II. Astronomical Applications

1 The Lyman alpha transition 2p - 1s in hydrogen

We calculate the spontaneous transition rate from the $n = 2, l = 1$ state to the ground ($n = 1, l = 0$) state of atomic hydrogen, producing the Lyman α line at 1216Å. As n changes, we look for the electric dipole moment. The selection rule requires l to change by unity, and since the ground state has $l = 0$ the upper state must be the $l = 1$ state.

The upper state is $|Xm\rangle = R_{2,1}(r)Y_{1,m}(\theta, \phi)$ where $R_{2,1}$ is the hydrogen radial wave function for $n = 2,\ l = 1$ and $Y_{1,m}$ is the spherical harmonic corresponding to $l = 1$ and $m = 1, 0, -1$, which latter is the component of angular momentum (divided by $\hbar$) in the z direction. We do not know which value of m our initial state has, but it will turn out that it doesn't matter (as it shouldn't — the transition doesn't depend on which way is up!). The lower state is $|Y\rangle = R_{1,0}(r)Y_{0,0}(\theta, \phi)$.

Matrix elements are

$$\langle Y|\mathrm{op}|X\rangle = \int R_Y^*(r)Y_Y^*(\theta,\phi)\ \mathrm{op}\ R_X(r)Y_X(\theta,\phi)\ r^2 dr d\Omega$$

The radial and angular parts of the hydrogen wave functions are:

$$R_{1,0}(r) = (2/a_0^{3/2})e^{-r/a_0}, \qquad R_{2,1}(r) = (r/\sqrt{24a_0^5})e^{-r/2a_0}$$

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}} \qquad Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} \qquad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

Remember that for the spherical harmonics Y

$$\int Y^*_{l',m'} Y_{l,m}\ d\Omega = \delta_{l',l}\ \delta_{m',m}.$$

The cartesian components of $\mathbf{r}$ can be written in polar coordinates as

$$x = r\ \sin\theta\cos\phi = r\ \sqrt{\frac{2\pi}{3}}\ (Y^*_{1,-1} - Y^*_{1,1})$$

$$y = r\ \sin\theta\sin\phi = r\ \sqrt{\frac{2\pi}{3}}\ (Y^*_{1,-1} + Y^*_{1,1})$$

$$z = r\ \cos\theta = r\ \sqrt{\frac{4\pi}{3}}\ Y^*_{1,0}$$

The second equalities in these expressions (got by inspection) will be used to calculate matrix elements, using the orthonormality of the spherical harmonics. Since $Y_Y^* = Y_{0,0}^*$ is constant, the angle integrals simplify to different applications of the orthonormality conditions on the Y's. We want $|\langle Y|\mathbf{r}|X\rangle|^2 = |\langle Y|x|X\rangle|^2 + |\langle Y|y|X\rangle|^2 + |\langle Y|z|X\rangle|^2$.

For example,

$$\langle Y|x|Xm\rangle = \int r^3 R_{1,0}(r) R_{2,1}(r)\, dr \int Y^*_{0,0}(\theta,\phi) \frac{x}{r} Y_{1,m}(\theta,\phi)\, d\Omega = F\sqrt{\frac{1}{6}}(\delta_{m,-1} - \delta_{m,1})$$

where F is the radial integral which is straightforward[1] to do and equals $(2^{15/2}/3^{9/2})a_0$.

Also,

$$\langle Y|y|Xm\rangle = F\sqrt{\frac{1}{6}}(\delta_{m,-1} + \delta_{m,1}), \qquad ; \ \langle Y|z|Xm\rangle = F\sqrt{\frac{1}{3}}\delta_{m,0}.$$

It follows that $r^2_{YX} = |\langle Y|\mathbf{r}|Xm\rangle|^2 = F^2/3 = 0.555 a_0^2$ whatever the value of m.

Now we can write down the spontaneous transition rate (Einstein A value) which is

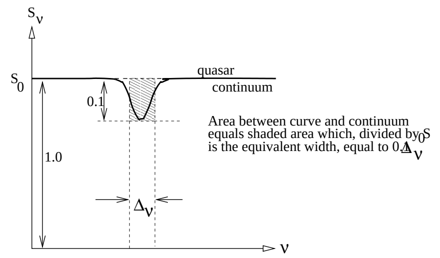
$$w_{spon}(2p \rightarrow 1s) = \frac{4\omega^3}{3\hbar c^3} \frac{e^2}{4\pi\epsilon_0} r^2_{YX} = 6.3\, 10^8 \ \ \mathrm{s}^{-1}.$$

This line, in the ultra-violet locally, is shifted into visibility at high redshift. The large value of transition rate means it is a very strong line in absorption, and hydrogen clouds in the line of sight to a distant ($z > 1.7$) quasar will show themselves as Lyman α lines at their own local redshift. The optical depth is (cf. sections 4.1 and 3.5; $n_u/n_l \simeq 0$)

$$\tau_\nu = l\kappa_\nu = N_l g_u \frac{\lambda^2}{8\pi} w_{spon}(2p \rightarrow 1s)\ \phi_\nu$$

where N_l is the column density of H atoms in the ground level and $g_u = (2l+1)_u = 3$.

Measuring column density from the depth of a spectrum line : We can determine the column density of an H cloud (assumed to have constant density and temperature throughout) which has a measured optical depth at the centre of the line.



If the flux density in the continuum on either side of the line is S_0, the line spectrum is $S_0\ e^{-\tau_\nu}$. The area between the spectrum and the extrapolated continuum (divided by the continuum value, and therefore measured in Hz) is the *equivalent width*:

$$\mathcal{W} = \int 1 - e^{-\tau_\nu}\, d\nu$$

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[1]

$$\int_0^\infty r^n e^{-\alpha r}\, dr = \left(-\frac{\partial}{\partial\alpha}\right)^n \int_0^\infty e^{-\alpha r}\, dr = \left(-\frac{d}{d\alpha}\right)^n \left(\frac{1}{\alpha}\right) = \frac{n!}{\alpha^{n+1}}$$

Reference to the diagram shows the area in question as a shaded block with the same depth as the line, and therefore the same effective width.

If the largest (central) value of τ_ν is much less than unity, then

$$\mathcal{W} \simeq \int \tau_\nu \, d\nu = N_l \frac{g_u}{g_l} \frac{\lambda^2}{8\pi} w_{spon}$$

where $N_l = \int n_l \, dl \simeq n_l \, l \;\; \mathrm{m}^{-2}$ is the column density of H in the lower *level* through the cloud.

Now apply this to a particular case. QSO 0000-26, a quasar at redshift 4.127, was observed by *Lu, Sargent, Womble, and Takada-Hidai 1996, Ap. J. 472, 509* to have an intense Lyman forest shortward of the Lyman α emission line at 6230Å (in the photometric R band).

Flux density S The quasar magnitude derived from the data of *Kennefick et al. 1996, Astr. J. 111, 1816* is R=22.4. The flux density from a zero magnitude source in R is 3.0 10^{-23} W m^{-2} Hz^{-1}, so the flux density from this source is 3.2 10^{-32} W m^{-2} Hz^{-1}.

Resolution $\Delta\nu$ The observed velocity width of the thermal profile (*cf* section 4.3) is approximately 20 km s^{-1} (resolved by the HIRES spectrometer on the Keck telescope), so we take (via Doppler effect) $\Delta\nu = 20 \;\; \mathrm{km\ s}^{-1} / 1216\mathring{A} = 1.64 \; 10^{11}$Hz, and envisage the spectrum as a set of resolution elements that wide (like the shaded box in the diagram).

Photons per resolved element The quasar flux in one resolution element $\Delta\nu$ is therefore 5.4 10^{-21} W m^{-2}, and since the effective area of the Keck telescope is 70 m^2, and we estimate a throughput efficiency of 0.1, and the integration time was 12000 s, the number of detected Joules per resolution element is $12000 \times 70 \times 0.1 \times 5.4 \; 10^{-21} = 4.5 10^{-16}$. The energy per photon in the R waveband is 3.2 10^{-19} J, and so the number of detected photons per resolution element of spectrum is 1400.

Signal-to-noise ratio The square root of 1400 is 37, which is the signal-to-noise ratio per resolution element of spectrum (*Lu et al.* quote between 25 and 35). If we see a dip in a resolution element equal to four times this standard deviation (a '4σ' measurement), a safe detection limit, it is a dip of 148 photons in that resolution element, a fractional dip of 0.1. This, multiplied by the element width $\Delta\nu = 1.64 \; 10^{11}$ gives

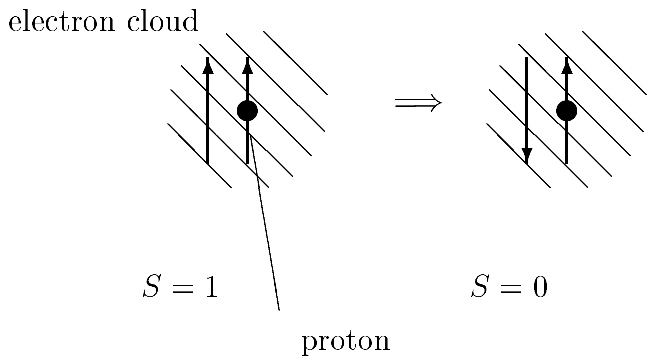
$$\mathcal{W} = 0.1\Delta\nu = \frac{3\lambda^2 w_{spon}}{8\pi} N_l$$

or

$$N_l = 0.1 \times \frac{8\pi}{3} \frac{\Delta\nu}{w_{spon}\lambda^2}$$

and in the present circumstances this is $N_l = N_{\mathrm{H}} = 7.4 \; 10^{15} \; \mathrm{m}^{-2} = 7.4 \; 10^{11} \; \mathrm{cm}^{-2}$. If the characteristic size is guessed to be 10pc the density must be $n_{\mathrm{H}} = 2.5 \times 10^{-8}$ cm^{-3} – it must be highly ionized (hence the guess at $T = 10^4$K, typical of HII regions). This, plus the near absence of a Gunn-Peterson effect, is the evidence for re-ionization of the Universe at early times, even in these protogalactic clouds.

2 The HI 21cm line



This is a spin-changing transition, with no change in the electronic orbital wave functions so no electric dipole or quadrupole moments, and is therefore magnetic dipole. It is a hyperfine structure transition, as the energy perturbation that splits the two S values of the ground state is the proton/electron spin interaction, and is therefore very small – the energy difference is 0.07 K, with the corresponding wavelength 21.1cm.

We calculate the spontaneous transition rate for $|X(S = 1)\rangle \rightarrow |Y(S = 0)\rangle$ by using the dipole formula, replacing the squared electric dipole $|e\mathbf{r}_{YX}|^2$ by the squared magnetic dipole $|\langle Y|(e\ 2\mathbf{s}/2mc)|X\rangle|^2$ associated with the electron spin (section I.3.7)[2] The spatial part of the integral in the transition matrix is unity, as the (purely spin) operator doesn't act on the orbital state which is the same before and after (*i.e.* $\psi(\mathbf{r})_Y = \psi(\mathbf{r})_X$); and there is no orbital ($\mathbf{L}$) matrix element because both before and after the state is the ground electronic state ($l = 0$). The remaining spin matrix element is between the upper state (X) in which spins are parallel (compounding to a spin of unity) and the lower state (Y) with proton and electron spins opposed, compounding to total spin zero.

The calculation is given in the appendix. Briefly, the states can be expressed in terms of individual or of combined spins. The initial state can be described as one of the three states $|+\rangle_e|+\rangle_p$, $(|+\rangle_e|-\rangle_p + |-\rangle_e|+\rangle_p)/\sqrt{2}$ and $|-\rangle_e|-\rangle_p$. These can be alternatively expressed as $|1, M_S\rangle$, $M_S = 1, 0, -1$. The final state, $|0, 0\rangle$ is also expressed as $(|+\rangle_e|-\rangle_p - |-\rangle_e|+\rangle_p)/\sqrt{2}$.

The spin operator $\mathbf{s} = s_x\mathbf{e}_x + s_y\mathbf{e}_y + s_z\mathbf{e}_z$ can be written in terms of the 'raising' and 'lowering' operators $s_x \pm is_y$ and s_z to arrive at

$$|\mathbf{s}_{YX}|^2 = (|s^+_{YX}|^2 + |s^-_{YX}|^2)/2 + |s_{z,YX}|^2.$$

The electron spin operators operate only on the electron spin function, and the upshot

[2]the spin operator should be the sum of electron and nuclear spins, but since each is multiplied by $h/2mc$, and $m_{proton} \gg m_{electron}$ the nuclear component is neglected.

is

$$|2\mathbf{s}_{XY}|^2 = \hbar^2, \qquad \text{any } M_S$$

(the independence of M_S, as for the Lyman α calculation, says that the result of an angle average should not depend on the direction of the chosen z-axis). The transition rate is therefore

$$w_{spon}(21\text{cm}) = \frac{4\omega^3}{3\hbar c^3}\frac{e^2}{4\pi\epsilon_0}\left(\frac{\hbar}{2mc}\right)^2 = 2.85\ 10^{-15}\ \text{s}^{-1} \simeq 10^7\ \text{y}$$

The critical density of this transition is $n_{\text{crit}} = 4.7\ 10^{-3}(T/1\,\text{K})^{0.77}\ \text{cm}^{-3}$ (*Kulkarni & Heiles in Hollenbach & Thronson 'Interstellar Processes'*). We may therefore assume that the levels are thermally populated (at a temperature far greater than 0.07K!). The statistical weights $(2S+1)$ are 3 and 1 for upper and lower energies, and we assume no other level is occupied, so 3/4 of H atoms are in the upper energy level. Thus the emissivity is

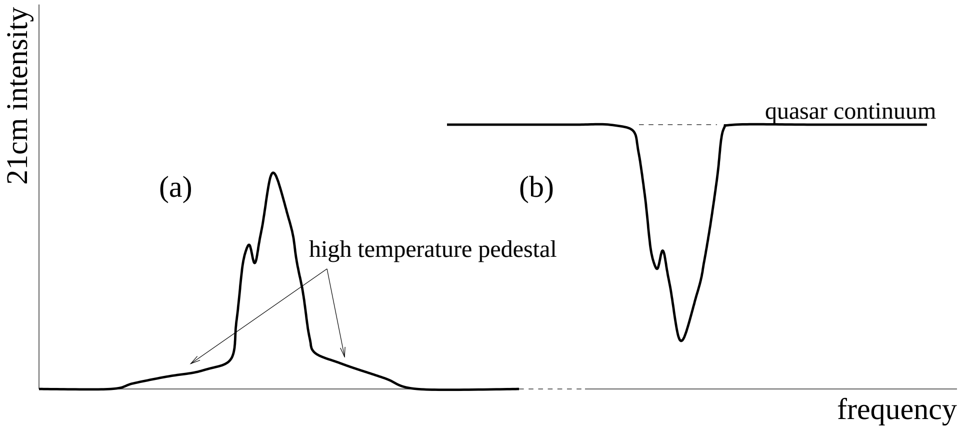
$$\mathcal{E}_\nu = \frac{h\nu}{4\pi} w_{spon} \frac{3n_{\text{H}}}{4}\phi_\nu = 1.6\ 10^{-40} n_{\text{H}}\phi_\nu.$$

The Rayleigh-Jeans limit ($h\nu \ll kT$) certainly applies in this case, and so

$\kappa_\nu = \mathcal{E}_\nu/B_\nu(T) = \mathcal{E}_\nu\lambda^2/2kT$, and

$$\tau_\nu = \frac{3hc^2 w_{spon}}{32\pi\nu kT} N_{\text{H}}\phi_\nu = 2.6\ 10^{-15}\left(\frac{N_{\text{H}}/1\ \text{cm}^{-2}}{T/1\ \text{K}}\right)\phi_\nu$$

The optical depth is inversely proportional to the gas kinetic temperature, while the emission is not. This has the following interesting consequence. If HI is observed in emission ($I_\nu = \mathcal{E}_\nu l$) in the plane of the galaxy, profile (a) might result. In absorption against a bright extragalactic continuum source in the same direction, profile (b) results, lacking the broad pedestal in profile (a). When first studied in detail (Radhakrishnan 1972, ApJ J suppl. 24) this indicated that there was a component, seen everywhere, that was at high temperature (≥ 1000 K). This result led directly to a 2-phase cloudy model of the interstellar medium.



Incidentally, the fact that in radio astronomy the Rayleigh-Jeans limit so often applies has led to the use of *brightness temperature* T_b (and antenna temperature and a host of cousins) as a measure of specific intensity.

$$T_b = I_\nu/(2k\nu^2/c^2)$$

Similarly, since velocity is related to frequency by the Doppler effect, velocity v is often used as the variable in the line profile.

$$\int I_\nu \, d\nu = \int T_b \, dv \ \times \ 2k\nu^3/c^3$$

and the line strength (area under the profile) is quoted in Kelvin km s^{-1}.

Other uses for 21cm radiation : mapping spiral arms in our Galaxy— mapping spiral arms in other galaxies—measuring velocity vs. radius in external spirals to detect dark halos by their gravitation—measuring velocity width in distant galaxies to estimate maximum rotational velocity, which correlates with luminosity (Tully-Fisher relation) to determine distances.

3 The CO molecule

At low excitation energies (collisions in a gas at a few 10's K, for instance), the molecule behaves like a rigid rotatator (dumbbell). The Hamiltonian is

$$H = \frac{\mathbf{J}^2}{2I}$$

where $\mathbf{J}$ is the angular momentum operator, and the eigenstates are represented by the spherical harmonics $Y_{JM}(\theta, \phi)$. The operator which is the square of the AM operator, $\mathbf{J}^2$, has eigenvalues $J(J+1)\hbar^2$, and the z component, J_z, has eigenvalues $M\hbar$ where $M = J, J-1, J-2, ... - J$. The moment of inertia I about the centre of mass is $\sum m_n r_n^2 = \mu R^2$ where the reduced mass μ is $6.8\mathrm{m_H}$ and the interparticle separation is 1.1Å. Thus

$$\frac{\hbar^2}{2I} = 2.7K$$

and the first few rotational levels are easily excited in cool gas.

The electric dipole moment $\mathbf{d} = e\bar{\mathbf{r}}$ is 0.11 Debye (4.8 Debye $\equiv |e| \times 1$Å, so $\bar{\mathbf{r}} =$ 0.0229Å), and is so small because the molecule is so nearly symmetric. The dipole moment operator in this case is the sum of $e_i \mathbf{r}_i$ over all the particles in the atom (28 electrons and two nuclei), but fortunately the electrons move so rapidly that their position can be related to the 'static' nuclei, and provided we exclude vibration of the nuclei the initial and final states of the electrons in this frame will be the same, and the integral with respect to electron positions gives a mean (expectation) value for the vector $e_i \mathbf{r}_i$, say $e\bar{\mathbf{r}}$, whose only change will be its (relatively) slow rotation in 3-space, for which the remaining wave functions are sperical harmonics.

The matrix elements $\langle Y|\mathbf{r}|X\rangle = \langle J'M'|\bar{\mathbf{r}}|JM\rangle$ are

$$\mathbf{r}_{YX} = \int Y^*_{J',M'}(\theta,\phi)\, \bar{\mathbf{r}}\, Y_{J,M}(\theta,\phi) d\Omega = \bar{r} \int Y^*_{J',M'}(\theta,\phi)\, \mathbf{n}\, Y_{J,M}(\theta,\phi) d\Omega.$$

These have exactly the same form as the angular part of the Lyman α calculation - at least if Y is a state with $J' = 0$ and X with $J = 1$, and so the squared modulus of the angle integral is 1/3 in this case as well. For other J values, tables of integrals of spherical harmonics give the algebraic functions of J, J' that result.

The transition rate is therefore

$$w_{spon}(J = 1 \to 0) = \frac{4\omega^3}{3\hbar c^3} \frac{e^2}{4\pi\epsilon_0} (\bar{r}^2/3) = 7.4\ 10^{-8}\ \mathrm{s}^{-1}.$$

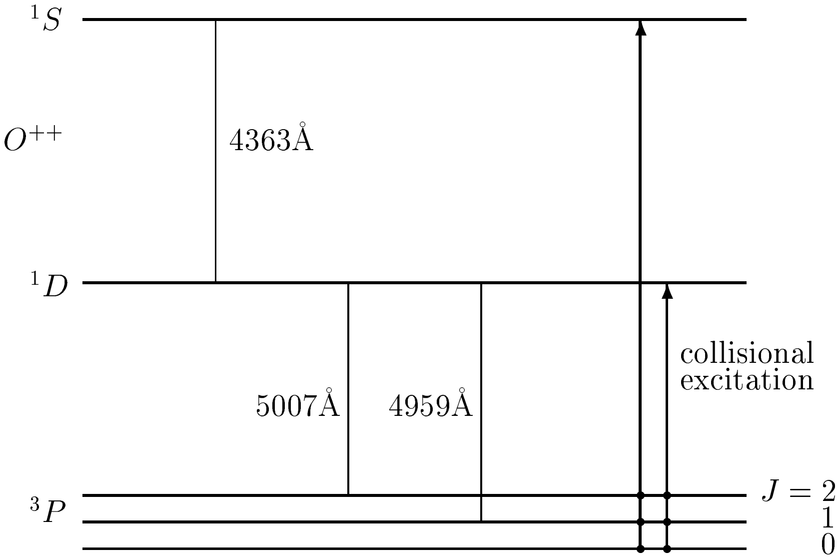
This is the main transition, radiating at 2.6mm, by which molecular gas has been detected and mapped in the Universe.

For interest, the rate for $J \to J - 1$ is the above rate times $3J/(2J+1)$.

4 Fine structure excited by electron collisions: diagnostic lines

4.1 the O^{++} ground state : $2p^2$

LS coupling gives three terms in the ground state: ^3P, ^1D, ^1S, and this is true for the isoelectronic sequence N^+, C, and for any other p^2 configuration.



Consider collisional excitation of the D term, and of the S term. The P term is treated as a single state. The important number is (*Osterbrock, AGN*[2]): $\langle \sigma v \rangle_{^1D \to ^3P} / \langle \sigma v \rangle_{^1S \to ^3P} = 7.75$. The critical densities (part I section 6.3) are high enough that we use the low density limit (each collision leads to a photon emission).

$$\mathcal{E}_{ul} = \frac{h\nu}{4\pi} n_l n_e \langle \sigma v \rangle_{lu} = \frac{h\nu}{4\pi} n_l n_e (g_u/g_l) \langle \sigma v \rangle_{ul} e^{-\Delta E/kT}$$

Applying this to $^3P \to ^1D$ and $^3P \to ^1S$ gives

$$\frac{\mathcal{E}_{4363\text{Å}}}{\mathcal{E}_{5007\text{Å}}} = \left(\frac{4}{3}\right) \frac{5007}{4363} \frac{\langle \sigma v \rangle_{(S,P)}}{\langle \sigma v \rangle_{(D,P)}} e^{-\Delta E_{4363}/kT} = 0.20 e^{-32900/T}.$$

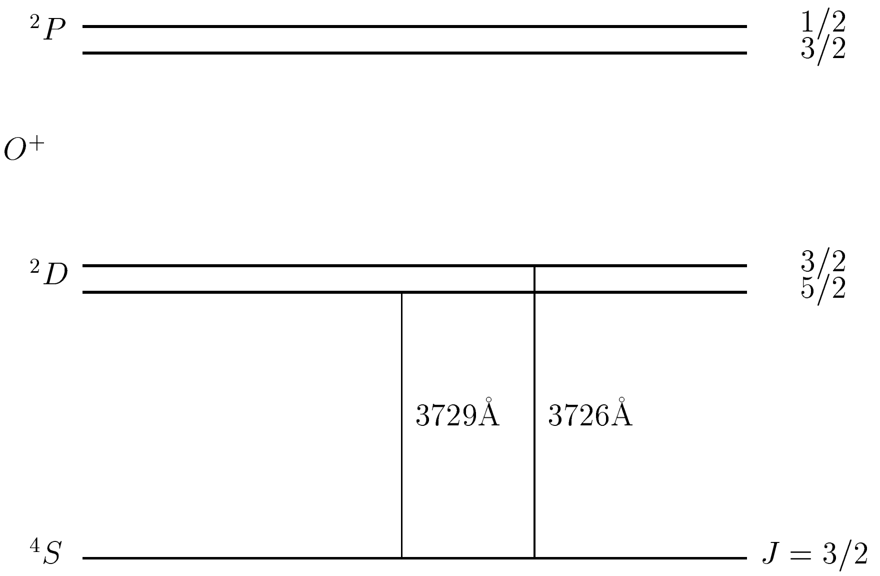
The factor (4/3) arises because approximately 3/4 of the transitions from the D level give the λ5007Å line.

Thus the intensity ratio of the 4363Å and 5007Å lines is highly temperature sensitive. Below 8000K the 4363Å line is hard to detect.

In very high density ($n_e >> 10^5$ cm^{-3}) HII regions, such as the very young 'ultra-compact HII regions', the critical density is exceeded, and a full level calculation is required, as given in part I, section 6.3.

4.2 the O^+ ground state : $2p^3$

(Also for N, S^+, etc)



Consider the equilibrium of the ^4S and ^2D terms. For each of the D levels separately

$$\frac{n_u}{n_l} = \frac{(g_u/g_l)e^{-(E_u-E_l)/kT}}{1 + n_{\rm crit,e}/n_e}$$

and so the ratio gives

$$\frac{n_u(3/2)}{n_u(5/2)} = \frac{2}{3}\,\frac{1 + n_{\rm crit,e(5/2)}/n_e}{1 + n_{\rm crit,e(3/2)}/n_e}.$$

The latter equality has neglected the small difference in energy between the two upper levels (only 29K); and the ratio of statistical weights $(2J+1)$ of the upper levels is 2/3. Now

$$n_{\rm crit,e}(3/2) = (g_l w_{spon}/\langle\sigma v\rangle)_{^2D_{\frac{3}{2}}\to{}^4S} = 1.6\ 10^4 {\rm cm}^{-3}$$

$$n_{\rm crit,e}(5/2) = (g_l w_{spon}/\langle\sigma v\rangle)_{^2D_{\frac{5}{2}}\to{}^4S} = 3.1\ 10^3 {\rm cm}^{-3}$$

at 10^4 K. The rate $\langle\sigma v\rangle)_{^2D_{\frac{3}{2}}\to{}^4S}$ equals $\langle\sigma v\rangle)_{^2D_{\frac{5}{2}}\to{}^4S}$.

The ratio of the emissivity of the lines at 3726Å and 3729Å is $w_{spon}(3/2)/w_{spon}(5/2)$ times the number ratio above, and gives therefore at *low* density

$$I_{3726}/I_{3729} = 0.67$$

while at high density

$$I_{3726}/I_{3729} = (2/3)\ w_{spon}(3/2)/w_{spon}(5/2) = 3.33$$

In between, in the density range $10^3 - 10^5$ cm^{-3}, the density dependence in the density ratio makes the intensity ratio a unique function of electron density, giving an excellent (and reddening-free) means of measuring density in ionized gas regions.

The $3p^2$ structure of S^+ is identical, producing the density sensitive line pair at 6716Å and 6732Å.

5 Quadrupole emission by H_2

The hydrogen molecule is *homopolar* and therefore has no dipole emission from transitions between ro/vibrational levels in the ground electronic state. These transitions are by electric quadrupole emission (no parity change in ground state, and no spin change, therefore no magnetic dipole transition).

The spontaneous transition rate is given (see section I.3.3 and I.3.7) by

$$w(\Omega)_{spon} d\Omega = \frac{\omega^3 d\Omega}{2\pi\hbar c^3}\frac{e^2}{4\pi\epsilon_0}\left|-i\mathbf{k}.\frac{1}{2}(\mathbf{rr})_{YX}.\mathbf{e}_{\mathbf{k},\alpha}\right|^2 = \frac{\omega^5 d\Omega}{8\pi\hbar c^5}\frac{e^2}{4\pi\epsilon_0}\left|\mathbf{n}.(\mathbf{rr})_{YX}.\mathbf{e}_{\mathbf{k},\alpha}\right|^2$$

Note that unit vector $\mathbf{n} = (c/\omega)\mathbf{k}$ is perpendicular to $\mathbf{e}_{\mathbf{k},\alpha}$. Without changing the result we can replace $\mathbf{rr}$ by $\mathbf{rr} - (1/3)r^2\mathbf{I}$, which has zero trace (sum of diagonal elements), since $\mathbf{n}.\mathbf{I}.\mathbf{e}_{\mathbf{k},\alpha} = 0$. This zero trace property will be useful later. We write $\mathbf{Q} = (\mathbf{rr} - (1/3)r^2\mathbf{I})_{YX}$ for convenience.

To find the transition rate in all directions and any polarization we need to sum over polarizations $\alpha = 1, 2$ and integrate over all photon directions $d\Omega$. The sum is as in the footnote to section I.3.3 with $\mathbf{n}.\mathbf{Q}$ taking the place of $\mathbf{r}_{YX}$, and so we need to evaluate the angle integral

$$F = \int_\Omega \left(|\mathbf{n}.\mathbf{Q}|^2 - |\mathbf{n}.\mathbf{Q}.\mathbf{n}|^2\right)\, d\Omega$$

Now $\mathbf{Q}$ is in general complex. Put $\mathbf{Q} = \mathbf{U} + i\mathbf{V}$, $\quad$ ($\mathbf{U}$, $\mathbf{V}$ real). Then

$$|\mathbf{n}.\mathbf{Q}|^2 = (\mathbf{n}.\mathbf{U})^2 + (\mathbf{n}.\mathbf{V})^2 \qquad \text{and} \qquad |\mathbf{n}.\mathbf{Q}.\mathbf{n}|^2 = (\mathbf{n}.\mathbf{U}.\mathbf{n})^2 + (\mathbf{n}.\mathbf{V}.\mathbf{n})^2$$

Since $\mathbf{U}, \mathbf{V}$ are real symmetric dyadics, they can be diagonalized by a frame rotation (orthogonal transform) in which vectors and dyadics change as follows :

$$\mathbf{n}' = \mathbf{R}.\mathbf{n}, \quad \mathbf{U}' = \mathbf{R}.\mathbf{U}.\mathbf{R}^{tr}, \quad \mathbf{R}.\mathbf{R}^{tr} = \mathbf{I}.$$

In this transform, $(\mathbf{n}.\mathbf{U}.\mathbf{n})^2$ and $(\mathbf{n}.\mathbf{U})^2$ are invariant (a similar but not necessarily identical rotation will diagonalize $\mathbf{V}$). Thus we can write for example

$$F_U = \int_\Omega \left((\mathbf{n}.\mathbf{U})^2 - (\mathbf{n}.\mathbf{U}.\mathbf{n})^2\right)\, d\Omega = \int_\Omega \left((\mathbf{n}'.\mathbf{U}')^2 - (\mathbf{n}'.\mathbf{U}'.\mathbf{n}')^2\right)\, d\Omega$$

Now $U' = u_1\mathbf{e}_x\mathbf{e}_x + u_2\mathbf{e}_y\mathbf{e}_y + u_3\mathbf{e}_z\mathbf{e}_z$ in the diagonalizing coordinate frame, and so

$$F_U = \int_\Omega \left(\sum n'^2_i u_i^2 - \left(\sum n'^2_i u_i\right)^2\right) d\Omega = 4\pi\left(\sum_i (\overline{n'^2_i} - \overline{n'^4_i})u_i^2 - \sum_{j\neq k}\overline{n'^2_j n'^2_k}u_j u_k\right)$$

where the overline denotes the angle average $\int(...)\, d\Omega/4\pi$. The angle integration is invariant to the frame rotation, and each direction cosine n'_i behaves in the same way to give

$$\overline{n'^2_i} = 1/3, \quad \overline{n'^4_i} = 1/5, \quad \overline{n'^2_j n'^2_k} = 1/15.$$

Thus

$$F_U = \frac{4\pi}{15}\left(2\sum_i u_i^2 - \sum_{j\neq k} 2u_j u_k\right).$$

Now we can use the zero trace property (preserved under rotation) $\sum u_i = 0$. Squaring this we get the second sum to equal $-\sum u_i^2$, and

$$F_u = \frac{4\pi}{5}\sum u_i^2.$$

Also Trace $\mathbf{U}.\mathbf{U}$ = Trace $\mathbf{U}'.\mathbf{U}' = \sum u_i^2$, so

$$F_U = \frac{4\pi}{5}\text{Trace }(\mathbf{U}.\mathbf{U})$$

and similarly for $\mathbf{V}$. Then since $\mathbf{U}$ and $\mathbf{V}$ are symmetric, Trace $\mathbf{Q}^*.\mathbf{Q}$ $(= |\mathbf{Q}|^2)$ equals the sums of the traces of $\mathbf{U}.\mathbf{U}$ and $\mathbf{V}.\mathbf{V}$. Finally

$$F = F_U + F_V = \frac{4\pi}{5}|\mathbf{Q}|^2$$

and the transition rate $X \to Y$ with a photon going in any direction and with any polarization is

$$w_{spon} = \frac{1}{10}\,\frac{\omega^5}{\hbar c^5}\,\frac{e^2}{4\pi\epsilon_0}\,|\mathbf{Q}|^2$$

The Born-Oppenheimer approximation allows us to calculate the dependence of the rate on J_X, J_Y values, by separating electronic, vibrational and rotational parts of the transition – the electrons move so fast that they populate a wave function determined by the instantaneous positions of the nuclei, specified in this case by their separation R. The vibrational wave functions with quantum number v are functions of R only. Rotation of the molecule is so slow that the moments of inertia are determined by the mean intermolecular distances, averaged over the vibrational states. Then for instance

$$|X\rangle = |electronic\rangle|v\rangle|JM\rangle$$

and transition matrix elements in the ground state (no electronic state change) of an operator Op are

$$\langle Y|\text{Op}|X\rangle = \langle J_Y M_Y|\overline{\text{Op}}|J_X M_X\rangle$$

where $\overline{\text{Op}}$ is the quantity $\langle v_Y|\langle\text{Op}(R)\rangle|v_X\rangle$, and $\langle\text{Op}(R)\rangle$ is the expectation value of operator with respect to the electronic states at internuclear separation R. These calculations are done in a frame in which the molecule is not rotating, say with the line joining the nuclei along the z-axis.

Now the rate for a transition from a given state X to a state Y should be summed over M_Y since the final orientation of the molecule is immaterial. The result is

$$w_{spon,tot} = \frac{1}{10}\,\frac{\omega^5}{\hbar c^5}\,\frac{e^2}{4\pi\epsilon_0}\sum_{M_Y}|\langle J_Y M_Y|\,\overline{\mathbf{rr} - \tfrac{1}{3}r^2\mathbf{I}}\,|J_X M_X\rangle|^2.$$

Now we introduce **spherical tensors** T_{km}, $m = -k, ... + k$. These are operators which transform under rotation of axes like spherical harmonics $Y_{km}(\theta,\phi)$, and like them consist of $(2k+1)$ elements for each value of k that they represent. The elements of any cartesian tensor can be expressed as a linear combination of the corresponding spherical tensor. For example a scalar is proportional to T_{00}, invariant to rotation; a vector V_i, $i = 1, 3$ can be expressed in terms of the three elements T_{1m}, and a *symmetrical, traceless* tensor (which has five independent elements) can be expressed in terms of T_{2m}. If the symmetrical traceless cartesian tensor is q_{ij}, then the spherical tensor components can be written (by comparison of the elements of $\mathbf{rr} - \frac{1}{3}r^2\mathbf{I}$ written in polar coordinates, with the values of $Y_{km}(\theta.\phi)$) :

$$T_0^2 = -\sqrt{\tfrac{3}{2}}q_{zz}$$
$$T_{\pm 1}^2 = \pm(q_{xz} \pm iq_{yz})$$
$$T_{\pm 2}^2 = -\tfrac{1}{2}(q_{xx} - q_{yy} \pm 2iq_{xy}).$$

The normalizing constant of proportionality has been chosen so that

$$\sum_m |T_{km}|^2 = \sum_{i,j} |q_{i,j}|^2$$

A state with known total angular momentum J and z component M, $|JM\rangle$, can be expressed in wave functions in a frame rotated with respect to the first. J will be the same, but the z component will not. However, the new state function $|JM\rangle_{new}$ will be a linear combination of the $|JM\rangle$ since these are a complete set for states of angular momentum J

$$|JM\rangle_{new} = \sum_{M}^{\prime} D^J_{M'M}|JM'\rangle.$$

Tops : If a rigid body is so described, the rotation can be from body-fixed to space-fixed frame, and in the body-fixed frame the wave function is a constant (not changing with ϕ, etc; it's fixed!). Thus the space-fixed wave function for a rigid body is a linear sum of D matrices. If the object has an axis of symmetry aligned with the body-fixed z axis, the modulus of the wave function should be independent of rotation by an arbitrary angle χ about the z axis, which can only be true if there is only one term on the right hand side (each is proportional to $e^{-iM'\chi}$). This means that the space-fixed state function is

$$|JKM\rangle = \sqrt{\frac{2J+1}{8\pi^2}}D^{*J}_{MK}(\phi,\theta,\chi).$$

Here K is the component of angular momentum about the axis of symmmetry and the complex conjugate is taken to get the correct χ dependence.

Since the spherical tensors transform like spherical harmonics which are themselves wave functions, they transform by the same rule. This means that symmetrical top matrix elements such as $\langle J'M'|T_{km}|JM\rangle = \int \Psi^*_{J_Y M_Y}\, T_{2m}\, \Psi_{J_X M_X} d\Omega$ transform under rotation with a matrix involving products of three D matrices integrated over all directions.

Unsurprisingly, the D matrices are related to the amplitudes of the angular momentum states resulting from coupling two angular momenta $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$:

$$|JM\rangle = \sum_{1,2} \langle J_1 M_1 J_2 M_2 | JM\rangle |J_1 M_1 J_2 M_2\rangle$$

The only non-zero coefficients are those for which $M = M_1 + M_2$ and $J_1 + J_2 \geq J \geq |J_1 - J_2|$. The coefficients are the Clebsch-Gordan coefficients, and Wigner $3j$ symbols are defined by

$$\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} = \frac{(-1)^{J_1+J_2-M_3}}{\sqrt{2J_3+1}} \langle J_1 M_1 J_2 M_2 | J_3 M_3\rangle$$

We can use the result (which comes from the orthonormality of the $|JM\rangle$ functions)

$$\int D^{J_1}_{M_1' M_1}\, D^{J_2}_{M_2' M_2} D^{J_3}_{M_3' M_3}\, d\Omega = 8\pi^2 \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1' & M_2' & M_3' \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}.$$

From this can be derived the following expression for matrix elements in the space-fixed frame in terms of matrix elements in the body-fixed frame of a symmetrical top:

$$\sum_{m,M_Y} |\langle \alpha_Y J_Y M_Y | T_{km} | \alpha_X J_X M_X \rangle|^2 = (2J_Y + 1) \begin{pmatrix} J_Y & k & J_X \\ -K_Y & \mu & K_X \end{pmatrix}^2 |\langle \alpha_Y | \overline{T}_{k\mu} | \alpha_X \rangle|^2$$

where α stands for internal quantum numbers (electronic, vibrational, spin, angular momentum about axis) and the last factor contains the matrix element in body-fixed coordinates.

In the case of ground state transitions in H_2, $k = 2$, $K_X = K_Y = 0$ and so $\mu = K_Y - K_X = 0$. The right hand side of the equation contains the factor

$$(2J_Y + 1) \begin{pmatrix} J_Y & 2 & J_X \\ 0 & 0 & 0 \end{pmatrix}^2$$

which by consulting tables of $3j$ symbols becomes (use $J = J_X$):

$$\frac{3}{2}\frac{(J+1)(J+2)}{(2J+1)(2J+3)} \quad J_Y = J + 2$$

$$\frac{J(J+1)}{(2J-1)(2J+3)} \quad J_Y = J$$

$$\frac{3}{2}\frac{J(J-1)}{2J-1)(2J+1)} \quad J_Y = J - 2$$

In the body-fixed frame, $\langle \alpha_Y | \overline{T}_{k\mu} | \alpha_X \rangle$ can be replaced by $\sqrt{2/3}\overline{q_{zz}}$, and the transition rate is

$$w_{spon,tot} = \frac{1}{10}\frac{\omega^5}{\hbar c^5}\frac{e^2}{4\pi\epsilon_0} |\langle \alpha_Y | \overline{q_{zz}} | \alpha_X \rangle|^2 f(J_x, J_Y)$$

and the matrix element can be written

$$\int_R \Psi^*_{v_Y}(R) \int_e \rho(\mathbf{r}_e; R)(2z^2 - x^2 - y^2)\, d\mathbf{r}_e\, \Psi_{v_X}(R)\, dR$$

where ρ is the squared modulus of the wave function for all the charges in the body-fixed frame, at a nuclear separation of R. The Hönl-London factors $f(J_x, J_Y)$ are evidently 2/3 of the three values given above.

6 Photoionization

Only the non-relativistic, electric dipole, transition will be considered. This calculation can be carried out exactly for hydrogen (and hydrogen-like atomic systems).

The initial state has the electron in the hydrogen ground state

$$\psi_X = a_0^{-3/2}\, e^{-r/a_0}$$

and the photon states are as usual specified by $N_{\mathbf{k},\alpha}$. and the final state has the electron in a continuum state Y and the photon occupancies are $N'_{\mathbf{k},\alpha}$.

Since momentum and energy must be conserved, there is a unique relationship between final photon and electron states; although these states are each in a continuum, the integral over final states in the Golden Rule need be over only one of these as a consequence of momentum conservation. It is conventional to integrate over the density of final electron states.

How is the final state, a free Coulomb field state specified?

The time-reversed situation is easier to grasp. Here a free electron in the Coulomb field of the ion is elastically scattered, and there is some probability that it is captured, *i.e. recombined*. The initial electron state is represented by a plane wave at infinity plus a radially outward-moving scattered wave at infinity (*Landau & Lifshitz, Quantum Mechanics, §123*), with axial symmetry,

$$\psi_{rec} \sim e^{ikz} + f(\theta)e^{ikr}/r.$$

By expanding the plane wave in spherical waves,

$$e^{ikz} \overset{r\to\infty}{\longrightarrow} \frac{1}{2ikr}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)[(-1)l+1e^{-ikr}+e^{ikr}]$$

In a Coulomb field the wave with axial symmetry will have the form

$$\psi_{rec}^{(+)} = \frac{1}{2k}\sum_{l=0}^{\infty} C_l R_{kl}(r)P_l(\cos\theta),$$

The constants C_l are chosen to be $(i^l/2k)(2l+1)e^{i\delta_l}$ so that this has the asymptotic form given above. The resulting wave functions

$$\psi_{rec}^{(+)} = \frac{1}{2k}\sum_{l=0}^{\infty} i^l(2l+1)e^{i\delta_l}R_{kl}(r)P_l(\cos\theta)$$

where $R_{kl}(r)$ are Coulomb continuum radial wave functions and δ_l are the associated phase shifts (e.g. *Landau & Lifshitz, Quantum Mechanics, §36*).

The time-reversal of this, namely the situation we want to describe of an electron being liberated and travelling to infinity, is got by taking the complex conjugate ($[e^{-i\omega t}]^* = e^{+i\omega t}$), and then reversing the sign of $\mathbf{k}$ (since it was reversed by reversing t). Noting that $P_l(-\cos\theta) = (-1)^l P_l(\cos\theta)$ we arrive at the form for the free electron wave function representing the ionized state – a plane wave plus an *in-going* spherical wave! – which is given by

$$\psi_{rec}^{(-)} = \frac{1}{2k}\sum_{l=0}^{\infty} i^l (2l+1) e^{-i\delta_l} R_{kl}(r) P_l(\cos\theta).$$

Since this is a dipole transition from the s state, only the p wave ($l = 1$) need be retained in this expansion. Thus the final electron state is

$$\psi_Y = \frac{3}{2k}\cos\theta R_{k1}(r)$$

Now we can calculate the dipole transition matrix element

$$\int \psi_Y^* \mathbf{e}.\mathbf{r}\psi_X \; dV.$$

Before doing so, however, we'll re-do the bookkeeping. it makes more sense for a continuum process like this to specify the transition rate by a cross section σ_ν. Remember that cross section equals rate divided by flux, and that flux in a given photon state is $N_{\mathbf{k},\alpha} c$,

$$d\sigma =$$