

## Influence of Atom-Atom Collisions on the Population Densities of Excited Atomic Levels

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The number densities of excited hydrogen atoms in a non-thermal plasma have been calculated on the basis of a coupled system of rate equations (25 levels) in which one accounts for electron-atom and atom-atom collisions. The calculated population densities depend strongly on the neutral particle density  $n_a$  when  $n_e/n_a \ll 1$ . When the electron temperature,  $T_e$ , is different from the gas temperature,  $T_g$ , the number densities of the excited levels are determined by  $T_g$  rather than by  $T_e$ . This is important in connection with the quantitative spectroscopy of plasmas.

### Introduction

For a non-thermal plasma, the population densities of the ground and of the excited levels have to be calculated from a coupled system of rate equations containing the various radiative and collisional rate coefficients. In all papers published up to now one only considered electronic collisions and the usual radiative transition processes. The influence of heavy particle collisions besides electronic collisions has always been ignored. However, as soon as the condition

$$n_a \langle \sigma_a^a v_a \rangle_{\text{atom-atom}} \gg n_e \langle \sigma_e^a v_e \rangle_{\text{electron-atom}} \quad (1)$$

is fulfilled the inelastic atom-atom collisions will be more efficient than the electron-atom encounters. Thus, the population densities will be determined by atomic collisions rather than by electronic ones. Due to the small efficiency for momentum transfer atom  $\rightarrow$  electron and the small atomic velocities (compared to those of the electrons) the atom-atom collisions can be estimated to be more effective than electron-atom collisions when the atomic number density  $n_a$  fulfills the condition

$$\begin{aligned} n_a/n_e &\gg \{(m_a + m_e)/2 m_e\} \{m_a/m_e\}^{1/2} f(i, T_e, T_g) \\ &\approx \frac{1}{2} (m_a/m_e)^{3/2} f(i, T_e, T_g) \end{aligned} \quad (2)$$

where  $f(i, T_e, T_g)$  is a function<sup>1</sup> depending on the principal quantum number  $i$  of the level considered, on the electron temperature  $T_e$  and on the gas temperature  $T_g$ . All levels for which this condition is fulfilled should depend on  $T_g$  rather than on  $T_e$ . It seems that this situation has not yet been treated quantitatively in the literature.

In this paper we study numerically the influence of collisions of hydrogen atoms on the level populations of hydrogen atoms. For reasons of simplicity in the establishment of the basic equations it is assumed that the plasma consists of atoms, electrons, and protons

only, the density of the  $H_2$ -molecules is assumed to be negligibly small compared to that of the H-atoms. Under actual conditions the  $H_2$ -molecules should not be omitted. However, inspection of the cross sections for atomic and molecular collisions shows that the results should not be very different (at least for the highly excited atomic levels) when the atomic number density  $n_a$  is replaced by the molecular number density.

### Basic Process and Equations

The following reaction processes are taken into account:

1. Ionization by electronic collisions and recombination by 3-body collisions (ion plus two electrons). For the  $i$ -th level, the reaction rates are

$$\begin{aligned} \text{ionization:} & \quad n_i n_e S_i^{(e)}, \\ \text{recombination:} & \quad n_+ n_e^2 Q_i^{(e)} \end{aligned}$$

where  $n_+$  is the proton number density. The subscript  $i$  denotes the principal quantum number. The reaction coefficients  $S_i^{(e)}$  and  $Q_i^{(e)}$  are functions of  $i$  and of the electron temperature  $T_e$ .

2. Photoionization and radiative recombination. For the  $i$ -th level, one has the reaction rates:

$$\begin{aligned} \text{ionization:} & \quad n_+ n_e (1 - A_i) R_i, \\ \text{recombination:} & \quad n_+ n_e R_i. \end{aligned}$$

The coefficient  $A_i$  accounts for the optical thickness of the transition  $i \rightarrow$  continuum.  $A_i$  may be identified with an effective escape factor for free-bound emission associated with level  $i$ . For  $A_i = 1$ , the transition continuum  $\rightarrow i$  is completely optically thin, thus, photoionization becomes equal to zero. The value  $A_i = 0$  means a complete optically opaque free-bound transition: The recombination rate will completely be balanced by the photoionization rate.

3. Excitation of level  $i$  by collisions of electrons with a lower lying level  $h$  and collisional de-excitation of level  $i$  by electronic collisions (superelastic collisions). The reaction rates are:

$$\begin{aligned} \text{excitation:} & \quad n_h n_e C_{hi}^{(e)}, \\ \text{de-excitation:} & \quad n_i n_e F_{ih}^{(e)}, \end{aligned} \quad h < i.$$

4. Spontaneous de-excitation of level  $i$  towards a lower lying level  $h$ , and the radiative excitation of level  $i$  due to the reabsorption of photons of frequency  $\nu_{ih}$ . As in the case of photoionization, the effect of the radiation field may be characterized by a gross escape factor  $A_{ih}$ . A plasma is optically opaque if  $A_{ih} = 0$ , and completely optically thin if  $A_{ih} = 1$ . Thus, the reaction rates write for the  $i$ -th level coupled with level  $h$ :

$$\begin{aligned} \text{radiative excitation:} & \quad n_i (1 - A_{ih}) A_{ih}, \\ \text{spontaneous de-excitation:} & \quad n_i A_{ih}. \end{aligned}$$

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<sup>1</sup>  $f(i, T_e, T_g)$  contains the form of the collision cross sections for collisions of the type  $e + a$  and  $a + a$ .



The  $A_{ih}$  are the Einstein coefficients. Induced emission is assumed to be contained in the coefficient

$$(1 - A_{ih}) A_{ih}.$$

5. Ionization by collisions with ground state hydrogen atoms ( $i=1$ ) of number density  $n_1$ , and 3-body collisional recombination. For the  $i$ -th level, the reaction rates are:

$$\begin{aligned} \text{ionization:} & \quad n_i n_1 S_i^{(1)}, \\ \text{recombination:} & \quad n_+ n_e n_1 Q_i^{(1)}. \end{aligned}$$

6. Excitation of level  $i$  by collisions of ground state hydrogen atoms ( $i=1$ ) of number density  $n_1$  with lower lying levels  $h$ , and the inverse process (superelastic collisions). The reaction rates are:

$$\begin{aligned} \text{excitation:} & \quad n_h n_1 C_{hi}^{(1)}, \\ \text{de-excitation:} & \quad n_i n_1 F_{hi}^{(1)}, \quad h < i. \end{aligned}$$

These six times two reaction processes must be coupled with the Boltzmann collision equations and with the radiative transfer equations. The solution of the radiative transfer equations is avoided by the introduction of the coefficients  $A_i$  and  $A_{ih}$ . These coefficients may be chosen arbitrarily. We have put:  $A_{i1}=0$ , all other  $A_{ih}=1$ , and all  $A_i=1$ . This corresponds to a plasma which is optically opaque towards the lines of the Lyman series. All other transitions are assumed to be optically thin. This case applies to many actual conditions.

We now assume a quasi-steady state ( $\partial/\partial t \equiv 0$ ) for the excited levels  $i > 1$  and a homogeneous plasma ( $\nabla_r \equiv 0$ ). The population densities can then be calculated from a coupled system of equations of the following kind:

$$\begin{aligned} \left( \frac{\partial n_i}{\partial t} \right)_{\text{collision, radiation}} = 0 = & \sum_{h < i}^{i-1} n_h \left[ n_e C_{hi}^{(e)} + n_1 C_{hi}^{(1)} \right. \\ & \left. + \frac{n_i}{n_h} (1 - A_{ih}) A_{ih} \right] \\ & + \sum_{k > i}^p n_k [n_e F_{ki}^{(e)} + n_1 F_{ki}^{(1)} + A_{ki}] \\ & + n_+ n_e [R_e + n_e Q_i^{(e)} + n_1 Q_i^{(1)}] \\ & - n_i \sum_{h < i}^{i-1} [n_e F_{ih}^{(e)} + n_1 F_{ih}^{(1)} + A_{ih}] \quad (3) \\ & - n_i \sum_{k > i}^p \left[ n_e C_{ki}^{(e)} + n_1 C_{ki}^{(1)} \right. \\ & \quad \left. + \frac{n_k}{n_i} (1 - A_{ki}) A_{ki} \right] \\ & - n_i \left[ n_e S_i^{(e)} + n_1 S_i^{(1)} \right. \\ & \quad \left. + \frac{n_+ n_e}{n_i} (1 - A_i) R_i \right] \end{aligned}$$

with  $i=2, \dots, p$ , where  $p$  is the highest still bound level. We considered  $p=25$  levels for the numerical evaluation. This is sufficient to see the effect we are interested in. It should be mentioned that the coupled system to be solved is non-linear in  $n_1$  when all 25 equations are considered. However, we are interested

in an extrem non-equilibrium situation, e. g. a recombining plasma, or a plasma in which a second group of electrons of low density  $n_e^*$  and high temperature  $T^*$  determines the ratio  $n_e/n_1$ , where  $n_e$  and  $T_e$  refer to the cold group. Under these conditions one may drop the rate equation belonging to level  $i=1$ . The remaining  $p-1=24$  equations are linear in  $n_2, n_3, \dots, n_p$  and all  $n_i > 1$  can be calculated when  $n_e, n_1, T_e, T_g$  are given. It should also be mentioned that a second group of hot electrons practically does not change the population densities of the higher excited levels provided that  $n_e^* \ll n_e, T^* \gg T$ . This has been checked numerically by solving a coupled system of rate equations for two groups of electrons, see Ref. <sup>2</sup>.

The results of the present calculations are independent on any assumption about a second group or the special state of the plasma, since the coupled system of rate equations treated here is only based on two assumptions: 1. quasi-steady state and 2. homogeneous, for  $i > 1$ . Under these two conditions the coupled system of rate equations can formally be solved when  $n_e, n_1, T_e$  and  $T_g$  are given. One needs no additional conditions.

The cross sections and rate coefficients used in this paper are the same as in Ref. <sup>3</sup> for the calculation of the collisional-radiative recombination coefficients.

### The Results

A few typical results are shown in Figs. 1 to 5. The Figs. 1 to 3 show how the number densities of the excited states change with  $n_e, n_1$  and  $T$ , when  $T=T_e=T_g$ . One sees that the number density  $n_i$  of the *highly excited levels* is practically independent from  $n_1$  for given values of  $n_e$  and  $T$ . However, the number densities of levels with *medium quantum numbers* strongly change with  $n_1$ . For low electron densities this effect is more pronounced than for high values of  $n_e$ .

It should be pointed out that the calculated number densities  $n_i$  become independent from  $n_1$  if  $n_1 < 10^4 n_e$ . The coefficient  $10^4$  corresponds approximately to the ratio  $(m_H/m_e)^{3/2}$  in the condition (2) when one assumes for the quantity  $f(i, T_e=T_g=T)$  the order of magnitude one.

The Figs. 4 and 5 show the population densities  $n_i$  when the gas temperature  $T_g$  is different from the electron temperature  $T_e$ . When  $n_e/n_1$  is sufficiently small the heavy particle collisions practically determine the population densities of all levels. This dependence has a consequence in connection with the temperature determination from the relative line intensities: By drawing the line intensities  $I$  divided by the statistical weight  $g$  in a semi-logarithmic scale as a function of the excitation energy  $E$  one obtains the temperature  $T$  from the slope  $\Delta \log(I/g)/\Delta E$ . In stead of  $\log(I/g)$  one may draw the quantity  $\log(n_i/g_i)$  as a function of  $1/i^2$ . This has been done for the values given in Fig. 5, the result is shown in Fig. 6.

One sees that it is practically not possible to obtain a temperature from the level populations belonging to low and medium principal quantum numbers. In this

<sup>2</sup> H. W. DRAWIN, Ann. Phys. Leipzig **17**, 374 [1966].

<sup>3</sup> H. W. DRAWIN, Z. Phys. **225**, 483 [1969].

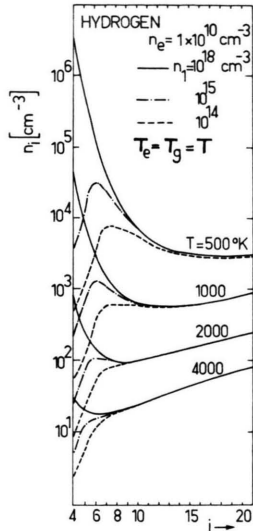


Fig. 1

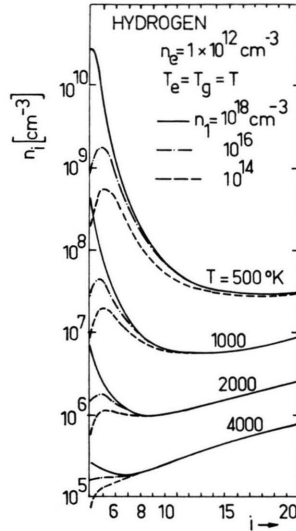


Fig. 2

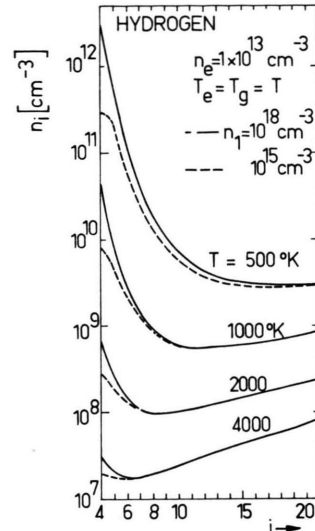


Fig. 3

Figs. 1 to 3. Population densities  $n_i$  of hydrogen levels when  $T_e = T_g = T$ . Lyman lines optically thick, all other transitions optically thin.

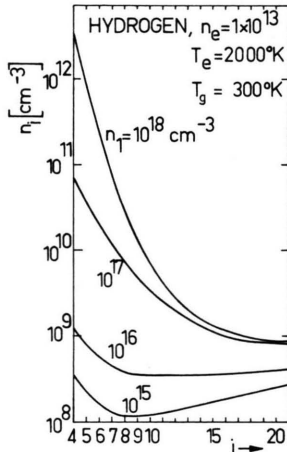


Fig. 4

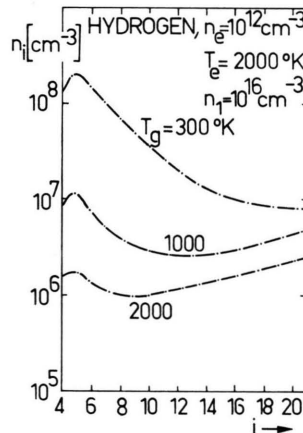


Fig. 5

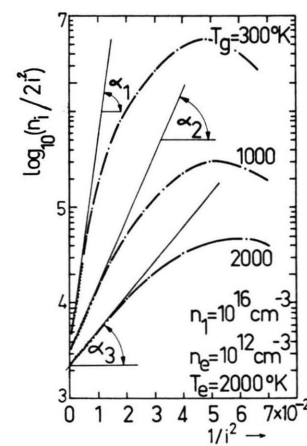


Fig. 6. Determination of the temperature from the slope of the population densities as a function of  $1/i^2$ . The temperatures obtained corresponds to the temperature  $T_g$ .

region of  $i$  one gets neither  $T_e$  nor  $T_g$ , the slope is a complicated function of  $T_e$ ,  $T_g$ ,  $n_e$ ,  $n_1$ , and  $i$ . A slope common to many levels can only be drawn for sufficient highly excited levels. The slopes (in Fig. 6) having angles  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  lead to the temperatures  $T = 300$  °K,  $1000$  °K, and  $2000$  °K, respectively. These are exactly the values of  $T_g$  initially used for calculating  $n_i$  from the coupled system of rate equations. *The slopes do not depend on  $T_e$  (!) provided  $n_e/n_1 \ll 1$ .*

This result may be generalized as follows: In a plasma of low ionization degree in which the electron

temperature is different from the gas temperature the spectral line intensities will give the gas temperature rather than the temperature of the electrons. To obtain  $T_g$  one has to evaluate the lines originating from highly excited levels. Intensities from low and medium levels do not permit a determination of  $T$ , if  $T_e \neq T_g$ . This result is in general agreement with recent measurements made by KLAN<sup>4</sup> on a P.I.G. discharge in helium gas.

I thank Miss F. EMARD for having written the computer programme.

<sup>4</sup> F. KLAN, Report I.P.P. 3/92 (1969), Institut für Plasmaphysik, Garching, and privat communication.