Calculating Level Populations of Ions in a Hot Plasma

Calculating the level population of an ion in collisional ionization equilibrium is conceptually quite simple. The most trivial example is that of a two level ion, with a ground state (1) and an excited state (2). In this case, the level population is calculated by balancing the excitation and de-excitation rates. Assume the collisional excitation rate is $\gamma_{1\to 2}(T)\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, the collisional de-excitation rate is $\gamma_{2\to 1}(T)\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, and the radiative rate is $A_{2\to 1}\,\mathrm{s}^{-1}$. Then in equilibrium the excitation rate equals the de-excitation rate so:

$$n_e p_1 \gamma_{1\to 2} = n_e p_2 \gamma_{2\to 1} + p_2 A_{2\to 1} \tag{1}$$

where p_1 and p_2 are the fractional level populations of level 1 and 2, respectively. In the case of a two-level atom, balancing the excitations and de-excitations into the ground state or the excitated state gives identical equations. This is not the case for atoms with more than 2 levels, however, as will be seen.

Continuing, we can solve equation (1) for p_2/p_1 we get

$$\frac{p_2}{p_1} = \frac{n_e \gamma_{1\to 2}}{n_e \gamma_{2\to 1} + A_{2\to 1}}. \tag{2}$$

Finally, using the requirement that $p_1 + p_2 = 1$, we get:

$$p_1 = \frac{n_e \gamma_{2\to 1} + A_{2\to 1}}{n_e(\gamma_{2\to 1} + \gamma_{1\to 2}) + A_{2\to 1}} \tag{3}$$

$$p_2 = \frac{n_e \gamma_{1\to 2}}{n_e(\gamma_{2\to 1} + \gamma_{1\to 2}) + A_{2\to 1}} \tag{4}$$

We can now consider the slightly more complex example of a three-level atom. In this case, we will have a larger number of excitation and de-excitation rates: $\gamma_{1\to 2}$, $\gamma_{1\to 3}$, $\gamma_{2\to 3}$, $\gamma_{3\to 1}$, $\gamma_{3\to 2}$, $\gamma_{2\to 1}$, $A_{2\to 1}$, $A_{3\to 1}$, and $A_{3\to 2}$. The method remains the same, however: in equilibrium, the excitation and de-excitation rates out of each level are balanced. Therefore, we can write the following equations:

$$p_1 + p_2 + p_3 = 1 \tag{5}$$

$$n_e(p_2\gamma_{2\to 1} + p_3\gamma_{3\to 1}) + p_2 A_{2\to 1} + p_3 A_{3\to 1} = n_e p_1(\gamma_{1\to 2} + \gamma_{1\to 3}) \tag{6}$$

$$n_e(p_1\gamma_{1\to 2} + p_3\gamma_{3\to 2}) + p_3 A_{3\to 2} = n_e p_2(\gamma_{2\to 1} + \gamma_{2\to 3}) + p_2 A_{2\to 1} \tag{7}$$

$$n_e(p_1\gamma_{1\to 3} + p_2\gamma_{2\to 3}) = n_e p_3(\gamma_{3\to 2} + \gamma_{3\to 1}) + p_3(A_{3\to 1} + A_{3\to 2}) \tag{8}$$

We now have four equations but only three variables (p_1, p_2, and p_3). This system is degenerate, and so one equation must be removed. This must be done with some care, however. Assume we randomly select a level i and remove it from the equations to be solved. If $A_{i\to j} \equiv \gamma_{i\to j} \equiv \gamma_{j\to i} \equiv 0$ for all j, then level i is not connected to any other level. Levels of this type must be removed from the level population calculation in any event, but removing it will not remove the degeneracy. The only level which we can guarantee will be connected to others is the ground state level. Therefore, removing the ground state balancing equation when calculating the level population assures that the population equations will be soluble.

Equations (8) can be written in matrix form, as follows:

$$\begin{bmatrix} 1 & 1 & 1 \\ n_e\gamma_{1\to2} & -n_e(\gamma_{2\to1}+\gamma_{2\to3})-A_{2\to1} & n_e\gamma_{3\to2}+A_{3\to2} \\ n_e\gamma_{1\to3} & n_e\gamma_{2\to3} & -n_e(\gamma_{3\to1}+\gamma_{3\to2})-A_{3\to2}-A_{3\to1} \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad (9)$$

Solving for the level population, then, is done by inverting this matrix equation. This method can easily be extended to n levels. Note the density dependence is explicitly included, since it affects the collisional rates but not the radiative rates.

Equation (9) covers the case of an ion in isolation. However, ionization and recombination can affect the results. Ionization to an excited level can occur, but is rare. However, recombination to an excited state can and does regularly happen, via two different processes: radiative recombination and dielectronic recombination. We will consider these separately.

In the case of radiative recombination to an excited level, the rate for recombination to the nth level is α_n^{RR}, in units of cm^3/s. The total rate per unit volume is $n_e n_{I^+}\alpha_n^{RR}$, where n_{I^+} is the density of the ionized atom.

Dielectronic recombination occurs when an electron recombines and simultaneously excites an electron in the recombined atom, resulting in a doubly-excited state. This can be resolved by auto-ionization or by radiative stabilization. In this latter case, first one electron radiatively transitions to a lower level (creating a satellite line) and then the atom is left in a singly excited state. The rate for such recombinations can be written as $\alpha_n^{DR} n_e n_{I^+}$, in recombinations per second.

The total recombination rate to an excited level n is therefore $n_e n_{I^+}(\alpha_n^{RR} + \alpha_n^{DR})$. We can now re-write equations 5-8 including this term and get:

$$p_1 + p_2 + p_3 = 1 \quad (10)$$

$$n_e(p_2\gamma_{2\to1} + p_3\gamma_{3\to1}) + p_2A_{2\to1} + p_3A_{3\to1} + n_e(\alpha_1^{DR} + \alpha_1^{RR})\frac{n_{I^+}}{n_I} = n_e p_1(\gamma_{1\to2} + \gamma_{1\to3}) \quad (11)$$

$$n_e(p_1\gamma_{1\to2} + p_3\gamma_{3\to2}) + p_3A_{3\to2} + n_e(\alpha_2^{DR} + \alpha_2^{RR})\frac{n_{I^+}}{n_I} = n_e p_2(\gamma_{2\to1} + \gamma_{2\to3}) + p_2A_{2\to1} \quad (12)$$

$$n_e(p_1\gamma_{1\to3} + p_2\gamma_{2\to3}) + n_e(\alpha_2^{DR} + \alpha_2^{RR})\frac{n_{I^+}}{n_I} = n_e p_3(\gamma_{3\to2} + \gamma_{3\to1}) + p_3(A_{3\to1} + A_{3\to2}) \quad (13)$$

Since this rate is not proportional to the any of the level populations of the recombined atom, it cannot be in the $N \times N$ matrix, but rather must be on the right hand side of the equation. In addition, all the rates in equation (9) are proportional to the atom density n_I, while the recombination rates are proportional to n_{I^+}. This requires adding the factor of n_{I^+}/n_I seen above.

Therefore in the case of the 3 level atom, we have for the matrix formulation:

$$\begin{bmatrix} 1 & 1 & 1 \\ n_e\gamma_{12} & -n_e(\gamma_{21}+\gamma_{23})-A_{21} & n_e\gamma_{32}+A_{32} \\ n_e\gamma_{13} & n_e\gamma_{23} & -n_e(\gamma_{31}+\gamma_{32})-A_{32}-A_{31} \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -n_e\frac{n_{I+}}{n_I}(\alpha_2^{RR}+\alpha_2^{DR}) \\ -n_e\frac{n_{I+}}{n_I}(\alpha_3^{RR}+\alpha_3^{DR}) \end{bmatrix} \tag{14}$$

Note that arrows have been left out of the subscripts; γ_{21} should be read as $\gamma_{2\to1}$.