III. QUANTUM PROCESSES INVOLVING BOUND ELECTRONS

7. Emission and Absorption in Atomic Systems

References:

- Rybicki & Lightman and Shu (the two texts)
- G. Herzberg, *Atomic Spectra and Atomic Structure*, 1944 (Dover Publications)

7.1 Review of Basic Atomic Physics

Up to now, we have considered radiation from a classical or macroscopic point of view. However, as we all know, some important properties of radiation (such as photon spin and momentum) cannot easily be explained or accounted for in these terms. The physics of the microscopic world differs in some important ways from that of the macroscopic world. I want to review briefly a few basic concepts pertaining to the "Alice-in-Wonderland" world of the atom where some of the classical theories of physics are not valid.

As an example, Maxwell's equations break down on the scale of atomic systems. The bound electron in an atom does not lose energy due to its accelerated motion but, in fact, is quite stable for long periods of time if it is in its ground state.

It's true that mass, momentum, and electric charge always have to be conserved. But, in the microscopic realm, there are three major differences arising from the quantum behavior of atomic systems:

(i) In a bound atom, the quantity "action" (which has units of energy $\times$ time or momentum $\times$ distance) can only change by *integral* multiples of h, Planck's constant. In quantitative terms, this can be written as Sommerfeld first expressed it:

$$\text{Action} \equiv \oint p_i \, dq_i = n_i h$$

where the integral extends over one period of the electron's motion, and p_i and q_i are the generalized momentum and its corresponding coordinate.

(ii) States of an atomic system whose characteristic actions differ by less than h cannot be distinguished. This is Heisenberg's "Uncertainty Principle".

(iii) Two particles with half-integer spin cannot occupy the same cell in phase space; that is, they cannot have the same position, momentum, and spin direction. This is the "Pauli Exclusion Principle".

The quantization of the atomic world even extends to phase space itself as we have seen and as statement (iii) above implies. Phase space volume has units of (action)^3 and the basic element is a cell of volume h^3. This follows from the Uncertainty Principle; particles within one phase cell are identical – that is, physically indistinguishable.

The existence of a fundamental volume in phase space is very important because it puts an upper limit on the density of fermions which obey the Pauli Exclusion Principle. For example, if we consider electrons, then the maximum number with momenta between p and $p + dp$ which can occupy a real volume V is

$$2V \times \frac{4\pi p^2\, dp}{h^3} .$$

The factor 2 here accounts for the fact that *two* electrons of opposite spin can fit into each cell without violating the Pauli rule. One can think of $8\pi p^2\, dp/h^3$ as the number of phase cells per unit volume of real space, each cell able to hold a maximum of one fermion.

If one is dealing with *bosons* with integer spin, then there is no limit in principle on the number of particles (or photons) which can occupy a phase space cell. However, one can argue (as we already have in §1.5 on p12) that a particular mean number can be expected for given physical conditions (e.g., density) and so, in this way, the *mean* boson density rather than the *maximum* density is determined by the fundamental phase space volume and Bose-Einstein or Boltzmann statistics.

As a further example of the quantization of the action principle, let's look at the possible angular momentum states of the atom and the selection rules which govern transitions between states. This is most easily done by considering the Bohr theory of the atom.

(a) Bohr-Sommerfeld Theory

The basic idea here is that angular momentum which has units of *action* is quantized in atomic systems. Consider the simple view of the atom which in the case of hydrogen consists of a single electron in orbit around a proton. In the more general case of a hydrogenic atom, there is a single electron moving in the Coulomb field of charge Ze outside closed shells. For a circular orbit,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r} \qquad \Longrightarrow \qquad r = \frac{Ze^2}{mv^2} .$$

The orbit radius cannot assume any value due to the quantization condition:

$$\oint mvr\, d\phi = 2\pi mvr = nh$$

which yields

$$r = \frac{n^2\hbar^2}{Zme^2} \qquad (n = 1, 2, 3, \ldots)$$

where $\hbar \equiv h/2\pi$. The Bohr radius $r_{\rm B}$ is associated with the smallest orbit ($n = 1$) for the hydrogen atom ($Z = 1$):

$$\begin{aligned} r_{\rm B} &= \frac{\hbar^2}{me^2} = 0.529\,\text{Å} , \\ v_{\rm B} &= \frac{e^2}{\hbar} = 2 \times 10^8\,\mathrm{cm\,s^{-1}} \sim 10^{-2}\mathrm{c} . \end{aligned}$$

This simplest of theories can be refined in at least three ways:

(i) Instead of the electron mass m, one should use the *reduced* mass, $\mu \equiv mM/(m+M)$, because the electron actually orbits the center of mass of the electron and the nucleus of mass M. Thus, deuterium (^{2}H) has slightly different energy states than does hydrogen (^{1}H).

(ii) In general, *elliptical* orbits are possible as well as circular ones. The quantization of angular momentum forces both the semi-major and the semi-minor axes to assume only *discrete* values. Applying Sommerfeld's action integral to both the radial and the azimuthal components of the momentum, p_r and p_ϕ, we can write

$$\begin{aligned} \oint p_r\, dr &= n_r h \,, \\ \oint p_\phi\, d\phi &= n_\phi h = (\ell + 1)\, h \,. \end{aligned}$$

The principle quantum number n is the sum of these two components: $n = n_r + n_\phi = n_r + \ell + 1$. One finds that the orbital axes are given by

$$\begin{aligned} a &= \frac{n^2\hbar^2}{Z\mu e^2} = \frac{n^2 r_{\mathrm{B}}}{Z} \qquad (n = 1, 2, 3, \ldots) \,, \\ b &= \frac{n(\ell+1)\hbar^2}{Z\mu e^2} = \frac{n(\ell+1) r_{\mathrm{B}}}{Z} \qquad (\ell = 0, 1, 2, \ldots, n-1) \,. \end{aligned}$$

Here, ℓ is the orbital momentum quantum number. Obviously, when $\ell = n - 1$ (the maximum value), the orbit is circular. Note that $\ell = 0$ does NOT correspond to a zero angular momentum orbit. However, in quantum mechanics, $\ell = 0$ *does* correspond to zero angular momentum of the *atom*, because the actual value of the angular momentum is $\sqrt{\ell(\ell+1)}\hbar$. This peculiar result is related to the Uncertainty Principle: if one specifies the angular momentum about one axis, it is *uncertain* about the other two axes. Thus, electron orbits are not confined to planes as they are in classical physics, but are free to rotate about *three* axes. This is consistent with the "electron cloud" picture of wave mechanics. For $\ell = 0$, the electron cloud has *spherical symmetry* because it does not rotate as a whole. For $\ell = 1$, the electron cloud is a rotating bar, and so on (see Herzberg, p44).

(iii) Sommerfeld applied relativistic mechanics to the Bohr atom and showed that the elliptical orbits precess about the center of mass just as Mercury precesses about the Sun. Wave mechanics, of course, tells us that not only the long axis rotates but also the *plane* of the orbit as well. Therefore, we shouldn't really picture electron orbits as miniature planetary orbits. But since each atomic state has a very definite angular momentum, it is still proper to think of electrons as moving about the nucleus (albeit in some complicated 3D fashion).

Note that the quantization of angular momentum is not some "axiom" of quantum mechanics but actually follows from the theory. One can find solutions of the Schrödinger equation only for *discrete* values of the angular momentum. That is, this is an *eigenvalue* problem. The easiest way to see this is to consider the De Broglie wavelength of an electron ($\lambda = h/mv$) in a circular orbit. The standing-wave condition that an integral number of waves fit into the circular orbit (namely, $n\lambda = 2\pi r$) is equivalent to Bohr's original quantization statement: $mvr = n\hbar$!

(iv) The Pauli Exclusion Principle limits the number of electrons in each orbital. The higher energy states obviously have a larger number of allowable angular momentum states (namely, $\ell = 0, 1, 2, \ldots, n-1$) and so will have higher statistical weights. That is, as n increases, more and more electrons will be allowed to occupy those states because more substates are available.

(b) **Energy States of a Hydrogenic Atom**

For circular orbits, the total energy is

$$E = -\frac{Ze^2}{r} + \frac{mv^2}{2} = -\frac{Ze^2}{r} + \frac{Ze^2}{2r} = -\frac{Ze^2}{2r} \, .$$

Since r is quantized ($r_n = n^2\hbar^2/Zme^2$), so is E; therefore,

$$E_n = -\frac{2\pi^2\mu e^4 Z^2}{n^2\hbar^2} \qquad \text{(use reduced mass)} \, .$$

In the absence of an external magnetic field and the weak interaction of the electron and nuclear spins, this energy is the same for all ℓ. That is, the energy depends only on the *semi-major* axis of the orbit – a classical result, as well, which applies to planets. A transition between two states n_1 and n_2 ($n_1 < n_2$, say) results in the absorption or emission of a photon of energy

$$h\nu = \frac{2\pi^2\mu e^4 Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where R is the Rydberg constant ($= 13.6\,\text{ev}$).

The interaction of the electron and nuclear spins results in a very small or "hyperfine" splitting of each state. The splitting is of order 10^{-5} ev and transitions between the two lowest states are responsible for the 21 cm line of atomic hydrogen.

There is a further splitting of each state in the presence of a magnetic field (Zeeman effect). This occurs because the orbital angular momentum of the electron gives rise to a loop current with an associated magnetic dipole. The magnitude of this dipole is $\sqrt{\ell(\ell+1)}\mu_{\mathrm{B}}$ ($\mu_{\mathrm{B}} \equiv$ the Bohr magneton $= e\hbar/2mc$) and the component along the magnetic field is "space quantized" according to

$$m_\ell \mu_{\mathrm{B}} \qquad (m_\ell = -\ell, -\ell+1, \ldots, 0, 1, 2, \ldots, \ell) \, .$$

Here, m_ℓ is the so called magnetic quantum number associated with ℓ; it distinguishes $2\ell + 1$ substates, each of which can be further split into two components corresponding to the two possible orientations of the electron spin relative to the external field (if it exists) or the nuclear spin (if it doesn't).

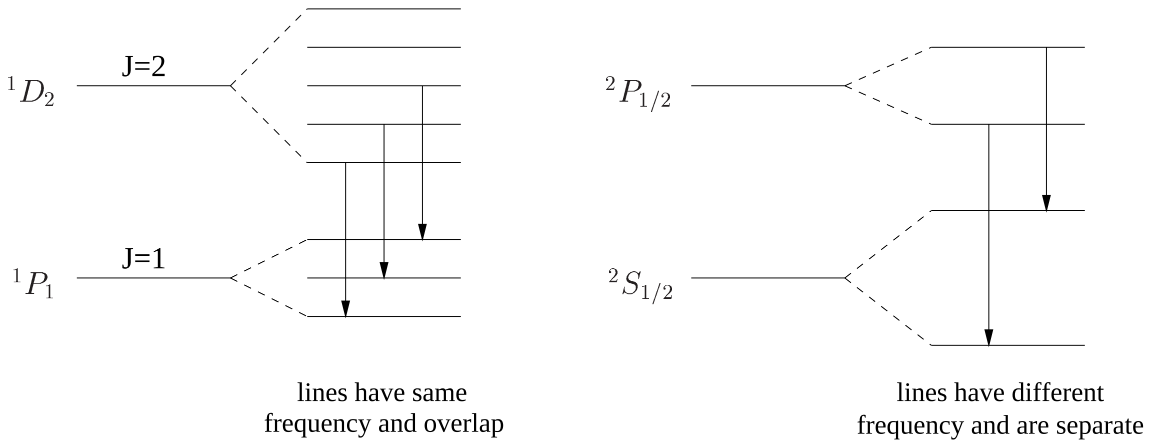
Actually, in the presence of *weak* fields, it is the *total* angular momentum J which is quantized (spatially, that is). This is the well-known Zeeman effect: $M_{\mathrm{J}} = -J, -J+1, \ldots, J$ with corresponding energies

$$E = E_o + \mathrm{g}\mu_{\mathrm{B}} H M_{\mathrm{J}}$$

where H is the magnetic field strength and E_o is the zero-field energy. Note that $B = \mu H$ and remember that for most astrophysical plasmas $\mu = 1$; therefore, from our perspective, there is no difference between H and B. Also, note that 'g' is the Landé "g-factor" which according to quantum mechanics is given by

$$\mathrm{g} = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

where Russell-Saunders coupling has been assumed (see later discussion of R-S versus j-j coupling). The g-factor varies between 1 for $S = 0$ (singlet states) and 2 for $L = 0$ but it can be less than unity for nonzero values of L and S. For example, examine the ${}^2P_{1/2}$ state on the next page; it has a g-factor of 2/3 (check it out). Note that when g $= 1$, transitions between corresponding substates of different J (or L) all have the same frequency ("normal" Zeeman effect) whereas, for g $\neq 1$, this isn't true ("anomalous" Zeeman effect):



(a) NORMAL ZEEMAN (b) ANOMALOUS ZEEMAN

As an historical note, I might point out that the designation "normal" was introduced *before* electron spin was discovered and, if one ignores spin, then the *normal* Zeeman effect is what one would expect. The "anomalous" (but more common) cases weren't understood until after the concept of spin appeared and then it was too late to change the terminology.

Before we leave the Zeeman effect, note that the g-factor for the singlet states on the left in the above diagram is 1 but it is 2/3 (P) and 2 (S) for the doublet states on the right.

Now consider *strong* magnetic fields in the presence of which the total orbital ($\boldsymbol{L}$) and spin ($\boldsymbol{S}$) angular momentum vectors precess separately about the field lines. That is, the total orbital and the total spin angular momenta are quantized separately ($M_{\rm L} = -L, -L+1, \ldots, L$ and $M_{\rm S} = -S, -S+1, \ldots, S$). This is the Paschen-Back effect which has an energy splitting according to

$$E = E_o + \mu_{\rm B} H M_{\rm L} + 2\mu_{\rm B} H M_{\rm S} \ .$$

For both the Zeeman and Paschen-Back effects, the lowest substate corresponds to the situation wherein the atomic magnetic dipole is *parallel* or in the same direction as the external field. In this state, the angular momentum vector is *anti*-parallel to the field because the electron's loop current is opposite in direction to its motion. In either case, the splitting is the same as far as the number of states is concerned – just the spacing is different.

In summary, there are four basic quantum numbers for each individual electron in an atom: n, ℓ, m_ℓ, and m_s. For each (n, ℓ), there are $2(2\ell+1)$ substates and since ℓ varies from 0 to $n-1$, the total number of states associated with the $n^{\rm th}$ shell is

$$\sum_{\ell=0}^{n-1} 2(2\ell+1) = 2n + 4\sum_{\ell=0}^{n-1} \ell = 2n + 4 \times \frac{1}{2} n(n+1) = 2n^2 \ .$$

That the statistical weight of the $n^{\rm th}$ level is proportional to n^2 should not be a surprise because we have already seen that the number of states with momentum p is proportional to

$$\frac{4\pi p^2}{h^3} \propto n^2 \qquad \text{since} \qquad p = n\hbar \ .$$

Thus, bound and free energy states have similar statistical weights.

We have seen that the atomic energy states are quantized in angular momentum with separation $\hbar$. Now recall that photons have spin momentum $\hbar$. In view of this, it should be obvious that if an atom absorbs or emits a *single* photon (the normal case) it can make a transition only to an *adjacent* angular momentum state. It can do this by changing the ℓ of one electron by one unit of $\hbar$ or by an electron spin flip. The spin flip, however, is a very low probability event due to the weak coupling of electromagnetic fields and electron spin. Therefore, the basic selection rule for *single* photon emission is $\Delta\ell = \pm 1$. Such a transition gives rise to *electric dipole* radiation – sometimes referred to as "permitted radiation". The atom radiates by changing its electric dipole moment. This is both a classical and quantum mechanical process which results in *plane or linearly polarized* radiation just like that from a dipole antenna (a wire strung between two poles!).

Single photon emission is a fairly high probability event if the atom or molecule has an electric dipole moment (some do not). A typical excited atom will radiate in about 10^{-8} s if it can make a $\Delta\ell = \pm 1$ transition. In situations where such a transition is not possible, *two-photon* emission can occur although it has very low probability. If it does take place, however, $\Delta\ell$ can be zero or some other value and the radiation has different polarization properties: *electric quadrapole*. Such "forbidden" transitions are very important in some astrophysical situations. Gaseous nebulae are good examples. Here, atomic energy states which are very close to the ground level (and can be collisionally excited only via $\Delta\ell = 0$ transitions) are "metastable" with lifetimes as long as *seconds*.

Sometimes an atom can radiate via a changing *magnetic* dipole moment (without changing its electric dipole moment). But this also is a low probability process (10^{-5} relative to electric dipole transitions). Transitions involving an electron spin flip (spin momentum changes by $\hbar$) are usually accompanied by magnetic dipole radiation. In such a line-emission event, $\Delta\ell$ could be zero for single photon emission but angular momentum would still be conserved. The 21-cm line emission from H I is a good example of such a low energy (10^{-6} ev) transition. A continuum example of magnetic dipole radiation is a precessing magnetic dipole as in a rotating neutron star. The spin-down of pulsars is due to this form of radiation and not the synchrotron emission from relativistic electrons in the magnetospheres of the stars.

(c) **Electron Configurations, Term Types, and Energy Level Diagrams**

This discussion began with the H-atom. Now let's consider the more general problem of an atom with more than one electron and address the following basic questions:

(i) How are the electrons distributed in the various shells; in particular, what is the electron configuration for the ground state? That is, what are the (n, ℓ) for each electron?

(ii) For a given electron configuration, what are the possible energy states (term types) corresponding to the different possible orientations of the orbital and spin angular momenta (characterized by m_ℓ and m_s)?

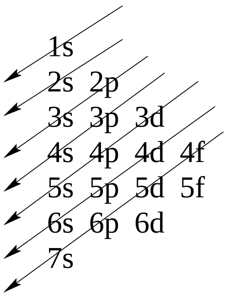
(iii) How are these possible states (terms) distributed in energy? In other words, what is the energy level diagram and which state is the *ground level*?

The first question is not too difficult to answer if one remembers the Pauli Exclusion Principle which dictates that no two electron can have the same n, ℓ, m_ℓ, and m_s. Given this, it is easy to see that the possible electronic states are as outlined in the table at the top of the next page.

POSSIBLE STATES OF AN ELECTRON

	K	L				M									N															
n	1	2				3									4															
ℓ	0	0	1			0	1			2					0	1			2					3						
	s	s	p			s	p			d					s	p			d					f						
m_ℓ	0	0	-1	0	+1	0	-1	0	+1	-2	-1	0	+1	+2	0	-1	0	+1	-2	-1	0	+1	+2	-3	-2	-1	0	+1	+2	+3
m_s	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
	K	L_1	L_2			M_1	M_2			M_3					N_1	N_2			N_3					N_4						

What is not obvious is how the electrons fill up the different ℓ states for heavier and heavier atoms. For heavy atoms, the higher ℓ states are not filled in a given n-shell until after the lower ℓ states in the $(n+1)$-shell. However, for atoms up to radium, the states *are* filled in a fairly orderly manner. The following empirical rule for filling orbitals works with just two or three exceptions up to $Z = 88$:



Ander & Sonnessa
Principles of Chemistry
MacMillan & Co. 1965
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Once the electron configuration for a particular atom or ion has been established, the next step is to determine the possible values of the total orbital angular momentum (L); they govern which term-types are present (S, P, D, F, G,...). This step can be done in a straightforward way by adding *vectorially* the ℓ-values for any two electrons, and then adding the ℓ of a third electron to the resulting L values, and so on. If you do this properly (respecting the Pauli Exclusion Principle), you quickly find that closed shells always have $L = 0$ ($\Longrightarrow$ S-state only) and so the terms for a particular atom are determined entirely by the electrons *outside* closed shells. These are the "valence" electrons. Silicon, for example, has two $3p$ electrons outside closed (filled) shells. One can conclude immediately that, in this ground state configuration, there are present S, P, and D terms because $1 \vec{+} 1 = 0, 1, 2$ ($\vec{+}$ is a *vectorial* plus or add).

L VALUES AND TERM SYMBOLS FOR TERMS WITH DIFFERENT ELECTRON CONFIGURATIONS

Electron Configuration	L	Term Symbol
sp	1	P
pp	0 1 2	S P D
pd	1 2 3	P D F
dd	0 1 2 3 4	S P D F G
ppp	0 1 1 1 2 2 3	S P P P D D F

Next, one finds the total spin momentum (S) by again adding vectorially the spins ($\frac{1}{2}\hbar$) of all the individual electrons present. Again, the total spin is determined entirely by the electrons outside closed shells because $S = 0$ for every filled shell. The spin S determines the multiplicity $(2S+1)$. Thus, hydrogen which has a single electron can have S only equal to $\frac{1}{2}$ and, hence, the multiplicity is $2 \times \frac{1}{2} + 1 = 2$. Therefore, the ground state of hydrogen is a "doublet" S-state (written as ^{2}S) because obviously $L = 0$.

Returning to silicon which has two p-electrons, we have

$$S = \frac{1}{2} \vec{+} \frac{1}{2} = 0 \text{ and } 1 \quad \Longrightarrow \quad \text{multiplicity} = 1 \text{ and } 3\,.$$

Thus, the ground configuration in this case consists of "singlet" and "triplet" states.

At this point, it is necessary to distinguish between *equivalent* electrons (same n and ℓ) and *nonequivalent* electrons (different n or ℓ). If we have two nonequivalent p-electrons, then as argued above, $L = 0, 1$, or 2 and $S = 0$ or 1. Therefore, there are singlet and triplet S, P, and D states:

$$^1\mathrm{S},\ ^1\mathrm{P},\ ^1\mathrm{D},\ ^3\mathrm{S},\ ^3\mathrm{P},\ ^3\mathrm{D}\,.$$

More examples are given in the first table below:

TERMS OF NON-EQUIVALENT ELECTRONS

Electron Configuration	Terms
$s\,s$	^{1}S, ^{3}S
$s\,p$	^{1}P, ^{3}P
$s\,d$	^{1}D, ^{3}D
$p\,p$	^{1}S, ^{1}P, ^{1}D, ^{3}S, ^{3}P, ^{3}D
$p\,d$	^{1}P, ^{1}D, ^{1}F, ^{3}P, ^{3}D, ^{3}F
$d\,d$	^{1}S, ^{1}P, ^{1}D, ^{1}F, ^{1}G, ^{3}S, ^{3}P, ^{3}D, ^{3}F, ^{3}G
$s\,s\,s$	^{2}S, ^{2}S, ^{4}S
$s\,s\,p$	^{2}P, ^{2}P, ^{4}P
$s\,s\,d$	^{2}D, ^{2}D, ^{4}D
$s\,p\,p$	^{2}S, ^{2}P, ^{2}D, ^{2}S, ^{2}P, ^{2}D, ^{4}S, ^{4}P, ^{4}D
$s\,p\,d$	^{2}P, ^{2}D, ^{2}F, ^{2}P, ^{2}D, ^{2}F, ^{4}P, ^{4}D, ^{4}F
$p\,p\,p$	^{2}S(2), ^{2}P(6), ^{2}D(4), ^{2}F(2), ^{4}S(1), ^{4}P(3), ^{4}D(2), ^{4}F(1)
$p\,p\,d$	^{2}S(2), ^{2}P(4), ^{2}D(6), ^{2}F(4), ^{2}G(2), ^{4}S(1), ^{4}P(2), ^{4}D(3), ^{4}F(2), ^{4}G(1)
$p\,d\,f$	^{2}S(2), ^{2}P(4), ^{2}D(6), ^{2}F(6), ^{2}G(6), ^{2}H(4), ^{2}I(2), ^{4}S(1), ^{4}P(2), ^{4}D(3), ^{4}F(3), ^{4}G(3), ^{4}H(2), ^{4}I(1)

TERMS OF EQUIVALENT ELECTRONS

Electron Configuration	Terms
s^2	^{1}S
p^2	^{1}S, ^{1}D, ^{3}P
p^3	^{2}P, ^{2}D, ^{4}S
p^4	^{1}S, ^{1}D, ^{3}P
p^5	^{2}P
p^6	^{1}S
d^2	^{1}S, ^{1}D, ^{1}G, ^{3}P, ^{3}F
d^3	^{2}P, ^{2}D(2), ^{2}F, ^{2}G, ^{2}H, ^{4}P, ^{4}F
d^4	^{1}S(2), ^{1}D(2), ^{1}F, ^{1}G(2), ^{1}I, ^{3}P(2), ^{3}D, ^{3}F(2), ^{3}G, ^{3}H, ^{5}D
d^5	^{2}S, ^{2}P, ^{2}D(3), ^{2}F(2), ^{2}G(2), ^{2}H, ^{2}I, ^{4}P, ^{4}D, ^{4}F, ^{4}G, ^{6}S

For two *equivalent* p-electrons, however, the Pauli Exclusion Principle eliminates the ^{1}P, ^{3}S, and ^{3}D states (refer to the second table above). Again, Si is a good example of this case. The absence of the triplet D state is easy to understand because the electron spins are parallel ($m_s = \frac{1}{2}$)

and also m_ℓ is the same for each electron. That is, in one combination of the m_ℓ's, they would be both $+1$ and in another combination both -1. This is a clear violation of the Pauli Exclusion Principle.

The absence of the ^{3}S and ^{1}P states, on the other hand, is much harder to explain. The best way to understand it is to consider all possible combinations of m_ℓ and m_s which satisfy the Pauli rule. There are 15 in all according to the table below. The values of $M_{\rm L} \equiv \sum m_\ell$ and $M_{\rm S} \equiv \sum m_s$ allow one to determine by elimination which combinations belong to the ^{1}D state (5 in all, denoted by a Δ in the last column), the ^{3}P states (9 in all, denoted by a + sign), and the ^{1}S state (1 combination only, indicated by the $\times$ symbol). So, you see that two equivalent p-electrons give rise to only the terms ^{1}S, ^{1}D, and ^{3}P and *no others*!

DERIVATION OF TERMS FOR TWO EQUIVALENT p-ELECTRONS

m_ℓ			$\sum m_\ell = M_{\rm L}$	$\sum m_s = M_{\rm S}$	State
$+1$	0	-1			
$\uparrow\downarrow$			$+2$	0	Δ
$\uparrow$	$\uparrow$		$+1$	$+1$	$+$
$\uparrow$	$\downarrow$		$+1$	0	Δ
$\downarrow$	$\uparrow$		$+1$	0	$+$
$\downarrow$	$\downarrow$		$+1$	-1	$+$
$\uparrow$		$\uparrow$	0	$+1$	$+$
$\uparrow$		$\downarrow$	0	0	Δ
$\downarrow$		$\uparrow$	0	0	$+$
$\downarrow$		$\downarrow$	0	-1	$+$
	$\uparrow\downarrow$		0	0	$\times$
	$\uparrow$	$\uparrow$	-1	$+1$	$+$
	$\uparrow$	$\downarrow$	-1	0	Δ
	$\downarrow$	$\uparrow$	-1	0	$+$
	$\downarrow$	$\downarrow$	-1	-1	$+$
		$\uparrow\downarrow$	-2	0	Δ

You will notice that, in the table for equivalent electrons, *four* p-electrons give the same term structure as *two* p-electrons. This is related to the fact that the combination of the two (6 p-electrons) makes a filled shell which corresponds to a singlet S-state. Similarly, the terms for *three* equivalent d-electrons (d^3) must be the same as those for *seven* equivalent d-electrons (d^7).

Now we can introduce the other standard quantum number J which is the *total* angular momentum obtained by adding vectorially L and S. The triplet P states which we have been examining are really three P states of different J. We have

$$J \;=\; |L \vec{+} S| = L+S, L+S-1, L+S-2, \ldots, |L-S| \;=\; 0,1,2$$

in this case. Thus, the ^{3}P term corresponds to the three states

$$^3\mathrm{P}_0,\ ^3\mathrm{P}_1,\ \text{and}\ ^3\mathrm{P}_2\ .$$

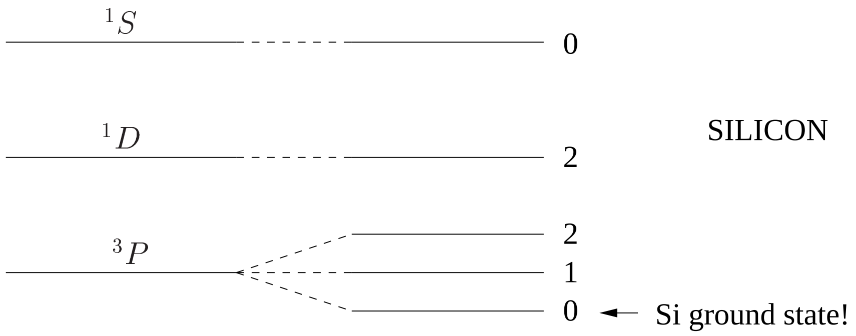
For the other example that we considered, hydrogen, $J = |0 \vec{+} \frac{1}{2}| = \frac{1}{2}$ and so the ground state is a $^2\mathrm{S}_{1/2}$ state which can be split in two by a magnetic field ($M_{\rm J} = \pm\frac{1}{2}$) or by a hyperfine interaction with the nuclear spin of the proton.

Returning to silicon again, we have *five* energy states belonging to the ground electron configuration (i.e., the non-excited atom): $^1\mathrm{S}_0$, $^1\mathrm{D}_2$, $^3\mathrm{P}_0$, $^3\mathrm{P}_1$, $^3\mathrm{P}_2$. In an energy level diagram, how would they be ordered? In particular, which one lies lowest and is, therefore, the ground state? In this regard, there are two useful rules which, strictly speaking, apply only to the ground configuration:

1. Of the terms given by equivalent electrons, those with the greatest multiplicity lie lowest, and of these, the lowest is the one with greatest L. This in known as "Hund's Rule".

2. Multiplets (singlets, doublets, triplets, quartets, etc.) formed from equivalent electrons are *regular* (energy increases with J) when *less* than half the shell is occupied but *inverted* when *more* than half the shell is filled. Exactly half full is a special case: levels are usually inverted in this situation but not always. If uncertain, one can refer to Moore's *A Multiplet Table of Astrophysical Interest*, National Bureau of Standards, 1972.

If we apply these rules to silicon, we easily arrive at the following energy level diagram which involves 5 states (that split into 15 in the presence of a magnetic field):



Note that electric dipole transitions between any two of these states are strictly *forbidden* because $\Delta\ell$ would be *zero* in all cases. It is interesting that doubly ionized oxygen (OIII) has exactly the same energy diagram as Si I (shown above) because it too has two p-electrons outside closed shells. In this case, the ^{1}D state lies about 1 ev above the ground state and can be easily populated by collisions in a gaseous nebula with a kinetic temperature of $10^4\,{}^\circ$K. Subsequent forbidden transitions down to the $^3\mathrm{P}_2$ and $^3\mathrm{P}_1$ states give rise to very strong nebular lines around 5000 Å. These are typically the strongest lines in the spectra of gaseous and planetary nebulae.

In the energy level diagram above, I drew the energy separation of the multiplet components as being *less* than the separation between the other terms. This is a feature or characteristic of Russell-Saunders coupling which we have been studying in the foregoing examples and which applies (at least approximately) in the majority of atoms. In R-S (or weak-field) coupling, the individual ℓ_i's for the outer electrons are more strongly coupled with each other than with their respective s_i's. Thus, we end up with an L and an S which weakly couple with each other to form various J-values. For some *heavy* atoms, on the other hand, the ℓ_i's couple more strongly with their associated s_i's to produce j_i's which then couple together more weakly to yield various J's. This latter process is called j-j coupling or (j,j)-coupling as used by Herzberg in his book. It results in the same number of terms, each with the same J as does Russell-Saunders coupling but they have to be labelled differently (and the multiplets have different energy spacings) because L and S no longer have any special meaning.

The various terms belonging to any electron configuration (ground or excited) can be found as shown above. For excited states, however, the exact ordering of the terms in energy is *not* always obvious because one is often dealing with non-equivalent electrons for which Hund's rule and the other don't really apply. The finer details of energy level diagrams aside, you should have some feeling for the general features of level diagrams.

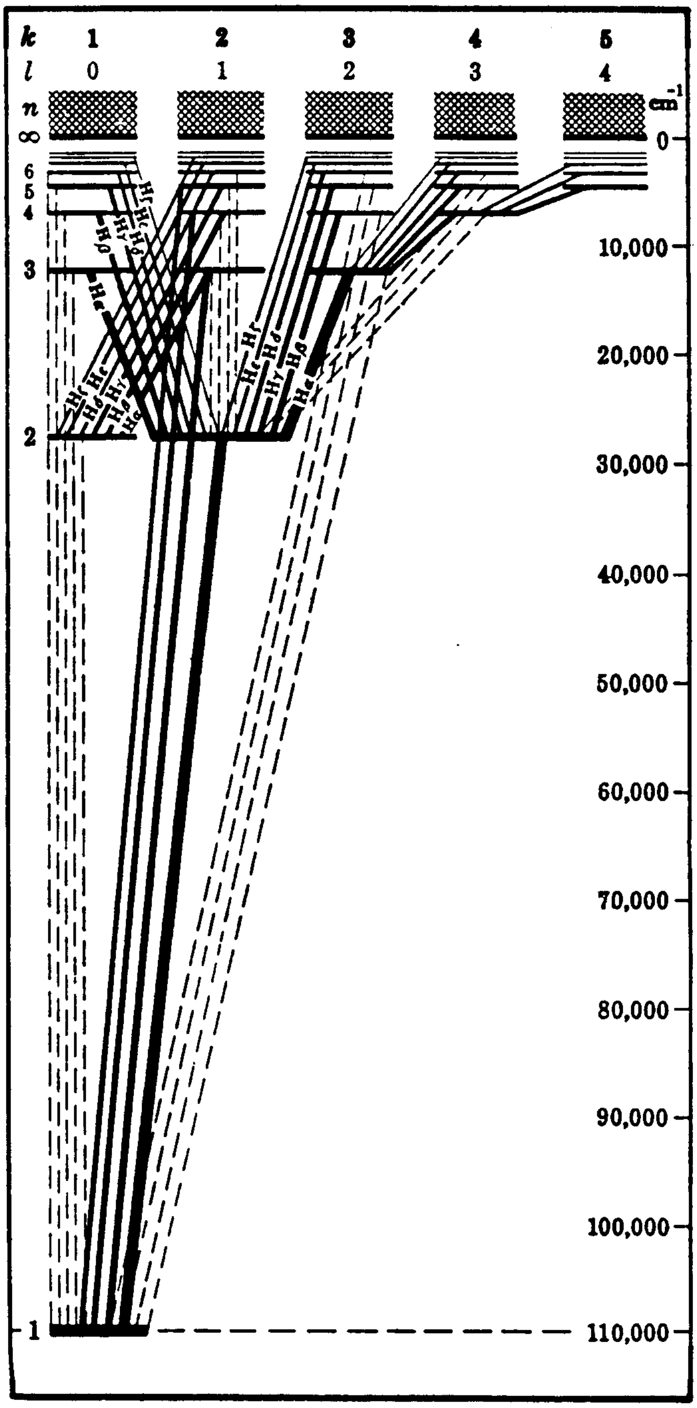


Fig. 7.11 – Energy level diagram for the hydrogen atom. The Balmer series is indicated, as usual, with H_α, H_β, H_γ, and so on. The broken lines refer to forbidden transitions. (From Herzberg's *Atomic Spectra and Atomic Structure*.)

The diagrams for hydrogen and the hydrogenic atoms and ions consist only of *doublets* for obvious reasons. The case of H is unique in that the terms for each n-level are essentially *degenerate* as shown in the above sketch. This is due entirely to the fact that the single electron moves in a *spherically symmetric* r^{-2} Coulomb field.

When one goes to the hydrogenic atoms (Li, for example), the single outer electron no longer moves in a r^{-2} field although it is still spherically symmetric. This situation leads to an energy shift of the terms, especially the doublet S-states. Electrons with small orbital angular momentum (i.e., low ℓ) move through a greater range in r (recall the Bohr-Sommerfeld orbits) and, hence, sense more of the non-point-charge field. Thus, the greater shift of the S-states relative to that of hydrogen as shown in the following diagram.

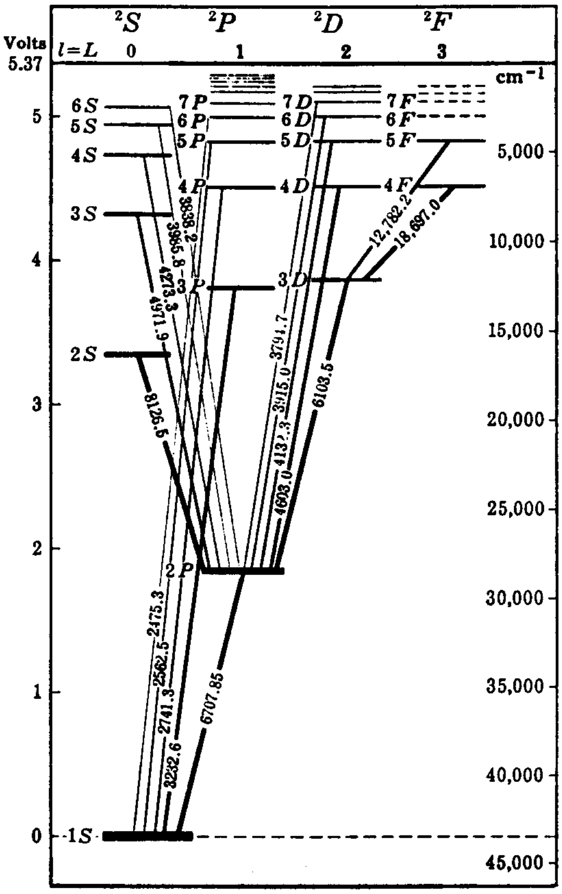


Fig. 7.12 – Energy level diagram for the Li atom. The wavelengths of the spectral lines are written on the connecting lines representing the transitions. Doublet structure is not included. Some unobserved levels are indicated by dotted lines.

Notice, however, that the high n states and the lower n – high ℓ states are more or less degenerate like H. This is because the electrons in these states see a more or less spherical r^{-2} Coulomb field.

When we go to atoms with two or more outer electrons, then terms with more than one multiplicity come in. Helium, for example, has singlet *and* triplet states as shown in the diagram on the following page. You can see that there is considerable difference between the energies of corresponding terms of different multiplicity. This is due to the Coulomb interaction of the outer electrons which now in general move in not only a non-inverse-square force field but also in a non-spherically symmetric one. Under these conditions, the individual angular momenta are no longer constant and so ℓ no longer has the same strict physical meaning. However, one can still treat the m_ℓ and m_s as "mean" quantum numbers and determine the term structure as described above. The *total* angular momentum J, of course, is still a constant and *does* have a physical significance.

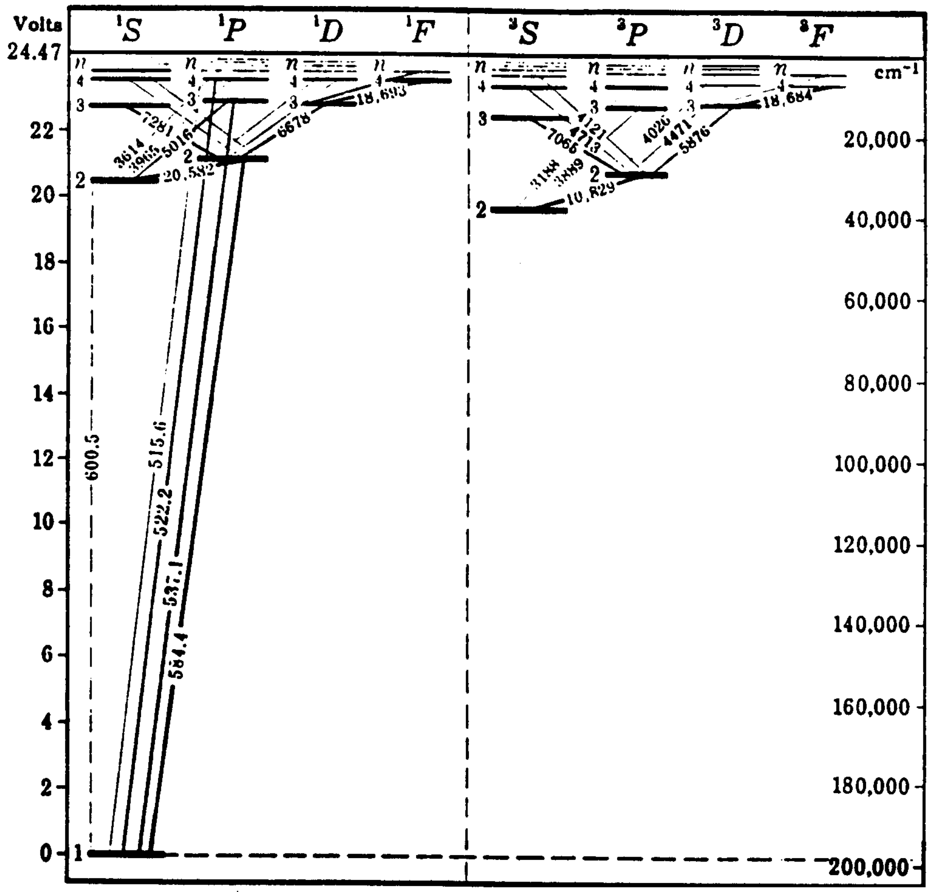


Fig. 7.13 – Energy level diagram for helium. The series in the visible and near ultraviolet regions correspond to the indicated transitions between terms with $n \geq 2$.

7.2 Derivation of Radiative Transition Rates

References:

- N. F. Mott 1960, *Elements of Wave Mechanics*
- Rybicki & Lightman, *Radiative Processes*

Here, we employ the semi-classical approach which treats the atom quantum mechanically but the incoming photons classically (that is, as a continuous wave or $\boldsymbol{E}$-field). The EM-wave forms a perturbation to the energies of the atomic states. We need derive only the absorption rates between bound states; the spontaneous and stimulated rates will follow automatically from the relationships between the Einstein coefficients. The photoionization and recombination rates can also be easily derived by generalizing the bound-bound rates to include a free upper state.

The physical rationale for the semi-classical approach is that while the EM-wave represents a large number of photons (as opposed to a single one) the absorption probability should be *linearly* proportional to time or the number of photons interacting with the atom. Therefore, we should be able in principle to extrapolate back to the quantum regime – that is, down to the effect of a single photon.

Perturbation Theory

The general Schröedinger equation is given by

$$\frac{\partial \Psi}{\partial t} = -\frac{iH}{\hbar}\,\Psi \quad \text{where} \quad H = -\frac{\hbar^2}{2m}\,\nabla^2 + V \ .$$

This is usually broken down by a separation of variables into

$$\Psi(q,t) = \psi(q)\,\phi(t) \quad \text{where} \quad \phi(t) = \mathrm{e}^{-iEt/\hbar}$$

from which we can easily derive

$$(H-E)\,\psi = 0$$

where

H is the Hamiltonian operator $= -\dfrac{\hbar^2}{2m}\,\nabla^2 + V$,
V is the potential energy,
E is the total energy (kinetic + potential),
q is shorthand for $\boldsymbol{q}$, a set of normalized phase space coordinates.

Now, let's consider the various "eigenstates" (or "stationary states") of the atom:

$$(H-E_n)\,\psi_n(q) = 0$$

where the $\psi_n(q)$ form an *orthonormal set* of wave functions.

We now add to the potential a small perturbation – a time-dependent term which represents the incident EM-wave. The potential perturbation $V(q,t)$ is included in the Schröedinger equation as follows:

$$-\frac{\hbar}{i}\,\frac{\partial \Psi}{\partial t} = H\,\Psi + V(q,t)\,\Psi \ .$$

Keep in mind that the equilibrium part of the potential energy is included in H and that, in what follows, V is only the perturbed part of the potential. [I'm being overly conservative in my notation!]

Before the arrival of the wave, we assume that the atom is in the ground state $n = 0$ (strictly speaking, we should use $n = 1$, but think of n as just a *label*). Thus, for $t < 0$,

$$\Psi(q,t) = \psi_o(q)\,\mathrm{e}^{-iE_o t/\hbar} \ .$$

For $t \geq 0$, the perturbed wave function Ψ may be expanded as a time-dependent superposition of the unperturbed eigenstates, signifying that we don't know precisely which state the atom is in:

$$\Psi(q,t) = \sum_n a_n(t)\,\psi_n(q)\,\mathrm{e}^{-iE_n t/\hbar} \ .$$

The coefficients $a_n(t)$ are now *time-dependent* and recalling that the $\psi_n(q)$ are orthonormal, we can calculate the coefficients if Ψ is known at any time. Note that $|a_n(t)|^2$ should be interpreted as the probability that the atom is in state n at time t. This is closely related to the absorption coefficient B_{on} that we are after since the latter is the probability per unit time that a transition takes place from the ground state up to level n.

Now to obtain a solution for $a_n(t)$, substitute the foregoing expression for Ψ into Schröedinger's equation:

$$-\frac{\hbar}{i}\sum_n \psi_n(q)\left[\frac{da_n}{dt} - \frac{i}{\hbar}\,a_n E_n\right]\mathrm{e}^{-iE_n t/\hbar} = H\sum_n a_n(t)\psi_n(q)\,\mathrm{e}^{-iE_n t/\hbar} + V\,\Psi$$

or

$$-\frac{\hbar}{i}\sum_n \frac{da_n}{dt}\,\psi_n(q)\,\mathrm{e}^{-iE_n t/\hbar} - \sum_n a_n(t)\,(H - E_n)\,\psi_n(q)\,\mathrm{e}^{-iE_n t/\hbar} = V\,\Psi \ .$$

But the terms $(H - E_n)\psi_n$ are all *zero* because the ψ_n are eigenstates. Thus,

$$\sum_n \frac{da_n}{dt}\,\psi_n(q)\,\mathrm{e}^{-iE_n t/\hbar} = -\frac{i}{\hbar}\,V\,\Psi \ .$$

To isolate da_n/dt, multiply by $\psi_n^*\,\mathrm{e}^{iE_n t/\hbar}$ and integrate over all space (i.e., over all q):

$$\frac{da_n}{dt} = -\frac{i}{\hbar}\,\mathrm{e}^{iE_n t/\hbar}\int \psi_n^*\,V\,\Psi\,d^3q \ .$$

We can obtain a good approximation by recalling that the initial state is Ψ_o and that the effect of the perturbing EM-field is small. Thus,

$$\Psi \simeq \Psi_o = \psi_o\,\mathrm{e}^{-iE_o t/\hbar} \qquad \text{(ground state)}$$

and

$$\frac{da_n}{dt} = -\frac{i}{\hbar}\,\mathrm{e}^{i\omega_{no}t}\int \psi_n^*\,V(q,t)\,\psi_o\,d^3q$$

where

$$\omega_{no} \equiv \frac{E_n - E_o}{\hbar} = 2\pi\nu_{no}$$

is the transition frequency. The integral is what is normally called a "matrix element"; it is a measure of the coupling of states 0 and n by the perturbing potential V.

We must now adopt a form for the potential V and for this purpose we invoke the so-called "dipole approximation":

$$V(q,t) = \frac{1}{2} ez\mathcal{E}_o\, \mathrm{e}^{-i\omega t}$$

which corresponds to a passing wave of the form

$$\mathcal{E}_o \cos(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t) = \frac{1}{2}\mathcal{E}_o \left[\mathrm{e}^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} + \mathrm{e}^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\right] .$$

If $\omega_{no} > 0$ (absorption), then only the first term makes a significant contribution. If $\omega_{no} < 0$ (stimulated emission), then it is the second term which dominates.

The expression for the perturbing potential assumes that the axis of polarization of the EM-wave is in the z-direction and that $\boldsymbol{E}$ is *constant* over the atomic scale; that is

$$\boldsymbol{k}\cdot\boldsymbol{r} \sim \frac{r_{\mathrm{B}}}{\lambda} \ll 1$$

which is reasonable for typical wavelengths. Thus, the potential associated with the electric field is proportional to

$$e\boldsymbol{E}\cdot\boldsymbol{r} = \frac{1}{2} ez\mathcal{E}_o\, \mathrm{e}^{-i\omega t} .$$

The factor ez is responsible for the "dipole" designation. This dipole potential couples states with different electric dipole moments, allowing transitions between them. These "permitted" transitions give rise to electric dipole radiation.

Now substitute the expression for $V(q,t)$ into the one for da_n/dt to obtain

$$\frac{da_n}{dt} = -\frac{ie}{2\hbar}\,\mathcal{E}_o \langle n|z|0\rangle\, \mathrm{e}^{i(\omega_{no}-\omega)t}$$

where I am using a short-hand notation for the "dipole matrix element":

$$\langle n|z|0\rangle \equiv \mathcal{Z}_{no} \equiv \int \psi_n^*\, z\, \psi_o\, d^3q .$$

Integrate with respect to time and take $\omega_{no} > 0$ (appropriate for absorption):

$$a_n(t) = \int_0^t \frac{da_n}{dt'}\, dt' = -\frac{ie}{2\hbar}\,\mathcal{E}_o \mathcal{Z}_{no} \frac{\left[\mathrm{e}^{i(\omega_{no}-\omega)t} - 1\right]}{i(\omega_{no}-\omega)}$$

which satisfies the initial condition $a_n(0) = 0$.

Now calculate the probability of a transition after time t per unit bandwidth of the incident radiation; this is a dimensionless quantity:

$$\frac{dP_n(t)}{d\nu} \equiv |a_n|^2 = \frac{1}{2}\left(\frac{e\mathcal{E}_o}{\hbar}\right)^2 |\mathcal{Z}_{no}|^2 \frac{[1-\cos(\omega_{no}-\omega)t]}{(\omega_{no}-\omega)^2} .$$

Note that when $\omega \to \omega_{no}$ (with t small), the probability $dP_n/d\nu \propto t^2$ which is an unpleasant surprise because we want the probability to grow *linearly* with time. However, not to worry because the relevant probability P_n must be obtained by integrating over the line. The foregoing equation shows clearly that this quantity grows quickly at line center but much more slowly off-center. Averaging over the line will give a weaker dependence on the time t.

Calculation of the Einstein B-Coefficient

First of all, let's convert or eliminate $\mathcal{E}_o$ in favor of the mean intensity J_ν of the incoming radiation:

$$\frac{\mathcal{E}_o^2}{8\pi} = U_\nu = \frac{4\pi}{c}\, J_\nu \quad \text{(per unit bandwidth)}.$$

Note the factor '8π' here rather than '4π'; this is due to the fact that $\mathcal{E}_o^2 = 2E_o^2$. Also, we should recognize that the dependence on z in the dipole matrix element is artificial in that the incoming wave has, in general, a random direction and random polarization. Thus, we should replace $|\mathcal{Z}_{no}|^2$ by an average over what might be called the "principal axes":

$$|\mathcal{Z}_{no}|^2 \longrightarrow \frac{1}{3}(|\mathcal{X}_{no}|^2 + |\mathcal{Y}_{no}|^2 + |\mathcal{Z}_{no}|^2) = \frac{1}{3}\,|\mathcal{D}_{no}|^2 \quad (\text{unit} = \text{cm}^2)$$

where $\mathcal{D}_{no}$ is the "principal dipole coupling constant".

Putting this together, we have

$$dP_n(t) = -\frac{32\pi^2 e^2}{2\hbar^2 c}\, J_\nu \left(\frac{|\mathcal{D}_{no}|^2}{3}\right) \frac{(1-\cos x)}{x^2/t^2}\, \frac{dx}{2\pi t}$$

where $x \equiv (\omega_{no} - \omega)t$ and $dx = -2\pi t\, d\nu$.

Now integrate over all frequency from 0 to ∞ (or over all x from $\omega_{no}t$ to $-\infty$) to get

$$P_n(t) = \frac{8\pi^2 e^2}{3\hbar^2 c}\, \bar{J}\, |\mathcal{D}_{no}|^2\, t \quad (\text{unit} = \text{s}^{-1})$$

where I have pushed the upper limit on x up to $+\infty$ (a reasonable approximation) and used the fact that

$$\int_{-\infty}^{\infty} \frac{(1-\cos x)}{x^2}\, dx = \pi\ .$$

Moreover, I have assumed that J_ν is slowly varying over the line profile width in the integral and replaced it by a frequency average, $\bar{J}$. Note that $P_n(t)$ is now *linearly* proportional to the time which makes more sense.

We are just one step away from the Einstein B-coefficient (more specifically B_{on}). Recall that B is defined as the probability (per unit time per unit intensity) of a transition (or absorption). Hence,

$$B_{on} = \frac{P_n(t)}{\bar{J}t} = \frac{8\pi^2 e^2}{3\hbar^2 c}\, |\mathcal{D}_{no}|^2$$

from which we can derive

$$A_{no} = \frac{2h\nu_{no}^3}{c^2}\, B_{on} = \frac{32\pi^3 e^2 \nu_{no}^3}{3\hbar c^3}\, |\mathcal{D}_{no}|^2\ .$$

Introduce a dimensionless oscillator strength which is consistent with an earlier definition (see p44 and the next page):

$$f_{on} \equiv \frac{8\pi^2 m\nu_{no}}{3h}\, |\mathcal{D}_{no}|^2\,,$$

which leads to the following expressions for the Einstein coefficients:

$$\begin{aligned} A_{no} &= \frac{8\pi^2 e^2 \nu_{no}^2}{mc^3}\, f_{on} \quad (\text{unit} = \text{s}^{-1})\,, \\ B_{on} &= \frac{4\pi^2 e^2}{mch\nu_{no}}\, f_{on} \qquad (\text{unit} = \text{s}^{-1}\,\text{erg}^{-1}\,\text{cm}^2)\,. \end{aligned}$$

The Bound-Bound Absorption Coefficient

Back in §2.5, we introduced the relationship between the scattering coefficient and the "oscillator strength"; we can now easily derive the corresponding relation for the absorption coefficient per atom:

$$a_{on} = \frac{1}{n_o}\int \alpha_\nu \, d\nu = \frac{h\nu_{no}}{4\pi}\, B_{on} = \frac{\pi e^2}{mc}\, f_{on} \quad (\text{unit} = \text{cm}^2\,\text{s}^{-1})$$

where n_o is the number of atoms per unit volume in the ground state and (remember) ν_{no} is the line-center frequency. We saw earlier that $\pi e^2/mc$ is the classical harmonic oscillator strength. Therefore, f_{on} is a measure of the absorption coefficient in units of the classical oscillator strength. This explains the origin of the name for f_{on} and why it is defined in such an apparently arbitrary way on the preceding page. Note that f_{on} is NOT a classical quantity – it is a quantum mechanical one!

Another useful property of f_{on} (as defined) is that it satisfies the Thomas-Kuhn "Summation Rule"; namely,

$$\sum_n f_{on} = N$$

where N is the total number of electrons in the atom and the sum is over all energy states. Note that this rule applies to *any* initial state, not just the ground state.

Clearly, for hydrogen ($N = 1$), f_{on} is always less than unity. In this case, f_{on} can be computed fairly easily because the eigenfunctions are known explicitly and exactly. See Table 10.1 in the text. For large n, $f_{on} \propto n^{-3}$ which shows that transitions from the ground state to high energy levels have low probability. Interestingly, recombinations from the continuum also depend on n in exactly the same way. Thus, high energy states tend to be bypassed "coming and going".

Selection Rules

The foregoing expressions for the transition probabilities can be used, in principle, to derive selection rules. In particular, if the matrix element or coupling constant for a particular transition is zero, then that transition is "forbidden". Without going into detail, it is possible to confirm the selection rule involving $\Delta\ell$ that we inferred earlier; namely,

$$\Delta\ell = \pm 1\,, \quad \Delta m_\ell = 0, \pm 1\,,$$

$$\Delta J = 0, \pm 1\,, \quad \Delta M_J = 0, \pm 1 \quad (0 \not\to 0)\ .$$

We know, of course, that forbidden transitions do have a finite but small transition probability. In the "dipole" approximation that we have been employing, they are zero because we neglected the size of the atom compared to the wavelength of the radiation. More explicitly, in the expression for the EM-wave, we wrote

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = 1 + i\boldsymbol{k}\cdot\boldsymbol{r} + \ldots$$

and neglected all terms but the first. The second term here would govern the quadrapole or "forbidden" transitions. It takes into account the change in the amplitude of $\boldsymbol{E}$ as the wave passes through the atom. This corresponds to a perturbation potential which is *nonlinear* in the spatial coordinates. It couples states with different electric quadrapole moments, enabling transitions between them.

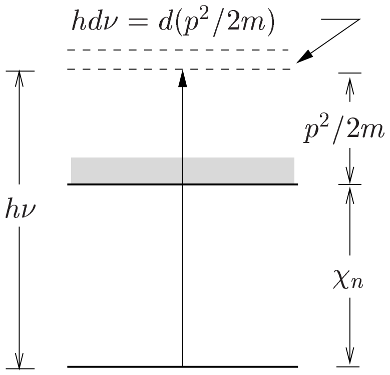
Bound-Free Transitions

In this case, photoionization occurs with the final state being one of a continuum of states. Essentially, the same formalism can be used, but we must treat the upper state as *unbound* and this makes the calculation of the matrix element more difficult because the wave function of the free electron is a more complicated function of the spatial coordinates.

Let me skip the details and just sketch the basic argument. In this case, our expression for $P_n(t)$ should be considered the transition probability per final state; that is, dP_ν/dN where ν denotes some frequency or energy in the continuum and dN is the number of final states in some energy or frequency band $d\nu$ (say). Thus, we write

$$B_{on} \longrightarrow B_{o\nu}\frac{d\nu}{dN} = \frac{32\pi^4 e^2}{3h^2 c}\,|\mathcal{D}_{\nu o}|^2 \quad (\text{unit} = \text{cm}^2\,\text{s}^{-1}\,\text{erg}^{-1})$$

which provides an expression for $B_{o\nu}$, the probability for a photoionization per unit bandwidth. Now, in some domain of dimension or scale L, the number of states available for our free electron in momentum range $p \rightarrow p + dp$ is



$$dN = L^3 \times \frac{8\pi p^2\,dp}{h^3} = \frac{8\pi L^3}{h^3}\,m^2 v\,d\left(\frac{p^2}{2m}\right) = \frac{8\pi L^3}{h^2}\,m^2 v\,d\nu\ ,$$

where I have identified a difference in electron kinetic energy, $d(p^2/2m)$, with a difference in photon energy, $d(h\nu)$. This analysis is for *nonrelativistic* velocities which is appropriate for thermal processes.

Now we have an expression for $dN/d\nu$, the number of free electron states per unit frequency interval from which we can derive the bound-free absorption coefficient per atom, per unit time, and per unit bandwidth:

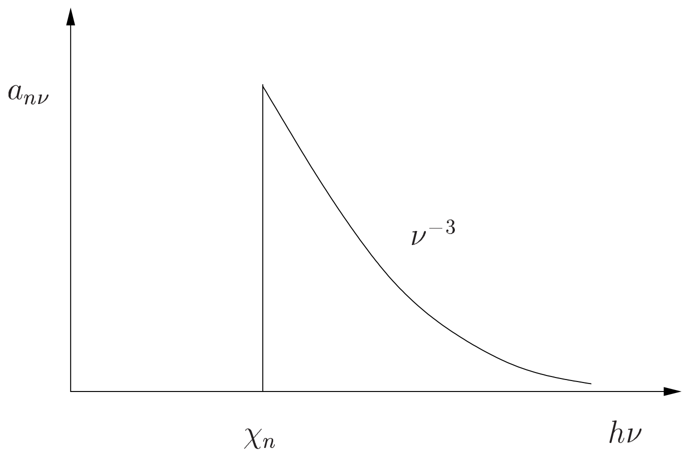
$$\begin{aligned} a_{o\nu} = \frac{h\nu}{4\pi}\,B_{o\nu} &= \frac{h\nu}{4\pi}\left(\frac{32\pi^4 e^2}{3h^2 c}\,|\mathcal{D}_{\nu o}|^2\right)\frac{8\pi L^3}{h^2}\,m^2 v \\ &= \frac{64\pi^4 m^2 e^2}{3h^3 c}\,v\nu L^3\,|\mathcal{D}_{\nu o}|^2 \qquad (h\nu > \chi_n;\text{unit} = \text{cm}^2)\ , \end{aligned}$$

where χ_n is the ionization potential (refer to the above sketch). The factor L^3 looks out of place here but it will cancel out because the free-electron wave function, involved in the matrix element $\mathcal{D}_{\nu o}$, scales like $L^{-3/2}$.

This is the basic argument which applies just as well to any initial state n (not only the ground state). For hydrogen, the wave functions for the bound (initial) state and the unbound (final) state are known and so the matrix element coupling the two states can be computed (although not easily!). The result is

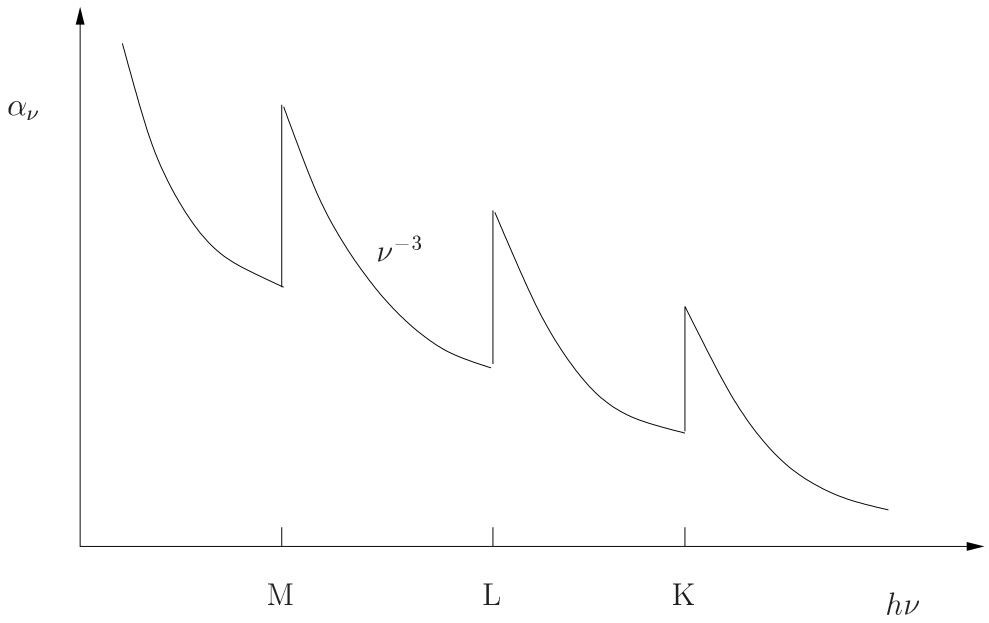
$$a_{n\nu} = \frac{64\pi^4 m e^{10} Z^4}{3\sqrt{3}h^6 c\nu^3 n^5}\,g_{\text{bf}}(\nu) \qquad (h\nu > \chi_n;\text{unit} = \text{cm}^2)$$

where g_{bf} is the b-f Gaunt factor which incorporates small quantum corrections to our EM-wave treatment; it is of order unity at the ionization edges, one of which is shown schematically in the following sketch:



Note that this "raw" ν^{-3} behavior (uncorrected for stimulated emission) is shared by the free-free absorption coefficient which we considered earlier although in that case there are no absorption edges, of course. The magnitude of $a_{n\nu}$ at the absorption edge ($h\nu = \chi_n$) is proportional to n as you can easily confirm by substituting $\chi_n \propto n^{-2}$ into the expression at the bottom of the preceding page.

The *total* absorption coefficient per atom will be a sum over all bound states whose ionization energies are *less than* $h\nu$. Here is a schematic representation:



Note how α_ν grows towards lower frequencies. The maximum α_ν corresponds to the n of the highest *bound* state; this will always be less than ∞ due to external perturbations such as particle interactions if not something else. The relative sizes of the spikes at absorption edges can increase or decrease with increasing frequency depending on the temperature which controls the populations in the various states.

In general, for multi-electron atoms, the wave functions and the corresponding absorption coefficients can be computed only approximately if, indeed, they can be evaluated at all. In many cases, laboratory measurements must be relied on for astrophysically important absorption data and, where such data is absent, one must make intelligent guesses based on the best theories available.

Recombination Coefficient

Now that we have the photoionization rate, we can estimate the recombination rate (or, more specifically, the recombination cross-section $\langle\sigma_n^{(r)}\, v\rangle$ for atomic level n, averaged over all velocities). To do this, we can assume thermodynamic equilibrium for which the photoionization rate exactly balances the recombination rate. Then, once we have an expression for the cross-section, we can drop the equilibrium assumption. We employed this approach earlier when deriving the relationships between the Einstein coefficients. All these atomic properties do not depend on whether or not thermodynamic equilibrium prevails.

Thus, we have for hydrogenic atoms, including stimulated emission,

$$N_e N_{\rm II}\, \sigma_n^{(r)}(v)\, v\, dv = 4\pi N_n \frac{B_\nu}{h\nu}\, \alpha_{n\nu}\, (1 - {\rm e}^{-h\nu/kT}) d\nu$$

where N_n is the number density of neutral atoms in state n, $N_{\rm II}$ is the ionized number density and $B_\nu/h\nu$ is the photon flux per unit bandwidth about ν. We now invoke Saha's equation to obtain an expression for

$$\frac{N_e N_{\rm II}}{N_{\rm n}} = \frac{g_e g_{\rm II}}{g_{\rm n}}\, \frac{(2\pi mkT)^{3/2}}{h^3}\, {\rm e}^{-\chi_n/kT}$$

where $\chi_n \equiv$ ionization potential for the $n^{\rm th}$ level ($\chi_1 = 13.6\,$ev for hydrogen). The statistical weights are easy to express: $g_{\rm n} = 2n^2$ and $g_e g_{\rm II} = 2 \times 1 = 2$ (again for H). Using these results and substituting for the Planck function B_ν (p11) and the photoionization rate $\alpha_{n\nu}$ (p117), we find after collecting terms

$$\sigma_n^{(r)}(v)\, v\, dv \equiv \sigma_n^{(r)}(\nu)\, d\nu = \frac{2^9 \pi^5 m e^{10} Z^4}{3\sqrt{3} h^3 c^3 n^3 \nu (2\pi mkT)^{3/2}}\, \frac{{\rm e}^{\chi_n/kT}}{{\rm e}^{h\nu/kT}}\, g_{\rm bf}(\nu)\, d\nu \ .$$

Note that I have introduced (and defined) a new cross-section, $\sigma_n^{(r)}(\nu)$, which is a different function of its argument than is $\sigma_n^{(r)}(v)$; the two have different units and deserve to be assigned different symbols (but I am too lazy to do so). Also, be aware that v and ν are related through energy conservation:

$$h\nu = \frac{1}{2} m v^2 + \chi_n \qquad \Longrightarrow \qquad h\, d\nu = m v\, dv \ .$$

Before computing the average cross-section over v or ν, let's derive an expression for $\sigma_n^{(r)}(\nu)$ which will be useful in the next section where we consider a comparison of recombination continuum and bremsstrahlung. Indeed, it will prove useful in any analysis involving gaseous nebulae or stellar ionization zones.

From the foregoing equation, it is easy to obtain

$$\sigma_n^{(r)}(\nu) \simeq 3.26 \times 10^{-6} \frac{Z^4 g_{\rm bf}(\nu)}{n^3 T_e^{3/2} \nu}\, \frac{{\rm e}^{\chi_n/kT_e}}{{\rm e}^{h\nu/kT_e}} \ \ {\rm cm^3\, s^{-1}\, Hz^{-1}} \qquad ({\rm h}\nu > \chi_{\rm n})$$

where the implication of thermodynamic equilibrium has been dropped by setting $T = T_e = T_{\rm kin}$. Note how the cross-section drops very quickly with increasing n and with increasing $h\nu$. That is, recombination is maximized for low-energy electrons dropping to the bottom of the Coulomb potential well. This is intuitively what we expect. Another point is that the n-dependence mimics that of the bound-bound transitions; the Einstein coefficients, A_{no} and B_{on}, and the Balmer decrement, D_n, are all proportional to n^{-3}.

Now let's evaluate the average over all velocities; this corresponds to integrating over the frequency range $(\chi_n/h, \infty)$:

$$\langle \sigma_n^{(r)}\, v \rangle = \int_0^\infty \sigma_n^{(r)}(v)\, v\, dv = \frac{2^9 \pi^5 m e^{10} Z^4\, \mathrm{e}^{\chi_n/kT_e}}{3\sqrt{3} h^3 c^3 n^3 (2\pi m k T)^{3/2}} \int_{\chi_n/h}^\infty \frac{g_{\rm bf}(\nu)}{\mathrm{e}^{h\nu/kT_e}}\, \frac{d\nu}{\nu}\ .$$

We can get a reasonable approximation to the integral in the foregoing expression by making the same low temperature assumption that we made before, namely

$$\frac{h\nu}{kT_e} > \frac{\chi_n}{kT_e} \gg 1\ .$$

We first write

$$\int_{\chi_n/h}^\infty \frac{g_{\rm bf}(\nu)}{\mathrm{e}^{h\nu/kT_e}}\, \frac{d\nu}{\nu} \simeq \bar{g}_{\rm bf} \int_{x_n}^\infty \frac{\mathrm{e}^{-x}}{x}\, dx = \bar{g}_{\rm bf}\, \mathrm{Ei}(x_n)$$

where $\mathrm{Ei}(x)$ is the exponential integral. Since $x_n \equiv \chi_n/kT_e$ is large at low T_e we can use the following asymptotic behavior:

$$\mathrm{Ei}(x) \simeq \frac{\mathrm{e}^{-x}}{x}\left(1 - \frac{1!}{x} + \frac{2!}{x^2} - \frac{3!}{x^3} + \ldots\right) \quad \text{(large } x\text{)}.$$

Taking only the first term, we have

$$\langle \sigma_n^{(r)}\, v \rangle \simeq \frac{2^8 \pi^4 e^{10} Z^4\, \bar{g}_{\rm bf}}{3\sqrt{3} h^3 c^3 n^3 \chi_n (2\pi m k T_e)^{1/2}} \propto \frac{1}{n T_e^{1/2}}\ .$$

For $kT_e \sim \chi_n$ or larger, then the temperature dependence departs a little from $T_e^{-1/2}$. (See M. J. Seaton, MNRAS, **119**, 81, 1959 for more details.) Note that the presence of the χ_n factor in the denominator transforms the n^{-3} dependence of the monochromatic cross-section to a simple n^{-1} dependence for the integrated form. (Again, I am guilty of laziness for leaving a subscript 'n' off the bf Gaunt factor.)

Recombination Continuum Versus Bremsstrahlung

From §3.1 (p50), we have for the bremsstrahlung emission

$$j_\nu(\text{ff}) = 5.44 \times 10^{-39} \frac{Z^2 N_e N_{\text{II}}}{T_e^{1/2}} \, \text{e}^{-h\nu/kT_e} \, \bar{g}_{\text{ff}}(\nu, T_e) \quad \text{ergs}\,\text{s}^{-1}\,\text{cm}^{-3}\,\text{Hz}^{-1}\,\text{sr}^{-1}$$

which involves a small change in notation. We can write down an analogous expression for the recombination continuum by using the monochromatic cross-section derived in the preceding section:

$$\begin{aligned} j_\nu(\text{fb}) &= N_e N_{\text{II}} \, \sigma_n^{(r)}(\nu) \, \frac{h\nu}{4\pi} \\ &= 1.71 \times 10^{-33} \, \frac{Z^4 N_e N_{\text{II}}}{n^3 T_e^{3/2}} \, \frac{\text{e}^{\chi_n/kT_e}}{\text{e}^{h\nu/kT_e}} \, g_{\text{bf}}(\nu) \quad \text{ergs}\,\text{s}^{-1}\,\text{cm}^{-3}\,\text{Hz}^{-1}\,\text{sr}^{-1} \; . \end{aligned}$$

Now, we can compare the recombination emission with the corresponding bremsstrahlung *at the same frequency*. For illustration, assume hydrogen ($Z = 1$) and neglect the Gaunt factors:

$$\frac{j_\nu(\text{fb})}{j_\nu(\text{ff})} \simeq \frac{3.14 \times 10^5}{n^3 T_e} \, \text{e}^{\chi_n/kT_e} \; .$$

Consider three cases:

(i) <u>Balmer continuum ($n = 2$) at $T_e = 10^4\,°\text{K}$:</u>

In this situation, $kT_e \sim 1\,\text{ev}$ and $\chi_2 = 13.6/2^2 = 3.4\,\text{ev}$. Thus,

$$\frac{j_\nu(\text{fb})}{j_\nu(\text{ff})} \simeq \frac{31.4}{2^3} \, \text{e}^{3.4} = 118 \; .$$

Conclusion: Balmer continuum dominates bremsstrahlung at low T_e. Note, however, that this is not true for higher-order continua due to the n^{-3} factor (see the third case below). The continuum that we see in the spectra of gaseous nebulae is primarily the result of hydrogen recombination to the $n = 2$ state.

(ii) <u>Balmer continuum ($n = 2$) at $T_e = 10^7\,°\text{K}$:</u>

In this higher temperature case, $kT_e \sim 1\,\text{Kev}$ and, again, $\chi_2 = 3.4\,\text{ev}$.

$$\frac{j_\nu(\text{fb})}{j_\nu(\text{ff})} \simeq \frac{0.0314}{2^3} = 0.0039 \; .$$

Conclusion: At high temperatures, bremsstrahlung catches up to recombination so that free-free emission will dominate by a large factor (the reciprocal of 0.0039 at $10^7\,°\text{K}$). Therefore, the hot intracluster gas in galaxy clusters cools predominantly by free-free emission. This continues to be true down to about $10^5\,°\text{K}$.

(iii) <u>radio continuum at $T_e = 10^4\,°\text{K}$:</u>

Take $\nu = 1\,\text{GHz}$ which corresponds to an energy of $h\nu = 4.14 \times 10^{-6}$ ev. This is much smaller that the thermal energy: $kT_e \sim 1\,\text{ev}$. Also, we require $\chi_n < h\nu$ from which we can get an estimate for n:

$$\chi_n = \frac{\chi_1}{n^2} \quad \Longrightarrow \quad \frac{1}{n^3} = \left(\frac{\chi_n}{\chi_1}\right)^{3/2} < \left(\frac{h\nu}{\chi_1}\right)^{3/2} \simeq \left(\frac{4.14 \times 10^{-6}}{13.6}\right)^{3/2} = 1.68 \times 10^{-10} \; .$$

Therefore,

$$\frac{j_\nu(\mathrm{fb})}{j_\nu(\mathrm{ff})} \simeq 31.4 \times 1.68 \times 10^{-10} \simeq 5.3 \times 10^{-9} \ .$$

CONCLUSION: Bremsstrahlung completely dominates in the radio for all but the highest T_e.

The bottom line here is that recombination can dominate free-free emission only at lower temperatures and for frequencies higher than those in the infrared.

STUDENT EXERCISE:

In the (T_e, ν)-plane delineate the regions where bremsstrahlung dominates recombination and vice-versa. Another exercise would be to compare the integrated emissions (over all frequencies) as a function of T_e. You should be able to confirm that above $10^5\,^\circ$K the integrated emission is dominated by thermal bremsstrahlung. From that temperature down to about $5 \times 10^4\,^\circ$K, recombination continuum dominates. Below that, forbidden line radiation is the dominant cooling mechanism.