Line transitions

1. Electron changes its binding energy in an atom (bound-bound transition)
   1b. Electron changes its binding energy in a molecule (bound-bound transition)

2. A molecule changes its binding energy (vibrations)

3. A molecule changes its rotational energy

Quantum mechanics is at work:
Discrete energies are relevant \( \implies \) radiative transitions produce line emission/absorption
no continuum (except ionization/recombination)

Statistical laws in case of Thermal Equilibrium (TE, at least Local . . . LTE)
Textbooks and further reading

1. Dopita & Sutherland: chap. 2 (more arguments in other chapters)

2. Rybicki – Lightman: chap. 1.6 (Einstein's Coefficients); chap 9; chap 10; chap 11

3. Tennison: (H spectrum & similarities, some molecular line theory/observations)
What can we learn?

1. Composition of a celestial body

2. Temperature (and other gas/plasma properties)

3. Abundances of various species (intensity of transitions) and excitation/ionization state

4. Motions:
   4.1 particles (line widths)
   4.2 clouds (line shift)

5. Pressure (relation with collisions, line broadening, turbulence)

6. Magnetic field (degenerate state, angular momentum becomes split if H is present)
Spectral lines in an optical spectrum (mostly atomic transitions)
Atomic spectra

Hydrogen at visual wavelengths

Joseph Ritter von Fraunhofer (1787 - 1826)
Basic concept of atomic structure (1)

Each electron is **bound** to its nucleus with a given **binding energy** which is **quantized** into various **LEVELS**, as predicted by QM, corresponding to **different distances to the nucleus**, i.e. the various levels correspond to different orbits in a sort of planetary system.

The **outermost electron** may change its binding energy, swapping between two LEVELS, either acquiring (absorption) or releasing (emission) energy $\hbar \nu$ via **radiative transitions** (warning... there are also **other types of energy transitions**!)

Such radiative transitions must obey strict **selection rules**.

The Ground State correspond to the maximum binding energy (which is negative).

To **IONIZE** an atom in the ground state an energy in excess to this maximum binding energy must be provided, i.e. the maximum binding energy defines the minimum ionization energy. E.g. for an H atom it is 13.6 eV (UV photons, 912 A)

*Obviously, real atoms are more complicated!*
Figure 6-12. Probability density plots of some hydrogen atomic orbitals. The density of the dots represents the probability of finding the electron in that region.

© 1983 University Science Books; "Quantum Chemistry" by Donald A. McQuarrie
contrary to classical theory of charges in motion, the electrons do not radiate in their curved orbits, except during a “transition”

Atomic spectra
basic concepts (3)

Quantum numbers:

\[ n - \text{main number} = 1, 2, 3, \ldots \text{defines the energy and the size of the “orbit”} \]

\[ a_n = a_o \frac{n^2}{Z} \quad a_o = 0.53 \text{ Å} \]

\[ l - \text{azimutal number} \ (\text{angular momentum, related to eccentricity}) \]

\[ 0, 1, 2, \ldots, n-1 \]

\[ \sqrt{1-e^2} = \frac{b}{a} = \frac{l+1}{n} \leq 1 \]

\[ m - \text{magnetic number} \ (\text{orbit orientation in case of magnetic field}) \]

\[ -l, -l+1, \ldots, 0, \ldots l-1, l \]

However… at a given main number (n), there is a tiny difference in energy between levels with different combination of l,m

this is not true (first order) for hydrogen, where there is a high degree of energy degeneracy (fine structure)

further extremely small energy structures (hyperfine structure) can be defined by the spin number \( s = (\pm 1/2) \)
Basic concept of atomic structure (4): Orbitals, as from n,l,m

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<thead>
<tr>
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<th>p (ℓ = 1)</th>
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Basic concept of atomic structure (5): Orbitals, as from n,l,m

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>Orbitals and sub-orbitals of Bound Electrons</th>
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<tr>
<td>0</td>
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<td>$d$</td>
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<tr>
<td>3</td>
<td>$f$</td>
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- **$s$** orbitals are spherical in shape.
- **$p$** orbitals have dumbbell shapes along the axes of the $x$, $y$, and $z$ directions.
- **$d$** orbitals are more complex, with four lobe shapes along the $x$, $y$, and $z$ axes, and two lobe shapes along the $d_{x^2-y^2}$ and $d_{z^2}$ directions.

For each $\ell$, the sub-orbitals are distinguished by $m_{\ell}$:
- $m_{\ell}$ can be $-\ell$ to $\ell$.
- For $\ell = 0$, $m_{\ell}$ can only be $0$.
- For $\ell = 1$, $m_{\ell}$ can be $-1$, $0$, or $1$.
- For $\ell = 2$, $m_{\ell}$ can be $-2$, $-1$, $0$, $1$, or $2$.
- For $\ell = 3$, $m_{\ell}$ can be $-3$, $-2$, $-1$, $0$, $1$, or $2$.

Note: 7 sub-orbitals are not pictured for $\ell = 3$. 

7 sub-orbitals not pictured.
Shape of f orbitals

- $f_{z^2} - \frac{3}{5} zr^2$
- $f_{x^2} - \frac{3}{5} xz^2$
- $f_{y^2} - \frac{3}{5} yr^2$
- $f_{xyz}$
- $f_{y(x^2 - z^2)}$
- $f_{x(z^2 - y^2)}$
- $f_{z(x^2 - y^2)}$
Basic concept of atomic structure (9): Filling the orbitals
Atomic spectra basic concepts (7)

Hydrogen:
simplest example for studying lines between various energy levels

The frequency $\nu$ of a photon emitted/absorbed during a transition between two levels $m$ and $n$ is

$$\nu_{nm} = c R_H \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \text{ Hz} ; \quad n > m > 0$$

$$R_H = \frac{2 \pi^2 e^4 m_e}{\hbar^3 c} = 1.1 \cdot 10^5 \text{ cm}^{-1} \rightarrow \text{Rydberg constant}$$

$\Rightarrow$ increasing $n$, lines get closer to a limiting frequency $\nu = \frac{c R_H}{m^2}$

$\Rightarrow$ if $m$ is large, lines of different series start at very close frequencies and produce a spectrum similar to a continuum (but it is not!)

[hydrogen-like atoms, He+, Li++, Be+++,... are obtained attributing the energy $E_n$ at each “level”]

$$E_n = -Z^2 \frac{R_H \mu \hbar c}{n^2} + \epsilon(n, l)$$
Hydrogen transitions in terms of energy:

\[ R_y = \frac{2\pi^2 e^4 m_e}{h^2 c} = 13.6 \text{ eV} \] (called 1 Rydberg)

\[ h\nu_{mn} = R_y \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \text{ eV} \quad ; \quad m > n > 0 \]

For a given pair of quantum numbers, decay and excitation can either generate (emission) or cancel (absorption) photons at the appropriate frequency/energy.
transitions obey to well known selection rules: $\Delta n, \Delta l, \Delta m,$
Atomic spectra

Hydrogen: Grotrian diagrams

UV, visible, IR
Atomic spectra

Hydrogen: main series

Free electrons

Balmer series

Paschen series

Lyman series

First level

Second level

Third level

Nucleus
> No continuum photons

> Typical of PN and HII regions
Atomic spectra

for an extremely detailed spectrum of the sun see
http://chinook.kpc.alaska.edu/~ifafv/lecture/fraunhofer.htm
Molecular spectra (1):

Molecules have 3-D structures capable to oscillate around the equilibrium distance, and may also change their rotation axis/velocity moving through energy levels defined by quantum mechanics.

**Electronic** (~eV energies, optical)
Electrons in individual atoms may move to a different energy level.

**Vibrational** (~0.1 – 0.01 eV, IR)

\( n \) is the vibrational quantum number.

\[
E_n = \left( n + \frac{1}{2} \right) h\nu_o - \left( n + \frac{1}{2} \right)^2 \frac{(h\nu_o)^2}{4D_e}
\]

\[
E_{n+1} - E_n = h\nu_o - (n+1) \frac{(h\nu_o)^2}{2D_e}
\]

With the quantum harmonic oscillator, the energy between adjacent levels is constant, \( h\nu_o \). With the Morse potential, the energy between adjacent levels decreases with increasing \( n \) as is seen in nature. It fails at the value of \( n \) where \( E_{n+1} - E_n \) is calculated to be zero or negative. The Morse potential is a good approximation for the vibrational fine structure at \( n \) values below this limit.
Molecular spectra (1b):

NIR composite spectra for various astrophysical bodies
Molecular spectra (1c): NIR & MIR, from vibrational transitions

Circinus galaxy - HST
Molecular spectra (2):

rotational (~meV, submm, mm & cm wavelengths)

rotational levels lie within vibrational levels

The rotational quantum number $J$ is related to the moment of inertia $I$, to the distance $r$ and to the rotational energy $E_{\text{rot}}$:

$$ J(J+1) = \frac{8 \pi^2 I r^2 E_{\text{rot}}}{\hbar^2} $$

$$ I = m_1 r_1^2 + m_2 r_2^2 $$
Molecular spectra (2b):

CO emission in a dense, cold cloud (a GMC!)
Molecular spectra (2c):

- 37 Identified Features
- 35 Unidentified Features
- ~6 lines per 100 km/s
- $T_{RMS} = 0.003$ K (theoretical)
Molecular spectra (2d): transitions with ALMA

The hot core in Orion KL (high mass SFR)
Optical ( & UV) spectra of galaxies

**QUASAR**

- **Ly α**
- **CIV**
- **CII**
- **MgII**
- **Hα**

 Flux Density, $I_\lambda$ (Arbitrary Units)

Rest Wavelength, $\lambda$ (Å)

- $\alpha_\lambda = -0.46$
- $\alpha_\lambda = -1.58$

**ELLIPICAL**

Typical UV–strong galaxy

- UV upturn

- Only BCGs

3C 273 and its Jet

**SPIRAL**

- ESO New Technology Telescope
- Hubble Space Telescope
- Palomar Sky Survey

$F_\lambda [10^{-15} \text{erg cm}^{-2} \text{s}^{-1} \text{Å}^{-1}]$

Wavelength [Å]
Atomic and molecular spectra: observational constraints

➢ Lines are not monochromatic

➢ Lines can be (red – blue) shifted

➢ Various elements may appear in the same spectrum (i.e. region ?)
  Projection effects ?
  Intrinsic association ?

➢ Line ratios are a diagnostic for temperature?

➢ Lines are generally associated to gaseous (plasma) fluids

➢ Lines appear either in emission or in absorption (* a background source is required!)
Einstein's coefficients (1)

They are used to describe radiative interactions involving bound-bound electron transitions, on the basis of quantum mechanics. Simplest example: an atom with two energy levels only (approx)

\[
E_{12} = E_2 - E_1 = h \nu_{12}
\]
Einstein's coefficients (2)

Given two atomic levels $U$ and $U,(with U > L)$ the following definitions hold:

Spontaneous emission:
$A_{UL} = \text{transition probability per unit time to go from level } U \text{ to } L \text{ by emission of a photon}$

Absorption:
$B_{LU} = \text{transition probability per unit time to go from level } L \text{ to } U \text{ via absorption of a photon}$

Stimulated emission:
$B_{UL} = \text{transition probability per unit time } U \rightarrow L \text{ via emission induced by incoming radiation}$

$\bar{J}$ represents the density of photons at the frequency $\nu_{UL}$ so that $h \nu_{UL}$ corresponds to the difference between the energy levels $U$ and $L$

$A_{UL}$ is given in $\text{sec}^{-1}$ units, $\frac{1}{A_{UL}}$ is the mean lifetime of the excited state
Einstein's coefficients (3)

The set of emitted photons is not monochromatic: the energy difference between the two levels is not infinitely sharp.

It is described by the line profile function (LPF) $\Phi (\nu)$ which is (sharply?) peaked at the frequency $\nu_{UL}$

$$\int_0^\infty \Phi (\nu) \, d\nu = 1$$

It represents how effectively photons with frequencies around $\nu_{UL}$ can cause transitions

$$\overline{J} \equiv \int_0^\infty J_\nu \Phi (\nu) \, d(\nu)$$

If $J_\nu$ changes slowly with $\nu$, then $\Phi (\nu)$ acts like a $\delta$ function.
Spectral line broadening (1)

Natural (Lorentz) broadening
an atom at an excited state has a finite lifetime
the energy difference is finite as well
the decay therefore follows the Heisenberg’s Principle in the form

\[ \Delta t \approx \frac{1}{A_{UL}} \]

\[ \Delta E = \Delta h \nu \]

\[ \Delta E \Delta t \geq \frac{h}{2\pi} \]

\[ \Delta E \Delta t = \Delta h \nu \frac{1}{A_{UL}} \geq \frac{h}{2\pi} \]

\[ \Delta \nu \geq \frac{A_{UL}}{2\pi} \]

and this is the minimum width allowed for the transition between levels U, L

WARNING: large/small values of imply broad/narrow lines
Doppler (thermal) broadening

Atoms are in (thermal) motion wrt the observer and the rest (atom) frame frequencies are either red- or blue- shifted. If $\nu_r$ is the radial velocity

$$\Delta \nu = \nu_{\text{obs}} - \nu_{\text{em}} = \nu_{\text{em}} \frac{\nu_r}{c}$$

It is possible to derive the radial velocity (redshift/blueshift)

$$\nu_r = c \frac{\nu_{\text{obs}} - \nu_{\text{em}}}{\nu_{\text{em}}}$$

the shape of the line is modified, the total energy is not

**N.B.** The centroid (= “natural frequency”) remains unchanged; only in the case that the whole cloud is moving, then also the centroid is (Doppler) shifted
Spectral line broadening (3) – $v_r$ and temperature

In case we are at thermal equilibrium (Maxwell-Boltzmann)

$$N(v_r)dv_r \approx N_0 v^2 e^{\frac{-m_a v_r^2}{2kT}} dv_r$$

where $m_a$ is the mass of the atom

$$-\frac{m_a c^2 (v_{obs} - v_{em})^2}{2kT v_{em}^2}$$

and in this case the Line Profile Function becomes (if we introduce the Doppler width)

$$N(v)dv \approx N_0 e^{-\frac{m_a v_r^2}{2kT v_{em}^2}} dv$$

$$\Delta v_D = \frac{v_{em}}{c} \sqrt{\frac{2kT}{m_a}}$$

$$\Phi(v) = \left(\Delta v_D \sqrt{\pi}\right)^{-1} \exp\left(-\frac{(v_{obs} - v_{em})^2}{(\Delta v_D)^2}\right)$$

Valid also in case of turbulence, once modified the Doppler width by introducing $\xi$, the rms of turbulent velocities (with Gaussian distribution)

$$\Delta v_D = \frac{v_{em}}{c} \sqrt{\frac{2kT}{m_a}} + \xi^2$$
Spectral line broadening (4)

the LPF for natural broadening is

\[ \Phi(\nu) = \frac{\gamma/4\pi^2}{(\nu_{\text{obs}} - \nu_{\text{em}})^2 + (\gamma/4\pi)^2} \quad \text{where} \quad \gamma = \sum_m A_{nm} \]

or \( \gamma = \gamma_u + \gamma_l \), in case there are transitions from a lower level too (inclusive of radiation field and appropriate \( B_{mn} \))

Collisional broadening

collisions introduce random changes to the phase of E/B field

\[ \Phi(\nu) = \frac{\Gamma/4\pi^2}{(\nu_{\text{obs}} - \nu_{\text{em}})^2 + (\Gamma/4\pi)^2} \]

where \( \Gamma = \gamma + 2\nu_{\text{coll}} \); \( \nu_{\text{coll}} \) is the frequency of collisions per unit time an atom experiences.

atoms hit other particles during emission (absorption). All broadening mechanisms coexist, with Doppler and Lorentz broadenings being dominant.
Spectral line shape produced by: (a) Doppler broadening and (b) natural and collision broadening (taken from Levi (1968)).
Test(1): Do we understand how it works?

question 1:

question 2:

question 3:
Test(2): Do we really understand how it works?

question 4:

question 5:

question 6:
Balmer JUMP/ Discontinuity:

Visible in continuum from stars

- **Origin:**
  bound-free transition, electrons from n=2 are ionised

- **Effect:**
  depression of the continuum

- **Depends on:**
  Density (composition) & Temperature of the region responsible for the absorption (largest in A-type stars)

- **Located at:**
  The Balmer series limit and higher energies
Four Statistical laws (for thermal equilibrium)

Maxwell – Boltzmann (velocities .aka. energy for particles)

\[
\frac{dN}{dv} \propto f(v) \propto v^2 e^{-\frac{mv^2}{2kT}} \approx v^2 e^{-\frac{v^2}{2\sigma^2}} \quad \text{where} \quad \sigma = \frac{kT}{m}
\]

Planck (spectral distribution for radiation)

\[
U(\nu) = \frac{4\pi}{c} B_\nu(T_P) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT_P}} - 1}
\]

Boltzmann (energy level occupation in atoms, molecules)

\[
\frac{N_U}{N_L} = \frac{g_U}{g_L} e^{-\frac{(E_U - E_L)}{kT_Bz}} = \frac{g_U}{g_L} e^{-\frac{h\nu_{UL}}{kT_Bz}}
\]

Saha (ionization states)

\[
\frac{N_{i+1}}{N_i} = 2 \frac{u_{i+1}}{u_i} \frac{1}{N_e} \sqrt{\left( \frac{2\pi m_e kT_S}{\hbar^2} \right)^3} e^{-\frac{(E_{i+1} - E_i)}{kT_S}}
\]

where \( \sqrt{\frac{2\pi m_e kT_S}{\hbar^2}} = \Lambda_{th} \) de Broglie thermal wavelength, and \( u_i = \sum_n g_{i,n} e^{-\chi_{i,n}/kT} \)
Atoms as oscillators: electric dipole transitions

Basic concept: e-m waves are radiated at the same frequency of an oscillating charge

\[ d(t) = q \cdot x_0 \cos(\omega t) \]

in terms of quantum mechanics, we have the wave function \( \Psi \) (probability density)

\[ \Psi(\vec{r}, t) = \psi(x, y, z) e^{-2\pi i(E/h)t} \]

space /time dependent

in turn, \( \psi(x, y, z) \equiv \psi(r, \Theta, \Phi) \) in case of central potential

\[ \psi(r, \Theta, \Phi) = \frac{R(r)}{r} Y(\Theta, \Phi) \quad \text{(spherical harmonics)} \]

\[ Y(\Theta, \Phi) = Y_{lm}(\Theta, \Phi) = \left[ \frac{(l - |m|)!}{(l + |m|)!} \frac{2l + 1}{4\pi} \right]^{1/2} (-1)^{|m|/2} P_l^{|m|} \cos \Theta e^{im\Phi} \]

\( P_l^{|m|} \) Legendre function, \( l \) & \( m \) integers
\( Y_{lm}(\Theta, \Phi) \rightarrow \text{eigenfunctions of the orbital angular momentum} \)
Atoms as oscillators: electric dipole transitions (2)

Basic concept: the dipole (i.e. nucleus + electron) may be written as

\[ d_x(t) = \int e \cdot x \, \Psi \, \Psi^* \, d\tau \]  (the same also for y, z)

and more in general for a generic transition from \( U \rightarrow L \)

\[ d^{UL}_x(t) = \int e \cdot x \, \Psi_U \, \Psi_L^* \, d\tau = \int e \cdot x \, \psi_U \, \psi_L^* \, e^{-2\pi i t (E_U - E_L)/\hbar} \, d\tau \]

(\text{the same also for } y, z)

Using 3-D notation

\[ \vec{d}^{UL}(t) = e \cdot \vec{R}^{UL}(t) \, e^{-2\pi i t (E_U - E_L)/\hbar} \]

where: \[ R^{UL}_x(t) = \int x \, \psi_U \, \psi_L^* \, d\tau \]  [the same for \( R^{UL}_y(t) \), \( R^{UL}_z(t) \)]

i.e. \[ \vec{R}^{UL}(t) = \int \vec{r} \, \psi_U \, \psi_L^* \, d\tau \]
Atoms as oscillators: electric dipole transitions

Emitted power & the meaning of $A_{UL}$: during dipole transitions

$$P(t) = \frac{2e^2}{3c^3} a^2(t) = \frac{2e^2}{3c^3} \omega^4 x_0^2 \cos^2(\omega t)$$

$$\langle P(t) \rangle = \frac{2e^2}{3c^3} \frac{\omega^4 x_0^2}{2} = \frac{32\pi^4}{3c^3} \nu^4 \left( \frac{e^2 x_0^2}{2} \right) = \frac{32\pi^4}{3c^3} \nu^4 \langle d_\lambda^2(t) \rangle$$

$$= A_{UL} \cdot h \nu_{UL} \quad (\text{i.e. number of transitions per unit time } \times \ h \nu_{UL})$$

Then we can derive the expression of the Einstein coefficient for spontaneous emission:

$$A_{UL} = \frac{32\pi^4 \nu^3}{3hc^3} \langle d_\lambda^2(t) \rangle$$

Going to 3-D

$$A_{UL} = \frac{64e^2 \pi^4 \nu^3}{3hc^3} \vec{R}_{UL} \vec{R}_{UL} = \frac{64\pi^4 \nu^3}{3hc^3} \left| P_{UL} \right|^2$$

where $\left| P_{UL} \right|$ is the power emitted for $U \rightarrow L$ transitions
the meaning of $A_{mn}$:

example:

$$x_0 = a_0 = 5.3 \times 10^{-9} \text{ cm (Bohr radius)}, \quad \nu_{mn} = 3.3 \times 10^{15} \text{ Hz (Lya limit)}$$

$$p = e a_0 / 2 = 1.3 \times 10^{-18} \text{ ues cm}$$

we get:

$$A_{\infty 1} = 3.5 \times 10^8 \text{ s}^{-1}$$

vectors $\vec{R}_{mn}$ can be arranged into a (symmetric) matrix and some elements are 0 meaning that the probability of the transition is 0, namely prohibited.

the value of the elements in the matrix may be interpreted as oscillator strength for that transition.

Electric dipole transitions:
Selection rules: $\Delta n$ arbitrary (but not 0), $\Delta l = \pm 1$ (parity change), $\Delta L = 0, \pm 1, \Delta S = 0 , \Delta J = 0, \pm 1$,
(for reference to notation see Rohlf, 1994 “Modern physics from $\alpha$ to Z_0”)

Some examples of $A_{mn}$ coefficients for electric dipole transitions

<table>
<thead>
<tr>
<th>Line</th>
<th>wavelength (Å)</th>
<th>oscillator strength</th>
<th>$A_{mn}$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman a</td>
<td>1215.67</td>
<td>0.41620</td>
<td>4.70E+008</td>
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<tr>
<td>Lyman b</td>
<td>1025.72</td>
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<td>5.58E+007</td>
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<tr>
<td>Lyman g</td>
<td>972.54</td>
<td>0.02899</td>
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<td>Lyman limit</td>
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<td>H d</td>
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<tr>
<td>H e</td>
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<td>H limit</td>
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<tr>
<td>P a</td>
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<tr>
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<tr>
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<td>0.06549</td>
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<tr>
<td>B limit</td>
<td>14584.00</td>
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</tbody>
</table>

From Allen's Astronomical quantities (p 70, 71) – warning! $A_{mn}$ different from Dopita & Sutherland “Astrophysics of the Diffuse Universe”, p 19
Atomic spectra diagrams

UV, visible, IR

Hydrogen: Grotrian diagrams
Atoms as oscillators: electric quadrupole transitions

The quadrupole term can be non zero when the dipole is 0 (prohibited transition, second term of expansion of potential vector $A$);

in this case the integral becomes

$$q_x(t) = \int e \cdot x^2 \Psi_U \Psi_L^* \, d\tau \quad (also \quad q_y(t), \quad q_z(t))$$

A similar expression for $A_{mn}$ can be derived as in the case of the dipole; all these transitions are termed (semi–) prohibited, but their probabilities ($A_{mn}$) although much smaller than in the dipole case, may be relevant

Selection rules: $\Delta n$ arbitrary, $\Delta l = 0 \pm 2, \Delta J = 0, \pm 1, \pm 2, \Delta L = 0, \pm 1, \pm 2$  
$\Delta S = 0, \Delta m = 0, \pm 1, \pm 2$
The magnetic dipole has to be considered and refers to hyperfine structure transitions, where energy levels differ by very small quantities.

Selection rules: $\Delta n = \Delta l = \Delta L = \Delta S = 0$, $\Delta J = 0, \pm 1$, $\Delta m = 0, \pm 1$

$$m(t) = m_o \cos(\omega t)$$

$$\langle P(t) \rangle = \frac{2}{3 c^3} \omega^4 \langle m^2(t) \rangle = \frac{32 \pi^4}{3 c^3} \nu^4 \langle m^2(t) \rangle$$

$$A_{mn} = \frac{64 \pi^4}{3 h} \frac{\nu^3}{c^3} |\mu_{mn}|^2$$

typical ratios for transitions:

$$\frac{A_Q}{A_D} \approx 3 \cdot 10^{-8} \quad \frac{A_M}{A_D} \approx 5 \cdot 10^{-5}$$

for Einstein B coefficients we need a bit more patience....
H hyperfine structure of Energy levels

For an electron the electric potential within an atom is not simply that from the Coulomb's law. Atoms with many e\(^-\) (Li,...C,N,O,...): the interaction between orbiting electrons and their spins raises the degeneracy of the “n” states so that each “l” level has a slightly different energy. The “m” levels remain undistinguishable unless an external strong magnetic field is applied to the atom (Zeeman splitting).

Further, there is a spin-orbit coupling providing further energy structure. Some atoms may have double, triple, multiple lines closely packed (see CaII, [OIII] doublet).

The binding energy does not depend on the main quantum number alone anymore!!!!!

\[ E_{nj}^{\text{exact}} = mc^2 \left( 1 + Z \alpha (n-j-1/2 + \sqrt{(j+1/2)^2 - Z^2 \alpha^2})^{-1} \right)^{-1/2} - 1 \] where \( j = l + s \)
Selection rules for electronic transitions

**Electric Dipole:**
\[ \Delta n = \text{arbitrary (no 0)} \]
\[ \Delta l = \pm 1 \text{ (parity change)} \]
\[ \Delta J = 0, \pm 1 \quad J=0 \rightarrow J = 0 \text{ forbidden} \]
\[ \Delta L = 0, \pm 1 \quad L=0 \rightarrow L = 0 \text{ forbidden} \]
\[ \Delta S = 0 \]

**Electric Quadrupole:**
\[ \Delta n = \text{arbitrary} \]
\[ \Delta l = 0 \pm 2 \text{ (no parity change)} \]
\[ \Delta J = 0, \pm 1, \pm 2 \quad J=0 \rightarrow J = 0 \text{ forbidden} \]
\[ \Delta L = 0, \pm 1, \pm 2 \quad L=0 \rightarrow L = 0 \text{ forbidden} \]
\[ \Delta S = 0 \]

**Magnetic Dipole:**
\[ \Delta n = \Delta l = 0 \]
\[ \Delta J = 0, \pm 1 \quad J=0 \rightarrow J = 0 \text{ forbidden} \]
\[ \Delta L = 0 \]
\[ \Delta S = 0, \pm 1 \]

\( n, l = \text{electron angular momentum} (=0,...n-1), \quad S = \text{total spin}, \quad L = \text{orbital angular momentum}, \quad J = L+S \text{ total angular momentum} \)
Determining electronic transitions

General notation for bound electrons:

\[ ns^i np^j nd^k \ 2S+1 \ L^J \]

where
n = principal quantum number
S = total spin (\(2S+1\) = multiplicity)
l_i = i-th electron angular momentum (=0,...n-1)
L = sum (l_i), total orbital angular momentum (inner full shells sum to 0)
J = L+S total angular momentum

Example: C_{\text{III}} transitions are resonance, intercombination, and forbidden

C_{\text{III}}: \( A(2s2p^{1P} \rightarrow 2s^2 \ ^1S) = 1.7 \cdot 10^9 \text{ s}^{-1} \)

C_{\text{III}}: \( A(2s2p^{3P} \rightarrow 2s^2 \ ^1S) = 97 \text{ s}^{-1} \)

[C_{\text{III}}]: \( A(2s2p^{3P} \rightarrow 2s^2 \ ^1S) = 5.2 \cdot 10^{-3} \text{ s}^{-1} \)
<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>m</th>
<th>state</th>
<th>( n^{2S+1} L )</th>
</tr>
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<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1s</td>
<td>( 1^2S )</td>
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<td>±2</td>
<td>±2</td>
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