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# Ionization in a dense hydrogen plasma: analytic solution of the master equation

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The master equation is solved analytically for the ionization in a dense hydrogen plasma involving single-quantum transitions. The derived expression for the observed ionization rate coefficient is valid for all temperatures at which the ionization time constant is long compared with the internal relaxation time constants. At high temperature, the observed ionization rate coefficient is determined by excitation and ionization from the ground level. At low temperature, a bottleneck occurs above the first excited state, and the expression reduces to a form foreseen by Bates as the counterpart to the network-like expression for recombination. The implications with regard to the temperature dependence of the rate coefficient are discussed.

## 1. INTRODUCTION

The kinetics of ionization and recombination in a plasma have been of considerable theoretical and experimental interest in recent years. Much of the work has been reviewed by Biberman, Yakubov & Vorob'ev (1971) and by Bates (1974*a*).

A milestone in the theoretical development is the work of Bates, Kingston & McWhirter (1962). In this work, the quasi-steady-state assumption was made that the only time-dependent populations were those of the ground state atoms and free electrons. An optically thin plasma, which included electronic excitation, de-excitation, ionization and (three-body) recombination, spontaneous radiation and radiative recombination, was considered. The collisional-radiative recombination and ionization coefficients were obtained by using the quasi-steady-state approximation.

An alternative theoretical approach which does not invoke the quasi-steady-state approximation is to seek the solution of the time-dependent relaxation equations. This approach facilitates a study of the temporal behaviour of the plasma by integrating the relaxation equations numerically (Gordiets, Gudzenko & Shelepsin 1968; Limbaugh & Mason 1971). The integration consumes much computing time, because the system of equations is stiff, so that the integration step-length must be very small. Also, the number of differential equations involved is large, one equation being required for each of the bound states as well as one for the continuum.

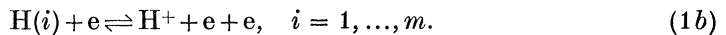
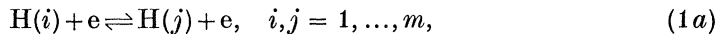
Recently, Hogarth & McElwain (1975 *a*) applied the boundary layer method and obtained an approximate solution for the relaxation equations of a dense hydrogen plasma. These authors set up and solved the master equation for the ionization–recombination reaction and showed that the ionization rate coefficient could be obtained from the largest eigenvalue of the relaxation matrix. The eigenvalue was computed numerically for a series of temperatures by Hogarth & McElwain (1975 *b*). Their work represents a substantial improvement over previous numerical studies in so far as the required labour of computing is concerned. Yet, for heavier atoms with phenomenally large numbers of bound states, the required computation is still formidable, and approximate procedures such as matrix condensation (Burgess & Summers 1969) are sometimes used.

The aim of this paper is to derive the analytic solution of the relaxation matrix for a dense plasma, and to elucidate from it the prominent microscopic features in dense plasma relaxations.

The organization of the paper is as follows. In § 2, the master equation is set up and the formal relations between the observed ionization rate coefficient and the normal modes of internal relaxation are derived. In § 3, the ionization rate coefficient is derived for a model system involving nearest-neighbour transitions only, and the derived expression is used to examine the rôles of the respective microscopic processes in the overall observed ionization rate in a dense hydrogen plasma. Numerical results are presented in § 4. The relevant implications regarding the temperature coefficient are discussed in § 5.

## 2. MASTER EQUATION

Following the work of Hogarth & McElwain (1975 *a, b*), we consider a dense and neutral hydrogen plasma, in which only collisional excitation–de-excitation and ionization–recombination processes need to be considered:



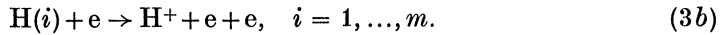
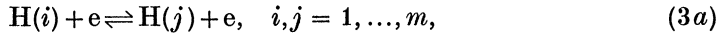
Transitions due to atom–atom, atom–ion or ion–ion collisions and any boundary effects are neglected (Bates *et al.* 1962; Hogarth & McElwain 1975 *a, b*). In reactions (1),  $\text{H}(i)$  denotes a hydrogen atom with principal quantum number  $i$ , and  $e$  denotes an electron. The high-lying bound states of the hydrogen atom are regarded as part of the continuum whence the principal quantum number of the atom ( $i$  and  $j$  in (1)) ranges from 1 to  $m$ . The degenerate states of a particular level are assumed to be populated according to their statistical weights. Furthermore, we assume an electron temperature  $T_e$  which remains constant throughout the reaction, whence the transition probabilities of reactions (1) are independent of time; it should be noted that under certain circumstances, the relaxation time associated with  $T_e$  is much shorter than that for the plasma decay (Bates & Kingston 1964 *a, b*).

The nonlinear master equation for the relaxation of the plasma may then be written as

$$dn_i/dt = n_e \left\{ \sum_{j=1}^m (n_j P_{ji} - n_i P_{ij}) + n_e^2 P_{ci} - n_i P_{ic} \right\}, \quad (2)$$

for  $i = 1, \dots, m$ , where  $n_e(t)$  is the electron concentration,  $n_i(t)$  is the number density of atoms in state  $i$ ,  $P_{ij}$  is the transition rate constant from state  $i$  to state  $j$ , with the subscript  $c$  denoting the continuum.

To obtain the ionization rate coefficient, one considers the system which involves ionization but no recombination (Hogarth & McElwain 1975 *a, b*), namely,



The master equation is then linear and may be cast in matrix notation:

$$(d/dt)|N\rangle = A|N\rangle, \quad (4)$$

where  $|N(t)\rangle$  is the population vector and

$$A_{ij} = n_e \left\{ (1 - \delta_{ij}) P_{ji} - \delta_{ij} \left[ \sum_{k=1}^m (1 - \delta_{ik}) P_{ik} + P_{ic} \right] \right\}. \quad (5)$$

The reader is referred to the papers of Hogarth & McElwain (1975 *a, b*) for the detailed derivations of the above results.

To solve for (4), we note that the transport matrix  $A$  may be symmetrized to  $B$ ,

$$B = E^{-\frac{1}{2}} A E^{\frac{1}{2}}, \quad (6)$$

where  $E$  is the fractional equilibrium population matrix.

$$E_{ij} = \tilde{n}_i \delta_{ij}, \quad (7)$$

where  $\tilde{n}_i$  is the fractional equilibrium population of hydrogen atom with principal quantum number  $i$  at temperature  $T_e$ . The matrix  $B$  is symmetric and negative-definite. Hence, it has eigenvalues  $\lambda_j$  and eigenvectors  $|X_j\rangle$  which satisfy the following:

$$B = X A X^T, \quad (8)$$

$$A_{ij} = \lambda_i \delta_{ij}, \quad (9)$$

and  $0 > \lambda_1 > \lambda_2 \geq \lambda_3 \geq \dots \geq \lambda_m$ . (10)

The solution of (4) is  $|N(t)\rangle = \exp(At) |N(0)\rangle$  (11a)

and hence 
$$n_i(t) = \tilde{n}_i^{\frac{1}{2}} \sum_{j=1}^m \exp(\lambda_j t) X_{ij} \sum_{k=1}^m \tilde{n}_k^{-\frac{1}{2}} X_{kj} n_k(0). \quad (11b)$$

At time  $t \ll 1/(\lambda_1 - \lambda_2)$ , the system goes through a transient during which the initial distribution of hydrogen atoms relaxes to a new distribution at a rate which depends

on  $-\lambda_2$ . Following the transient (at  $t \gg 1/(\lambda_1 - \lambda_2)$ ), the new distribution decays at a much slower rate which depends on  $-\lambda_1$ , and (11) reduces to

$$n_i(t) \simeq \tilde{n}_i^{\frac{1}{2}} \sum_{k=1}^m \tilde{n}_k^{-\frac{1}{2}} X_{k1} n_k(0) \exp(\lambda_1 t) X_{i1}. \quad (12)$$

The initial transient corresponds to internal relaxation while the latter phase characterizes the ionization process. Explicitly the ionization rate approaches

$$dN_{\text{H}}/dt = -S_{\text{obs}} n_{\text{e}} N_{\text{H}}, \quad (13)$$

where  $N_{\text{H}}$  is the total concentration of hydrogen atoms,

$$N_{\text{H}}(t) = \sum_{i=1}^m n_i(t), \quad (14)$$

and the observed ionization rate coefficient  $S_{\text{obs}}$  is just

$$S_{\text{obs}} = -\lambda_1/n_{\text{e}}. \quad (15)$$

To solve for  $\lambda_1$ , we factorize the transport matrix  $\mathbf{A}$  into

$$\mathbf{A} = \mathbf{Q} - \mathbf{K} \quad (16)$$

with 
$$Q_{ij} = n_{\text{e}} \left\{ (1 - \delta_{ij}) P_{ji} - \delta_{ij} \sum_{k=1}^m (1 - \delta_{ik}) P_{ik} \right\} \quad (17)$$

and 
$$K_{ij} = n_{\text{e}} \delta_{ij} P_{ic}. \quad (18)$$

The matrix  $\mathbf{Q}$  then consists only of transitions between the bound states of the atom, and is stochastic with zero column-sums. Again we note that it may be symmetrized to  $\mathbf{R}$ ,

$$\mathbf{R} = \mathbf{E}^{-\frac{1}{2}} \mathbf{Q} \mathbf{E}^{\frac{1}{2}}. \quad (19)$$

The symmetrized matrix  $\mathbf{R}$  has eigenvalues  $\gamma_j$  and eigenvectors  $|Y_j\rangle$  which satisfy the following

$$\mathbf{R} = \mathbf{Y} \mathbf{\Gamma} \mathbf{Y}^{\text{T}} \quad (20)$$

$$\Gamma_{ij} = \gamma_i \delta_{ij}, \quad (21)$$

$$0 = \gamma_1 > \gamma_2 \geq \gamma_3 \geq \dots \geq \gamma_m, \quad (22)$$

and 
$$|Y_1\rangle = \mathbf{E}^{\frac{1}{2}} |1\rangle, \quad (23)$$

where all the elements in  $|1\rangle$  are unity. The zero eigenvalue  $\gamma_1$  in (22) and the equilibrium eigenvector  $|Y_1\rangle$  in (23) ensure the conservation of particles and the attainment of Boltzmann equilibrium at infinite time in the absence of ionization.

Using (16)–(19), we rewrite the eigenvalue equation (8) in the iterative form:

$$|X_k\rangle = (\mathbf{R} - \lambda_k \mathbf{I})^{-1} \mathbf{K} |X_k\rangle. \quad (24)$$

Substituting (20) and (21) into (24) gives

$$|X_k\rangle = \mathbf{Y} (\mathbf{\Gamma} - \lambda_k \mathbf{I})^{-1} \mathbf{Y}^{\text{T}} \mathbf{K} |X_k\rangle. \quad (25)$$

Since  $\mathbf{K}$  is diagonal, (25) reduces to

$$X_{ik} = \sum_{l=1}^m \sum_{j=1}^m Y_{ij} Y_{lj} (\gamma_j - \lambda_k)^{-1} K_{ll} X_{lk}. \quad (26)$$

Using (18), (22) and (23), one obtains

$$n_e^{-1} X_{ik} = (-\lambda_k)^{-1} \tilde{n}_i^{\frac{1}{2}} \sum_l \tilde{n}_l^{\frac{1}{2}} P_{lc} X_{lk} + \sum_{j=2}^m Y_{ij} (\gamma_j - \lambda_k)^{-1} \sum_l Y_{lj} P_{lc} X_{lk}, \quad (27)$$

where the  $l$ -summations are now over states from which ionization occurs. Thus, for a system with  $r$  such states, (27) leads to a system of  $r$  equations in  $r$  unknowns,  $\lambda_k$  and the  $(r-1)$  ratios of  $X_{lk}$ , given  $\mathbf{Y}$ ,  $\mathbf{\Gamma}$  and  $\mathbf{K}$ . It might appear at first sight that (27) is more tractable than the eigenvalue equation (8). This is not so in actual fact because the equation is nonlinear. Rather, it is useful because one can establish from it the relations between the normal modes of internal relaxation ( $\gamma_j$  and  $|Y_j\rangle$ ) and those of ionization ( $\lambda_j$  and  $|X_j\rangle$ ) (Yau & Pritchard 1978*a, b*). Such relations, together with others between  $\lambda_j$  and  $\gamma_j$  derived from *a priori* considerations, lead easily to explicit solutions of  $\lambda_1$ , at least for simple realistic model systems. In particular, it may be shown that

$$\lambda_1 = \alpha(Q_{11} - K_{11}) \quad (28a)$$

$$\approx \alpha(\gamma_2 - K_{11}), \quad (28b)$$

where  $0 < \alpha < 1$  and  $\alpha$  is physically a fractional measure of the deviation of population from the Boltzmann distribution due to the ionization reaction. Of course  $\alpha$  is unknown *a priori*. However, a first approximation may be obtained by noting that in a plasma, ionization probability and excitation probability from the ground state are small compared with those from the excited states. This implies that the population distributions of the excited states are strongly affected by the ionization whereas that of the ground state is not. Hence, we have

$$\alpha \approx 1 - \tilde{n}_1. \quad (29)$$

Note also that except at very high temperature,  $K_{11} \ll -Q_{11}$ . Hence, to simplify (27), we make the approximation that

$$\gamma_j - \lambda_1 \approx \tilde{n}_1 \gamma_j, \quad (30)$$

$j \geq 2$ , whence we obtain

$$n_e^{-1} X_{i1} = \sum_l \left\{ -\tilde{n}_i^{\frac{1}{2}} \lambda_1^{-1} \tilde{n}_l^{\frac{1}{2}} + \sum_{j=2}^m Y_{ij} Y_{lj} \tilde{n}_1^{-1} \gamma_j^{-1} \right\} P_{lc} X_{li}. \quad (31)$$

Let us examine the validity of the approximation (30) in more detail. At low temperature, the excited states are hardly populated ( $\tilde{n}_i \ll 1$  for  $i > 1$ ) and ionization is much slower than internal relaxation. Thus  $\tilde{n}_1 \approx 1$  and  $|\lambda_1| \ll |\gamma_j|$  for  $j > 2$ ; (30) is therefore an excellent approximation. As the temperature increases, the ionization rate becomes comparable with the internal relaxation rate, and  $(\gamma_j - \lambda_1)$  no longer approximates to  $\gamma_j$ . Nevertheless, (30) holds for  $j = 2$  as long as the excitation

probability from the ground state is smaller than any of those from the excited states. For the other eigenvalues  $\gamma_j, j > 2$ , two possibilities arise. If the eigenvalues are widely spaced, with  $|\gamma_j| \gg |\gamma_2|$  for  $j > 2$ , then the  $j > 2$  terms are small compared with the  $j = 2$  term in the  $j$ -summation in (31). Hence, little error is introduced into (31) even though (30) fails to hold for  $j > 2$ . On the other hand, if the eigenvalues  $\gamma_j$  are closely spaced, then  $\gamma_j$  is approximately  $\gamma_2$  for all  $j > 2$  and (30) is thus valid for all  $j > 2$ . Note, however, that at very high temperature when  $\tilde{n}_1$  is exceedingly small, the error in (30) becomes large even though the approximation in (29) is excellent, namely,  $\alpha \rightarrow 1$ , because the ionization probability from the ground state becomes comparable with the corresponding excitation probabilities. This temperature range is indeed beyond our interest, because the ionization mode ( $\lambda_1$  and  $|X_1\rangle$ ) and the transient relaxation modes ( $\lambda_j$  and  $|X_j\rangle, j > 2$ ) are no longer separable, and the description of the ionization process using a single eigenvalue becomes less meaningful. Hogarth and McElwain (1975*a*) have shown that the ionization rate coefficient may be characterized by  $-\lambda_1$ , provided that

$$\epsilon = (\lambda_1/\lambda_2)^{\frac{1}{2}} \quad (32)$$

$$\ll 1. \quad (33)$$

We see that the approximation (29) is valid at all temperatures for which  $\epsilon \ll 1$ .

### 3. RATE COEFFICIENT

The temperature of experimental interest ranges from a small percentage of  $\theta$  to about  $\theta$ , where  $\theta = I_1/k$ ,  $I_1$  and  $k$  being respectively the ionization energy from the ground state, and the Boltzmann constant. Our objective in this section is to derive the ionization rate constant for a model system that is simple enough as to allow transparent analytic solutions, and yet is realistic enough at all these temperatures. To this end, we note that in the transition probability matrix  $Q$ , transitions between neighbouring levels are dominant. Indeed, for all  $i$ ,  $P_{i, i+1}$  is greater than  $P_{ij}, j > i + 1$ , by at least an order of magnitude in this temperature range. Also, the ionization probability from the topmost bound level,  $P_{mc}$ , exceeds all the  $P_{ic}, i < m$ . Hence, we shall consider the simplified system in which only transitions between neighbouring levels are allowed, whence

$$P_{ij} = 0, \quad |j - i| > 1, \quad (34)$$

and

$$P_{ic} = 0, \quad i < m. \quad (35)$$

To assess the consequence of the first simplification (34), one may examine its effect on the internal relaxation behaviour of the system. Table 1 compares the slowest relaxation eigenvalues  $\gamma_2$  for a system allowing all transitions with those for a system allowing nearest-neighbour transitions only, calculated by using the collisional transition rate coefficients of Johnson (1972) for hydrogen with 20 bound levels ( $m = 20$ ). At the temperatures shown (4000–64 000 K), the agreement is better than 20 %, indicating that (34) does represent a semiquantitative approximation

to the full transition matrix; this conclusion is not inconsistent with the results of Brocklehurst (1970).

The consequence of assuming (35) is less obvious. Certainly, the approximation is valid for the ground and low-lying excited states, where the ionization probabilities are small. On the other hand, the ionization probabilities from the high-lying excited states are quite large. Fortunately, however, the observed ionization rate coefficient does not in fact depend strongly on the microscopic ionization processes at these states; we recall that it is this property that justifies the treatment of the very high-lying excited states as an extension of the continuum in the first place. Thus, (35) is expected to lead to little error in the derived ionization rate coefficient, provided that the ionization probabilities from the low-lying states are small.

TABLE 1. INTERNAL RELAXATION EIGENVALUE  $-\gamma_2$

temp K	$-\gamma_2$ , full matrix cm <sup>3</sup> s <sup>-1</sup>	$-\gamma_2$ , tridiagonal matrix cm <sup>3</sup> s <sup>-1</sup>
4 <sup>3</sup> †	1.06 <sup>-8</sup>	1.03 <sup>-8</sup>
8 <sup>3</sup>	1.08 <sup>-9</sup>	1.02 <sup>-9</sup>
1.6 <sup>4</sup>	1.34 <sup>-10</sup>	1.23 <sup>-10</sup>
3.2 <sup>4</sup>	7.98 <sup>-10</sup>	6.81 <sup>-10</sup>
6.4 <sup>4</sup>	5.36 <sup>-9</sup>	4.28 <sup>-9</sup>

† The index gives the power of 10 to be multiplied with the entry.

With the introduction of (35), (31) reduces drastically to give

$$-\lambda_1 = \tilde{n}_m \{n_e^{-1} P_{mc}^{-1} + V_{mm}\}^{-1}, \quad (36)$$

where the quantity 
$$V_{mm} = -(1/\tilde{n}_1) \sum_{i=2}^m Y_{mi}^2 / \gamma_i \quad (37)$$

is shown in the appendix to be 
$$V_{mm} = \sum_{j=1}^{m-1} V_j, \quad (38)$$

with 
$$V_j = \tilde{n}_m \left( \sum_{k=1}^j n_k \right)^2 / n_e \tilde{n}_1 \tilde{n}_j P_{j,j+1}, \quad j = 1, \dots, m-1, \quad (39)$$

for a system obeying (34). The observed ionization rate coefficient  $S_{\text{obs}}$  is then explicitly

$$S_{\text{obs}} = \left\{ \frac{1}{\tilde{n}_m P_{mc}} + \frac{1}{\tilde{n}_1} \sum_{j=1}^{m-1} \frac{\left( \sum_{k=1}^j \tilde{n}_k \right)^2}{\tilde{n}_j P_{j,j+1}} \right\}^{-1}. \quad (40)$$

Several properties of the rate coefficient  $S_{\text{obs}}$  are apparent in (40). First, the observed rate coefficient represents a co-operative effect of the respective excitation transitions, in the sense that the latter behave like a series of capacitors, leading to a resultant rate coefficient which is rather like the effective capacitance of a series of capacitors. This is perhaps intuitively obvious for systems with nearest-neighbour transitions only; for systems which allow other transitions as well, the



corresponding physical picture is expected to be more complicated. Indeed, at low temperatures (below 10 000 K in hydrogen) when  $\tilde{n}_1 \rightarrow 1$ , (40) approaches

$$S_{\text{obs}} = \left\{ \sum_{j=1}^m (\tilde{n}_j P_{j, j+1})^{-1} \right\}^{-1}, \quad (41)$$

where  $P_{m, m+1}$  denotes  $P_{mc}$ . This expression is complementary to that derived by Bates for the recombination coefficient  $\alpha_{\text{obs}}$  using an electrical network analogy (Bates & Kingston 1964*c*; Bates 1974*b*). Note, however, that the applicability of (40) is more restricted than is the corresponding expression of Bates (1974*b*) for the recombination coefficient; the latter is valid for systems involving radiative transitions as well, whereas (40) is valid only for systems where radiative transitions are unimportant or where the radiation field has a temperature  $T_e$ .

Equation (40) is useful in identifying the rôles of the respective microscopic processes in the overall ionization. Specifically, if we define

$$V_m = (n_e P_{mc})^{-1}$$

as a generalization to  $V_j$ ,  $j < m$ , then the observed ionization rate coefficient is predominantly controlled by the process associated with the largest  $V_j$  term,  $V_{\text{max}}$ . Figure 1 is a logarithmic plot of  $V_j/V_m$  for hydrogen at 4000, 8000 and 12000 K, again calculated by using the collisional transition rates of Johnson (1972) with 20 bound levels. The fact that  $V_m$  is much smaller than  $V_{\text{max}}$  at all these temperatures, indicates that the observed ionization rate coefficient does not depend strongly on the ionization probability  $P_{mc}$  and provides a plausible justification for (35). The location of  $V_{\text{max}}$  simply corresponds to the bottleneck. Indeed, it is of interest to compare the ionization of atomic hydrogen with the dissociation of molecular hydrogen in this regard. In the latter, the bottleneck occurs at highly excited states near the dissociation limit, and is broad in the sense that excitation processes associated with several levels are of importance in determining the overall rate, at all temperatures of experimental interest (Yau & Pritchard 1978*b*). This compares with the ionization of hydrogen (figure 1) where the bottleneck occurs in the low-lying excited states at all interesting temperatures. Indeed, as the temperature increases, the bottleneck is shifted towards the ground level, so that at high temperatures, the observed ionization rate coefficient depends predominantly on the excitation rate coefficient  $P_{12}$  from the ground level to the first excited level. Such temperature dependence of the bottleneck is to be found in a system which allows all transitions also. Indeed, at high temperature, the observed ionization rate is simply the sum of all the excitation probabilities plus the ionization probability from the ground level, as is given by (28*a*). Note also that the bottleneck is relatively sharp, in the sense that only excitation processes associated with a few states are of importance in determining the observed ionization rate. Such behaviour was first observed semiquantitatively by Byron, Stabler & Bortz (1962) in their studies of collisional-radiative recombination. Indeed, their empirical correction factor  $\gamma$  may be understood as the ratio of  $V_{\text{max}}$  to the sum of  $V_j$  in the present context.

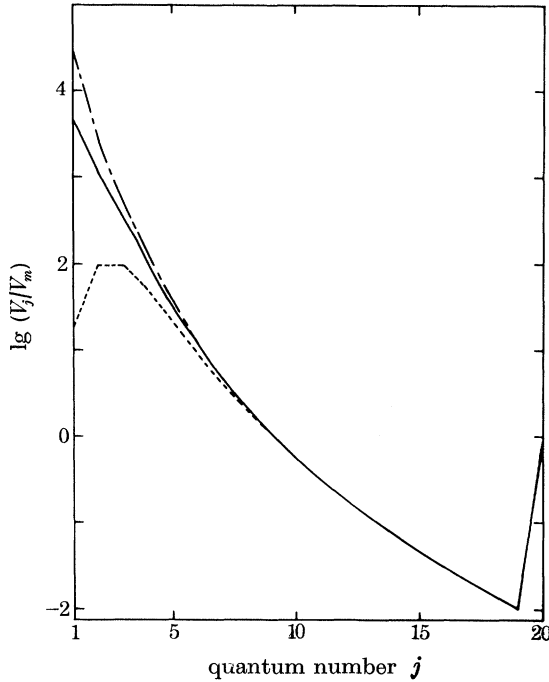


FIGURE 1. Study of bottleneck effects in collisional ionization of hydrogen at 4000, 8000 and 12 000 K.  $V_j$  is contribution from level  $j$  to the overall ionization time,  $1/S_{\text{obs}}$ ; equation (39).  $V_j \gg V_m$  for small  $j$ . Thus,  $S_{\text{obs}}$  depends predominantly on the excitation processes from the low-lying states. - - -, 4000 K; —, 8000 K; — · —, 12 000 K.

#### 4. RESULTS

Given the collisional transition probabilities  $P_{ij}$  and  $P_{ic}$ , it is straightforward to compute the observed ionization rate coefficient as a function of temperature by using (40). For atomic hydrogen, a complete set of data for  $P_{ij}$  and  $P_{ic}$  has been given by Johnson (1972). In the present calculation,  $m$  is taken to be 20, and the actual ionization limit (13.6 eV) is used. In Johnson's paper, a reduced ionization limit was introduced, which increases the ionization probabilities  $P_{ic}$  slightly. Since the observed ionization rate coefficient  $S_{\text{obs}}$  is in any case insensitive to the ionization probability  $P_{ic}$  in (40), the effect of the reduction in the ionization limit on the observed rate coefficient is clearly minimal.

Table 2 summarizes the results of the relevant calculations and illustrates the numerical properties of the formal results in §§ 2 and 3. Columns 2–6 refer to solutions of the complete system, namely, the one with all transitions allowed. Columns 7–10 refer to the tridiagonal system, which allows only nearest-neighbour transitions. It is immediately apparent from inspection that all the corresponding entries in the two systems are very similar, showing that the tridiagonal system indeed represents a fair approximation to the complete one.

TABLE 2. IONIZATION AND INTERNAL RELAXATION RATE COEFFICIENTS

In this table (and also in table 1), all rate coefficients are given in second order form i.e. for  $n_e = 1 \text{ cm}^{-3}$ .

temp K	full matrix				tridiagonal matrix		
	$\frac{-\gamma_2}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{K_{11}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{-\gamma_2 + K_{11}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{S_{\text{obs}}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{S_{\text{obs}}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{S_{\text{obs}}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{-\gamma_2}{\text{cm}^3 \text{ s}^{-1}}$
4 <sup>3+</sup>	1.06 <sup>-8</sup>	1.27 <sup>-26</sup>	1.06 <sup>-8</sup>	5.67 <sup>-22</sup>	4.38 <sup>-22</sup>	4.38 <sup>-22</sup>	1.03 <sup>-8</sup>
6 <sup>3</sup>	3.36 <sup>-9</sup>	8.67 <sup>-21</sup>	3.36 <sup>-9</sup>	5.67 <sup>-17</sup>	4.97 <sup>-17</sup>	4.97 <sup>-17</sup>	3.12 <sup>-9</sup>
8 <sup>3</sup>	1.08 <sup>-9</sup>	7.68 <sup>-18</sup>	1.08 <sup>-9</sup>	1.08 <sup>-14</sup>	9.98 <sup>-15</sup>	9.98 <sup>-15</sup>	5.45 <sup>-4</sup>
1 <sup>4</sup>	4.67 <sup>-10</sup>	4.70 <sup>-16</sup>	4.67 <sup>-10</sup>	2.22 <sup>-13</sup>	2.07 <sup>-13</sup>	2.07 <sup>-13</sup>	4.40 <sup>-10</sup>
1.2 <sup>4</sup>	2.56 <sup>-10</sup>	7.52 <sup>-15</sup>	2.56 <sup>-10</sup>	1.61 <sup>-12</sup>	1.50 <sup>-12</sup>	1.50 <sup>-12</sup>	2.40 <sup>-10</sup>
1.4 <sup>4</sup>	1.69 <sup>-10</sup>	5.57 <sup>-14</sup>	1.69 <sup>-10</sup>	6.59 <sup>-12</sup>	6.05 <sup>-12</sup>	6.05 <sup>-12</sup>	1.57 <sup>-10</sup>
1.6 <sup>4</sup>	1.34 <sup>-10</sup>	2.54 <sup>-13</sup>	1.34 <sup>-10</sup>	1.90 <sup>-11</sup>	1.72 <sup>-11</sup>	1.72 <sup>-11</sup>	1.23 <sup>-10</sup>
3.2 <sup>4</sup>	7.98 <sup>-10</sup>	6.19 <sup>-11</sup>	8.60 <sup>-10</sup>	8.25 <sup>-10</sup>	6.51 <sup>-10</sup>	6.47 <sup>-11</sup>	6.81 <sup>-10</sup>
6.4 <sup>4</sup>	5.36 <sup>-9</sup>	1.24 <sup>-9</sup>	6.60 <sup>-9</sup>	6.59 <sup>-9</sup>	4.26 <sup>-9</sup>	4.06 <sup>-9</sup>	4.28 <sup>-9</sup>
1.28 <sup>5</sup>	1.58 <sup>-8</sup>	6.68 <sup>-9</sup>	2.25 <sup>-8</sup>	2.25 <sup>-8</sup>	1.20 <sup>-8</sup>	9.46 <sup>-9</sup>	1.21 <sup>-8</sup>
				$\frac{S_{\text{obs}}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{S_{\text{obs}}}{\text{cm}^3 \text{ s}^{-1}}$	$\frac{S_{\text{obs}}}{\text{cm}^3 \text{ s}^{-1}}$	
				(eqn 32)	(eqn 40)	(eqn 32)	
				2.10 <sup>-7</sup>	4.38 <sup>-22</sup>	4.38 <sup>-22</sup>	1.87 <sup>-7</sup>
				5.24 <sup>-5</sup>	4.97 <sup>-17</sup>	4.97 <sup>-17</sup>	5.21 <sup>-5</sup>
				5.13 <sup>-4</sup>	9.98 <sup>-15</sup>	9.98 <sup>-15</sup>	5.45 <sup>-4</sup>
				1.77 <sup>-3</sup>	2.07 <sup>-13</sup>	2.07 <sup>-13</sup>	1.94 <sup>-3</sup>
				3.91 <sup>-3</sup>	1.50 <sup>-12</sup>	1.50 <sup>-12</sup>	4.33 <sup>-3</sup>
				6.78 <sup>-3</sup>	6.05 <sup>-12</sup>	6.05 <sup>-12</sup>	7.58 <sup>-3</sup>
				1.02 <sup>-2</sup>	1.72 <sup>-11</sup>	1.72 <sup>-11</sup>	1.14 <sup>-2</sup>
				4.19 <sup>-2</sup>	6.51 <sup>-10</sup>	6.47 <sup>-11</sup>	4.66 <sup>-2</sup>
				9.03 <sup>-2</sup>	4.26 <sup>-9</sup>	4.06 <sup>-9</sup>	9.47 <sup>-2</sup>
				1.46 <sup>-1</sup>	1.20 <sup>-8</sup>	9.46 <sup>-9</sup>	1.43 <sup>-1</sup>

† The index gives the power of 10 to be multiplied with the entry.

For the complete system, the calculated values of  $S_{\text{obs}}$  are in exact agreement with the results of Hogarth & McElwain, except at 4000 and 6000 K: the slight discrepancies of less than 1 % here are attributed to their use of a reduced ionization limit and possibly to the different numerical methods of solution used. The ratio of  $(-\gamma_2 + K_{11})$  to  $S_{\text{obs}}$ , columns 4 and 5, approaches unity above 32 000 K, the temperature beyond which the ionization probability from the ground level,  $K_{11}$ , becomes comparable with the slowest internal relaxation rate  $-\gamma_2$ , and the parameter  $\epsilon$  in (32) becomes comparable with unity. (Both  $-K_{11}/\gamma_2$  and  $\epsilon$  exceed 0.1 above 64 000 K.)

Similar behaviour is found in the tridiagonal system, namely,  $\gamma_2$  approaches  $\lambda_1$  (since  $K_{11}$  is assumed to be zero here) and  $\epsilon$  becomes comparable with unity above 32 000 K. The analytic solution for  $S_{\text{obs}}$  from (40) is given together with the numerical solution; agreement is seen to be excellent up to 32 000 K. Note that the solutions for the tridiagonal system and the full system agree to within 20 % up to this temperature. To the extent that the collisional transition probability data are uncertain to this order of magnitude, we feel that the analytic solution for the tridiagonal system represents an acceptable approximation to the full numerical solution up to this temperature. Above this temperature, the ionization probability  $P_{ic}$  from the ground level becomes appreciable compared with the excitation probabilities, and the observed ionization rate coefficient  $S_{\text{obs}}$  approaches the sum of the ionization probability and excitation probabilities from the ground level. Note however that the meaning of a single time-independent ionization rate coefficient becomes less well defined at these high temperatures as  $\epsilon$  becomes comparable with unity. The results at and above 64 000 K are therefore less meaningful, and are given only for comparison and completeness.

The rate-quotient law is obeyed up to first order in  $\epsilon$  in the relaxation of a dense plasma (Hogarth & McElwain 1975 *a, b*), namely,

$$n_e S_{\text{obs}} = -\lambda_1 \{1 + O(\epsilon^2)\} \quad (42)$$

and 
$$n_e \beta_{\text{obs}} = -\lambda_1 K_{\text{eq}}^{-1} \{1 + O(\epsilon^2)\} \quad (43)$$

with 
$$\beta_{\text{obs}} = \alpha_{\text{obs}} n_e^{-1}, \quad (44)$$

where  $\beta_{\text{obs}}$  is the three-body recombination rate coefficient and  $K_{\text{eq}}$  is the Saha equilibrium constant. One may therefore compute  $\beta_{\text{obs}}$  using the relation

$$\beta_{\text{obs}} = S_{\text{obs}}/K_{\text{eq}}. \quad (45)$$

Table 3 gives the value of  $\beta_{\text{obs}}$  calculated by using (40) and (45) up to 16 000 K. Above this temperature, the populations of the high-lying excited states become appreciable and the Saha equilibrium constant is very sensitive to the number of bound levels assumed; this causes the recombination coefficient  $\beta_{\text{obs}}$  calculated from (45) to become meaningless, and it is therefore not given for temperatures above 16 000 K. The values of  $\beta_{\text{obs}}$  of Johnson & Hinnov (1973) and of Hogarth & McElwain (1975 *b*) are also given in the table for comparison. The three calculations

are in essential agreement. Also, the calculated values of  $\beta_{\text{obs}}$  agree with the experiment of Funahashi & Takeda (1969) between 10 000 and 20 000 K to within a factor of five.

TABLE 3. RECOMBINATION COEFFICIENT  $\beta_{\text{obs}}$

temp K	$\beta_{\text{obs}}/(\text{cm}^3 \text{s}^{-1})$		
	eqn (45)	Johnson & Hinnov (1973)	Hogarth & McElwain (1975)
$4^3 \dagger$	$9.80^{-26}$	$1.3^{-25}$	$1.17^{-25}$
$6^3$	$1.18^{-26}$	—	$1.27^{-26}$
$8^3$	$2.14^{-27}$	$2.3^{-27}$	$2.22^{-27}$
$1^4$	$6.13^{-28}$	—	$6.35^{-28}$
$1.2^4$	$2.44^{-28}$	—	$2.56^{-28}$
$1.4^4$	$1.24^{-28}$	—	$1.32^{-28}$
$1.6^4$	$7.84^{-29}$	$7.5^{-29}$	$8.50^{-29}$

† The index gives the power of 10 to be multiplied with the entry.

TABLE 4. ACTIVATION ENERGY  $E_{\text{act}}$  FOR THE IONIZATION RATE COEFFICIENT

temp K	$E_{\text{act}}$ , full matrix eV/atom	$E_{\text{act}}$ , tridiagonal matrix eV/atom
$4^3 \dagger$	12.4	12.5
$1.6^4$	10.2	10.0
$6.4^4$	12.5	10.8
$2.56^5$	17.0	14.0
$1.024^6$	7.5	5.7
$4.096^6$	-71.8	-65.7

† The index gives the power of 10 to be multiplied with the entry. Ionization energy = 13.6 eV, first excitation energy = 10.2 eV.

## 5. DISCUSSION

It has been customary to interpret kinetic data in plasma relaxation experiments in terms of a postulated mechanism, with the interpretation based upon certain empirical trends in experimental observations. Thus, for example, the ionization of an inert-gas atom in a shock wave has been postulated as a two-step process, namely, excitation from the ground state to the first excited state followed by ionization from there at a much faster rate; the postulate is based upon the experimental observation that the temperature coefficient of the observed ionization rate coefficient  $E_{\text{act}}$ , where

$$E_{\text{act}} = -d \ln S_{\text{obs}}/d(1/kT), \quad (46)$$

is close to the excitation energy (McLaren & Hobson 1968). Detailed theoretical expressions which explicitly relate the rate coefficients of the respective microscopic excitation processes to the observed rate coefficient, such as equation (40), may shed some light on such interpretations at an atomic level.

Thus, in the ionization of a dense hydrogen plasma, equation (40) does support the above postulated mechanism at high temperature, namely, that the ionization rate is determined by the rate of activation from the ground level to the first excited level. It also shows, however, that this does not necessarily imply that the activation energy  $E_{\text{act}}$  will be close to the first excitation energy. Indeed,  $E_{\text{act}}$  at such temperatures is simply the temperature coefficient of the overall rate of the relevant excitation processes; the latter depends on both the excitation energy and the energy dependence of the excitation cross sections, and may even become negative at very high temperature, as shown in table 4.

At low temperature, on the other hand, equation (40) suggests that the postulated mechanism no longer holds. The  $1 \rightarrow 2$  excitation is no longer the sole rate-determining step. Rather, the observed ionization rate is determined by excitation processes associated with more than one excited levels above the first excited level. Also, the observed temperature coefficient  $E_{\text{act}}$  may no longer be identified with the temperature coefficient of any particular transition, though it should be close to the first excitation energy. Table 4 lists the temperature coefficient  $E_{\text{act}}$  for the ionization rate coefficient for a dense hydrogen plasma between  $4 \times 10^3$  and  $4 \times 10^6$  K for both the complete system and the tridiagonal system. The agreement between the two is good at all temperatures shown (but the figures at and above 64 000 K should be taken as illustration of the theoretical result only in view of the discussions in § 4 regarding the rate coefficient at these temperatures).

Although the above deductions from equation (40) are applicable, strictly speaking, only to a model hydrogenic plasma restricted to nearest-neighbour transitions, one may expect from the results of table 4 that equation (40) not only describes the basic physical features for an actual dense hydrogen plasma where all transitions are allowed, but also for other dense atomic plasma, since the transition probabilities and energy-level structures in different plasma are qualitatively similar; this despite the fact that in the latter systems, we are dealing primarily with atom-atom rather than electron-atom collisions.

In respect of the latter point, we note two, as yet unexplained, results obtained in shock-wave ionization studies of the inert gases. For argon (McLaren & Hobson 1968) it has been shown (McElwain, Wagschal & Pritchard 1970) that the observed rate data in the temperature range 8000–12 000 K can be fitted satisfactorily to a two-state reaction scheme, whereas there is no two-state model solution for the data at 7000 K: thus, the ionization process for argon at 7000 K appears to be in a similar régime to that indicated in figure 1 and table 4 for hydrogen at 4000 K. On the other hand, similar experiments show an activation energy slightly (1 eV) lower than the first excitation energy for xenon, and the preliminary result for neon appears to be lower (Ward 1969); in view of the wide range of temperature coefficients exhibited in table 4 for the ionization rate for hydrogen, there seems no reason to be unduly suspicious of these apparently anomalous results, and it would appear that they both merit further investigation.

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## REFERENCES

- Bates, D. R. 1974*a* *Case Stud. Atom. Phys.* **4**, 57–92.  
 Bates, D. R. 1974*b* *Proc. R. Soc. Lond. A* **337**, 15–20.  
 Bates, D. R. & Kingston, A. E. 1964*a* *Proc. R. Soc. Lond. A* **279**, 10–31.  
 Bates, D. R. & Kingston, A. E. 1964*b* *Proc. R. Soc. Lond. A* **279**, 32–38.  
 Bates, D. R. & Kingston, A. E. 1964*c* *Proc. Phys. Soc.* **83**, 43–47.  
 Bates, D. R., Kingston, A. E. & McWhirter, R. W. P. 1962 *Proc. R. Soc. Lond. A* **267**, 297–312.  
 Biberman, L. M., Yakubov, I. T. & Vorob'ev, V. S. 1971 *Proc. Inst. elect. electron. Engrs* **59**, 555–572.  
 Brocklehurst, M. 1970 *Mon. Not. R. astr. Soc.* **148**, 417–434.  
 Burgess, A. & Summers, H. P. 1969 *Astrophys. J.* **157**, 1007–1021.  
 Byron, S., Stabler, R. C. & Bortz, P. I. 1962 *Phys. Rev. Lett.* **8**, 376–379.  
 Funahashi, A. & Takeda, S. 1969 *J. Phys. Soc. Japan.* **27**, 182–186.  
 Gordiets, B. F., Gudzenko, L. I. & Shelepsin, L. A. 1968 *J. quant. Spectrosc. Radiat. Transfer* **8**, 791–804.  
 Hogarth, W. L. & McElwain, D. L. S. 1975*a* *Proc. R. Soc. Lond. A* **345**, 251–263.  
 Hogarth, W. L. & McElwain, D. L. S. 1975*b* *Proc. R. Soc. Lond. A* **345**, 265–276.  
 Johnson, L. C. 1972 *Astrophys. J.* **174**, 227–236.  
 Johnson, L. C. & Hinnov, E. 1973 *J. quant. Spectrosc. Radiat. Transfer.* **13**, 333–358.  
 Limbaugh, C. C. & Mason, A. A. 1971 *Phys. Rev. A* **4**, 2368–2377.  
 McElwain, D. L. S., Wagschal, L. & Pritchard, H. O. 1970 *Physics Fluids* **13**, 2200–2202.  
 McLaren, T. I. & Hobson, R. M. 1968 *Physics Fluids* **11**, 2162–2172.  
 Ward, T. V. 1969 Ph.D. thesis, The Queen's University of Belfast.  
 Yau, A. W. & Pritchard, H. O. 1978*a* *Can. J. Chem.* (in the press).  
 Yau, A. W. & Pritchard, H. O. 1978*b* *J. Phys. Chem.* (in preparation).

## APPENDIX

To derive (38) from (37), we define

$$Z_i = \sum_{l=2}^m \frac{Y_{il}Y_{ml}}{\gamma_l}, \quad i = 1, 2, \dots, m. \quad (\text{A } 1)$$

Since  $\mathbf{R} |Y_l\rangle = \gamma_l |Y_l\rangle$ ,  $l = 1, 2, \dots, m$ , (\text{A } 2)

and  $0 = \gamma_1 > \gamma_2 > \dots > \gamma_m$ , summing (A 2) over  $l$  leads to

$$\sum_{l=2}^m \sum_{k=1}^m R_{ik} Y_{kl} Y_{ml} \gamma_l^{-1} = \sum_{l=2}^m Y_{il} Y_{ml}. \quad (\text{A } 3)$$

Using the orthogonality property,

$$\sum_{l=1}^m Y_{il} Y_{kl} = \delta_{ik}, \quad (\text{A } 4)$$

we obtain

$$\mathbf{R} |Z\rangle = |\zeta\rangle, \quad (\text{A } 5)$$

where

$$\zeta_i = \delta_{im} - Y_{i1} Y_{m1} \quad (\text{A } 6)$$

$$= \delta_{im} - \tilde{n}_i^{\frac{1}{2}} \tilde{n}_m^{\frac{1}{2}}. \quad (\text{A } 7)$$

In (A 5),  $\mathbf{R}$  is singular. To solve for  $|\zeta\rangle$ , we define as generalization of  $\mathbf{R}$  and  $|\zeta\rangle$  a perturbed  $\mathbf{R}^{(h)}$  and  $|\zeta^{(h)}\rangle$ , where

$$R_{ij}^{(h)} = R_{ij}^{(0)} - h\delta_{im}\delta_{jm}, \quad (\text{A } 8)$$

and

$$\zeta_i^{(h)} = \delta_{im} - Y_{i1}^{(h)} Y_{m1}^{(h)} \quad (\text{A } 9)$$

$$= \delta_{im} - \tilde{n}_i^{\frac{1}{2}} \tilde{n}_m^{\frac{1}{2}} g_i g_m, \quad (\text{A } 10)$$

where  $|Y_j^{(h)}\rangle$  is the  $j$ th eigenvector for the perturbed matrix  $\mathbf{R}^{(h)}$ . Note that  $|\zeta^{(0)}\rangle \equiv |\zeta\rangle$  and  $g_i \rightarrow 1$  as  $h \rightarrow 0$ . Straightforward manipulation then gives

$$Z_m = h^{-1} \left\{ g_m \sum_{i=1}^m \tilde{n}_i g_i - 1 \right\}. \quad (\text{A } 11)$$

To obtain  $g_i$ , we solve the eigenvalue equation

$$\mathbf{R}^{(h)} |Y_1^{(h)}\rangle = \gamma_1^{(h)} |Y_1^{(h)}\rangle, \quad (\text{A } 12)$$

where  $h$  is vanishingly small, and obtain

$$\gamma_1^{(h)} = -\tilde{n}_m h \quad (\text{A } 13)$$

and

$$g_i = C \left\{ 1 - \tilde{n}_m h \left[ \sum_{j=1}^m \left( \sum_{k=1}^m \tilde{n}_k \right) / n_e \tilde{n}_j P_{j, j+1} \right] \right\} \quad (\text{A } 14)$$

where  $C$  is the normalization constant, with

$$\sum_{i=1}^m \tilde{n}_i g_i^2 = 1. \quad (\text{A } 15)$$

Substitution of (A 11), (A 14) and (A 15) into (37) leads to (38) and (39).