Ay 126: Selection Effects & Forbidden lines

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It was readily observed that some lines are bright and some are faint. The Bohr model failed to explain the intensities of the lines. The physics of intensities of lines had to await the development of quantum mechanics.

1 QM treatment

Let us consider absorption of an incident beam by a cell containing gas, say sodium. The electric field has a time variable amplitude which acts upon the electron. So we have to use the full Schrodinger equation (i.e. time dependent):

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{1}$$

The interaction of radiation with the atom adds a new Hamilton ("interaction Hamilton"). Since it is a perturbation the stationary eigen wavefunctions obtained derived from the unperturbed Hamiltonian

$$\Big[\frac{\mathbf{p}^2}{2m_e} + V\Big]\psi_n = E_n\psi_n, \qquad \langle\psi_i|\psi_j\rangle = \delta_{ij} \tag{2}$$

can be used as the basis set and a Fourier approach for the time domain part:

$$\Psi = \sum_n a_n(t)\psi_n \exp(-iE_n/\hbar) \tag{3}$$

We select $a_i(0) = 1$ for a particular state i at time, $t = 0$; naturally $a_{j\neq i} = 0$. Then $|a_j(t)|^2$ is the probability of finding the atom in an excited j after a time t.

The electric and magnetic field can be written in terms of the vector potential, $\mathbf{A}$ and electrostatic field, ϕ:

$$\mathbf{E} \;=\; -\nabla\phi - \frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}, \qquad \mathbf{B} = \nabla\times\mathbf{A}. \tag{4}$$

The radiation field can be regarded as superposition of plane waves periodic in time:

$$\mathbf{A} = \mathbf{A_0}\Big[e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} + e^{-i(\omega t - \mathbf{k}\cdot\mathbf{r})}\Big] \tag{5}$$

The magnetic field can be ignored and the force on the electron is

$$\mathbf{F} = -e\nabla\phi - \frac{e}{c}\frac{\partial \mathbf{A}}{\partial t}. \tag{6}$$

We are interested in changes of the states of atom with time rather than state of the radiation field (that is the beam is much stronger than any consequence of it acting on the atom). Thus we can assume that the time and spatial components of the wave function are separable. From the force equation we see that $p_E = \frac{e}{c}\mathbf{A}$ acts as a momentum. Thus the perturbed Hamilton is

$$H = \frac{1}{2m_e}\Big(\mathbf{p} + \frac{e\mathbf{A}}{c}\Big)^2 + e\phi + V. \tag{7}$$

Unless there are very strong electric fields[1] we can ignore ϕ. After additional simplifications (not shown here) Schrodinger's equation becomes

$$i\hbar\frac{\partial \Psi}{\partial t} = \Bigg[-\frac{\hbar^2}{2m_e}\nabla^2 + \frac{i\hbar e}{m_e c}\mathbf{A}\times\nabla + \frac{e^2}{2m_e c^2} + V\Bigg]\Psi \tag{8}$$

The $\mathbf{A}^2$ is related to two-photon process and unless the beam is intense it can be ignored and thus

$$i\hbar\frac{\partial \Psi}{\partial t} = \Bigg[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e}{m_e}\mathbf{A}\cdot\mathbf{p} + V\Bigg]\Psi \tag{9}$$

The perturbing Hamilton is

$$H' = \frac{e}{m_e c}(\mathbf{A}\cdot\mathbf{p}) \tag{10}$$

The trial wavefunction (Equation 3) is then applied to the Schrodinger equation (Equation 1) and the desired solution, the transition probability per unit time, is

$$\frac{|a_j(t)|^2}{t} = \frac{2\pi e^2}{\hbar}A_0^2\Big|\Big\langle j\Big|\frac{\mathbf{e}\cdot\mathbf{p}}{m_e c}\exp(i\mathbf{k}\cdot\mathbf{r})\Big|i\Big\rangle\Big|^2\delta(E_j - E_i) \tag{11}$$

$$= \frac{2\pi}{\hbar}|\langle j|H'|j\rangle|^2\delta(E_j - E_i). \tag{12}$$

Here $\mathbf{e}$ is a unit vector along $\mathbf{E}$. [The $|a_j(t)|^2$ increases linearly with time (for small t) and thus the division by t. It can also be expressed as a rate by the usual differential approach.]

[1] I should look into possible astrophysical settings. Ditto for two-photon process; see below.

1.1 Approximation

The terminology of transition – dipole, quadrupole, magnetic – come from the approximations to $\exp(i\mathbf{k}\cdot\mathbf{r})$ in Equation 12. The first element of this exponential is the dipole. Let the wavelength of the incident radiation be λ. The other length scale is the size of the atom, a_0/Z. For optical photons, $\lambda \gg a_0/Z$ and thus the electric field is essentially constant over the atom. This constant electric field then polarizes the atom. We can use the commutation relations between $\mathbf{r}$ and $\mathbf{p}$ and switching to the notation of A and B coefficients, find

$$B_{ij} = \frac{2\pi}{\hbar^2}|\langle j|\mathbf{e}\cdot\mathbf{r}|i\rangle|^2. \tag{13}$$

Note that $|\langle \mathbf{r}Ii\rangle|^2 \sim a_0^2$ and using The B coefficient to obtain the A coefficient we can find

$$A \approx \frac{\omega^3}{\hbar c^3}(ea_0)^2 \sim 10^8\,\mathrm{s}^{-1} \tag{14}$$

2 Selection Rules

2.1 Allowed Transitions

The strongest transitions (with the largest A-coefficients) are those with large electric dipole term. The following selection rules must be satisfied:

1. Parity must change
2. One electron jumps to any another energy state ($|\Delta n| \geq 1$) but $\Delta l = \pm 1$.
3. $\Delta L = 0, \pm 1$
4. $\Delta J = 0, \pm 1$ with $\Delta J = 0 \rightarrow 0$ forbidden
5. $\Delta S = 0$

An allowed transition is denoted without square brackets.

2.2 Semi-forbidden or Intersystem Transitions

These satisfy all the rules of allowed transitions except $\Delta S \neq 0$. These are called as "semi"-forbidden or "inter-combination" of "inter-system" lines. Examples are transitions between singlet and triplet levels of Helium.

Such transitions have a single "]" on the right side of the line, e.g. N II]2143.4 Å$^3\mathrm{P}_2 - ^5\mathrm{S}^o_2$. The A-coefficients are a million times weaker.

2.3 Forbidden Transitions

Forbidden lines do not satisfy one or more of the four conditions listed above. They encompass a range of transitions (electric quadrupole or magnetic dipole) and the A coefficients are another factor of 10^2 to 10^6 weaker than those of semi-forbidden lines. The most famous forbidden lines are those resulting from transitions of the various terms associated with a ground state nl (Figure 1).

Ground configuration	Terms (in order of increasing energy)	Examples
$...ns^1$	$^2S_{1/2}$	H I, He II, C IV, N V, O VI
$...ns^2$	$^1S_0$	He I, C III, N IV, O V
$...np^1$	$^2P^o_{1/2,3/2}$	C II, N III, O IV
$...np^2$	$^3P_{0,1,2}$, $^1D_2$, $^1S_0$	C I, N II, O III, Ne V, S III
$...np^3$	$^4S^o_{3/2}$, $^2D^o_{3/2,5/2}$, $^2P^o_{1/2,3/2}$	N I, O II, Ne IV, S II, Ar IV
$...np^4$	$^3P_{2,1,0}$, $^1D_2$, $^1S_0$	O I, Ne III, Mg V, Ar III
$...np^5$	$^2P^o_{3/2,1/2}$	Ne II, Na III, Mg IV, Ar IV
$...np^6$	$^1S_0$	Ne I, Na II, Mg III, Ar III

Figure 1:

2.4 Highly Forbidden Transitions

The weakest lines with inverse A coefficients approaching millions of years (!) are transitions between the magnetic momentum of the electron and that of the the nucleus.

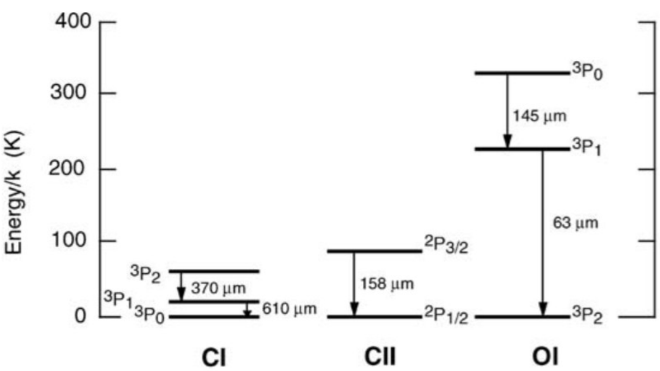
Table 5.1. Selection rules for atomic spectra. Rules 1, 2 and 3 must always be obeyed. For electric dipole transitions, intercombination lines violate rule 4 and forbidden lines violate rule 5 and/or 6. Electric quadrupole and magnetic dipole transitions are also described as forbidden.

	Electric dipole	Electric quadrupole	Magnetic dipole
1.	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$	$\Delta J = 0, \pm 1, \pm 2$ Not $J = 0 - 0, \frac{1}{2} - \frac{1}{2}, 0 - 1$	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$
2.	$\Delta M_J = 0, \pm 1$	$\Delta M_J = 0, \pm 1, \pm 2$	$\Delta M_J = 0, \pm 1$
3.	Parity changes	Parity unchanged	Parity unchanged
4.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
5.	One electron jumps Δn any $\Delta l = \pm 1$	One or no electron jumps Δn any $\Delta l = 0, \pm 2$	No electron jumps $\Delta n = 0$ $\Delta l = 0$
6.	$\Delta L = 0, \pm 1$ Not $L = 0 - 0$	$\Delta L = 0, \pm 1, \pm 2$ Not $L = 0 - 0, 0 - 1$	$\Delta L = 0$

Figure 2: Summary of Selection Rules (Tennyson, J. 2005).

3 Famous Fine-structure lines

The most important forbidden lines in the interstellar medium. Only CI, CII, OI, SiII, SII, and FeII are present in the neutral medium. They are also present in the ionised medium, but generally in smaller amounts than more ionised species. The collision strengths Ω_{ul} are for collisions with electrons at a temperature of 10^4 K. The critical densities $n_{crit} = A_{ul}/\langle\sigma_{ul} v\rangle$ correspond to collisions either with electrons (for $T_e \simeq 10^4$ K), or with H_2 molecules when between round brackets (for $T_k \simeq 100$K).



Ion	Transition l–u	λ μm	A_{ul} s^{-1}	Ω_{ul}	n_{crit} cm^{-3}
C I	$^3P_0-^3P_1$	609.1354	7.93×10^{-8}	–	(500)
	$^3P_1-^3P_2$	370.4151	2.65×10^{-7}	–	(3000)
C II	$^2P_{1/2}-^2P_{3/2}$	157.741	2.4×10^{-6}	1.80	47 (3000)
N II	$^3P_0-^3P_1$	205.3	2.07×10^{-6}	0.41	41
	$^3P_1-^3P_2$	121.889	7.46×10^{-6}	1.38	256
	$^3P_2-^1D_2$	0.65834	2.73×10^{-3}	2.99	7700
	$^3P_1-^1D_2$	0.65481	9.20×10^{-4}	2.99	7700
N III	$^2P_{1/2}-^2P_{3/2}$	57.317	4.8×10^{-5}	1.2	1880
O I	$^3P_2-^3P_1$	63.184	8.95×10^{-5}	–	2.3×10^4 (5×10^5)
	$^3P_1-^3P_0$	145.525	1.7×10^{-5}	–	3400 (1×10^5)
	$^3P_2-^1D_2$	0.63003	6.3×10^{-3}	–	1.8×10^6
O II	$^4S_{3/2}-^2D_{5/2}$	0.37288	3.6×10^{-5}	0.88	1160
	$^4S_{3/2}-^2D_{3/2}$	0.37260	1.8×10^{-4}	0.59	3890
O III	$^3P_0-^3P_1$	88.356	2.62×10^{-5}	0.39	461
	$^3P_1-^3P_2$	51.815	9.76×10^{-5}	0.95	3250
	$^3P_2-^1D_2$	0.50069	1.81×10^{-2}	2.50	6.4×10^5
	$^3P_1-^1D_2$	0.49589	6.21×10^{-3}	2.50	6.4×10^5
	$^1D_2-^1S_0$	0.43632	1.70	0.40	2.4×10^7
Ne II	$^2P_{1/2}-^2P_{3/2}$	12.8136	8.6×10^{-3}	0.37	5.9×10^5
Ne III	$^3P_2-^3P_1$	15.5551	3.1×10^{-2}	0.60	1.27×10^5
	$^3P_1-^3P_0$	36.0135	5.2×10^{-3}	0.21	1.82×10^4
Si II	$^2P_{1/2}-^2P_{3/2}$	34.8152	2.17×10^{-4}	7.7	(3.4×10^5)
S II	$^4S_{3/2}-^2D_{5/2}$	0.67164	2.60×10^{-4}	4.7	1240
	$^4S_{3/2}-^2D_{3/2}$	0.67308	8.82×10^{-4}	3.1	3270
S III	$^3P_0-^3P_1$	33.4810	4.72×10^{-4}	4.0	1780
	$^3P_1-^3P_2$	18.7130	2.07×10^{-3}	7.9	1.4×10^4
S IV	$^2P_{1/2}-^2P_{3/2}$	10.5105	7.1×10^{-3}	8.5	5.0×10^4
Ar II	$^2P_{1/2}-^2P_{3/2}$	6.9853	5.3×10^{-2}	2.9	1.72×10^6
Ar III	$^3P_2-^3P_1$	8.9914	3.08×10^{-2}	3.1	2.75×10^5
	$^3P_1-^3P_0$	21.8293	5.17×10^{-3}	1.3	3.0×10^4
Fe II	$^6D_{7/2}-^6D_{5/2}$	35.3491	1.57×10^{-3}	–	(3.3×10^6)
	$^6D_{9/2}-^6D_{7/2}$	25.9882	2.13×10^{-3}	–	(2.2×10^6)