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The rate coefficients for the processes of $(n - n')$-mixing in collisions of Rydberg atoms $\mathrm{H}^*(n)$ with H(1s) atoms

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Abstract

This paper presents the results of semi-classical calculations of rate coefficients of $(n - n')$-mixing processes in collisions of Rydberg atoms $\mathrm{H}^*(n)$ with H(1s) atoms. These processes have been modelled by the mechanism of the resonant energy exchange within the electron component of the $\mathrm{H}^*(n) + \mathrm{H}$ collisional system. The calculations of the rate coefficients, based on this model, were performed for the series of principal quantum numbers, n and n', and atomic, T_a, and electronic, T_e, temperatures. It was shown that these processes can be of significant influence on the populations of Rydberg atoms in weakly ionized plasmas (ionization degree $\lesssim 10^{-4}$), and therefore have to be included in appropriate models of such plasmas.

1. Introduction

This paper presents a further necessary investigation of two groups of inelastic collisional processes $\mathrm{H}^*(n) + \mathrm{H}$ and $\vec{\mathrm{e}}_k + \mathrm{H}^+ + \mathrm{H}$, where $\mathrm{H} = \mathrm{H(1s)}$, $\mathrm{H}^*(n)$ is a hydrogen atom in a Rydberg state with the principal quantum number n, and $\vec{\mathrm{e}}_k$ is a free electron with energy ϵ_k.

The first group of processes is $(n - n')$-mixing, both excitation:

$$\mathrm{H}^*(n) + \mathrm{H} \rightarrow \begin{cases} \mathrm{H}^*(n' = n + p) + \mathrm{H}, \\ \mathrm{H} + \mathrm{H}^*(n' = n + p), \end{cases} \tag{1}$$

and de-excitation:

$$\mathrm{H}^*(n) + \mathrm{H} \rightarrow \begin{cases} \mathrm{H}^*(n' = n - p) + \mathrm{H}, \\ \mathrm{H} + \mathrm{H}^*(n' = n - p), \end{cases} \tag{2}$$

where $p \geqslant 1$.

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A second group of processes consists of chemi-ionization:

$$\mathrm{H} + \mathrm{H}^*(n) \rightarrow \vec{\mathrm{e}}_k + \begin{cases} \mathrm{H}^+ + \mathrm{H}, \\ \mathrm{H} + \mathrm{H}^+, \end{cases} \tag{3}$$

and chemi-recombination processes:

$$\vec{\mathrm{e}}_k + \mathrm{H}^+ + \mathrm{H} \rightarrow \begin{cases} \mathrm{H} + \mathrm{H}^*(n), \\ \mathrm{H}^*(n) + \mathrm{H}. \end{cases} \tag{4}$$

Note that the resonant energy exchange within the electronic component of the collisional system was considered to be the main mechanism in these processes. It is different from the inelastic processes in $\mathrm{H}^*(n) + \mathrm{M}$ and $\vec{\mathrm{e}}_k + \mathrm{H}^+ + \mathrm{H}$ collisions, caused by direct interactions between the outer electron and atom or molecule M, whose electronic state remains unchanged during collisions (see [1–3]).

Processes (3) and (4) were extensively investigated. In [4], a semi-classical theory of the process (3) was formulated, and later in [5, 6] the method was developed to calculate the rate coefficients of (3) and (4). The method was finalized in [7, 8], where the rate coefficients were calculated for the equilibrium ($T_\mathrm{e} = T_\mathrm{a}$) and non-equilibrium ($T_\mathrm{e} > T_\mathrm{a}$) hydrogen plasmas, in wide domains of n, T_a and T_e. In [9], the rate coefficients of (3) and (4) were calculated for the Sun's photosphere. Results in [8, 9] showed that for weakly ionized hydrogen plasmas (ionization degree $\sim 10^{-4}$), these processes should be the dominant mechanisms for the population of Rydberg atoms, in comparison with other ionization and recombination processes. This was confirmed in [10], by calculations with the programme PHOENIX for modelling stars' atmospheres.

The total population of Rydberg atoms in weakly ionized hydrogen plasmas, as well as their distribution with respect to quantum numbers, is important for plasmas' kinetics. Therefore, apart from chemi-ionization and chemi-recombination processes, the processes of $(n - n')$-mixing must be taken into account. In [11, 12] it was found that the cross-sections for processes (1) and (2) were of an order of magnitude higher than that of the corresponding gas-kinetic processes. It suggested that apart from (3) and (4), processes (1) and (2) must be included for a full analysis of inelastic Rydberg atom–atom collisions and their influence on the Rydberg atom populations in weakly ionized hydrogen plasmas. This is illustrated in figure 1, where dashed arrows show links between Rydberg states and the continuum caused by (3) and (4), and bold arrows show links between Rydberg states themselves caused by processes (1) and (2).

The analysis of $(n - n')$-mixing processes is based on calculations of rate coefficients as functions of n, n' and atomic temperature T_a. We developed a semi-classical method for the rate coefficients of processes (1) and (2) within the Rydberg domain of principal quantum numbers ($n \gg 1$). The method was applied for a series of n, p, T_a and T_e, in domains of their values typical for a weakly ionized hydrogen plasma, similar to those in [7, 8]. The results allowed us to compare (1) and (2) with the corresponding inelastic electron–atom collisional processes.

2. A resonant mechanism of inelastic processes

In experiments [13], a high efficiency of $(n - n')$-mixing in symmetrical atom–Rydberg atom scattering in weakly ionized gas plasmas has been established. The theoretical explanation in [11] introduced the mechanism of the resonant energy exchange within the electronic component of the given collisional system, satisfying the constraint:

$$R \ll r_n, \tag{5}$$

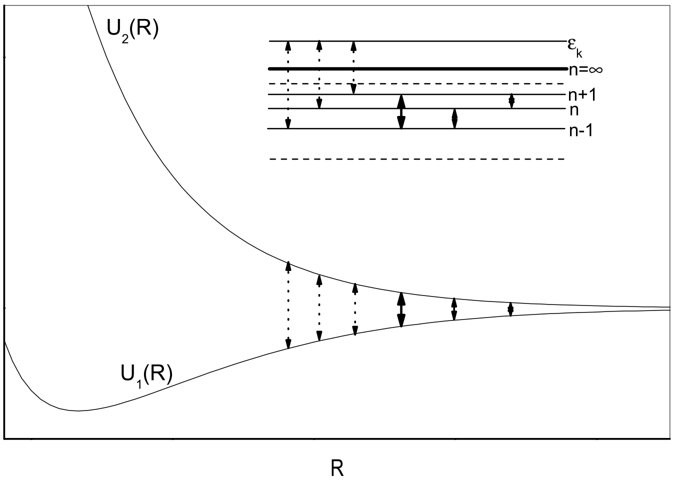

Figure 1. A diagram showing the resonant mechanism in chemi-ionization/recombination channels (dashed arrows), and $(n - n')$-mixing channels (full arrows).

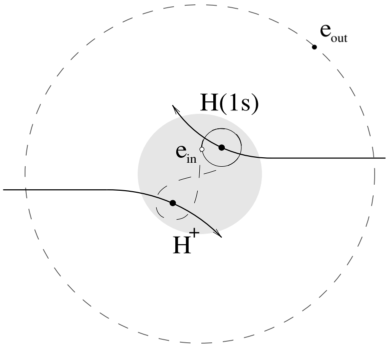

Figure 2. A diagram showing $H^*(n)$ + H(1s) collisions in the system of the mass centre; e_{in} and e_{out} are the inner and outer electron, respectively. The shaded area marks the internuclear distances satisfying constraint (5).

where $r_n \sim n^2$ is the average radius of the Rydberg atom in the state with a principal quantum number n, and R is the internuclear distance. This mechanism has been described in detail in [12, 4], and its main points will be summarized here.

Under condition (5), processes (1) and (2) were modelled as the interaction between a non-Coulomb part of the $H^*(n)$ atom's outer electron potential and a subsystem $H^+ + H$ (see figure 2). The electronic Hamiltonian H of the system was written as:

$$H = H_{mi}(R) + H_e + V_d, \tag{6}$$

where $H_{mi}(R)$ is a Hamiltonian of the subsystem $H^+ + H$, H_e describes an outer weakly bound electron in a Coulomb field and V_d is the non-Coulomb potential. Because only slow collisions were considered, the electronic state of the subsystem $H^+ + H$ was described as a superposition of the ground $|1, R\rangle$ and first excited $|2, R\rangle$ adiabatic electronic states of the molecular ion H_2^+. These states satisfy the Schrödinger equation:

$$H_{mi}(R)|i, R\rangle = U_i(R)|i, R\rangle, \qquad i = 1, 2, \tag{7}$$

where $U_{1,2}(R)$ are corresponding adiabatic terms. These terms as functions of R are shown in figure 1, in accordance with [14]. The delocalization of the electrons of the system is shown in figure 2. The state of an outer electron $|n\rangle$ satisfies the equation:

$$\mathrm{H}_e|n\rangle = \epsilon_n|n\rangle, \tag{8}$$

where $\epsilon_n = -Ry/n^2$. In the dipole approximation the operator V_d is expressed as:

$$V_d = \frac{e\vec{r}\cdot\vec{d}}{r^3} \tag{9}$$

where $\vec{r}$ is the radius vector of the outer electron, e is its charge, $r = |\vec{r}|$ and $\vec{d}$ is the dipole momentum operator of the subsystem $\mathrm{H}^+ + \mathrm{H}$.

In [11], the relative movement of nuclei in the collisional subsystem $\mathrm{H}^+ + \mathrm{H}$ was approximated by straight trajectories, and the influence of an outer electron on the electronic state of the system was neglected. Under these assumptions, the system was characterized by the dipole momentum $\vec{d}_{12}(t)$ as a known oscillating function of time t and frequency $\omega_{12}(R(t)) = [U_2(R(t)) - U_1(R(t))]/\hbar$. The probabilities of $n \to n' \neq n$ transitions were calculated from the solutions of a non-stationary Schrödinger equation with Hamiltonian $\mathrm{H}_e + [e\vec{r}\cdot\vec{d}_{12}(t)]/r^3$. The probabilities were used to estimate the cross-sections for processes (1) and (2), and for $n \approx 10$.

This approximation had previously shown a resonant characteristic of the considered processes. For every $n \to n'$ transition, the dominant role was played by surroundings of two resonant points $R = R_{n;n'}$, where $R_{n;n'}$ is determined from

$$U_2(R_{n;n'}) - U_1(R_{n;n'}) = |\epsilon_{n'} - \epsilon_n|. \tag{10}$$

In resonant points the transition frequency is $|\epsilon_{n'} - \epsilon_n|/\hbar = \omega(R_{n;n'})$.

Note that the same mechanism was applied in [15] for rate coefficient calculations of some chemi-ionization processes similar to (3), but in $A^*(n) + A$ collisions in the case of alkali metals. The same approach for such chemi-ionization processes was used in [16, 17].

The next step in a theoretical approach to the inelastic processes in symmetrical atom–Rydberg atom collisions was presented in [12]. The model was improved to include the influence of the electronic state of the outer electron on the electronic state of the subsystem atom–core of the Rydberg atom. The electronic state of the whole system was described as a superposition of the states $|1, R; n'\rangle = |1, R\rangle|n'\rangle$ and $|2, R; n'\rangle = |2, R\rangle|n'\rangle$. In accordance with (7) and (8), these states satisfy the equations:

$$[\mathrm{H}_{mi}(R) + \mathrm{H}_e]|i, R; n'\rangle = U_{i;n'}|i, R; n'\rangle, \tag{11}$$

where

$$U_{i;n'} = U_i(R) + \epsilon_{n'}, \tag{12}$$

and $i = 1, 2$. In [4, 12] it was explained why the electron spin has been neglected. The probabilities for $n \to n' \neq n$ transitions were calculated from the non-stationary solutions of a Schrödinger equation with a Hamiltonian given by (6) and (9), and the corresponding initial condition at $n' = n$. The probabilities were used to calculate the cross-sections of processes (1) and (2), for a series of initial and final quantum numbers n and n'.

This model explained some characteristics of processes (1) and (2), which was of importance for further analysis. It was confirmed that these processes were strongly resonant. This means that the excitation and de-excitation processes (1) and (2) are exclusively linked to transitions $|2, R; n\rangle \to |1, R; n' = n + p\rangle$ and $|1, R; n\rangle \to |2, R; n' = n - p\rangle$, respectively. Both transitions take place in the vicinity of resonant points $R = R_{n;n'}$, which can be interpreted as points of intersection of terms $U_{2;n}$ and $U_{1;n'}$ for $n' > n$, or $U_{1;n}$ and $U_{2;n'}$ for $n' < n$.

Table 1. $R_{n;n+p}/a_0$ values calculated from (10) for $n' = n + p$.

	p				
n	1	2	3	4	5
4	6.776	6.252	6.016	5.883	5.799
5	7.497	6.941	6.680	6.528	6.430
6	8.084	7.504	7.224	7.056	6.946
7	8.580	7.981	7.685	7.505	7.384
8	9.008	8.394	8.086	7.895	7.766
9	9.386	8.760	8.441	8.241	8.104
10	9.724	9.088	8.760	8.553	8.409

In other words, the mechanism of processes (1) is a resonant energy exchange within the electronic component of the collisional system $H^*(n) + H$ (see figure 1 for an illustration). It was shown in [12] that for (1) in domains $n,\ n' \gg 1$, the cross-section can be obtained from the probabilities of $n \to n'$ transitions by applying first-order perturbation theory. It was also observed that the domains of neighbouring resonant points (for example, $R_{n;n'}$ and $R_{n;n'+1}$) partially overlap. The efficiency of processes (1) and (2) is also caused by the fact that the resonant distances $R_{n;n'}$, satisfying (5), at $n \gg 1$ are several times larger than the atomic unit length a_0. This is illustrated in table 1 by the factor $R_{n;n+p}/a_0$, calculated for $4 \leqslant n \leqslant 10$ and $1 \leqslant p \leqslant 5$.

The straight trajectory approximation applied in [11, 12] could not be used for the cross-section calculations of processes (1) in domains of small collisional velocities, where this approximation was valid only for large impact parameters. Because of this, in [4] a different approximation was used: in the collisional system $H^*(n) + H$ in domains of internuclear distances satisfying (5), the initial electronic state of the subsystem $H^+ + H$ was assumed to be either in $|1, R\rangle$ or in $|2, R\rangle$ states with the probability 1/2. In the case of chemi-ionization processes (3), initially in the state $|2, R\rangle$, the relative movement of the nuclei in the $H^*(n) + H$ system was described by the trajectory calculated in the potential $U_2(R)$. The chemi-ionization process was treated as a result of the system's transition from the initial bound electronic state $|2, R; n\rangle = |2, R\rangle|n\rangle$ of the whole system into final continuum states, as illustrated in figure 1. Hence the processes of (3) type were described by the decay approximation and corresponding decay rates, which were used in [5] for the semi-classical method for rate coefficient calculations.

Note that these models can be applied both to processes (1) and (3). In [18], a method for rate coefficient calculations in $(n - n')$-mixing processes was presented. It was applied in the case of weakly ionized plasmas, where the collisional velocities are small (with collisional energies $E \lesssim 1$ eV). Processes (1) were modelled as a decay of the system's initial electronic state $|2, R; n\rangle$, and characterized by the decay rate. A modified version of the semi-classical method in [18] is used here for the rate coefficient calculations of processes (1) and (2).

3. The rate coefficients

Consider the case when the subsystem $H^+ + H$ of the collisional system $H^*(n) + H$ is in the initial electronic state $|2, R\rangle$, which means that the nuclei are moving in the potential $U_2(R)$. This movement is described by the trajectory defined by the impact parameter and collisional energy. The transitions $n \to n + p$, $p \geqslant 1$, will be treated as a result of the decay of the system initial electronic state $|2, R; n\rangle = |2, R\rangle|n\rangle$ in domains of internuclear distances satisfying (5). In these domains it is assumed that the decay is a continuous process taking place along the trajectory. The assumption is based on the well-known concept of 'smearing' part of a discrete spectre into a corresponding continuum.

We introduce an initial Rydberg state of an outer electron $|n\rangle = |n, l, m\rangle$ and blocks of Rydberg states $|n'\rangle = |n', l', m'\rangle$ with fixed quantum numbers l' and m', satisfying:

$$n + p_1 \leqslant n' \leqslant n + p_2, \tag{13}$$

where in the general case we have

$$p_2 \geqslant p_1 \geqslant 1. \tag{14}$$

Every block containing $p_2 - p_1 + 1$ discrete states corresponds to a block of continuous states characterized by quantum numbers n'', l' and m', where n'' is continuously changed from $n + p'_1$ to $n + p'_2$, and energies $\epsilon_{n''}$, satisfying

$$\int_{\epsilon_{n+p'_1}}^{\epsilon_{n+p'_2}} \rho_{n;n''}(l', m')\,\mathrm{d}\epsilon_{n''} = p_2 - p_1 + 1, \tag{15}$$

$$\int_{\epsilon_{n+p'_1}}^{\epsilon_{n+p'_2}} f_{n;n''}(l, m; l', m')\rho_{n;n''}(l', m')\,\mathrm{d}\epsilon_{n''} = f(n, p_1, p_2; l', m'). \tag{16}$$

Here $\rho_{n;n''}(l', m')$ is the density of continuous states $|n'', l', m'\rangle$, $f_{n;n''}(l, m; l', m')$ is the oscillator strength for $|n, l, m\rangle \to |n'', l', m'\rangle$ transitions and $f(n, p_1, p_2)$ is the total oscillator strength for the transition of the outer electron from the $|n, l, m\rangle$ state to a given block of Rydberg states. We will assume that $\epsilon_{n''} = -Ry/n''^2$ in order to have an appropriate distribution of continuous states, and

$$\rho_{n;n''}(l', m') = \frac{\mathrm{d}n''}{\mathrm{d}\epsilon_{n''}} = \frac{n''^3}{2Ry}. \tag{17}$$

From equation (15) it follows that the parameters $p'_{1,2}$ must satisfy the expression

$$p'_2 - p'_1 = p_2 - p_1 + 1. \tag{18}$$

While in [18] we had $p'_1 = p_1$ and $p'_2 = p_2 + 1$, here p'_1 and p'_2 are given as:

$$p'_1 = p_1 - \Delta p, \qquad p'_2 = p_2 + 1 - \Delta p, \qquad 0 \leqslant \Delta p < 1, \tag{19}$$

where it is assumed that $\Delta p = \Delta p(n, p_1, p_2)$.

Let $|2, R; n, l, m\rangle = |2, R\rangle|n, l, m\rangle$ be the initial state of the system $\mathrm{H}^*(n) + \mathrm{H}$ in the domain of internuclear distances satisfying (5). The described resonant mechanism generates transitions into the final states $|1, R; n', l', m'\rangle = |1, R\rangle|n', l', m'\rangle$ in the vicinity of the point $R = R_{n;n'}$. Because these transitions are treated as results of continuous decay of the initial state, the total transition probability of the outer electron from the state $|n, l, m\rangle$ into the blocks of Rydberg states defined by equation (13) is identified with the total transition probability into blocks of continuous states. These are described in a quasi-static approximation, similarly to the chemi-ionization processes in [4], and are characterized by the decay rate

$$W^{n''}_{n;l,m} = \frac{2\pi}{\hbar}\sum_{l',m'} |\langle n, l, m; 2, R_{n;n''}|V_d|1, R_{n;n''}; n'', l', m'\rangle|^2 \rho_{n;n''}(l', m'). \tag{20}$$

Here $|1, R_{n;n''}; n'', l', m'\rangle = |1, R_{n;n''}\rangle|n'', l'm'\rangle$, dipole interaction operator V_d is given by equation (9), and $R_{n;n''}$ is the internuclear distance which satisfies:

$$U_2(R_{n;n''}) - U_1(R_{n;n''}) = \epsilon_{n;n''}, \tag{21}$$

where

$$\epsilon_{n;n''} = \epsilon_{n''} - \epsilon_n. \tag{22}$$

States $|1, R; n'', l', m'\rangle$ will be treated through matrix elements in (20). Namely, we will assume that: the expression for element $\langle n, l, m; 2, R|V_d|1, R; n'', l', m'\rangle$ can be obtained from the expression for element $\langle n, l, m; 2, R|V_d|1, R; n', l', m'\rangle$ by substituting n' with n''; the squares of moduli of matrix elements $|\langle n, l, m; 2, R|V_d|1, R; n', l', m'\rangle|^2$ can be written [19] as

$$|\langle n, l, m; 2, R|V_d|1, R; n', l', m'\rangle|^2 = \frac{m^2\hbar^4}{e^2}(\epsilon_{n'} - \epsilon_n)^4 |\langle n, l, m|r_R|n', l', m'\rangle|^2 |\langle 1, R|d_R|2, R\rangle|^2. \tag{23}$$

Here m is the mass of electrons, and r_R and d_R denote the projections of the outer electron radius $\vec{r}$ and dipole momentum operator $\vec{d}$ of the subsystem $\mathrm{H}^+ + \mathrm{H}$ onto the internuclear axis, respectively. Using equation (20) we then have

$$W^{n''}_{n;l,m} = \frac{2\pi m^2}{\hbar^5 e^2}\epsilon^4_{n;n''} \sum_{l',m'} |\langle n, l, m|r_R|n''(R), l', m'\rangle|^2 |\langle 1, R|d_R|2, R\rangle|^2 \rho_{n;n''}(l', m'). \tag{24}$$

The next step in our model is to introduce the average decay rate $W_{n;n''}$ of the initial collisional system $\mathrm{H}^*(n) + \mathrm{H}$, defined as:

$$W_{n;n''} = \frac{1}{n^2}\sum_{l,m} W^{n''}_{n;l,m}. \tag{25}$$

In the quasi-static approximation we have

$$\sum_{l,m}\sum_{l',m'} |\langle n, l, m|r_R|n'', l', m'\rangle|^2 = \frac{1}{3}\sum_{l,m}\sum_{l',m'} |\langle n, l, m|\vec{r}|n'', l', m'\rangle|^2. \tag{26}$$

Assuming that R in the domain relevant for the process is several times larger than the atomic unit length, we have [4, 12]

$$|\langle 1, R|d_R|2, R\rangle|^2 = \frac{e^2R^2}{4}. \tag{27}$$

From equations (17), (24), (26) and (27), the average decay rate $W_{n;n''}$ is:

$$W_{n;n''} = \frac{\pi m}{4\hbar^3}\epsilon^3_{n;n''}\frac{n''^3}{2Ry} f_{n;n''} R^2_{n;n''}, \tag{28}$$

where $f_{n;n''}$ is the average oscillator strength for the $n \to n''$ transition, given by

$$f_{n;n''} = \frac{1}{n^2}\sum_{l,m}\sum_{l',m'} f^{n'';l',m'}_{n;l,m}, \tag{29}$$

$$f^{n'';l',m'}_{n;l,m} = \frac{2m}{3\hbar^2}(\epsilon_{n''} - \epsilon_n)|\langle n, l, m|r_R|n''(R), l', m'\rangle|^2. \tag{30}$$

The expression for $f_{n;n''}$ is obtained by substituting n' with n'' in the expression for $f_{n;n'}$ from [19]:

$$f_{n;n''} = \frac{2^5}{3\sqrt{3}\pi} n \left(\frac{n''}{n''^2 - n^2}\right)^3 g_{n;n''}, \tag{31}$$

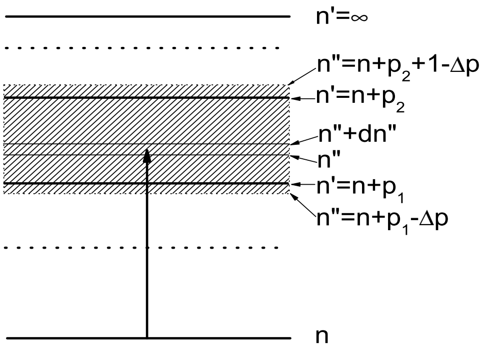

Figure 3. A diagram showing the partial 'smearing' of a discrete Coulomb spectre into a continuum.

where $g_{n;n''}$ is the Gaunt factor. After substituting $\epsilon_{n''}$ and ϵ_n into equation (28) with their expressions, we have finally

$$W_{n;n''} = \frac{R^2_{n;n''}}{3\sqrt{3}n^5} g_{n;n''}. \tag{32}$$

This expression is the same as the decay rate of the initial state of the system $H^*(n) + H$, in the case of chemi-ionization processes [4]. In domain $n \gg 1$ a function $g_{n;n''}$ is slowly changing for different n'', and we can assume:

$$g_{n;n''} = g_{n;n'=n+p}, \tag{33}$$

for $n' - \Delta p \leqslant n'' < n' + 1 - \Delta p$. Note that the expression (32) was considered in [20] for processes (1) for $n' > n$, which are similar to chemi-ionization processes. However, the expression here is based on equation (31) applied for $f_{n;n''}$.

Further procedures for rate coefficients for processes (1) are the same as for chemi-ionization processes (3), described in detail in [5]. Because of this, only the main steps will be presented here. For transitions $n \to (n'', n'' + \mathrm{d}n'')$, illustrated in figure 3, the differential probability, differential cross-section and differential rate coefficient are given by:

$$\mathrm{d}P_{n;n''} = \frac{1}{2}(2W_{n;n''}\,\mathrm{d}t) = W_{n;n''}\frac{\mathrm{d}R}{v_{\mathrm{rad}}(b, E, R_{n;n''})}, \tag{34}$$

$$\mathrm{d}\sigma_{n;n''}(E) = 2\pi \int_0^{b_{\max}(E, R_{n;n''})} \mathrm{d}P_{n;n''} b^2\,\mathrm{d}b, \tag{35}$$

$$\mathrm{d}K_{n;n''}(T_{\mathrm{a}}) = \int_{\epsilon_{n;n''}}^{\infty} f_{T_{\mathrm{a}}}(E) v(E)\,\mathrm{d}\sigma_{n;n''}\sqrt{E}\,\mathrm{d}E, \tag{36}$$

where b and E are the impact parameter and collisional energy, $R_{n;n''}$ is defined by equation (21), and $v(E) = (2E/\mu)^{1/2}$ is the radial velocity:

$$v_{\mathrm{rad}}(b, E, R_{n;n''}) = \left\{\frac{2E}{\mu}\left[E - U_2\left(R_{n;n''} - \frac{Eb^2}{R^2_{n;n''}}\right)\right]\right\}^{1/2}. \tag{37}$$

μ is the reduced mass of collisional particles, $f_{T_\mathrm{a}}(E)$ is the Maxwell distribution function for atomic temperature T_a, normalized by the condition

$$\int_0^\infty f_{T_\mathrm{a}}(E)\sqrt{E}\,\mathrm{d}E = 1. \tag{38}$$

A parameter $b_\mathrm{max}(E, R_{n;n''})$ is calculated from the equation:

$$v_\mathrm{rad}(b_\mathrm{max}, E, R_{n;n''}) = 0, \tag{39}$$

and $E_\mathrm{min}(n; n'') = U_2(R_{n;n''})$. From equations (22) and (34)–(39) the differential rate coefficient $\mathrm{d}K_{n;n''}$ is written as:

$$\mathrm{d}K_{n;n''}(T_\mathrm{a}) = \frac{2\pi}{3\sqrt{3}}\frac{e^2}{\hbar a_0^3} n^{-5} g_{n;n''} X(R_{n;n''}) \left\{ R^4 \exp\left[-\frac{U_2(R)}{kT_\mathrm{a}}\right]\right\}_{R=R_{n;n''}} \mathrm{d}R, \tag{40}$$

where a_0 is the atomic unit length, and $X(R_{n;n''})$ is:

$$X(R_{n;n''}) = \frac{\Gamma\left(\frac{3}{2}, \frac{-U_1(R_{n;n''})}{kT_\mathrm{a}}\right)}{\Gamma\left(\frac{3}{2}\right)}, \tag{41}$$

$\Gamma(3/2, x)$ i $\Gamma(x)$ being incomplete and complete gamma functions.

$K_{n;n+p_1,n+p_2}(T_\mathrm{a})$ denotes the total rate coefficient of processes (1) for the transitions of an outer electron of the system $\mathrm{H}^*(n) + \mathrm{H}$ into all states with the principal quantum number n' from domain (13). This is calculated using

$$K_{n;n+p_1,n+p_2}(T_\mathrm{a}) = \int_{n+p_1-\Delta p}^{n+p_2+1-\Delta p} \mathrm{d}K_{n;n''}(T_\mathrm{a}). \tag{42}$$

A similar method to this for calculating $K_{n;n+p_1,n+p_2}(T_\mathrm{a})$ was applied in calculating the coefficient of continuous absorption from a block of Rydberg states, the rate coefficient for electron–ion photo-recombination with free electron transition in a given block of Rydberg states (see [21, 22]), and for electron–ion–atom recombination [1]. The oscillator strength was assumed to be a continuous function of the principal quantum number.

To calculate the rate coefficient of processes (1) for fixed n and $n' = n + p$, denoted by $K_{n;n+p}(T_\mathrm{a})$, we will use that:

$$K_{n;n+p}(T_\mathrm{a}) = K_{n;n+p_1,n+p_2}(T_\mathrm{a}), \tag{43}$$

for $p_1 = p_2 = p$, and

$$K_{n;n+p_1,n+p_2}(T_\mathrm{a}) = \sum_{p=p_1}^{p_2} K_{n;n+p}(T_\mathrm{a}), \tag{44}$$

for $1 \leqslant p_1 < p_2$. From (33), (40), (42) and (43) it follows that $K_{n;n+p}(T_\mathrm{a})$ can be written as:

$$K_{n;n+p}(T_\mathrm{a}) = \frac{2\pi}{3\sqrt{3}}\frac{(ea_0)^2}{\hbar} n^{-5} g_{n;n+p} \int_{R_\mathrm{min}(n,n+p)}^{R_\mathrm{max}(n,n+p)} X(R) \exp\left[-\frac{U_2(R)}{kT_\mathrm{a}}\right] \frac{R^4\,\mathrm{d}R}{a_0^5}, \tag{45}$$

where $R_\mathrm{min}(n, n + p)$ and $R_\mathrm{max}(n, n + p)$ are calculated from equations

$$\epsilon(R = R_\mathrm{min}) = \epsilon_{n+p+1-\Delta p} - \epsilon_n, \qquad \epsilon(R = R_\mathrm{max}) = \epsilon_{n+p-\Delta p} - \epsilon_n, \tag{46}$$

$$\epsilon(R) = U_2(R) - U_1(R). \tag{47}$$

So far it has been assumed that the parameter $\Delta p = \Delta p(n, p_1, p_2)$ satisfies equations (16) and (19). However, equations (44) and (45) are in accordance with (15)–(19) for any n, p_1 and p_2 if $\Delta p(n, p_1, p_2) = \text{const}$. This parameter is a slowly varying function of n, p_1 and p_2, if $n \gg 1$. Hence we will consider the case $p_1 = p_2 = 1$, and the parameter Δp is calculated from equation

$$\int_{n+1-\Delta p}^{n+2-\Delta p} \frac{2^5}{3\sqrt{3}\pi} n \left(\frac{n''}{n''^2 - n^2} \right)^3 \mathrm{d}n'' = \frac{2^5}{3\sqrt{3}\pi} n \left[\frac{n+1}{(n+1)^2 - n^2} \right]^3 . \tag{48}$$

Within the domain $4 \leqslant n \leqslant 10$, the parameter Δp is practically constant, and we will assume its value $\Delta p = 0.380$, this corresponding to $n = 5$.

The rate coefficients $K_{n;n-p}(T_\mathrm{a})$ for de-excitation processes (2) are obtained from the thermodynamic balance principle

$$K_{n-p;n}(T_\mathrm{a}) N(n-p) N(1) = K_{n;n-p}(T_\mathrm{a}) N(n) N(1). \tag{49}$$

$N(1)$ is the concentration of atoms H(1s). $N(n-p)$ and $N(n)$ are concentrations of Rydberg atoms $\mathrm{H}^*(n-p)$ and $\mathrm{H}^*(n)$, given by expressions

$$\begin{aligned} N(n-p) &= N(1)(n-p)^2 \exp\left(-\frac{Ry + \epsilon_{n-p}}{kT_\mathrm{a}} \right), \\ N(n) &= N(1) n^2 \exp\left(-\frac{Ry + \epsilon_n}{kT_\mathrm{a}} \right). \end{aligned} \tag{50}$$

Finally, we have:

$$K_{n;n-p}(T_\mathrm{a}) = K_{n-p;n}(T_\mathrm{a}) \frac{(n-p)^2}{n^2} \exp\left(\frac{\epsilon_{n-p;n}}{kT_\mathrm{a}} \right), \tag{51}$$

with $\epsilon_{n-p;n}$ given by (10) with $n' = n - p$.

4. Results and discussion

The rate coefficients $K_{n;n+p}(T_\mathrm{a})$ and $K_{n;n-p}(T_\mathrm{a})$ for processes (1) and (2) are calculated in the domains of n and T_a corresponding to conditions in weakly ionized hydrogen plasmas. The results for $K_{n;n+p}(T_\mathrm{a})$ with $4 \leqslant n \leqslant 10$, $1 \leqslant p \leqslant 5$ and $3000\,\mathrm{K} \leqslant T_\mathrm{a} \leqslant 7000\,\mathrm{K}$ are obtained from (45) and presented in table 2. The values for $U_{1,2}(R)$ and $\epsilon(R)$ can be obtained from data in [14] or from analytical expressions in [23]; the Gaunt factor $g_{n;n+p}$ is approximated as in [24]. The rate coefficients $K_{n;n-p}(T_\mathrm{a})$ are calculated from (51) using coefficients $K_{n-p;n}(T_\mathrm{a})$.

The relative influence of processes (1) and (2) in weakly ionized hydrogen plasmas is established by comparison with electron–atom collisional processes:

$$\vec{\mathrm{e}}_k + \mathrm{H}^*(n) \rightarrow \vec{\mathrm{e}}_{k'} + \mathrm{H}^*(n'), \tag{52}$$

where $n' = n \pm p$. The rate coefficients of processes (52) are denoted with $\alpha_{n;n'}(T_\mathrm{e})$.

A similar comparison has been made in [18] where the rate coefficients for processes (52) were obtained from data in [25]. However, later we found that such $\alpha_{n;n'}(T_\mathrm{e})$ values in domains $4 \leqslant n \leqslant 20$ and $4000\,\mathrm{K} \leqslant T_\mathrm{a} \leqslant T_\mathrm{e} \leqslant 20\,000\,\mathrm{K}$ are 7–12 times higher than the more accurate ones obtained in [26]. This error greatly underestimated the influence of processes (1) and (2). Here the rate coefficients $\alpha_{n;n\pm p}(T_\mathrm{e})$ for processes (52) are taken from [26]. A relative efficiency of processes (1) and (2) is given by the parameter $F_{n;n\pm p}(T_\mathrm{a}, T_\mathrm{e})$:

$$F_{n;n\pm p}(T_\mathrm{a}, T_\mathrm{e}) = \frac{K_{n;n\pm p}(T_\mathrm{a}) N(n) N(1)}{\alpha_{n;n\pm p}(T_\mathrm{e}) N(n) N_e} = \frac{K_{n;n\pm p}(T_\mathrm{a}) \eta_{ea}}{\alpha_{n;n\pm p}(T_\mathrm{e})}, \tag{53}$$

$$\eta_{ea} = \frac{N(1)}{N_e}, \tag{54}$$

where N_e is the concentration of free electrons.

Table 2. Excitation rate coefficients $K_{n;n+p}(T_a)$ (10^{-9} cm^3 s^{-1}).

		$T_a(10^3\text{K})$								
n	p	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0
4	1	4.4232	5.0133	5.4997	5.9047	6.2456	6.5355	6.7845	7.0003	7.1887
	2	0.7228	0.8997	1.0576	1.1973	1.3205	1.4293	1.5256	1.6112	1.6876
	3	0.2401	0.3155	0.3860	0.4506	0.5092	0.5621	0.6098	0.6528	0.6917
	4	0.1091	0.1483	0.1861	0.2216	0.2544	0.2844	0.3118	0.3367	0.3595
	5	0.0592	0.0824	0.1053	0.1270	0.1474	0.1662	0.1835	0.1994	0.2140
5	1	3.3708	3.5901	3.7604	3.8960	4.0061	4.0972	4.1736	4.2385	4.2943
	2	0.7642	0.8574	0.9332	0.9956	1.0476	1.0916	1.1291	1.1614	1.1895
	3	0.3020	0.3502	0.3906	0.4246	0.4534	0.4781	0.4995	0.5180	0.5343
	4	0.1524	0.1808	0.2050	0.2257	0.2435	0.2589	0.2723	0.2840	0.2944
	5	0.0887	0.1069	0.1227	0.1364	0.1482	0.1585	0.1676	0.1755	0.1825
6	1	2.2484	2.3282	2.3886	2.4356	2.4731	2.5038	2.5292	2.5507	2.5690
	2	0.6072	0.6488	0.6812	0.7069	0.7278	0.7451	0.7596	0.7719	0.7825
	3	0.2658	0.2902	0.3096	0.3252	0.3380	0.3487	0.3577	0.3654	0.3721
	4	0.1435	0.1591	0.1716	0.1818	0.1903	0.1974	0.2035	0.2087	0.2132
	5	0.0875	0.0982	0.1068	0.1139	0.1198	0.1248	0.1291	0.1328	0.1360
7	1	1.4721	1.5029	1.5258	1.5434	1.5574	1.5687	1.5780	1.5859	1.5925
	2	0.4415	0.4599	0.4739	0.4848	0.4935	0.5006	0.5065	0.5116	0.5158
	3	0.2065	0.2182	0.2272	0.2344	0.2401	0.2449	0.2488	0.2522	0.2550
	4	0.1166	0.1246	0.1308	0.1357	0.1397	0.1430	0.1458	0.1482	0.1502
	5	0.0735	0.0792	0.0837	0.0873	0.0902	0.0926	0.0946	0.0964	0.0978
8	1	0.9787	0.9913	1.0007	1.0078	1.0134	1.0180	1.0217	1.0248	1.0275
	2	0.3144	0.3228	0.3291	0.3339	0.3378	0.3409	0.3435	0.3457	0.3475
	3	0.1538	0.1595	0.1638	0.1672	0.1699	0.1721	0.1739	0.1755	0.1768
	4	0.0897	0.0938	0.0969	0.0993	0.1013	0.1029	0.1042	0.1053	0.1063
	5	0.0580	0.0610	0.0633	0.0651	0.0666	0.0678	0.0688	0.0697	0.0704
9	1	0.6669	0.6724	0.6764	0.6795	0.6819	0.6839	0.6855	0.6868	0.6879
	2	0.2248	0.2288	0.2318	0.2340	0.2358	0.2373	0.2385	0.2395	0.2404
	3	0.1136	0.1165	0.1186	0.1203	0.1216	0.1227	0.1236	0.1243	0.1249
	4	0.0679	0.0700	0.0716	0.0729	0.0738	0.0747	0.0753	0.0759	0.0764
	5	0.0447	0.0463	0.0476	0.0485	0.0493	0.0499	0.0504	0.0508	0.0512
10	1	0.4663	0.4688	0.4707	0.4721	0.4732	0.4740	0.4748	0.4754	0.4759
	2	0.1629	0.1649	0.1663	0.1675	0.1684	0.1691	0.1697	0.1701	0.1706
	3	0.0843	0.0859	0.0870	0.0878	0.0885	0.0890	0.0895	0.0899	0.0902
	4	0.0514	0.0525	0.0534	0.0540	0.0545	0.0550	0.0553	0.0556	0.0559
	5	0.0343	0.0352	0.0359	0.0364	0.0368	0.0372	0.0374	0.0377	0.0379

Calculated values of $F_{n;n+p}(T_a, T_e)$ for $4 \leqslant n \leqslant 10$, $1 \leqslant p \leqslant 5$, $T_e = 5 \times 10^3$, 1×10^4 and 2×10^4 K, $T_a = 5 \times 10^3$ K, and $\eta = 10^4$, are presented in figures 4–6. The parameters' ranges correspond to plasmas with an ionization degree $\sim 10^{-4}$, which was analysed previously in [7, 8, 10, 27]. For $7 < n \leqslant 10$ the efficiency of processes (1) is comparable to that of processes (52), while for $n \leqslant 7$ processes (1) are dominant. This is true for both equilibrium ($T_e = T_a$, figure 4) and non-equilibrium plasmas ($T_e > T_a$, figures 5, 6). The same is valid for processes (2). Therefore, the influence of these processes in the modelling of weakly ionized plasmas and the interpretation of experimental results must be taken into account.

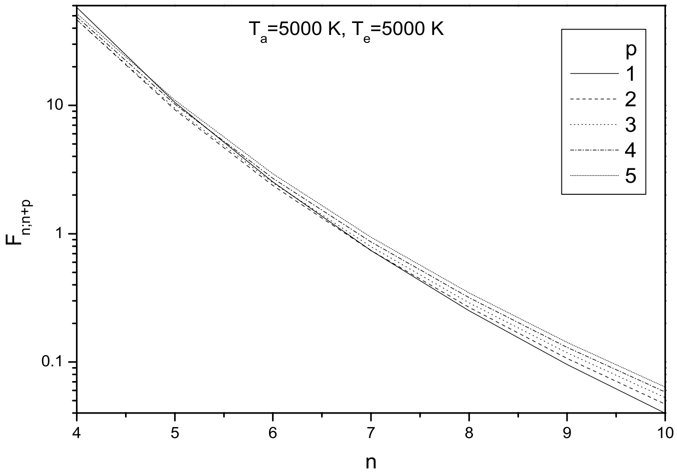

Figure 4. Parameter $F_{n;n+p}(T_\mathrm{a}, T_\mathrm{e})$ values given by equation (53) for $T_\mathrm{a} = 5000$ K and $T_\mathrm{e} = 5000$ K.

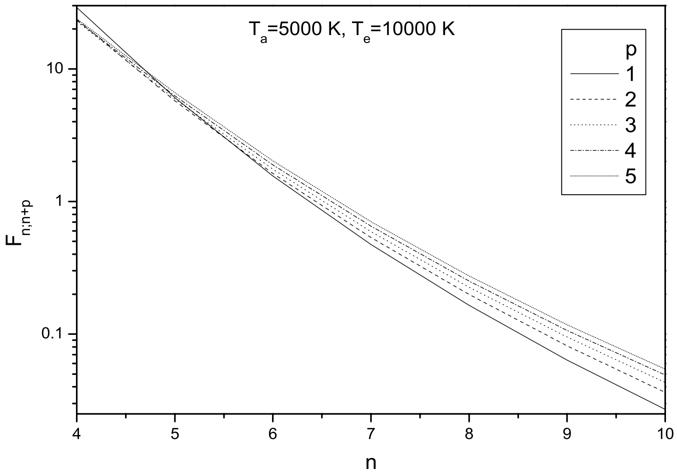

Figure 5. Same as in figure 4 but for $T_\mathrm{e} = 10\,000$ K.

Note that in [10] the significance of processes (3) and (4) on Rydberg states in weakly ionized plasmas (stars' photosphere with effective temperatures of around 4000 K) has been established. It was shown that they are important for at least up to $n = 20$, and dominant for $n \leqslant 7$. A similar effect is expected for processes (1) and (2). Also, it is important that excitation processes (1) and chemi-ionization processes (3), due to the established sameness of their decay rate expressions, can be treated from now on in the frame of a unique numeric procedure.

The $(n - n')$-mixing processes in atom–Rydberg atom collisions can be important for other atomic systems. We are thinking here of $\mathrm{He}^*(n) + \mathrm{He}(1\mathrm{s}^2)$, and $\mathrm{A}^*(n) + \mathrm{A}$ collisions where A is an alkali atom in a ground state.

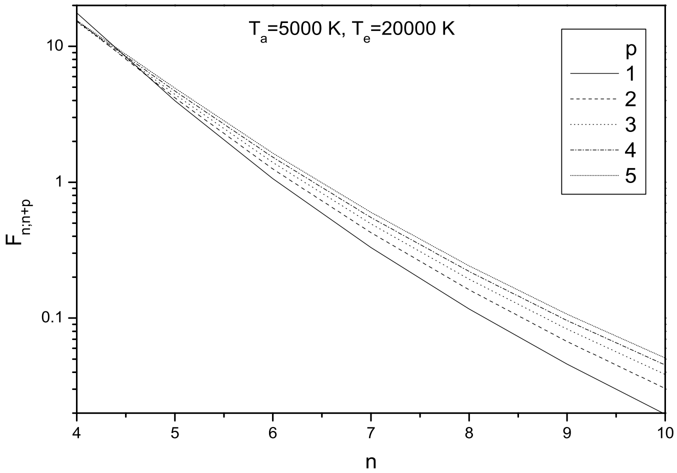

Figure 6. Same as in figure 4 but for $T_e = 20\,000$ K.

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