Chapter 3

Formation of the spectrum

This chapter corresponds to chapters 4 and 5 of [3].

3.1 Einstein coefficients

For practical calculations of radiative transfer one needs to know absorption, emission and scattering coefficients, i.e., the probabilities of radiative processes and the abundances of particles in states required for these processes. These abundances are influenced not only by the investigated radiative processes, but, generally, by all possible processes between the particles. These processes can be treated as some chemical reactions

$$X_1 + X_2 + \dots \Leftrightarrow X'_1 + X'_2 + \dots \, . \tag{3.1}$$

From the phenomenological point of view, the rates of reactions per unit time and unit volume of space in each direction of the reaction are proportional (with constants characterizing the probability of the reaction) to the product of densities $n_1 n_2 \dots$ and $n_{1'} n_{2'} \dots$. However, the balance of the reaction can be described also on a more detailed level of transitions between particular elementary quantum states of both ingoing and outgoing particles (including, e.g. their kinetic degrees of freedom). In this case the product of densities should be replaced by the product of the distribution functions normalized per quantum state (i.e. the occupation numbers). If we assume the distributions into the states of the participating particles to be known, the macroscopic rates can be then obtained by the averaging of the elementary probabilities over the distribution of initial states and by summation over the final states of particles participating in the reaction. Hereafter, wee shall thus investigated the reaction (3.1) as a transition between particular quantum states.

In the detailed equilibrium, the numbers of reactions in both directions are balanced,

$$f_1 f_2 \dots P_{(12\dots \to 1'2'\dots)} = f_{1'} f_{2'} P_{(1'2'\dots \to 12\dots)} \, . \tag{3.2}$$

For example, in the case of decay of a particle in an upper excited state X_u into a lower state X_l with simultaneous emission of another particle p,

$$X_u \Leftrightarrow X_l + p \, , \tag{3.3}$$

the detailed balance

$$f_u P_{ul} = f_l f_p P_{lu} \tag{3.4}$$

(where P_{ul}, P_{lu} stand for the probabilities normalized per single states of u, l and p of the reaction in its corresponding directions), will occur, if the distribution of the particle p will be

$$f_p = \frac{f_u P_{ul}}{f_l P_{lu}} \; . \tag{3.5}$$

If the populations of both states $X_{u,l}$ are in thermodynamic equilibrium, i.e., if they satisfy the Boltzmann distribution $f_{u,l} \sim \exp(-E_{u,l}/kT)$, we thus find that the particle p carrying the difference between energies of both states, $E_p = E_u - E_l$, must obey the Boltzmann distribution corresponding to the same temperature,

$$f_p = \frac{P_{ul} \exp(-\frac{E_u}{kT})}{P_{lu} \exp(-\frac{E_l}{kT})} = \frac{P_{ul}}{P_{lu}} \exp(-\frac{E_p}{kT}) \; . \tag{3.6}$$

It is thus obvious that this description is inappropriate just in the desired case of radiative processes, because the equilibrium distribution of photons is given by the Planck distribution instead of the Boltzmann one.

The difference between the behaviour of photons and the above described behaviour of the non-quantum particle p consists in their bosonic nature, which makes the rates of their reactions dependent not only on the densities of particles incoming to the reaction, but also on the densities (occupation numbers of final states) of the outgoing bosons (and fermions, if they also participate in the reaction). Consequently, if the particle p in the process (3.3) should be a photon, the above given classical description (3.4) of the statistical equilibrium must be modified by enhancing the left hand side for the contribution of the so called 'induced emission' (to distinguish it from the simple 'spontaneous emission'), i.e., a process in which another photon (in the same state as the emitted one) participates. Let us denote the probability of spontaneous emission by one atom in the state u per unit time[1] into the chosen states l of the atom and p of the photon

$$P_{ul}^{\text{sp.}} = \frac{c}{h\nu} A_{ul} \; . \tag{3.7}$$

In addition to this spontaneous emission, the upper state can emit the photon by spontaneous emission with probability proportional to the occupation number of the emitted photon (due to its interaction with the already existing photon in this state),

$$f_p P_{ul}^{\text{ind.}} = \frac{c}{h\nu} I B_{ul} \; . \tag{3.8}$$

The process in opposite direction can occur only if the absorbed atom yields the energy needed for the excitation of the atom. Consequently, the probability of absorption (during a unit of time per atom in the l-state in a given radiation field) is proportional to the occupation number of photons,

$$f_p P_{lu} = \frac{c}{h\nu} I B_{lu} \; . \tag{3.9}$$

The equation of statistical balance of radiative processes, which should replace the non-quantum equation (3.4), thus reads

$$f_u A_{ul} + f_u I B_{ul} = f_l I B_{lu} \; . \tag{3.10}$$

[1]Note that according to Eqs. (4-2) – (4-4), or their use in (4-10), in [3, p. 78] the Einstein coefficients A_{ul}, B_{ul} and B_{lu} are introduced as probabilities per light-travel time of unit length, not per the unit time, and they give the energy, not the number of emitted photons. The corresponding multiplicator given by the speed and energy of photons cancels from the rate equations, however it must be included or skipped self-consistently in the treatment of radiative transfer as well as of the statistical equilibrium.

The detailed equilibrium of this reaction thus takes place if the distribution of photons given in terms of the specific intensity satisfies

$$I = \frac{f_u A_{ul}}{f_l B_{lu} - f_u B_{ul}} = \frac{A_{ul}}{B_{ul}} \frac{1}{\frac{f_l B_{lu}}{f_u B_{ul}} - 1} \ . \tag{3.11}$$

In thermodynamic equilibrium the states of the atom should be populated according to the Boltzmann distribution

$$\frac{f_l}{f_u} = \exp(-\frac{E_l - E_u}{kT}) = \exp(\frac{h\nu}{kT}) \ , \tag{3.12}$$

where we have used the relation $E_u - E_l = h\nu$ of conservation of the energy, and the intensity

$$I = \frac{A_{ul}}{B_{ul}} \frac{1}{\frac{B_{lu}}{B_{ul}} \exp(\frac{h\nu}{kT}) - 1} \tag{3.13}$$

should be equal to the Planck's black-body radiation

$$B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp(\frac{h\nu}{kT}) - 1} \tag{3.14}$$

with the same temperature T. It is possible only if the Einstein coefficients (up to now treated as characteristics of three independent quantum processes) will satisfy the Milne – Einstein relations

$$A_{ul} = \frac{2h\nu^3}{c^2} B_{ul} \ , \tag{3.15}$$

$$B_{ul} = B_{lu} \ . \tag{3.16}$$

In practice, we often denote as one atomic level not a single quantum state (e.g. l, u) but the so-called 'gross-state', i.e. a set of sub-states with (approximately) equal energies (e.g. L, U). The probability of transitions between these gross-states depends generally on the inner distribution of population of the initial states, e.g.

$$P_{UL} = \frac{\sum_{ul} f_u P_{ul}}{\sum_u f_u} \ . \tag{3.17}$$

However, in thermodynamic equilibrium, the populations f_u are equal in the whole set U of states u, i.e. the population of the gross-state is

$$f_U \equiv \sum_u f_u = g_U f_u \ , \tag{3.18}$$

where g_U is the statistical weight of the level, and hence

$$P_{UL} = \frac{1}{g_U} \sum_{ul} P_{ul} \ . \tag{3.19}$$

To calculate the contribution of the process (3.3) to the collisional term (2.10) on the right-hand side of equation of radiative transfer, we must re-normalize the number of individual processes from the single atom to the unit of volume

$$\left(\frac{\delta I}{\delta s}\right)_c \equiv \epsilon - \alpha I = n_u A_{ul} + n_u I B_{ul} - n_l I B_{lu} \ , \tag{3.20}$$

where $n_{u,l}$ are the volume densities of the atom in the corresponding state. The terms here correspond to the spontaneous emission, induced emission and the true absorption. Comparing the absolute term and the term linear in I, we find (taking into account also the Milne – Einstein relations) the emissivity

$$\epsilon = n_u A_{ul} = \frac{2h\nu^3}{c^2} n_u B_{ul} \ , \tag{3.21}$$

and the opacity

$$\alpha = n_l B_{lu} - n_u B_{ul} = n_l B_{ul}(1 - \frac{n_u}{n_l}) \ , \tag{3.22}$$

in which the true absorption is reduced for the negative absorption, i.e. the induced emission. The term in brackets is equal to $\left(1 - \exp(-\frac{h\nu}{kT})\right)$ in thermodynamic equation. However, if the thermodynamic equilibrium between the population of the upper and the lower level is violated, the populations must be substituted explicitly. In the case of 'negative temperature', i.e. the inversion $n_u > n_l$ the absorption coefficient is negative and the radiative transfer leads to the laser-effect, i.e. an exponential grow of the intensity.

Exercise 3 *Derive the relations between the overall Einstein coefficients for gross-states of degenerated atomic levels and those corresponding to individual sub-levels. Derive the Milne – Einstein relations (3.15), (3.16) for them. Hint: Sum the rate equation (3.10) for all sublevels and require the same form of the overall equation.*

3.2 Interaction of quantum systems with radiation field

Let us investigate a particle (atom, ion or molecule) described by its Hamiltonian H_P with quantum eigenstates $|a\rangle$,

$$H_P|a\rangle = E_{P,a}|a\rangle \ , \tag{3.23}$$

cf. e.g., [1, Chap. X]. The eigenvalues $E_{P,a}$ may be either in a discrete or in a continuous spectrum of the energy (the later case corresponds in fact to a system of particles, e.g., ion + electron).

The state of one photon is described by the momentum $\vec{p}$ and polarization $\vec{e}$ and will be denoted by the ket-vector $|\vec{p}\,\vec{e}\rangle$. However, the radiation field has a variable number of photons, and its state must be thus described in the representation of the second quantization, i.e., by the eigenstates

$$|N_1, N_2, ...\rangle = (N_1!N_2!...)^{-1/2} \eta_1^{N_1} \eta_2^{N_2} ...|0\rangle \tag{3.24}$$

of operators of number of particles

$$\mathcal{N}_j = \eta_j \bar{\eta}_j \ , \tag{3.25}$$

in the states $|\vec{p}_j\vec{e}_j\rangle|_{j=1}^{\infty}$. Here η_j, $\bar{\eta}_j$ and $\mathcal{N}_j$ are the creation operator, annihilation operator and the occupation number in the j-th state, resp., and $|0\rangle$ is the vacuum state. The Hamiltonian of a free radiation field reads

$$H_R = \sum_j E_{R,j}\mathcal{N}_j \ , \tag{3.26}$$

where

$$E_{R,j} = h\nu_j = c|\vec{p}_j| \tag{3.27}$$

is the energy of a photon in the j-th state.

The whole system of the particle plus the radiation field can be described by the ket-vectors

$$|a, N_1, N_2, ...\rangle = |a\rangle|N_1, N_2, ...\rangle \tag{3.28}$$

in the product space, and its Hamiltonian is

$$H = H_P + H_Q + H_R \ , \tag{3.29}$$

where H_Q is the interaction Hamiltonian intermediating the mutual influence between the particle and the radiation field. We can treat it as a small perturbation of the unperturbed Hamiltonian H_P+H_R of a noninteracting particle and field, which has the eigenvectors (3.28). This perturbation will thus cause a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ with the probability per unit time of

$$P_{if} = \frac{4\pi^2}{h}|\langle f|H_Q|i\rangle|^2\delta(E_i - E_f) \tag{3.30}$$

(E_i, E_f being the energies of the whole system). If the interaction Hamiltonian is expanded into a series in operators η_j, $\bar{\eta}_j$,

$$H_Q = V_0 + \sum_j(U_j\eta_j + \bar{U}_j\bar{\eta}_j) + \sum_{jk}(U_{jk}\eta_j\bar{\eta}_k + V_{jk}\eta_j\eta_k + \bar{V}_{jk}\bar{\eta}_j\bar{\eta}_k) + \dots \ , \tag{3.31}$$

where V_0, U_j, U_{jk}, V_{jk} etc. are some operators in the space of states of the particle (i.e., of kets $|a\rangle$; $\bar{U}_j, \bar{V}_{jk}$ etc. are the corresponding complex conjugates), the individual terms of this expansion can be interpreted as perturbations causing the transition of the particle only (V_0), transition with simultaneous emission or absorption of one photon at the state j (U_j or $\bar{U}_j$), transition with simultaneous absorption of photon at the state k and emission of another one at the state j (U_{jk}), transition with simultaneous emission of two photons (V_{jk}) and so on.

For instance, the probability of the absorption of a photon at state $|\vec{p}\vec{e}\rangle$ by transition of the particle from the lower state $|l\rangle$ to the upper state $|u\rangle$ can be evaluated according to Eq. (3.30) if we choose

$$|i\rangle = |l, N\rangle \quad \text{and} \quad |f\rangle = |u, N-1\rangle \ , \tag{3.32}$$

where N is the occupation number of the state $|\vec{p}\vec{e}\rangle$ and the occupation numbers of other states are skipped for brevity. Following the expansion (3.31),

$$\langle f|H_Q|i\rangle = \langle u|\bar{U}|l\rangle\langle N-1|\bar{\eta}|N\rangle = \sqrt{N}\langle l|U|u\rangle \ , \tag{3.33}$$

and hence according to (3.30) the probability of the absorption is

$$P_{lu} = \frac{4\pi^2}{h}N|\langle l|U|u\rangle|^2\delta(E_l + h\nu - E_u) \ . \tag{3.34}$$

In a similar way, to evaluate the probability of emission of a photon by the transition from the upper state $|u\rangle$ to the lower state $|l\rangle$ of the particle, we must choose

$$|i\rangle = |u, N\rangle \quad \text{and} \quad |f\rangle = |l, N+1\rangle \ . \tag{3.35}$$

Consequently, we find from (3.31),

$$\langle f|H_Q|i\rangle = \langle l|U|u\rangle\langle N+1|\eta|N\rangle = \sqrt{N+1}\langle l|U|u\rangle \ , \tag{3.36}$$

and the final probability of the emission

$$P_{ul} = \frac{4\pi^2}{h}(N+1)|\langle l|U|u\rangle|^2\delta(E_l + h\nu - E_u) \ . \tag{3.37}$$

The polarization of a photon can have two possible values only, while its momentum fills the whole 3-dimensional space. The number N of photons in the state $|\vec{p}\,\vec{e}\rangle$ is thus equal to the distribution function f of photons, i.e., according to Eq. (2.3), proportional to the specific intensity of the radiation field. Following Eq. (3.34), the probability of the absorption is thus proportional to the intensity of the radiation, which is in agreement with our assumption in the phenomenological description of radiative transfer (cf. Eq. (2.10)), as well as its treatment using Einstein coefficients (cf. Eq. (3.20)). However, the probability of the emission is, following Eq. (3.37), a sum of two terms, one being also linear in the intensity (the induced emission) and the other (the spontaneous emission) being constant. Values of all these terms are determined by the same matrix element $\langle l|U|u\rangle$, which is the quantum-field reason for the validity of Milne – Einstein relations (3.15) and (3.16) justified originally by the thermodynamic reasoning.

For practical calculations of the transition probabilities we must know (in addition to the eigenstates of the atom itself) the interaction Hamiltonian H_Q. For an electron (i.e., a charged particle with a magnetic moment associated with its spin) in an electromagnetic field the interaction Hamiltonian can be expressed as

$$H_Q = \frac{e}{mc}(\vec{p}\vec{A}) + \frac{e^2}{2mc^2}(\vec{A}\vec{A}) - \mu(\vec{\sigma}\vec{H}) \, , \tag{3.38}$$

where $\vec{p}$ is the momentum, e the charge, m the mass and $\vec{\sigma}$ the spin of the particle, $\mu = \frac{eh}{4\pi mc}$ is the Bohr magneton. $\vec{A}$ is the vector potential of the electromagnetic field, which is the superposition of contributions of individual harmonic modes

$$\vec{A} = \sum_j \sqrt{\frac{hc^2}{2\pi V \nu_j}} \vec{e}_j \left(\bar{\eta}_j \exp\left(ik_j x\right) + \eta_j \exp\left(-ik_j x\right)\right) \, , \tag{3.39}$$

where k_j is the wave 4-vector, i.e., $k_j x \equiv \frac{2\pi}{h}(\vec{p}_j\vec{x} - E_j t)$. The magnetic field can thus be expressed as

$$\vec{H} = \vec{\nabla} \times \vec{A} = i \sum_j \sqrt{\frac{hc^2}{2\pi V \nu_j}} [k_j \times \vec{e}_j] \left(\bar{\eta}_j \exp\left(ik_j x\right) - \eta_j \exp\left(-ik_j x\right)\right) \, . \tag{3.40}$$

Substituting (3.39) and (3.40) into (3.38) and comparing the result with (3.31), we find the operator corresponding to the one-photon emission and/or absorption to be

$$U_j = \sqrt{\frac{hc^2}{2\pi V \nu_j}} \left(\frac{e}{mc}(\vec{p}\vec{e}_j) + i\mu(\vec{\sigma}.[k_j \times \vec{e}_j])\right) \exp\left(-ik_j x\right) \, . \tag{3.41}$$

Following Eq. (3.37), the probability of the spontaneous emission thus reads

$$P_{ul}^{\mathrm{sp.}} = \frac{2\pi c^2}{V \nu_j} |\langle l| \left(\frac{e}{mc}(\vec{p}\vec{e}_j) + i\mu(\vec{\sigma}.[k_j \times \vec{e}_j])\right) \exp\left(-ik_j x\right)|u\rangle|^2 \delta(h\nu + E_l - E_u) \, . \tag{3.42}$$

Expanding the exponential into the Taylor series ($\exp(-ik_j x) = 1 - ik_j x + ...$) we get the matrix element of the transition as a sum of dipole, quadrupole and higher-order multipole terms of the electric (the terms with $(\vec{p}\vec{e}_j)$) and magnetic (the terms with $(\vec{\sigma}.[k_j \times \vec{e}_j])$) radiation.

3.3 Thermodynamic equilibrium

It is well known from thermodynamics that the distribution function of any system determines its entropy (related to the amount of information contained in the distribution function), which, according to the third law of thermodynamics, is non-decreasing function of time. An isolated system thus relaxes to the state of thermodynamic equilibrium for which the corresponding equilibrium distribution function is the maximum of the entropy and is dependent only on the values of conserved quantities of the system (like its energy, momentum, number of particles etc.). Some of them can be eliminated (like the momentum by the choice of the system rest-frame), to others there correspond some 'intensity'-quantities (like the temperature to the energy or chemical potential to the number of particles), which must have the same value for each (mutually interacting) subsystems of the system in the thermodynamic equilibrium.

An example, which will be of primary importance for our opacity calculations, is the case of non-quantum particles (i.e., particles for which their bosonic or fermionic nature can be neglected, e.g., owing to their small density), for which the thermodynamic equilibrium is described by the Boltzmann distribution

$$f = f_0 \exp(-\frac{E}{kT}) \, , \tag{3.43}$$

where E is the energy of the state of the particle. The special cases of this distribution are, e.g., the Maxwell distribution of particles velocities (for which $E = \frac{1}{2}mv^2$), the excitation (of electron levels or vibration and rotation modes of molecules), ionization equilibria, or the barometric formula for density of particles in a potential (e.g., the gravity) field ($E = m\Phi$).

Stellar atmosphere is not an isolated system and it is not in thermodynamic equilibrium. However, the relaxation times for reaching the equilibrium are so short for some subsystems of the atmosphere that these subsystem are nearly in equilibrium with some values of the temperature and the other parameters, which are determined by the balance with other subsystems. We thus use to approximate the inner distribution of such subsystems by a state of thermodynamic equilibrium (TE), with corresponding (mutually different) temperatures. This TE is often (nearly) valid for the above mentioned kinetic degrees of freedom in small parts of volume of the atmosphere. In principle, the kinetic temperatures in the same volume element of the atmosphere can be different for different kinds of particles, if they are heated or cooled in a different rate and the exchange of the energy between them is slower than their own Maxwellization (what is the case between the light electrons and heavy ions). However, these differences are mostly negligible. Due to the fast interaction between most (first of all the higher) excitation states of ions with the kinetic degrees of freedom, the distribution of the former tends to the TE with the same temperature and it is thus used to denote the corresponding kinetic temperature as the local temperature of the atmosphere (which is a function of position). If this equilibrium (with the same temperature) is reached by all degrees of freedom, or if we simplify the problem by this assumption, the corresponding state of the atmosphere is denoted as the local thermodynamic equilibrium (LTE). If at least some of the degrees of freedom have different population, their state (and the state of the whole atmosphere) is denoted as non-LTE.

A simple example of LTE is the Boltzmann distribution of electron excitation levels, in which the numerical density of ions at excitation level k is

$$n_k = n \frac{g_k}{Z(T)} \exp(-\frac{E_k}{kT}) = n \frac{g_k}{U(T)} \exp(-\frac{E_k - E_0}{kT}) \, , \tag{3.44}$$

where n is the total numerical density of the ion (in any level), g_k is the statistical weight of the level k and

$$U(T) \equiv Z(T) \exp(\frac{E_0}{kT}) = \sum_k g_k \exp(-\frac{E_k - E_0}{kT}) \tag{3.45}$$

is the so called partition function.[2] Let us note, that the partition function diverges for the infinite number of levels. In practice, in the limited volume available for a single atom, only a

[2] Obviously, U corresponds to populations expressed in terms of the excitation energy $E_k - E_0$, where E_0 is the

finite number of electron orbits can exist due to their dimensions increasing with the excitation energy. Nonetheless, the estimate of the maximum number of levels can non-negligibly influence the calculations of their populations in the case of smaller densities.

Another example of the Boltzmann distribution is the Maxwell distribution of particles into their kinetic degrees of freedom, for which the population of elementary quantum state reads

$$f(x,p) = f_0 \exp(-\frac{p^2}{2mkT}) \ . \tag{3.46}$$

The normalizing constant f_0 has to be found from the condition for the total number N particles in a reference volume V,

$$N = nV = \int f(x,p)\frac{d^3p d^3x}{h^3} = V \int f_0 \exp(-\frac{p^2}{2mkT})\frac{d^3p}{h^3} = V f_0 \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \ . \tag{3.47}$$

We thus see, that its inverse is proportional to the partition function $Z_{\rm kin}$ for the kinetic degrees of freedom,

$$Z_{\rm kin}(T) \equiv \frac{n}{f_0} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \ . \tag{3.48}$$

If a particle has both the inner and the kinetic degrees of freedom (or some other in addition), its energy is the sum of the corresponding energies ($E = E^{\rm in} + E^{\rm kin} + ...$) and the equilibrium distribution as well as its overall partition function are products of the corresponding terms for each degree of freedom ($f = f_{\rm in} f_{\rm kin} ...$, $Z = Z_{\rm in} Z_{\rm kin} ...$).

Another important consequence of the Boltzmann distribution in thermodynamic equilibrium is the ionization equilibrium, which is a special case of thermal equilibrium of any chemical reaction

$$\sum_i \nu_i X_i \Leftrightarrow \sum_j {\nu'}_j {X'}_j \tag{3.49}$$

between particles X_i and X_j (cf. Eq. (3.1); here ν, ν' are the stechiometric coefficients giving the number of particles of the same kind). The left- and the right- hand side of this equation can be treated as two possible composite states of the same physical system. In thermodynamic equilibrium their abundances

$$n_L \equiv \Pi_i (n_i)^{\nu_i} \qquad \text{and} \qquad n_R \equiv \Pi_j ({n'}_j)^{{\nu'}_j} \tag{3.50}$$

(in any possible energetic state of each side of Eq. (3.49)) will thus be proportional to their partition functions

$$n_L = n\frac{Z_L}{Z} \qquad \text{and} \qquad n_R = n\frac{Z_R}{Z} \ , \tag{3.51}$$

where $n \equiv n_L + n_R$, $Z \equiv Z_L + Z_R$,

$$Z_L \equiv \sum_{k_i} \exp(-\frac{1}{kT}\sum_i E_{i,k_i}) = \Pi_i (Z_i)^{\nu_i} \qquad \text{and} \qquad Z_R = \Pi_j ({Z'}_j)^{{\nu'}_j} \tag{3.52}$$

(k_i denotes possible energetic states of the particle X_i). Each particle has the kinetic degree of freedom with the partition function $Z_{\rm kin}$ given by Eq. (3.48), and it can have also inner degrees

energy of the ground level, while Z is referred to any choice of zero energy.

of freedom with $Z_{\rm in}$ given by Eq. (3.45). The equilibrium abundances of individual particles participating in the reaction (3.49) thus satisfy the equation

$$\frac{\Pi_i(n_i)^{\nu_i}}{\Pi_j(n'_j)^{\nu'_j}} = \frac{\Pi_i(Z_i)^{\nu_i}}{\Pi_j(Z'_j)^{\nu'_j}} = \frac{\Pi_i(U_i \exp(-\frac{E_{i0}}{kT})(2\pi h^{-2} m_i kT)^{\frac{3}{2}})^{\nu_i}}{\Pi_j(U_j \exp(-\frac{E_{j0}}{kT})(2\pi h^{-2} m_j kT)^{\frac{3}{2}})^{\nu'_j}} \ . \tag{3.53}$$

In the special case of the ionization[3] of j-times ionized atom X to the ion X_{j+1}

$$X_j \Leftrightarrow X_{j+1} + e \ , \tag{3.54}$$

We find the Saha equation

$$\frac{n_j}{n_{j+1} n_e} = \frac{U_j \exp(-\frac{E_{j,0}}{kT})}{2U_{j+1} \exp(-\frac{E_{j+1,0}}{kT})(2\pi h^{-2} m'_e kT)^{\frac{3}{2}}} \equiv K_j \ , \tag{3.55}$$

where $m'_e = m_e m_{j+1}/m_j$ is the reduced mass of the electron. If we know the total density n_X of atoms X (in any ionization state) and the electron density n_e, we can solve (for a given temperature) the set of J linear equations ($j = 0, 1, ... J-1$) and the normalization condition

$$\sum_{j=0}^{J} n_j = n_X \ , \tag{3.56}$$

for $J+1$ unknown variables n_j. If n_e is also unknown and it has to be determined from the ionization equilibrium at the fixed temperature either for given densities n_{X_k} of all kinds (labeled by k) of atoms (i.e., when the density of the plasma is fixed in addition to its chemical composition) or for a given numerical density n of all free particles

$$n_e + \sum_k n_{X_k} = n \tag{3.57}$$

(i.e., for fixed pressure $P = nkT$ of the gas) we must solve the sets of Saha equations (3.55) and their normalization conditions (3.56) for all k simultaneously with the condition of quasineutrality (the balance of charge)

$$n_e = \sum_{k,j} j n_{k,j} \tag{3.58}$$

either for fixed n_{X_k} in the former case or fixed only the relative abundances $x_k \equiv n_{X_k}/(n - n_e)$ in the later case. For instance, in a pure hydrogen plasma including also the negative ion ($n_{-1} \equiv n_{\rm H^-}$) at fixed pressure the set of equations reads

$$\begin{aligned}
n_{-1} &= n_0 n_e K_{-1} \ , &(3.59)\\
n_0 &= n_1 n_e K_0 \ , &(3.60)\\
n_e &= n_1 - n_{-1} \ , &(3.61)\\
n &= n_e + n_1 + n_0 + n_{-1} \ , &(3.62)
\end{aligned}$$

which yields a quadratic equation

$$n_e^2 K_0 (1 + n K_{-1}) + 2n_e - n = 0 \ , \tag{3.63}$$

[3] The same results can be obtained both from the set of these subsequent ionizations or from the set of direct ionizations of the neutral atom, $X_0 \to X_j + je$. It is obvious, that a set of equations of the type (3.49) can be handled as a set of (homogeneous, also negative ν_i are allowed) linear algebraic equations.

with two solutions (one of which is unphysical)

$$n_e = \frac{\pm\sqrt{1 + nK_0(1 + nK_{-1})} - 1}{K_0(1 + nK_{-1})} \, . \tag{3.64}$$

For a mixture of hydrogen and helium the corresponding equation for n_e is of the 5th degree (or the 4th if H^- is neglected) and its degree increases with the number of ions included. In practice it is thus solved numerically either by straightforward iterations of n_e or by linearization in its perturbations.

Exercise 4 *Investigate the ionization equilibrium of hydrogen plasma with constant density. Find the general equation for n_e, its solution neglecting H^- and its perturbation due to H^-.*