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

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

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 → 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

$$n_a/n_e \gg \{(m_a+m_e)/2\,m_e\}\{m_a/m_e\}^{1/2} f(i, T_e, T_g) \approx \tfrac{1}{2}(m_a/m_e)^{3/2} f(i, T_e, T_g) \qquad (2)$$

where $f(i, T_e, T_g)$ is a function [1] 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

ionization: $n_i\, n_e\, S_i^{(e)}$,

recombination: $n_+\, n_e^2\, Q_i^{(e)}$

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:

ionization: $n_+\, n_e (1-\Lambda_i)\, R_i$,

recombination: $n_+\, n_e\, R_i$.

The coefficient Λ_i accounts for the optical thickness of the transition $i \rightarrow$ continuum. Λ_i may be identified with an effective escape factor for free-bound emission associated with level i. For $\Lambda_i = 1$, the transition continuum $\rightarrow i$ is completely optically thin, thus, photoionization becomes equal to zero. The value $\Lambda_i = 0$ 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:

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

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 ν_{ih}. As in the case of photoionization, the effect of the radiation field may be characterized by a gross escape factor Λ_{ih}. A plasma is optically opaque if $\Lambda_{ih} = 0$, and completely optically thin if $\Lambda_{ih} = 1$. Thus, the reaction rates write for the i-th level coupled with level h:

radiative excitation: $n_i (1-\Lambda_{ih})\, A_{ih}$,

spontaneous de-excitation: $n_i\, A_{ih}$.

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

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

$$(1-\Lambda_{ih})\,A_{ih}\,.$$

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:

ionization: $n_i\,n_1\,S_i^{(1)}$,

recombination: $n_+\,n_e\,n_1\,Q_i^{(1)}$.

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:

excitation: $n_h\,n_1\,C_{hi}^{(1)}$

de-excitation: $n_i\,n_1\,F_{hi}^{(1)}$, $h<i$.

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 Λ_i and Λ_{ih}. These coefficients may be chosen arbitrarily. We have put: $\Lambda_{i1}=0$, all other $\Lambda_{ih}=1$, and all $\Lambda_i=1$. 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 populaton densities can then be calculated from a coupled system of equations of the following kind:

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

with $i=2,\ldots,p$, 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 $n_2, n_3, \ldots, n_p$ 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. [2].

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. [3] 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 posible to obtain a temperature from the level populations belonging to low and medium principal quantum numbers. In this

[2] H. W. Drawin, Ann. Phys. Leipzig **17**, 374 [1966].

[3] H. W. Drawin, Z. Phys. **225**, 483 [1969].

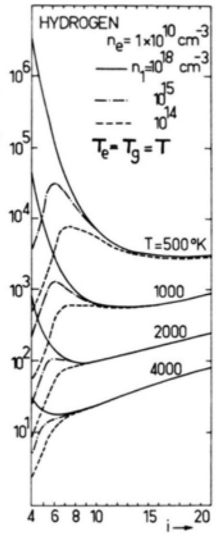

Fig. 1

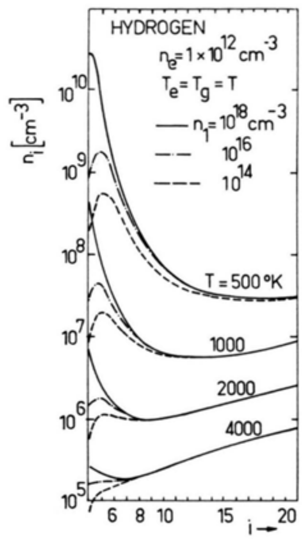

Fig. 2

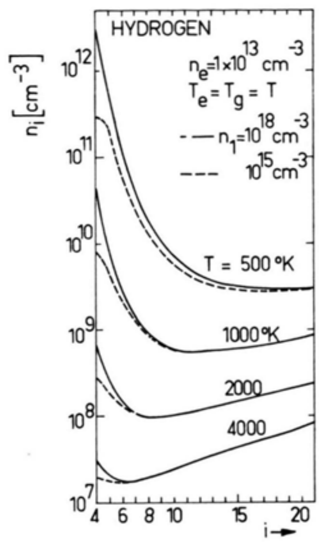

Fig. 3

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.

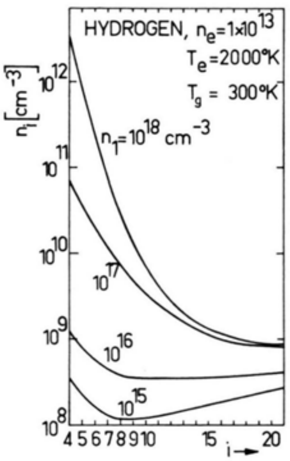

Fig. 4

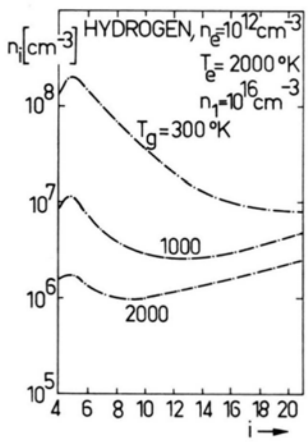

Fig. 5

Figs. 4 to 5. Population densities n_i of hydrogen levels when $T_e = T_g = T$. Lyman lines optically thick, all other transitions optically thin.

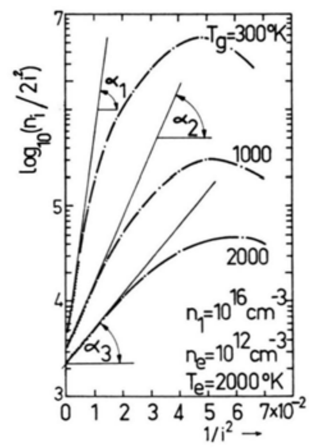

Fig. 6. Determination of the temperature from the slope of the population densities as a function of $1/i^2$. The temperatures obtained corresponds to the temperature T_g.

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 α_1, α_2, and α_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 no 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 [4] on a P.I.G. discharge in helium gas.

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

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