e n_\ell k_{\ell u} = A_{u\ell} n_u$$

$$\frac{n_u}{n_\ell} = \frac{n_e k_{\ell u}}{A_{u\ell}}$$

$$= \frac{n_e}{A_{u\ell}} \beta \frac{\langle \Omega_{u\ell} \rangle}{g_\ell} T^{-1/2} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

where $A_{u\ell}$ is the Einstein coefficient for spontaneous emission. Then, the line emissivity is given by

$$4\pi j_{u\ell} = E_{u\ell} A_{u\ell} n_u = E_{u\ell} n_e n_\ell k_{\ell u}$$

$$= n_e n_\ell E_{u\ell} \frac{8.62942 \times 10^{-6}}{T^{1/2}} \frac{\langle \Omega_{u\ell} \rangle}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right) \text{ [erg cm}^{-3} \text{ s}^{-1}\text{]}$$

$$4\pi j_{u\ell} \simeq \beta \chi n_e^2 E_{u\ell} T^{-1/2} \frac{\langle \Omega_{u\ell} \rangle}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

proportional to density-square

Here, $\beta = \left(\frac{2\pi\hbar^4}{km_e^2}\right)^{1/2} = 8.62942 \times 10^{-6}$

$$\chi = n_\ell / n_e$$

For low temperature, the exponential term dominates because few electrons have energy above the threshold for collisional excitation, so that the line rapidly fades with decreasing temperature.

At high temperature, the $T^{-1/2}$ term controls the cooling rate, so the line fades slowly with increasing temperature.

- In the high-density limit, the level population are set by the Boltzmann equilibrium, and the line emissivity is

$$\frac{n_u}{n_\ell} = \frac{g_u}{g_\ell} \exp\left(-\frac{E_{u\ell}}{kT}\right)$$

$$4\pi j_{u\ell} = E_{\ell u} A_{u\ell} n_u$$

$$= n_\ell E_{\ell u} A_{u\ell} \frac{g_u}{g_\ell} \exp\left(-\frac{E_{\ell u}}{kT}\right)$$

$$4\pi j_{u\ell} \simeq \chi n_e E_{\ell u} A_{u\ell} \frac{g_u}{g_\ell} \exp\left(-\frac{E_{\ell u}}{kT}\right)$$

proportional to density

Here, the line flux scales as n_e rather than n_e^2 , but the line flux tends to a constant value at high temperature.

- Critical density is defined as the density where the radiative depopulation rate matches the collisional de-excitation for the excited state.

$$A_{u\ell} n_u = n_e n_u k_{u\ell}$$

$$n_{\text{crit}} = \frac{A_{u\ell}}{k_{u\ell}}$$

$$\rightarrow n_{\text{crit}} = A_{u\ell} \frac{g_u}{\beta \langle \Omega_{u\ell} \rangle} T^{1/2}$$

$$= 1.2 \times 10^3 \frac{A_{u\ell}}{10^{-4} \text{ s}^{-1}} \frac{g_u}{\langle \Omega_{u\ell} \rangle} \left(\frac{T}{10^4 \text{ K}} \right)^{1/2} [\text{cm}^{-3}]$$

- At densities higher than the critical density, collisional de-excitation becomes significant, and the forbidden lines will be weaker as the density increases.
- At around the critical density, the “line emissivity vs density” plotted in log-log scale changes slope from +2 to +1.

- As can be seen in Tables and the formula, **collisional de-excitation is negligible for resonance and most forbidden lines in the ISM.**

| Ion | ℓ | u | | | $n_{\text{H,crit}}(u)$ | |
|-------|----------------------|----------------------|-------------------|----------------|--|---|
| | | | E_ℓ/k (K) | E_u/k (K) | $\lambda_{u\ell}$ (μm) | $T = 100 \text{ K}$ (cm^{-3}) |
| C II | $^2\text{P}_{1/2}^o$ | $^2\text{P}_{3/2}^o$ | 0 | 91.21 | 157.74 | 2.0×10^3 |
| CI | $^3\text{P}_0$ | $^3\text{P}_1$ | 0 | 23.60 | 609.7 | 620 |
| | $^3\text{P}_1$ | $^3\text{P}_2$ | 23.60 | 62.44 | 370.37 | 720 |
| O I | $^3\text{P}_2$ | $^3\text{P}_1$ | 0 | 227.71 | 63.185 | 2.5×10^5 |
| | $^3\text{P}_1$ | $^3\text{P}_0$ | 227.71 | 326.57 | 145.53 | 2.3×10^4 |
| Si II | $^2\text{P}_{1/2}^o$ | $^2\text{P}_{3/2}^o$ | 0 | 413.28 | 34.814 | 1.0×10^5 |
| Si I | $^3\text{P}_0$ | $^3\text{P}_1$ | 0 | 110.95 | 129.68 | 4.8×10^4 |
| | $^3\text{P}_1$ | $^3\text{P}_2$ | 110.95 | 321.07 | 68.473 | 9.9×10^4 |
| | | | | | | 1.5×10^3 |

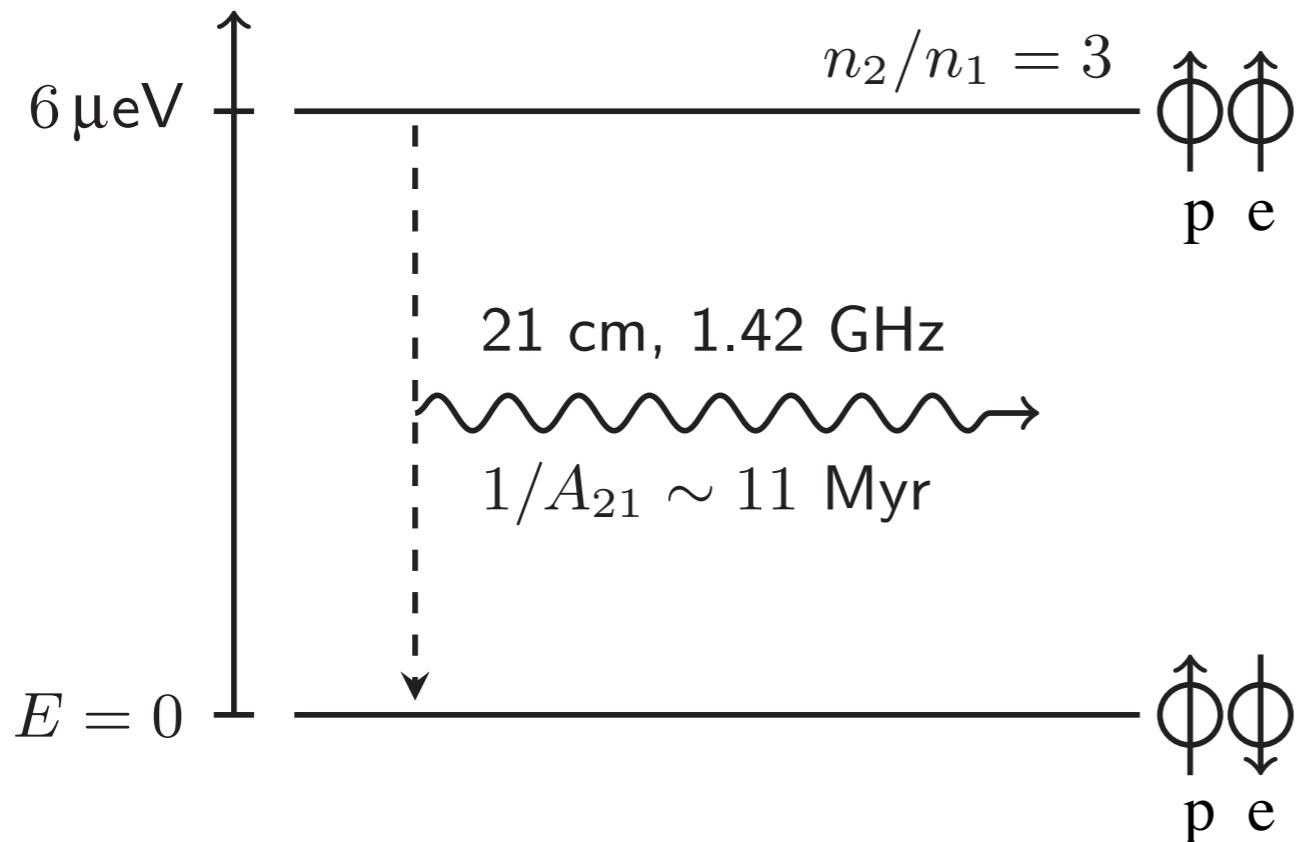
Table 17.1 in [Draine]

- However, it is not true for the 21 cm hyperfine structure line of hydrogen.
 - The critical density for 21cm line is

$$n_{\text{crit}} \sim 10^{-3} (T/100 \text{ K})^{-1/2} [\text{cm}^{-3}]$$
 - $A_{u\ell} = 2.88 \times 10^{-15} [\text{s}^{-1}]$
 - The levels are thus essentially in collisional equilibrium in the cold neutral medium.

| Ion | Transition l-u | λ μm | A_{ul} s^{-1} | Ω_{ul} | n_{crit} cm^{-3} |
|--------|---------------------------------------|----------------------------|-----------------------------|---------------|---------------------------------------|
| C I | $^3\text{P}_0 - ^3\text{P}_1$ | 609.1354 | 7.93×10^{-8} | – | (500) |
| | $^3\text{P}_1 - ^3\text{P}_2$ | 370.4151 | 2.65×10^{-7} | – | (3000) |
| C II | $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ | 157.741 | 2.4×10^{-6} | 1.80 | 47 (3000) |
| N II | $^3\text{P}_0 - ^3\text{P}_1$ | 205.3 | 2.07×10^{-6} | 0.41 | 41 |
| | $^3\text{P}_1 - ^3\text{P}_2$ | 121.889 | 7.46×10^{-6} | 1.38 | 256 |
| | $^3\text{P}_2 - ^1\text{D}_2$ | 0.65834 | 2.73×10^{-3} | 2.99 | 7700 |
| | $^3\text{P}_1 - ^1\text{D}_2$ | 0.65481 | 9.20×10^{-4} | 2.99 | 7700 |
| N III | $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ | 57.317 | 4.8×10^{-5} | 1.2 | 1880 |
| O I | $^3\text{P}_2 - ^3\text{P}_1$ | 63.184 | 8.95×10^{-5} | – | $2.3 \times 10^4 (5 \times 10^5)$ |
| | $^3\text{P}_1 - ^3\text{P}_0$ | 145.525 | 1.7×10^{-5} | – | $3400 (1 \times 10^5)$ |
| | $^3\text{P}_2 - ^1\text{D}_2$ | 0.63003 | 6.3×10^{-3} | – | 1.8×10^6 |
| O II | $^4\text{S}_{3/2} - ^2\text{D}_{5/2}$ | 0.37288 | 3.6×10^{-5} | 0.88 | 1160 |
| | $^4\text{S}_{3/2} - ^2\text{D}_{3/2}$ | 0.37260 | 1.8×10^{-4} | 0.59 | 3890 |
| O III | $^3\text{P}_0 - ^3\text{P}_1$ | 88.356 | 2.62×10^{-5} | 0.39 | 461 |
| | $^3\text{P}_1 - ^3\text{P}_2$ | 51.815 | 9.76×10^{-5} | 0.95 | 3250 |
| | $^3\text{P}_2 - ^1\text{D}_2$ | 0.50069 | 1.81×10^{-2} | 2.50 | 6.4×10^5 |
| | $^3\text{P}_1 - ^1\text{D}_2$ | 0.49589 | 6.21×10^{-3} | 2.50 | 6.4×10^5 |
| | $^1\text{D}_2 - ^1\text{S}_0$ | 0.43632 | 1.70 | 0.40 | 2.4×10^7 |
| Ne II | $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ | 12.8136 | 8.6×10^{-3} | 0.37 | 5.9×10^5 |
| Ne III | $^3\text{P}_2 - ^3\text{P}_1$ | 15.5551 | 3.1×10^{-2} | 0.60 | 1.27×10^5 |
| | $^3\text{P}_1 - ^3\text{P}_0$ | 36.0135 | 5.2×10^{-3} | 0.21 | 1.82×10^4 |
| Si II | $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ | 34.8152 | 2.17×10^{-4} | 7.7 | (3.4×10^5) |
| S II | $^4\text{S}_{3/2} - ^2\text{D}_{5/2}$ | 0.67164 | 2.60×10^{-4} | 4.7 | 1240 |
| | $^4\text{S}_{3/2} - ^2\text{D}_{3/2}$ | 0.67308 | 8.82×10^{-4} | 3.1 | 3270 |
| S III | $^3\text{P}_0 - ^3\text{P}_1$ | 33.4810 | 4.72×10^{-4} | 4.0 | 1780 |
| | $^3\text{P}_1 - ^3\text{P}_2$ | 18.7130 | 2.07×10^{-3} | 7.9 | 1.4×10^4 |
| S IV | $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ | 10.5105 | 7.1×10^{-3} | 8.5 | 5.0×10^4 |
| Ar II | $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ | 6.9853 | 5.3×10^{-2} | 2.9 | 1.72×10^6 |
| Ar III | $^3\text{P}_2 - ^3\text{P}_1$ | 8.9914 | 3.08×10^{-2} | 3.1 | 2.75×10^5 |
| | $^3\text{P}_1 - ^3\text{P}_0$ | 21.8293 | 5.17×10^{-3} | 1.3 | 3.0×10^4 |
| Fe II | $^6\text{D}_{7/2} - ^6\text{D}_{5/2}$ | 35.3491 | 1.57×10^{-3} | – | (3.3×10^6) |
| | $^6\text{D}_{9/2} - ^6\text{D}_{7/2}$ | 25.9882 | 2.13×10^{-3} | – | (2.2×10^6) |

H I 21 cm



Schematic of the hyperfine transition of the ground electronic state of hydrogen, due to the spin flip from parallel to anti-parallel alignment of the proton-electron pair.

An atom will typically remain in the excited state for about 11 Myr before decaying. This is much greater than the collisional time between atoms in an H I gas. Thus **the two hyperfine states are in collisional equilibrium** and the level populations are in a Boltzmann distribution with excitation temperature equal to the kinetic temperature of the gas, $T_{\text{ex}} = T_{\text{gas}}$

$$\frac{n_2}{n_1} - \frac{g_2}{g_1} e^{-E_{21}/kT} \simeq 3$$

Here, $g_1 = 1$ and $g_2 = 3$.

$E_{21}/k = 0.07 \text{ K}$ is much smaller than ISM temperatures (and the temperature of the cosmic background radiation ($T_{\text{CMB}} \simeq 3 \text{ K}$)).

Therefore, the exponential term is near unity.

[Line diagnostics]

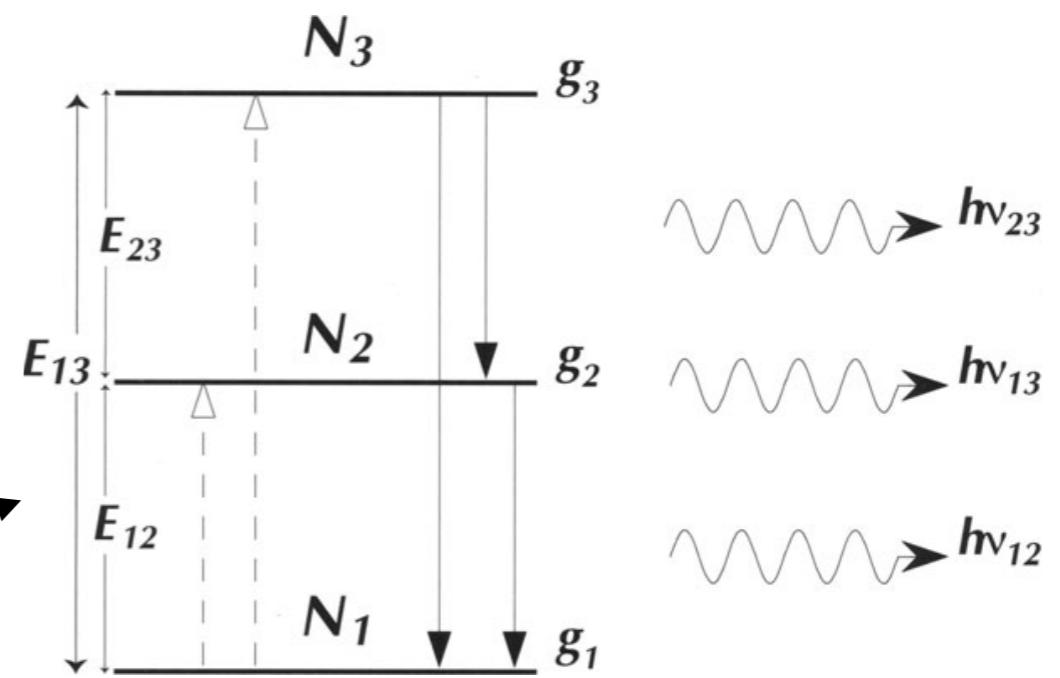
- **The Three-Level Atom (Line diagnostics)**

- Let C_{ij} be the collision rate ($C_{ij} = n_e k_{ij} \text{ s}^{-1}$) between any two levels. The equations of statistical equilibrium for a three level atom are

$$N_1 C_{13} + N_2 C_{23} = N_3 (C_{31} + C_{32} + A_{32} + A_{31})$$

$$N_1 C_{12} + N_3 (C_{32} + A_{32}) = N_2 (C_{23} + C_{21} + A_{21})$$

$$N_1 + N_2 + N_3 = 1$$



- **Electron temperature**

- ◆ Ions in which $E_{12} \sim E_{23}$
- ◆ In the low density limit, collisional de-excitation of the excited levels can be ignored. Therefore,

$$C_{31} \sim C_{32} \sim 0.$$

Also, because of the increasing threshold energies to excite each level, $N_3 \ll N_2 \ll N_1$ so that the equations are reduced to

$$N_3 = \frac{N_1 C_{13}}{(A_{32} + A_{31})}$$

$$N_2 = \frac{N_1 C_{12}}{A_{21}}$$

If we now form the line intensity ratio for the $3 \rightarrow 2$ and $2 \rightarrow 1$ transitions, we have

$$\begin{aligned}\frac{F_{32}}{F_{21}} &= \frac{E_{23}N_3A_{32}}{E_{12}N_2A_{21}} \\ &= \frac{E_{23}A_{32}C_{13}}{E_{12}(A_{32} + A_{31})C_{12}} \\ &= \frac{E_{23}A_{32}k_{13}}{E_{12}A_{31}k_{12}} \\ &= \frac{E_{23}A_{32}\Omega_{13}}{E_{12}A_{31}\Omega_{12}} \exp\left(-\frac{E_{23}}{kT}\right)\end{aligned}$$



collisional rate coefficients for excitation

$$k_{13} = \frac{\beta}{T^{1/2}} \frac{\Omega_{13}}{g_1} e^{-E_{31}/kT}$$

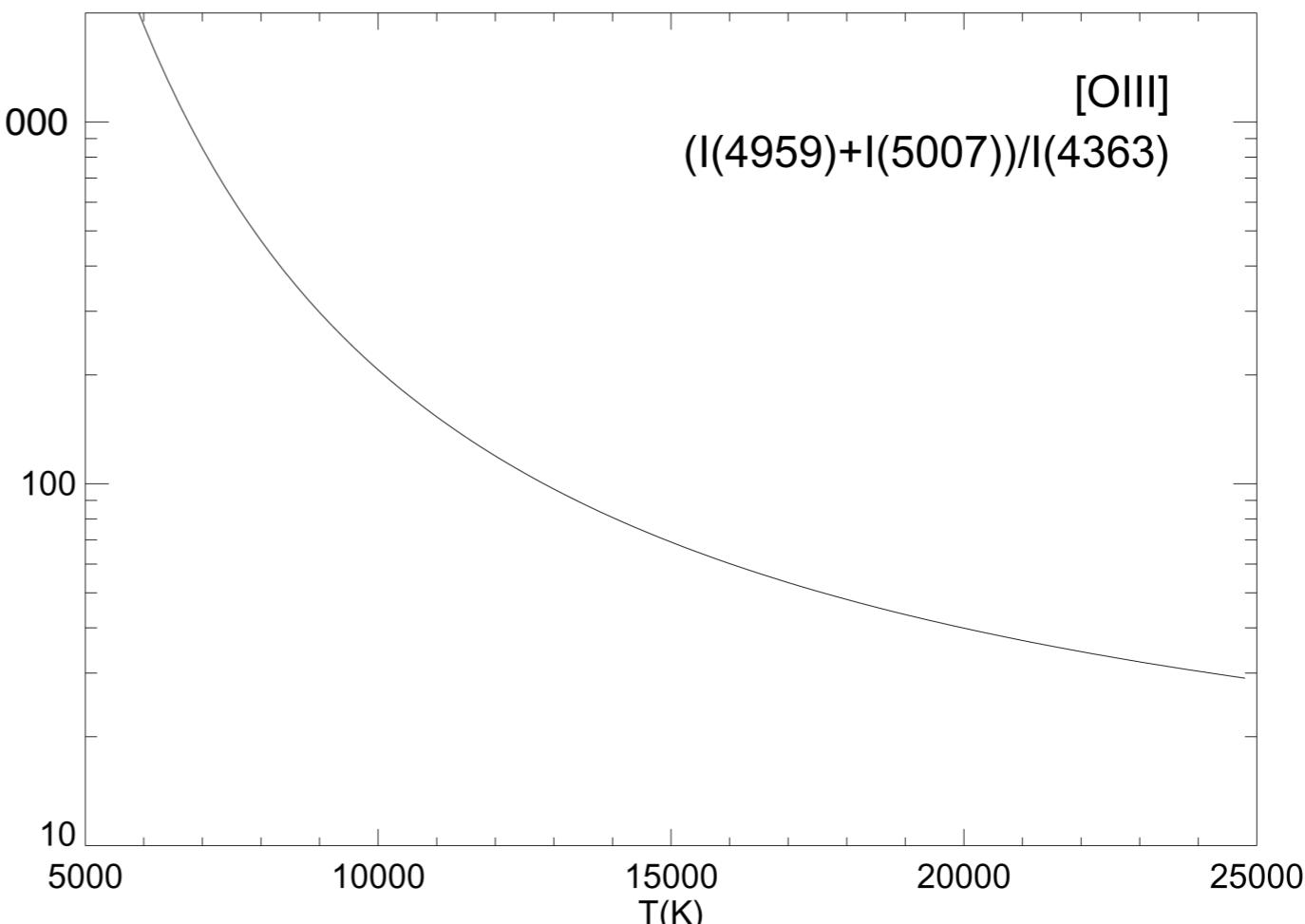
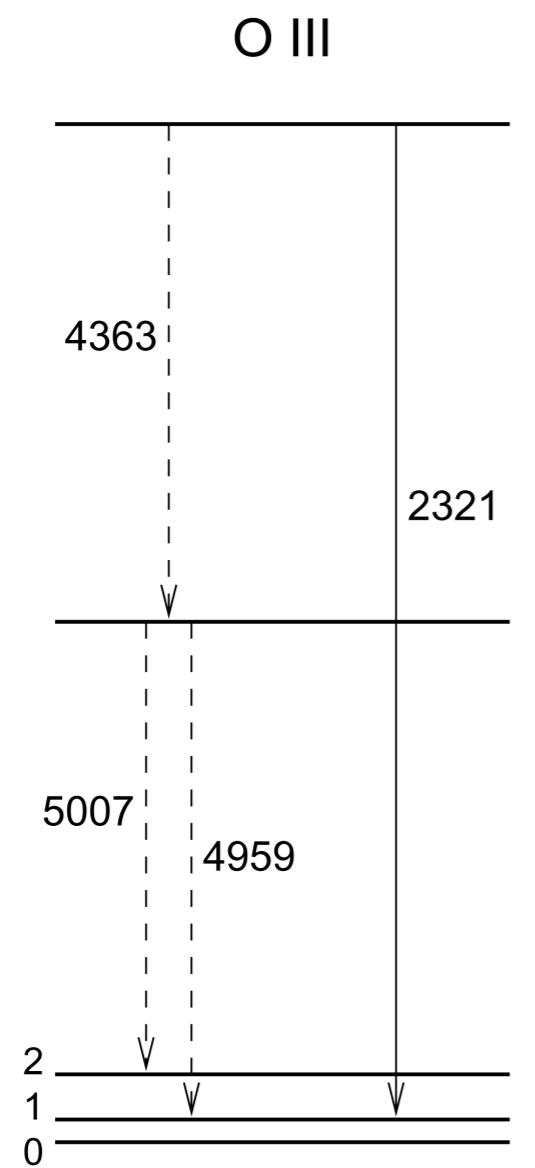
$$k_{12} = \frac{\beta}{T^{1/2}} \frac{\Omega_{12}}{g_1} e^{-E_{21}/kT}$$

provided that A_{32} is very much less than A_{31} .

Because this line ratio depends on the temperature, it can be used to measure the electron temperature in the plasma.

Temperature

Use two levels with different excitation energy.



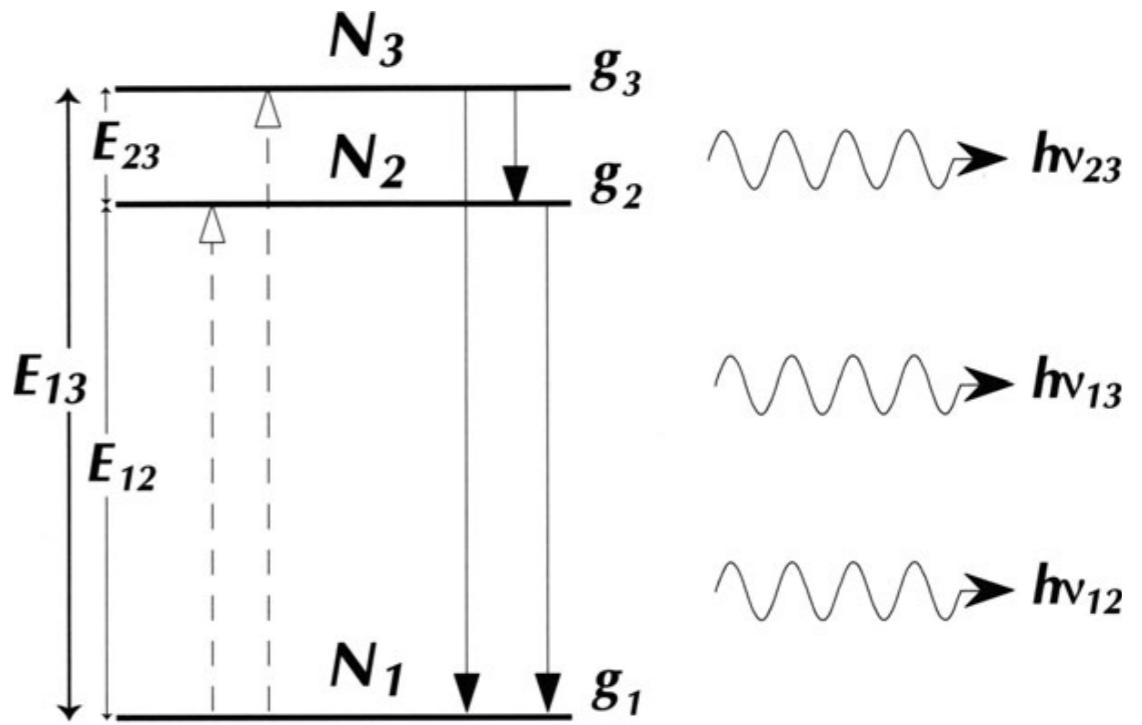
$$\frac{I(4959 + 5007)}{I(4364)} = \frac{7.7 \exp(-3.29 \times 10^4 / T)}{1 + 4.5 \times 10^{-4} n_e T^{-1/2}}$$

- **Electron density**

- ♦ Ions in which $E_{23} \ll E_{12}$
- ♦ In low density limit,
we can neglect collisional induced transitions
between the higher levels.

$$N_1 C_{13} = N_3 A_{31}$$

$$N_1 C_{12} = N_2 A_{21}$$



$$\frac{F_{31}}{F_{21}} = \frac{E_{31} A_{31} N_3}{E_{21} A_{21} N_2} = \frac{E_{31} C_{13}}{E_{21} C_{12}} \sim \frac{\Omega_{31}}{\Omega_{21}} \exp\left(-\frac{E_{21}}{kT}\right) \sim \frac{\Omega_{31}}{\Omega_{21}} = \frac{g_3}{g_2}$$

using the quantum-mechanical sum rule for collision strengths.

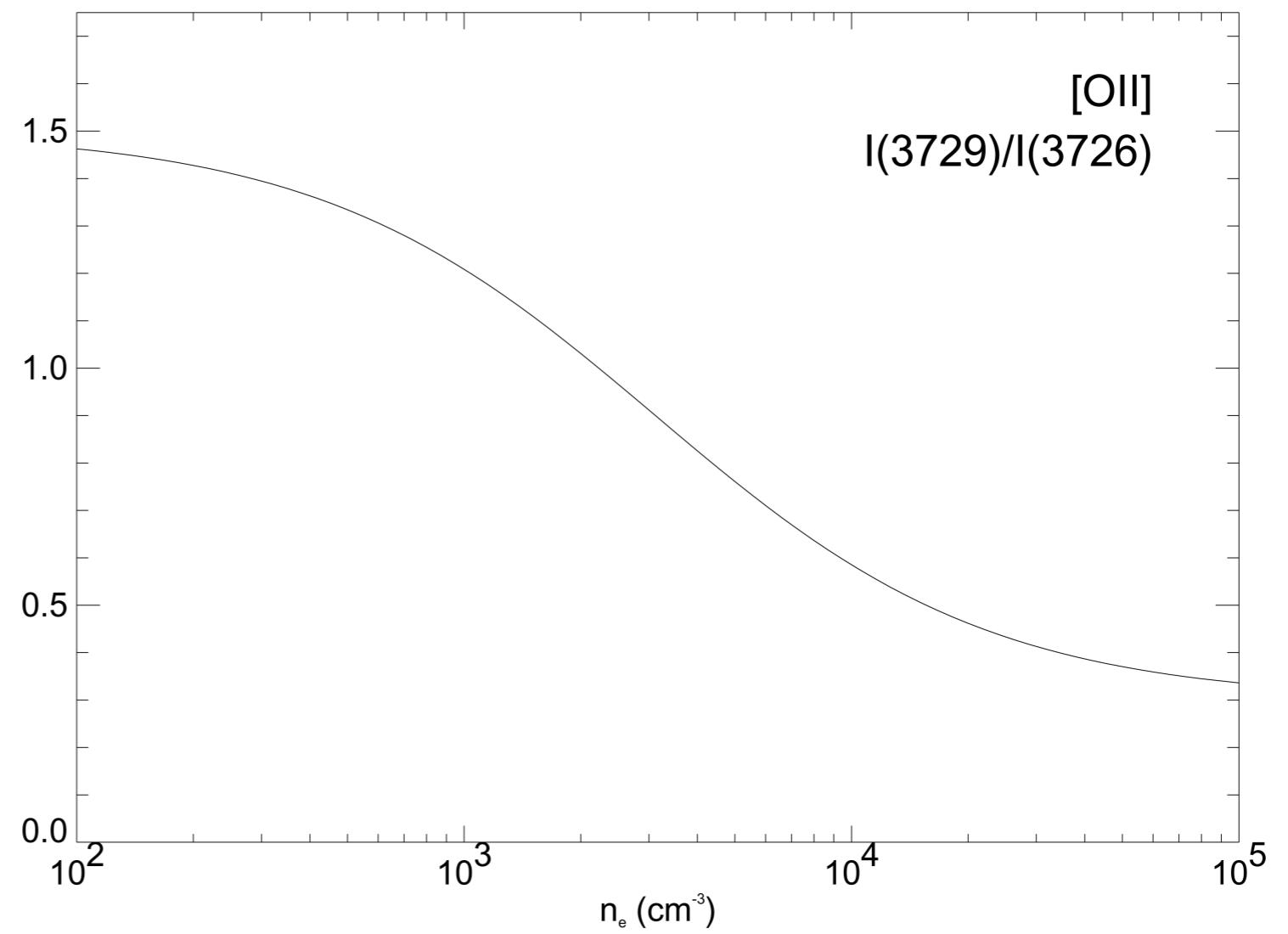
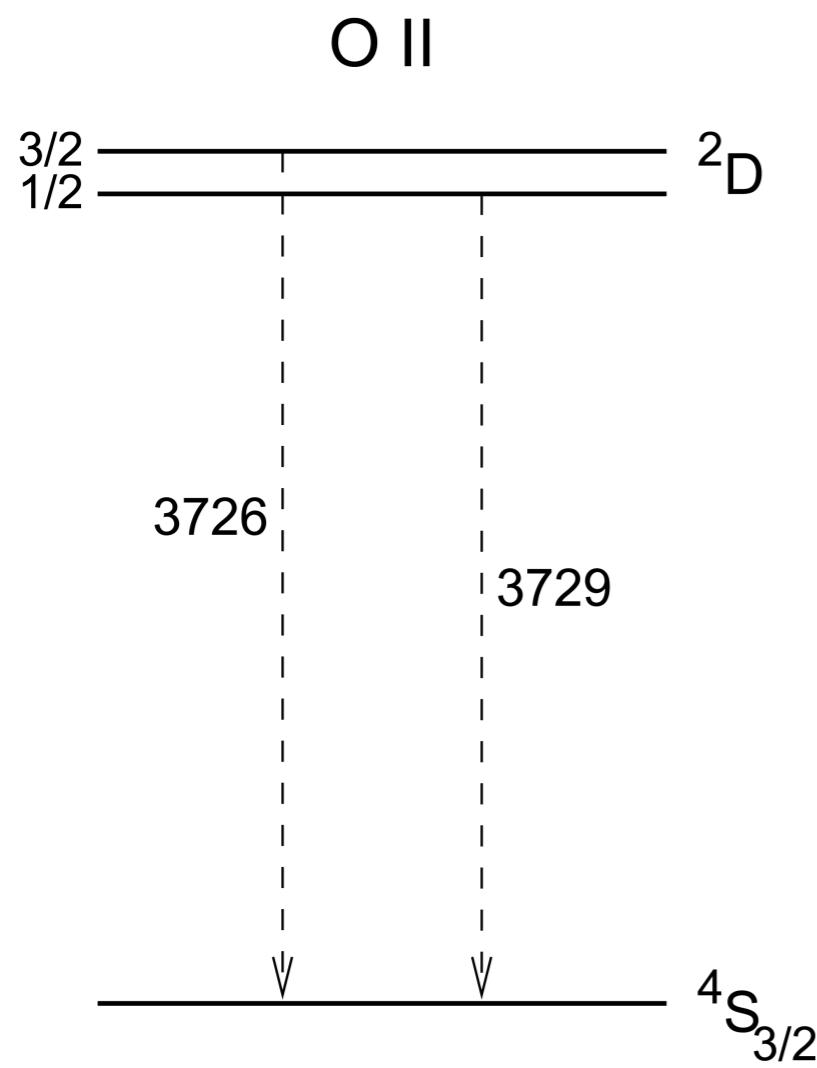
- ♦ In high density limit, the upper levels are populated according to their Boltzmann ratios,

$$\frac{F_{31}}{F_{21}} = \frac{E_{31} A_{31} N_3}{E_{21} A_{21} N_2} \sim \frac{A_{31} g_3}{A_{21} g_2} \quad \leftarrow \quad \frac{N_3}{N_2} = \frac{g_3}{g_2} e^{-\frac{E_{23}}{kT}} \approx 1$$

- ♦ Therefore, the line ratio can be used as density diagnostics in the regime between the critical densities for de-excitation of each of the transitions.

Density

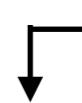
Choose atom with two levels with almost same excitation energy.



[Absorption Coefficient in terms of Einstein coefficients]

- The Einstein coefficients are useful means of analyzing absorption and emission processes. However, we often find it even more useful to use cross section because the cross section has a natural geometric meaning.
- (pure) Absorption cross section:**
 - The number density of photons per unit frequency interval is $u_\nu/h\nu = (4\pi/c)J_\nu/h\nu$. Let $\sigma_\nu = \sigma_0\phi_\nu$ be the cross section for absorption of photons for the transition $\ell \rightarrow u$. Then, the absorption rate is

$$\left(\frac{dn_u}{dt} \right)_{\ell \rightarrow u} = n_\ell \int d\nu \sigma_\nu \frac{4\pi J_\nu}{h\nu} \approx n_\ell \frac{4\pi}{h\nu_0} \sigma_0 \int d\nu J_\nu \phi_\nu = n_\ell \frac{4\pi}{h\nu_0} \sigma_0 \bar{J} \Rightarrow n_\ell B_{\ell u} J$$


 $\sigma_\nu = \sigma_0\phi_\nu$

- Here, we assumed that J_ν does not vary appreciably over the line profile of the cross section. Therefore, we derive a simple relation between the absorption cross section and the Einstein B coefficient:

$$\frac{4\pi}{h\nu_0} \sigma_0 = B_{\ell u} \rightarrow \sigma_0 = \frac{h\nu_0}{4\pi} B_{\ell u}$$

- If the cross section has a normalized profile of ϕ_ν , we can write the absorption cross section as follows:

$$\sigma_\nu = \frac{h\nu_0}{4\pi} B_{\ell u} \phi_\nu \quad \text{with} \quad \int \phi_\nu d\nu = 1$$

[Einstein Coefficients and Oscillator Strengths]

- Recall resonance scattering cross-section and the Einstein relations:

$$\sigma_{lu}(\nu) = \frac{\pi e^2}{mc} \frac{\gamma/4\pi^2}{(\nu - \nu_0)^2 + (\gamma/4\pi)^2}$$

Lorentz profile

$$g_l B_{lu} = g_u B_{ul}$$

$$A_{ul} = \frac{2h\nu_{lu}^3}{c^2} B_{ul}$$

where $\nu_{lu} \equiv \frac{E_u - E_l}{h} (\nu_0)$

- The Einstein (absorption) B coefficient associated with a classical oscillator can be defined in terms of the total energy extracted from a beam of radiation.

$$\int_0^\infty \sigma_{lu}(\nu) d\nu = \frac{\pi e^2}{mc} \equiv B_{lu}^{\text{classical}} \frac{h\nu_{lu}}{4\pi} \quad \rightarrow \quad B_{lu}^{\text{classical}} = \frac{4\pi}{h\nu_{lu}} \frac{\pi e^2}{mc}$$

It is convenient to define the **absorption and emission oscillator strengths** (f_{lu} and f_{ul}) by the formulae:

$$B_{lu} = B_{lu}^{\text{classical}} f_{lu} = \frac{4\pi^2 e^2}{h\nu_{lu} mc} f_{lu} \quad B_{ul} = \frac{4\pi^2 e^2}{h\nu_{ul}} f_{ul} \quad (\text{note that } \nu_{ul} = -\nu_{lu} < 0 \text{ and } f_{ul} < 0)$$

The oscillator strength (or f value) is the factor which corrects the classical result. The quantum mechanical process can be interpreted as being due to a (fractional) number f of equivalent classical electron oscillators of the same frequency.

-
- In quantum mechanics, the absorption oscillator strength is given by

$$f_{lu} = \frac{2m}{3\hbar^2 g_l e^2} (E_u - E_l) \sum |d_{lu}|^2 \quad d_{lu} \equiv \langle \phi_u | e\mathbf{r} | \phi_l \rangle$$

where the sum is over all substates of the upper and lower levels.

We also have the following relations.

$$\begin{aligned} g_l f_{lu} &= -g_u f_{ul} \\ g_u A_{ul} \equiv -\frac{8\pi^2 e^2 \nu_{ul}^2}{mc^3} g_u f_{ul} &= \frac{8\pi^2 e^2 \nu_{lu}^2}{mc^3} g_l f_{lu} \\ \sigma(\nu) &= \frac{\pi e^2}{mc} f_{lu} \\ &= \frac{\pi e^2}{mc} f_{lu} \phi(\nu) \end{aligned}$$

- *Thomas-Reiche-Kuhn sum rule*

$$\sum_{n'} f_{nn'} = N = \text{ total number of electrons in the atom}$$

Here, the summation is over all states of the atom. Where there is a close shell and a smaller number q of electrons outside the closed shells that are involved in a more limited set of transitions, we also have

$$\sum_{n'} f_{nn'} = q$$

where the sum is now only over those states involve transitions of these outer electrons.

We note that $f \sim 1$ for strong allowed transitions.

[Line Broadening Mechanisms]

- Atomic levels are not infinitely sharp, nor are the lines connecting them.
 - (1) Doppler Broadening
 - (2) Natural Broadening
 - (3) Collisional Broadening
- **Doppler Broadening**

The simplest mechanism for line broadening is the Doppler effect. An atom is in thermal motion, so that the frequency of emission or absorption in its own rest frame corresponds to a different frequency for an observer.

Each atom has its own Doppler shift, so that the net effect is to spread the line out, but not to change its total strength.

The change in frequency associated with an atom with velocity component v_z along the line of sight (say, z axis) is, to lowest order in v/c , given by

$$\nu - \nu_0 = \nu_0 \frac{v_z}{c}$$

Doppler shift: $\left[\frac{\nu}{\nu_0} = \frac{1}{\gamma(1 - \beta \cos \theta)} \rightarrow \nu \approx \nu_0 (1 + \beta \cos \theta) \rightarrow \nu - \nu_0 = \frac{\nu_0 v_z}{c} \right]$

Here, ν_0 is the rest-frame frequency.

The number of atoms having velocities in the range $(v_z, v_z + dv)$ is proportional to

$$f(v_z)dv_z = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z$$

From the Doppler shift formula, we have

$$v_z = \frac{c(\nu - \nu_0)}{\nu_0} \rightarrow dv_z = \frac{cd\nu}{\nu_0}$$

Therefore, the strength of the emission is proportional to

$$\exp\left(-\frac{mv_z^2}{2kT}\right) dv_z \propto \exp\left[-\frac{mc^2(\nu - \nu_0)^2}{2\nu_0^2 kT}\right] d\nu$$

Then, the normalized profile function is

$$\phi(\nu) = \frac{1}{\Delta\nu_D \sqrt{\pi}} e^{-(\nu - \nu_0)^2 / (\Delta\nu_D)^2} \quad \text{where } \Delta\nu_D = \frac{\nu_0}{c} v_{\text{th}}$$

$\Delta\nu_D$ is the Doppler width.

$$v_{\text{th}} = \sqrt{\frac{2kT}{m}}$$

v_{th} is the thermal velocity.

The line-center cross section for each atom, neglecting stimulated emission, is therefore

$$\begin{aligned}\sigma_{\nu_0} &= B_{12} \frac{h\nu}{4\pi} \phi(\nu_0) = \frac{1}{\Delta\nu_D \sqrt{\pi}} \frac{h\nu_0}{4\pi} B_{12} \quad \leftarrow \quad \phi(\nu_0) = \frac{1}{\Delta\nu_D \sqrt{\pi}} \\ &= \frac{\pi e^2}{mc} f_{12} \frac{1}{\Delta\nu_D \sqrt{\pi}}\end{aligned}$$

In addition to thermal motions, there can be turbulent velocities associated with macroscopic velocity fields. **When the scale of the turbulence is small in comparison with a mean free path (microturbulence)**, the turbulent motions are accounted for by an effective Doppler width.

$$\Delta\nu_D = \frac{\nu_0}{c} \left(\frac{2kT}{m} + v_{\text{turb}}^2 \right)^{1/2}$$

where v_{turb} is a root-mean-square measure of the turbulent velocities. This assumes that the turbulent velocities also have a Gaussian distribution.

The convolution of two Gaussian functions with the widths (standard deviations) σ_1 and σ_2 is a Gaussian function with the width of σ , given by:

$$\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}$$

- **Natural Broadening**

A certain width to the atomic level is implied by the uncertainty principle, namely, that the spread in energy ΔE and the duration Δt in the state must satisfy $\Delta E \Delta t \sim \hbar$.

The spontaneous decay of an atomic state n proceeds at a rate of the **damping parameter (Einstein A coefficient for the spontaneous emission)**, which is **the reciprocal of the mean lifetime of the upper state**,

$$\gamma = A_{u\ell}$$

where u and ℓ denote the upper and lower states, respectively.

The coefficient of the wave function of state n is of the form $e^{-\gamma t/2}$ and then the energy decays proportional to $e^{-\gamma t}$. We then have an emitted spectrum determined by the decaying sinusoid type of electric field. The spectral profile is of the form, which is called a **Lorentz (or natural, or Cauchy) profile**,

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

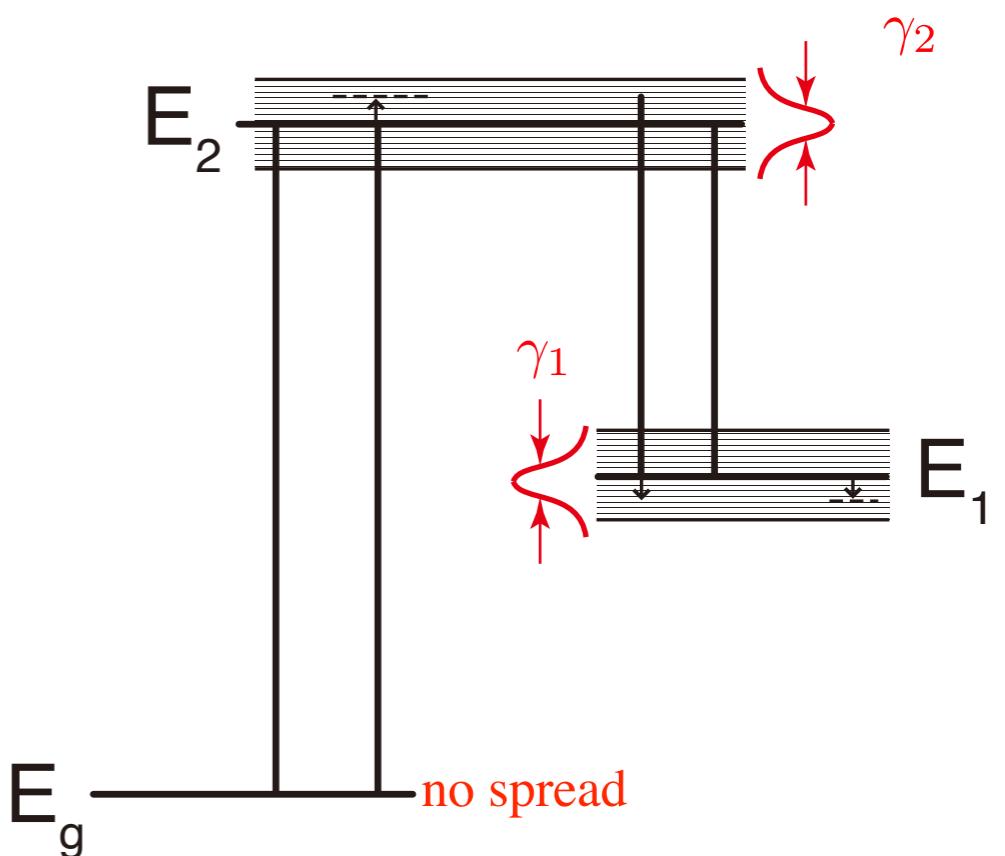
The above profile applies to cases in which only the upper state is broadened (no broadening in the lower state).

Semiclassical (Weisskopf-Woolley) Picture of Quantum Levels

- In the semiclassical picture, each level is viewed as a continuous distribution of sublevels with energies close to the energy of the level (E_n).
 - The distribution of sublevels are explained by the Heisenberg Uncertainty Principle. The level has a lifetime $\Delta t = 1/A$ (A = Einstein A coefficient) and a spread in energy about $\Delta E \approx \hbar/\Delta t = \hbar A$.

$$\Delta E \Delta t \approx \hbar$$

- The ground level has no spread in energy because $\Delta t = \infty$.
- The atom is in a definite sublevel of some level.



- A transition in a spectral line is considered to be an instantaneous transition between a definite sublevel of an initial level to a definite sublevel of a final level.
- The energy spread of sublevels is described by a Lorentzian profile with the damping parameter of $\gamma = A$.***
- This picture implies that the emission line profile is the same as the absorption line profile.***

If both the upper and lower state are broadened, then the line profile is the convolution of two Lorentz profiles, which is another Lorentz profile with $\gamma = \gamma_2 + \gamma_1$.

$$\gamma = \gamma_2 + \gamma_1$$

Note that $\gamma_1 = 0$ if the lower state is the ground state.

where γ_2 and γ_1 are the widths of the upper and lower states involved in the transition.

The longer an excited state exists, the narrower the line width so that metastable states can have very narrow lines (if the thermal Doppler broadening is not important). In general, the damping parameter is given by

$$\gamma = \sum_{n'} A_{nn'}$$

where **the sum is over all states n' of lower energy**.

- The semiclassical picture postulates that in the process of photon scattering, an atom stays in a given sublevel unless there are elastic collisions that cause a transitions to a different sublevel. Thus if there are no elastic collisions, the next transition starts from the same sublevel where the previous transition ended.

- **Collisional Broadening (by elastic collision)**

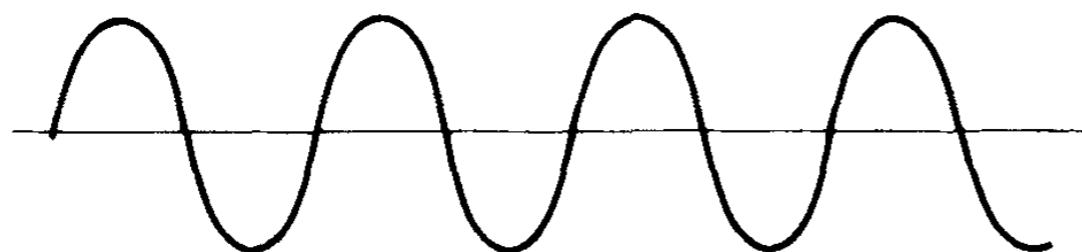
The Lorentz profile applies even to certain types of collisional broadening mechanisms.

If the atom suffers collisions with other particles while it is emitting, the phase of the emitted radiation can be altered suddenly. If the phase changes completely randomly at the collision times, then information about the emitting frequencies is lost.

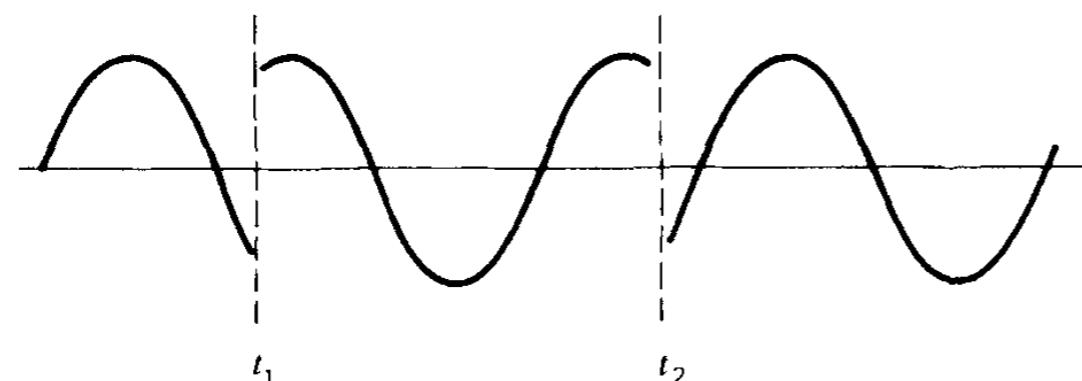
If the collisions occur with frequency ν_{col} , that is, each atom experiences ν_{col} collisions per unit time on the average, then the profile is

$$\phi(\nu) = \frac{\Gamma/4\pi^2}{(\nu - \nu_0)^2 + (\Gamma/4\pi)^2} \quad \text{where} \quad \Gamma = \gamma + 2\nu_{\text{col}}$$

Collisions dominate in high density environments.



purely sinusoidal



random phase interruptions by atomic collisions

For derivation of the above formula, see Problem 10.7 of Rybiki & Lightman and Chapter 11 of Atomic Spectroscopy and Radiative Processes [Degl'Innocenti].

- **Combined Doppler (Gaussian) and Lorentz Profiles**

Atoms shows both a Lorentz profile plus the Doppler effect. In this case, we can write the profile as an average of the Lorentz profile over the various velocity states of the atom:

$$\phi(\nu) = \frac{\Gamma}{4\pi^2} \int \frac{f(v_z)}{(\nu - \nu'_0)^2 + (\Gamma/4\pi)^2} dv_z$$

Here, $f(v_z)$ is the Maxwell velocity distribution and ν'_0 is the line center in the rest frame of the atom with a velocity v_z .

$$\nu'_0 = \nu_0 + \nu_0 (v_z/c)$$

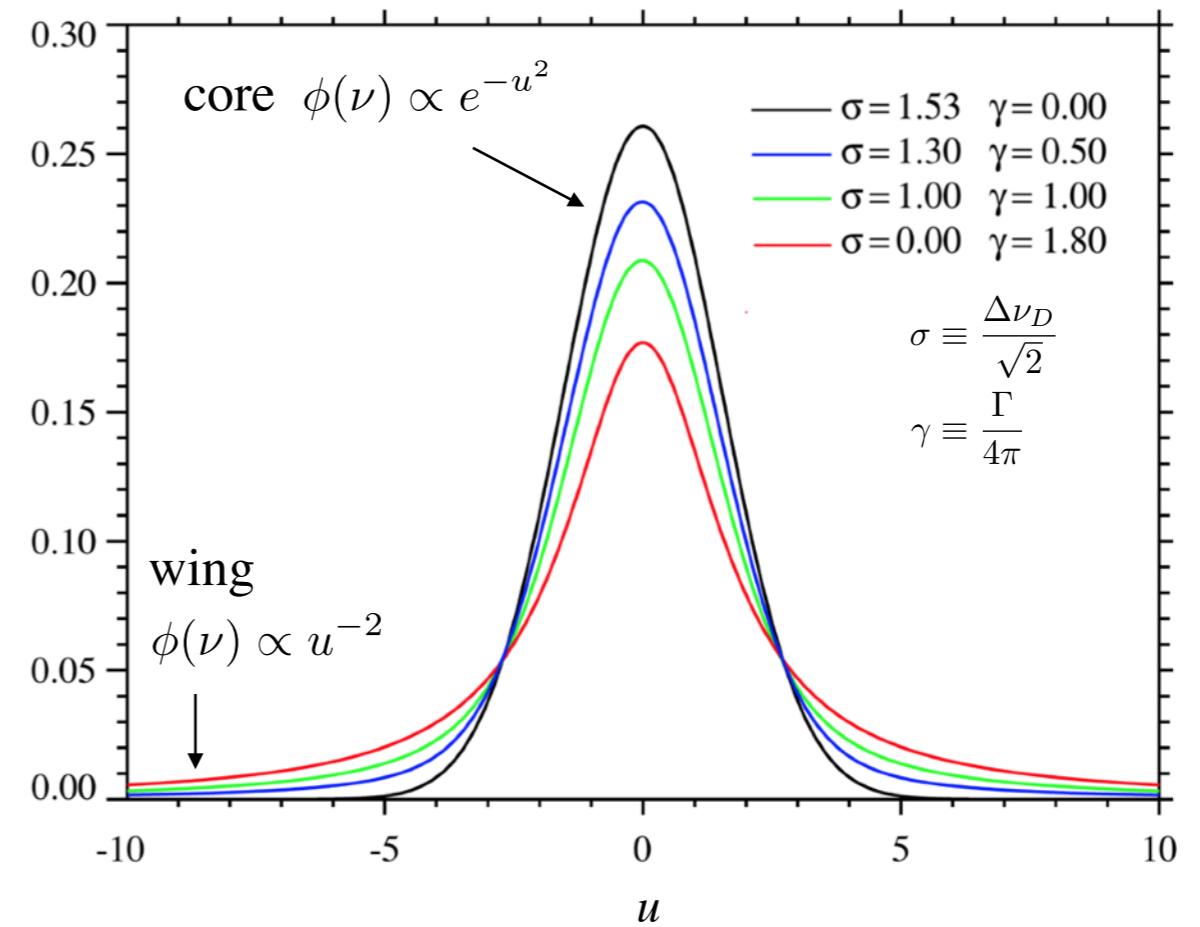
$$f(v_z) = \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left(-\frac{mv_z^2}{2kT} \right) \quad \text{Here, } m \text{ is the hydrogen mass.}$$

Therefore,

$$\phi(\nu) = \frac{\Gamma}{4\pi^2} \int_{-\infty}^{\infty} \frac{(m/2\pi kT)^{1/2} \exp(-mv_z^2/2kT)}{(\nu - \nu_0(1 + v_z/c))^2 + (\Gamma/4\pi)^2} dv_z$$

Changing the variable in integration to $y = mv_z^2/2kT$, the profile can be written using the Voigt function.

$$\begin{aligned}\phi(\nu) &= \frac{1}{\Delta\nu_D \sqrt{\pi}} H(u; a) \\ H(u; a) &\equiv \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{(u - y)^2 + a^2} \\ u &\equiv \frac{\nu - \nu_0}{\Delta\nu_D} \\ a &\equiv \frac{\Gamma}{4\pi \Delta\nu_D} \\ \nu_D &= \frac{\nu_0}{c} \sqrt{\frac{2kT}{m}}\end{aligned}$$



The “core” of the line is dominated by the Doppler (Gaussian) profile, whereas the “wings” are dominated by the Lorentz profile.

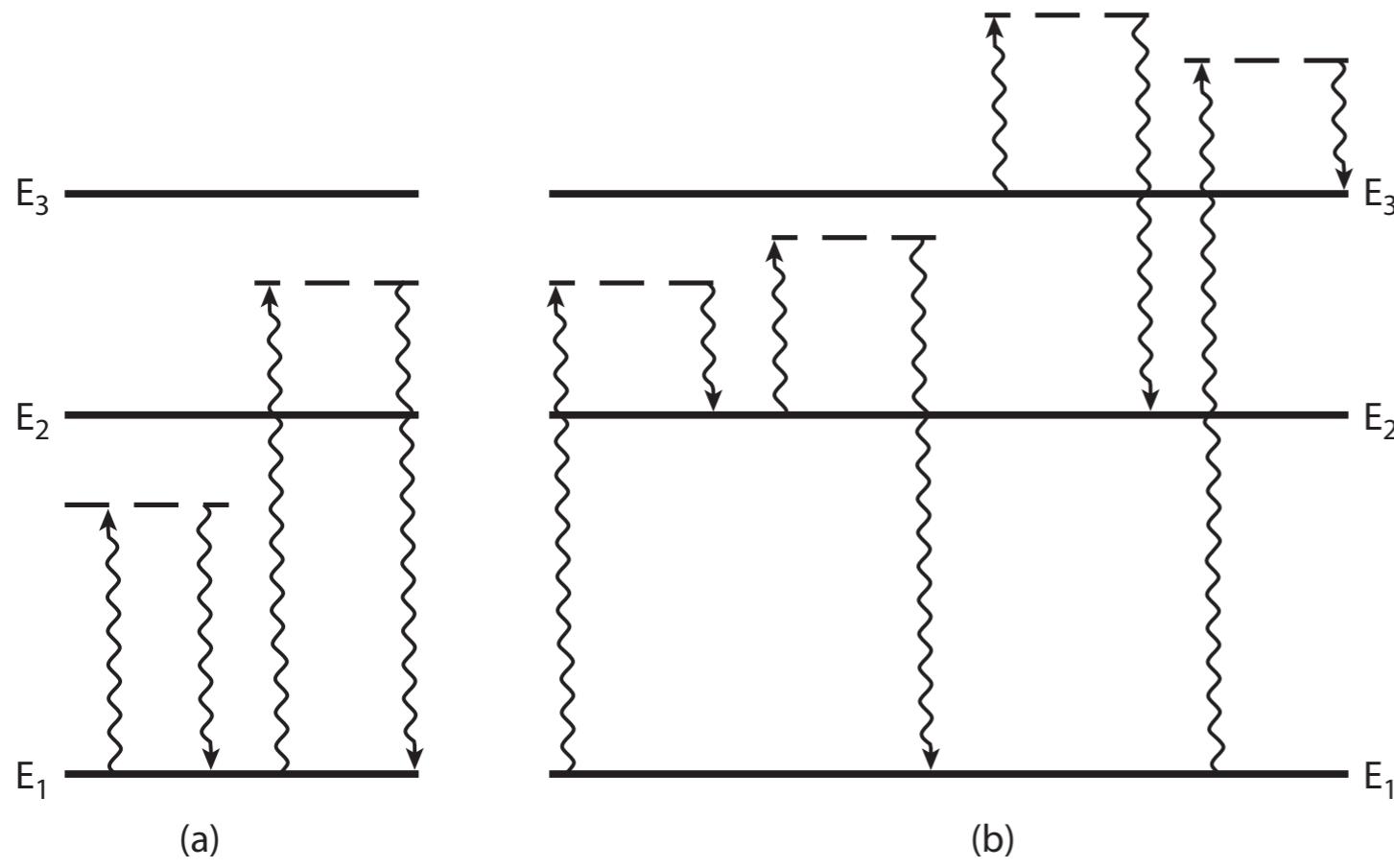
Rayleigh and Raman Scattering

- Rayleigh scattering and Raman scattering by atoms and molecules affect radiation over a wide range of frequencies.

These processes are very efficient when the frequency of an incident photon is close to resonance with a bound-bound transition in the scattering center.

In **Rayleigh scattering**, an incident photon raises a bound electron from an eigenstate of the scattering center to an intermediate state (that is not an eigenstate of the system), followed by the direct return of the electron to the original eigenstate with the release of a photon of the same frequency as the input photon. Like Thomson scattering, **Rayleigh scattering is coherent**.

In **Raman scattering**, an incident photon raises an electron from an eigenstate of the scattering center to an intermediate state followed by a jump of the electron to a different eigenstate of the system, along with the release of a photon having a frequency different from that of the input photon. Unlike Thomson and Rayleigh scattering, **Raman scattering is noncoherent**.



Examples of (a) Rayleigh scattering and (b) Raman scattering. Solid lines are energy eigenstates of the scattering center. Dashed lines are intermediate states that are not eigenstates of the system.

[Hubeny & Mihala] Theory of Stellar Atmosphere

Molecular Structure

[Introduction]

- The Make-Up of Molecules and Solids

Atoms can be combined to form molecules or solids.

The properties of these compounds depend greatly on the way their constitutive atoms are bonded together, by their electrons.

- Molecular Bonding

Chemical bonds are the result of the overlap between the outer orbitals of two atoms whose valence shell is not full.

Despite their mutual repulsion, sharing electrons leads to a lower energy state, in which a stable bonded molecule is formed.

The atomic spacing in a molecule or a solid is of the order of a few Å.

- Valence shell

The outer shell is called the valence shell. It contains the electrons responsible for molecular bonds and shaping the optical properties of solids.

The chemical bond depends on the tendency of its atoms: (i) to share electrons; (ii) to form cations, by losing one or several electrons; or (iii) to form anions, by gaining one or several electrons.

- So far, about 200 molecules have been detected in the interstellar and circumstellar medium by direct observation of their spectra. These molecules are ones which contain up to 13 atoms.

- Molecules formed from two atoms are called diatomics while those formed from more than two atoms are described as polyatomic.
- Because molecular binding energies are relatively small, i.e., generally less than ionization energies, molecules are only found in cooler, or less active, astronomical environments.

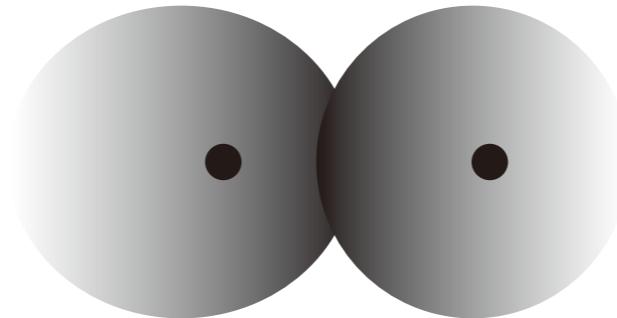
Polyatomic molecules are only a significant component of matter at temperatures below about 4000 K. Diatomic systems can survive to somewhat higher temperatures and may be found in environments with temperatures up to about 8000 K.

- The Structure, and hence the spectra, of molecules are more complicated than atoms in two ways:
 - There is no single charge center about which electrons move. The electronic wavefunctions therefore have lower symmetry, making them harder to calculate and harder to work with.
 - The nuclei themselves move, giving rise to both rotational and vibrational motions of the atoms within the molecule. These motions give rise to discrete spectra.

[Born-Oppenheimer Approximation]

- **Born-Oppenheimer approximation:**

- To a very good approximation, the motions of the electrons and nuclei could be treated separately. The electrons move much faster than the nuclei.
- *This come about because of the great difference between the masses of the electron and a typical nuclei.*
- The slowly moving nuclei only sense the electrons as a kind of smoothed-out cloud. As the nuclei move the electrons have sufficient time to adjust to adiabatically the new nuclear positions. (***It is like flies buzzing round an elephant - as the elephant moves the flies move with it.***) The nuclei then feel only an equivalent potential that depends on the internuclear distance and on the particular electronic state.

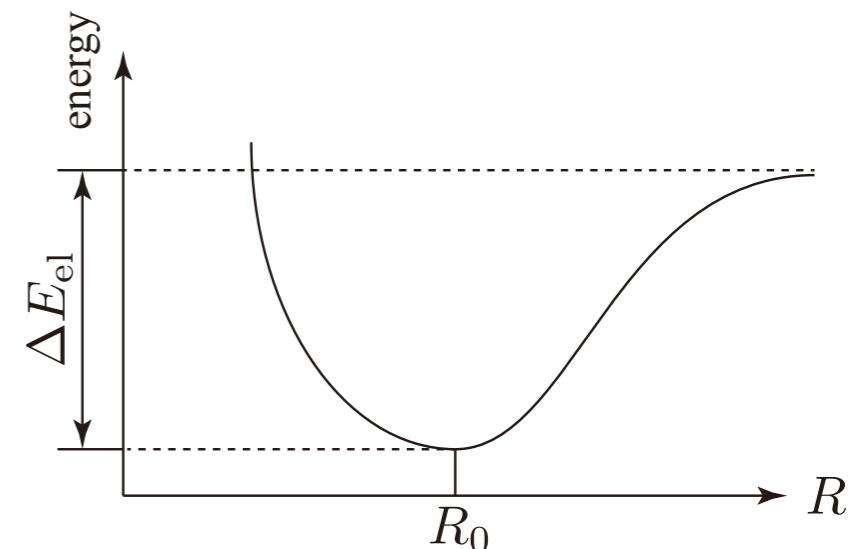


- One separates the wavefunction for the motions of electrons from the wavefunction for the motions of the nuclei. One can then consider the electronic wavefunction separately for each position of nuclei, as if the nuclei are held fixed.
- Due to very different energies of the **electronic, vibrational, and rotational states**, these interactions can be assumed to be decoupled. The separation of wavefunctions is referred to as the Born-Oppenheimer approximation. Under the Born-Oppenheimer approximation, the total wavefunction is a product of the nuclear, electronic, vibrational, and rotational wavefunctions.

$$\psi_{\text{tot}} = \psi_{\text{nuc}} \psi_{\text{el}} \psi_{\text{vib}} \psi_{\text{rot}}$$

- Order of magnitude of energy levels

- Electronic energy:



As the separation between the two atoms $R \rightarrow 0$ (at very small R), the overall interactions are strongly repulsive. There is repulsion due to nuclear-nuclear interaction whose potential depends on $Z_A Z_B / R$. There is also repulsion due to the electron-electron interactions, which also behave approximately as $1/R$. However, these repulsive interactions are largely cancelled by the attractive electron-nuclear interaction.

As $R \rightarrow \infty$, the molecule is pulled apart and it separates into atoms in a process known as dissociation. The energy of the system at dissociation is clearly just the sum of the atomic exchange.

At intermediate R , to get binding there must be some region of R where the molecular energy is less than the sum of the atomic energies. In this case, the electronic state is described as ‘attractive’ and there is a minimum in the potential energy curve.

For a diatomic molecule, a stable chemical bond can form between two atoms that approach within a distance of each other comparable to the Bohr radius $a_0 = \hbar^2/m_e c^2$. Then, the electron energy will be given by

$$E_{\text{elect}} \sim m_e v^2 = \frac{p^2}{m_e} \sim \frac{\hbar^2}{m_e a_0^2} \quad (\leftarrow p \times a_0 \sim \hbar, \text{ uncertainty relation}) \quad \Rightarrow \text{visible/UV (a few eV)} \\ (a \sim 1 \text{ \AA})$$

- **Vibrational energy:**

If the two nuclei are displaced from the equilibrium separation R_0 by a displacement comparable to $\xi \sim a_0$, they will vibrate about the equilibrium position with a frequency ω_{vib} such that **the vibrational energy contained in the motion and displacements of the two nuclei (of typical mass M) will be comparable to the depth of the electronic potential well.**

$$M\omega_{\text{vib}}^2 a_0^2 \sim E_{\text{elect}}$$

where ω = frequency of vibration.

M = mass of the molecule.

Then, the vibrational energy is

$$E_{\text{vib}} \sim \hbar\omega \sim \left(\frac{m_e}{M}\right)^{1/2} \frac{\hbar^2}{m_e a^2} \sim \left(\frac{m_e}{M}\right)^{1/2} E_{\text{elect}} \quad \Rightarrow \text{Near-IR / Mid-IR}$$

- **Rotational energy:**

The nuclei can also rotate about each other. Then, the energy of rotation is

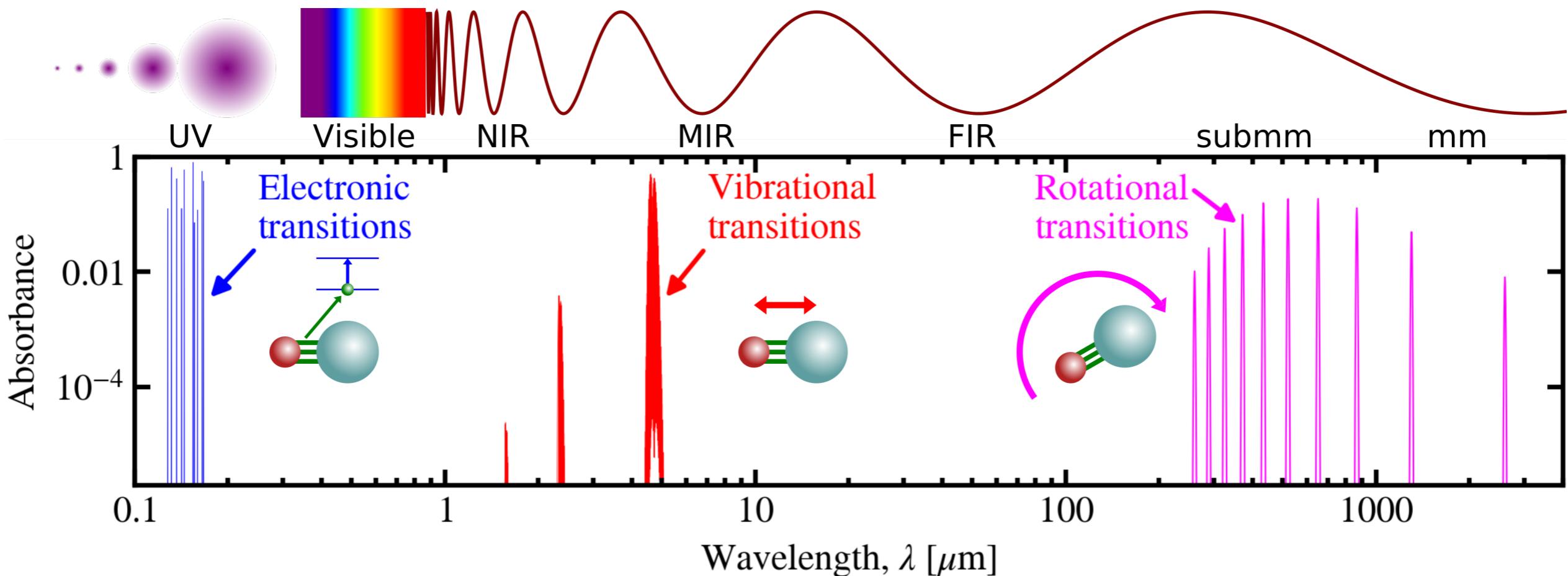
$$E_{\text{rot}} \sim \frac{L^2}{2I} \sim \frac{\hbar^2 \ell(\ell + 1)}{2I} \quad \Rightarrow \text{radio}$$

where I is the moment of inertia of the molecule: $I = Ma_0^2$. Therefore, we obtain

$$E_{\text{rot}} \sim \left(\frac{m_e}{M}\right) E_{\text{elect}}$$

In summary, $E = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}}$

| |
|--|
| $E_{\text{elect}} : E_{\text{vib}} : E_{\text{rot}} = 1 : \left(\frac{m_e}{M}\right)^{1/2} : \left(\frac{m_e}{M}\right)$ |
| for hydrogen ~ 0.02 ~ 0.0005 |



Molecular transitions.

The different types of transitions are illustrated with the CO molecule.

[credit: Frédéric Galliano]

Schrödinger equation for a diatomic molecule

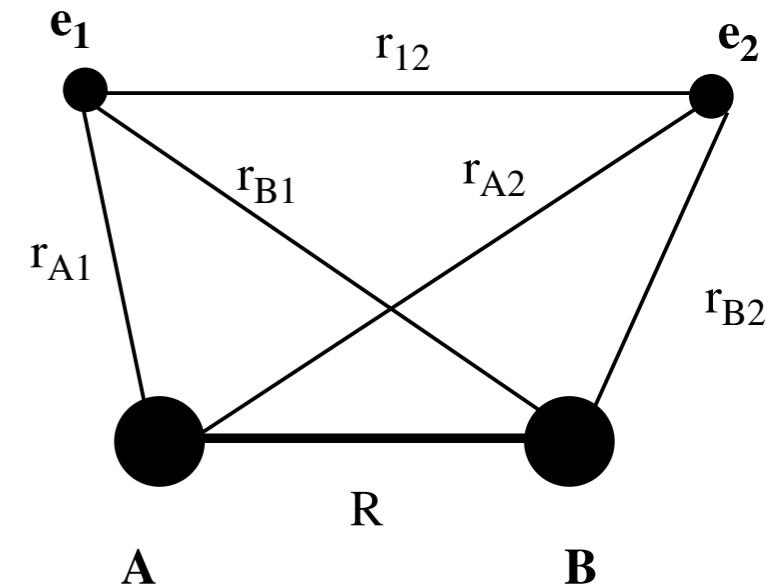
For a diatomic molecule with N electrons,

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E \right) \Psi(\mathbf{R}_A, \mathbf{R}_B, \{\mathbf{r}_i\}) = 0$$

The first two terms are the kinetic energy operators for the motions of nuclei A and B, the third term gives the kinetic energy operator for the electrons, V_e is the potential and E is the total energy of the system.

The potential is given by the various Coulomb interactions within the molecule:

$$V_e = - \sum_{i=1}^N \frac{Z_A e^2}{r_{Ai}} - \sum_{i=1}^N \frac{Z_B e^2}{r_{Bi}} + \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{e^2}{r_{ij}} + \frac{Z_A Z_B e^2}{R}$$



- (1) attraction of the electrons by nucleus A
 - (2) attraction of the electrons by nucleus B
 - (3) electron-electron repulsion
 - (4) nuclear-nuclear repulsion
- Born-Oppenheimer approximation: One can write the wave function as a product of electronic and nuclear wave functions.

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \{\mathbf{r}_i\}) = \psi_e(\{\mathbf{r}_i\}) \psi_n(\mathbf{R}_A, \mathbf{R}_B)$$

Then the equation becomes

$$\left[\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 - E \right) \psi(\mathbf{R}_A, \mathbf{R}_B) \right] \psi(\{\mathbf{r}_i\}) + \left[\left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e \right) \psi(\{\mathbf{r}_i\}) \right] \psi(\mathbf{R}_A, \mathbf{R}_B) = 0$$

- In this case the **electronic wavefunction** satisfies the following equation:

$$\left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e \right) \psi_e(\mathbf{r}_i) = E_e \psi_e(\mathbf{r}_i)$$

This equation is solved separately for each value of the internuclear separation R .

Then, the resulting eigenvalue E_e is the electronic energy at R and gives the electronic potential $V(R) = E_e$ upon which the nuclei move.

The equation for the wavefunction of nuclei is obtained to be

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V(R) - E \right) \psi_n(\mathbf{R}_A, \mathbf{R}_B) = 0 \quad \text{where } V(R) \equiv E_e.$$

Here, E (the eigenvalue) is the total energy of the system.

-
- The Schrödinger equation for the nuclei:

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V(R) - E \right) \psi_n(\mathbf{R}_A, \mathbf{R}_B) = 0 \quad \text{where } V(R) \equiv E_e.$$

The equation deals with three types of motions of the nuclei: (1) translation of the whole system, (2) vibrations, and (3) rotations. The motions can be separated into the translational motion of the center-of-mass of the system plus the internal motion of one body in a ‘central’ potential, which depends on the distance between the particles. The effective mass of this one-body problem is the reduced mass:

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

The Schrödinger equation for nuclear motion, neglecting the translational motion, becomes:

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(R) - E \right] \psi_n(\mathbf{R}) = 0$$

where $\mathbf{R} = (R, \theta, \phi)$. R is the internuclear separation, (θ, ϕ) is the orientation of the molecular axis relative to the laboratory z -axis.

The vibrational and rotational motion cannot be separated rigorously. However, as a good first approximation, the vibration and rotational motion may be separated.

$$\psi_n(\mathbf{R}) = \psi_{\text{vib}}(R)\psi_{\text{rot}}(\theta, \phi)$$

Then, we obtain two equations for the rotational motion and vibrational motion:

angular equation: $\left\{ -\frac{\hbar^2}{2\mu R^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - E_r \right\} \psi_{\text{rot}}(\theta, \phi) = 0$

 the angular part of the Laplacian operator ∇^2

radial equation: $\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) - E_v \right] \psi_{\text{vib}}(R) = 0$

(1) The solution of the angular equation is:

$$\begin{aligned} \psi_{\text{rot}}(\theta, \phi) &= Y_{JM}(\theta, \phi) \\ E_r &= \frac{\hbar^2}{2\mu R^2} J(J+1) \end{aligned}$$

(2) The potential $V(R)$ is not a simple function and thus the radial equation has no general algebraic solution. But, we can approximate $V(R)$ about its minimum by a parabola:

$$\begin{aligned} V(R) &= V(R_e) + \frac{1}{2} \left. \frac{d^2V}{dR^2} \right|_{R=R_e} (R - R_e)^2 + \mathcal{O}((R - R_e)^3) && \xleftarrow{\frac{dV}{dR} = 0 \text{ at } R = R_e} & \frac{dV}{dR} = 0 \text{ at } R = R_e \\ &= V_0 + \frac{1}{2} k(R - R_e)^2 + \dots \end{aligned}$$

Setting the zero of energy at the minimum potential, $V_0 = V(R_e) = 0$, the radial equation becomes

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_e)^2 - E_v \right] \psi_{\text{vib}}(R) = 0$$

This is the QM equation for the harmonic oscillator with the spring constant k . The energy levels of this equation are:

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right)$$

$$\text{where } \omega = \left(\frac{k}{\mu} \right)^{1/2}, \quad v = 0, 1, 2, \dots$$

