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On the validity of collisional–radiative models

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Abstract

I derive strict conditions for the validity of the collisional–radiative (CR) models widely used in plasma physics, and show that conditions on the eigenvectors of the full matrix of rates must be satisfied and that, in contrast to the conventional view, the eigenvalues have secondary importance. I use the results to analyse some CR models for molecular hydrogen.

Keywords: Theoretical modelling

1. Introduction

Collisional-radiative (CR) models have been successfully used in plasma physics for some time [1–10] Some details of their mathematical structure have been given [11].

The fundamental problem is to solve

$$\dot{\mathbf{n}} = \mathbf{M}(n_1, \ldots, n_m)\mathbf{n} + \mathbf{\Gamma}(n_1, \ldots, n_m). \tag{1}$$

Here $\mathbf{M}(n_1, \ldots, n_m)$ is an $N \times N$ matrix of rates and $\Gamma(n_1, \ldots, n_m)$ is a source provided by collisions between pairs of species whose (fixed) densities specify the plamsa environment; $\mathbf{n}$ is a vector whose components are the densities of the atomic, ionic and molecular states whose dynamics is to be calculated. Typically, a large number of species whose densities vary with a broad range of timescales must be included in (1). The purpose of a CR model is to reduce the number of species whose fate must be calculated explicitly.

The solution of (1) is

$$\mathbf{n}(t) = \exp(\mathbf{M}t)\mathbf{n}(0) + \exp(\mathbf{M}t)\int_0^t \exp(-\mathbf{M}t')\,\mathrm{d}t'\,\mathbf{\Gamma}. \tag{2}$$

This is supposed to be adequately approximated by

$$\mathbf{n}_P(t) = \exp(\mathbf{M}_{\mathrm{eff}}t)\mathbf{n}'_P(0) + \exp(\mathbf{M}_{\mathrm{eff}}t) \times \int_0^t \exp(-\mathbf{M}_{\mathrm{eff}}t')\,\mathrm{d}t'\,\mathbf{\Gamma}'_P, \tag{3}$$

$$\mathbf{n}_Q(t) = \Omega\mathbf{n}_P(t) - \mathbf{M}_Q^{-1}\mathbf{\Gamma}_Q, \tag{4}$$

so that $\mathbf{n}_P$ satisfies

$$\dot{\mathbf{n}}_P = \mathbf{M}_{\mathrm{eff}}\mathbf{n}_P + \mathbf{\Gamma}'_P \tag{5}$$

with initial condition $\mathbf{n}'(0)$, where the quantities $\mathbf{n}'_P(0)$, $\mathbf{\Gamma}'_P$ and Ω are defined below.

In Eq. (3), I have assumed that the states have been partitioned into two classes P and Q and define two projection operators P and Q, which project out the classes. For convenience we order the states, and therefore $\mathbf{M}$ so that the P states come first, and the Q states second, so that (1) becomes

$$\begin{bmatrix}\dot{\mathbf{n}}_P \\ \dot{\mathbf{n}}_Q\end{bmatrix} = \begin{bmatrix}\mathbf{M}_P & \mathbf{H} \\ \mathbf{V} & \mathbf{M}_Q\end{bmatrix}\begin{bmatrix}\mathbf{n}_P \\ \mathbf{n}_Q\end{bmatrix} + \begin{bmatrix}\mathbf{\Gamma}_P \\ \mathbf{\Gamma}_Q\end{bmatrix}, \tag{6}$$

where $P\mathbf{M}P = \mathbf{M}_P$, $P\mathbf{M}Q = \mathbf{H}$, $Q\mathbf{M}P = \mathbf{V}$, $Q\mathbf{M}Q = \mathbf{M}_Q$, $\mathbf{n}_P = P\mathbf{n}$, $\mathbf{n}_Q = Q\mathbf{n}$, $\mathbf{\Gamma}_P = P\mathbf{\Gamma}$ and $\mathbf{\Gamma}_Q = Q\mathbf{\Gamma}$. We assume that there are N_P P states and N_Q Q states. Traditionally, this division is made on physical grounds, with the assumption that all the P space states vary 'slowly', whereas all the Q space states vary 'rapidly'. In this paper, I show that this view is inadequate, and that the inadequacy can be serious if a CR model including molecules is needed.

A proper discussion of the solutions of (1) requires knowledge of the eigen*vectors* of $\mathbf{M}$ as well as the eigenvalues. Let us define $\mathbf{T}$ as an $N \times N$ matrix whose columns are the normalized eigenvectors of $\mathbf{M}$, arranged

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in order of increasing absolute value of the eigenvalues and

$$\mathbf{D} = \mathrm{diag}\left\{\lambda^{(1)}, \lambda^{(2)}, \ldots, \lambda^{N_P}, \lambda^{N_P+1}, \ldots, \lambda^{(N)}\right\} \tag{7}$$

as the diagonal matrix of eigenvalues $\lambda^{(k)}$, also in increasing order of absolute magnitude.

It is convenient to subdivide $\mathbf{T}$ as

$$\mathbf{T} = \begin{bmatrix} \mathbf{T}_P & \boldsymbol{\Delta} \\ \boldsymbol{\delta} & \mathbf{T}_Q \end{bmatrix}, \tag{8}$$

where $\mathbf{T}_P$ is an $N_P \times N_P$ submatrix, so that, $\mathbf{T}_P$ represents the P space part of the eigenvectors which correspond to the P space eigenvalues. Similarly, $\mathbf{T}_Q$ is the $N_Q \times N_Q$ submatrix which represents the Q space part of the eigenvectors which correspond to the Q space eigenvalues. $\boldsymbol{\Delta}$ is the P space part of the eigenvectors corresponding to the Q space eigenvalues and $\boldsymbol{\delta}$ the Q space part of the eigenvectors corresponding to the P space eigenvalues.

Similarly, defining

$$\mathbf{D}_P = \mathrm{diag}\left\{\lambda^{(1)}, \lambda^{(2)}, \ldots, \lambda^{(N_P)}\right\}. \tag{9}$$

It is straightforward, but tedious to show that

$$\mathbf{M}_{\mathrm{eff}}\mathbf{T}_P = \left[\mathbf{M} - \mathbf{H}\mathbf{M}_Q^{-1}\mathbf{V}\right]\mathbf{T}_P = [\mathbf{T}_P + \mathrm{O}(\boldsymbol{\delta})]\mathbf{D}_P. \tag{10}$$

Thus, only if [1] $\boldsymbol{\delta} \ll 1$, then the P space part of the eigenvectors corresponding to the P space eigenvalues are, to an adequate approximation the eigenvectors of $\mathbf{M}_{\mathrm{eff}}$, with eigenvalues $\lambda^{(k)}$, $k = 1, \ldots, N_P$. This, as we shall see, is a key requirement. Furthermore, if both $\boldsymbol{\delta} \ll 1$ *and* $\mathbf{T}_Q^{-1}\boldsymbol{\delta} \ll 1$, we can invert the matrix $\mathbf{T}$ to order $\boldsymbol{\delta}$ and calculate $\exp(\mathbf{M}t)$ explicitly. We can therefore derive the solution of Eq. (1) for times much greater than $1/|\lambda^{(N_P+1)}|$. The algebra is not reproduced here, but the result is that [2]

$$\{\exp(\mathbf{M}t)\mathbf{n}(0)\}_P = \exp(\mathbf{M}_{\mathrm{eff}}t)\mathbf{n}'_P(0) \tag{11}$$

with

$$\mathbf{n}'_P(0) = \mathbf{n}_P(0) - \Delta\mathbf{T}_Q^{-1}\mathbf{n}_Q(0) \tag{12}$$

and

$$\{\exp(\mathbf{M}t)\mathbf{n}(0)\}_Q = \boldsymbol{\delta}\mathbf{T}_P^{-1}\mathbf{n}_P(t) \tag{13}$$

as well as

$$\left\{\exp(\mathbf{M}t)\int_0^t \exp(-\mathbf{M}t')\,\mathrm{d}t'\,\boldsymbol{\Gamma}\right\}_P = \exp(\mathbf{M}_{\mathrm{eff}}t)\int_0^t \exp(-\mathbf{M}_{\mathrm{eff}}t')\,\mathrm{d}t'\,\boldsymbol{\Gamma}'_P(+C_P) \tag{14}$$

with

$$\boldsymbol{\Gamma}'_P = \boldsymbol{\Gamma}_P - \Delta\mathbf{T}_Q^{-1}\boldsymbol{\Gamma}_Q \tag{15}$$

and

$$\left\{\exp(\mathbf{M}t)\int_0^t \exp(-\mathbf{M}t')\,\mathrm{d}t'\,\boldsymbol{\Gamma}\right\}_Q = \delta\mathbf{T}_P^{-1}\exp(\mathbf{M}_{\mathrm{eff}}t)\int_0^t \exp(-\mathbf{M}_{\mathrm{eff}}t')\,\mathrm{d}t'\,\boldsymbol{\Gamma}'_P - \mathbf{M}_Q^{-1}\boldsymbol{\Gamma}_Q, \tag{16}$$

so that

$$\Omega = \boldsymbol{\delta}\mathbf{T}_P^{-1} \tag{17}$$

and Eq. (5) is indeed satisfied. Now if

$$|\lambda^{(N_P)}| \ll |\lambda^{(N_P+1)}|, \tag{18}$$

then we can show that

$$\boldsymbol{\delta}\mathbf{T}_P^{-1} = -\mathbf{M}_Q^{-1}\mathbf{V}, \tag{19}$$

$$\Delta\mathbf{T}_Q^{-1} = \mathbf{H}\mathbf{M}_Q^{-1} \tag{20}$$

and C_P is negligible.

2. Discussion

Comparing the above results with the conventional expressions for a CR model, we can see that

1. The proper criterion for validity is given in terms of the eigenvectors of the rate matrix $\mathbf{M}$.
2. The correct population coefficients are given by the substitutions
$$-\mathbf{M}_Q^{-1}\mathbf{V} \to \delta\mathbf{T}_P^{-1}, \quad \mathbf{H}\mathbf{M}_Q^{-1} \to \Delta\mathbf{T}_Q^{-1}. \tag{21}$$
3. There is *no* requirement for the Q space timescales to be very much shorter than the P space timescales, but if they are, (and if a valid CR model can be constructed according to the eigenvector criteria), then the conventional CR model is recovered. Notice, however, that if the eigenvector criteria are not satisfied, then no CR model is valid, whatever the eigenvalues of $\mathbf{M}$.

Thus, there are two distinct criteria. First, and more important, are the smallness of $\boldsymbol{\delta}$ and $\mathbf{T}_Q^{-1}\boldsymbol{\delta} \ll 1$, which

[1] I define the size of column n of length m in an $m \times n$ matrix $v_{m,n}$ through the l_1 (Manhatten) norm $\|\mathbf{v}\|_1^{(n)}$ viz

$$\|\mathbf{v}\|_1^{(n)} = \sum_{k=1}^{m} |v_{k,n}|$$

and the 'size' of the matrix $\mathbf{v}$ as $\max_n\{\|\mathbf{v}\|_1^{(n)}\}$. This definition is used in expressions involving $\boldsymbol{\delta} \ll 1$ etc.

[2] There is also a correction to $\mathbf{n}_P$ given by

$$C_P = -\Delta\mathbf{T}_Q^{-1}\mathbf{M}_Q^{-1}\boldsymbol{\Gamma}_Q,$$

which I shall not discuss. It corresponds to a contribution which arises from the equilibration of the Q space part of the source term on a timescale less than $1/\lambda^{N_P+1}$.

guarantee that the solution of the CR equations entirely within the P space is an acceptable approximation to the P space part of the full solution. This is essential. Secondly, the smallness of the P space eigenvalues in comparison to the Q space eigenvalues is required only to ensure that the initial Q space contribution (or Q space source term contribution) to the P space is given by $-\mathbf{H}\mathbf{M}_Q^{-1}$, and that the Q space densities in equilibrium with the P space states are given by $-\mathbf{M}_Q^{-1}\mathbf{V}$. If these expressions are replaced by $-\boldsymbol{\Delta}\mathbf{T}_Q^{-1}$ and $\boldsymbol{\delta}\mathbf{T}_P^{-1}$, respectively, then there is no requirement on the relative sizes of the eigenvalues of $\mathbf{M}$. Conversely, if a CR model with suitably small $\boldsymbol{\delta}$ has been constructed, but for which the eigenvalue criterion fails, then $-\boldsymbol{\Delta}\mathbf{T}_Q^{-1}$ and $\boldsymbol{\delta}\mathbf{T}_P^{-1}$ *must* be used for the population coefficients. Thus, this analysis shows that although the population coefficients are only given by the traditional expressions under restricted circumstances, the effective rate coefficients themselves (the components of $\mathbf{M}_{\text{eff}}$) are correctly given by the traditional expression (Eq. (10)).

Finally, if $\boldsymbol{\delta}$ and $\mathbf{T}_Q^{-1}\boldsymbol{\delta}$ are not small, it is not possible to construct an adequate CR model, even if the eigenvalue criterion is satisfied. Notice also, that if indeed $\boldsymbol{\delta} \ll 1$, then Eq. (13) implies that the Q space densities are all small in comparison to the P space densities.

3. Applications

Eq. (8) is important, not only because it determines the validity of possible CR models, but also because it can be used to generate them. The main problem with finding valid CR models is the determination of the P and Q spaces. A permutation of the ordering of the states in $\mathbf{n}$ has a 1–1 correspondence with the permutation of the rows in $\mathbf{T}$, so that permuting the rows of $\mathbf{T}$ to make the bottom left-hand corner small – which is numerically straightforward – enables possible P spaces to be identified. The results of a treatment based on this idea are shown below, in Table 1. Further details can be found in [15].

It is not the purpose of this work to discuss the atomic and molecular data which is used to construct a realistic rate matrix – details can be [12] – but it is important to understand which states are treated in Eq. (1), and which processes are included in $\mathbf{M}$. The states are:

1. All 15 vibrational levels of the electronic ground state of H_2.
2. The molecular ion H_2^+ (vibrationally unresolved).
3. The negative ion H^-.
4. 23 electronically excited molecular singlet states (vibrationally unresolved).
5. 23 electronically excited molecular triplet states (vibrationally unresolved).
6. The atomic hydrogen states $H(n),\ n = 1, \ldots, 19$ (unresolved in angular momentum).

The electron and proton densities are fixed and equal. The results presented here are for an electron density of $n_e = 10^{19}$ m^{-3}, and an electron temperature of 6.77 eV. Notice that fixing the electron and proton densities leads to a source $\boldsymbol{\Gamma}$ of neutral hydrogen due to recombination (three-body and radiative).

The atomic hydrogen states are coupled by all the usual radiative and electron–atom and electron–ion collision processes [10], and the electron–molecule analogues of all these processes are also included. Specifically molecular processes:

1. Electron impact vibrational transitions, $H_2(v) + e \rightarrow H_2(v') + e$.
2. Dissociative recombination, $H_2^+ + e \rightarrow H + H^*$.
3. Ion conversion, $p + H_2(v) \rightarrow H + H_2^+$.
4. Dissociative attachment, $H_2(v) + e \rightarrow H + H^-$

are included, and the H^- also undergoes:

1. Charge capture, $p + H^- \rightarrow H + H^*$.
2. Electron impact detachment, $e + H^- \rightarrow e + e + H$.

Thus, the rate matrix $\mathbf{M}$ contains all the processes which are thought to lead to molecular enhanced recombination (MAR) [13]. More details of the rates used in this work can be found in [14].

As we see in Table 1 only certain specific P spaces lead to valid CR models. Furthermore, there is no clear distinction between the fastest P space timescale τ_P and the slowest Q space timescale τ_Q. This is a feature of a

Table 1
The timescales and P spaces for the valid CR models discussed in the text with the parameters[a]

N_P	τ_P (μs)	τ_Q (μs)	ϵ	P Space states
1	26	9	7^{-4}	H(1s)
2	9	6	0.3	$H_2(0)$, H(1s)
4	4	3	0.5	$H_2(0–2)$, H(1s)
17	0.2	0.2	1^{-3}	$H_2(0–14)$, H_2^+, H(1s)
18	0.2	0.05	5^{-3}	$H_2(0–14)$, H_2^+, H^-, H(1s)
19	0.05	0.01	0.3	$H_2(0–14)$, H_2^+, H^-, $H_2[c^3\Pi]$, H(1s)

[a] $\tau_P(N_P)$ is the fastest timescale included in the CR model with N_P states; $\tau_Q(N_P)$ is the slowest timescale which this CR model treats as instantaneous. ϵ is an estimate of the accuracy of the CR model, given by the norm $\|\mathbf{T}_Q^{-1}\delta\|$, which is generally greater than $\|\delta\|$. a^b means $a \times 10^b$.

CR model with molecules. In contrast, if only atoms are present, then for the same environmental parameters

$\tau_P = 26\ \mu s, \quad \tau_Q = 8\ ns,$

so that in this case there is a clear division of timescales.

4. Summary

In this paper, I have used the designation CR in the sense in which it is often used in plasma physics, that is, to describe a model which identifies a set of 'P space' species, whose motion must be followed in detail, and a set of 'Q space' species whose behaviour can be derived from the behaviour of the P space states. Traditionally, the Q space contains those species which come to equilibrium rapidly, and the P space contains the remainder. However, a rather formal analysis of the rate equations which describe the time development of the species shows that this view is untenable. A more thorough discussion, which examines the eigenvectors of the rate matrix demonstrates that the validity of CR models must be based on properties of these eigenvectors, and that the timescales for equilibrium are not crucial. Furthermore, the so-called 'population coefficients', which relate P and Q space populations must, in general, be written in terms of the rate matrix eigenvectors. Only in the traditional case where, additionally, the P and Q space states develop on very different timescales can the population coefficients be written in terms of the rate matrix itself. In general, the problem with the construction of a CR model for the simplification of an arbitrary rate matrix is the identification of the P space. Fortunately, an algorithm based on the eigenvector criterion can be constructed which enables potential P spaces to be identified. There may be more than one P space and therefore more than one CR model associated with a given rate matrix. Different P spaces correspond to different time resolutions associated with the CR model. However, once the P space has been determined, the treatment described above can be used to reduce Eq. (1) to Eq. (5), which is the fundamental task of the CR model.

In summary, the description of the dynamics of molecules in fusion plasmas has complications which have sometimes been overlooked. This paper describes some of these problems and how they can be overcome. Nevertheless, the message is that CR models including molecules are very much more complicated than those which include only atoms, and physical intuition is not always a good guide to molecular behaviour.

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