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The Numerical Solution of a Nonlinear Master Equation

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The numerical formulation for the nonlinear master equation for the dissociation and recombination of a diatomic molecule is presented. Making the necessary variable and similarity transformation, the equation becomes more tractable from a computational viewpoint. The set of differential equations are formally uncoupled, and a nonlinear integral equation is solved. Knowing the solution to this equation, the solution for the set is easily achieved.

1. INTRODUCTION

In considering a nonequilibrium phenomenon which can be characterized by a Markovian stochastic process, a master equation is, at times, an adequate description of the system. In formulating a relatively general problem, consider a subsystem with particle density P_S dispersed in a heat bath with particle density P_N, with the added condition $P_S \ll P_N$. Initially, this subsystem of particles is in a nonequilibrium distribution, and as time evolves, it is allowed to relax via interactions between the subsystem particles and by interacting with the heat bath, which is at some initial temperature. Since the particle density P_S is much less then the heat bath density, the former interactions can be neglected.

From the principle of detailed balancing, the system must relax from any given distribution to a equilibrium distribution provided there exist no external constraints on the system. Consequently, the system of equations must take an arbitrary distribution with a time arrow to a steady state.

In the dissociation and recombination (RD) of a diatomic molecule in which the subsystem is composed of diatomic molecules dispersed in a heat bath (an inert gas), the energy transfer processes which bring about RD can categorized essentially into two types: first, the interaction of the heat bath with the diatomic molecules in which quanta of translational energy are converted into vibrational energy for the molecule; and second; vibrational-vibrational transfer processes, which are

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extremely efficient. However, due to the particle density condition, the latter process is negligible.

The mathematical model [1–6] which describes the vibrational relaxation is a set of non-linear differential equations with a conservation condition

$$\frac{dn(i)}{dt} = \sum_{j=0}^{m-1} \{W(i \mid j)[M]\, n(j) - W(j \mid i)[M]\, n(i)\}$$

$$+ [M]\, \overline{W}(i \mid \epsilon)\, n^2(\epsilon) - [M]\, \overline{W}(\epsilon \mid i)\, n(i) \quad \text{(Ref. [7])} \tag{1.0}$$

$$\sum_{i=0}^{m-1} n(i) + 1/2n(\epsilon) = N, \tag{1.1}$$

where $n(i)$ is the instantaneous concentration of molecules in the i-th state in which there are $m - 1$ discrete vibrational levels, $[M]$ is the concentration of the third body and is time invariant, $n(\epsilon)$ is the number of atoms, and N is a constant. Equation (1.0) is a rate equation in which the term $W(i \mid j)\, [M]\, n(j)$ is the rate of transition of molecules from the j-th to the i-th vibrational level. The quantity $W(i \mid j)$ is the transition probability between the two discrete states, $\overline{W}(i \mid \epsilon)$ is the averaged transition probability between the continuum and the discrete level, and $\overline{W}(\epsilon \mid i)$ is the converse of $\overline{W}(i \mid \epsilon)$.

The problem in solving (1.0) is that the system of equations are quite large, and also pathological. Any standard numerical integrator [8–9] will fail, because of the multitude of calculation that must be done for each time step. A transformation is proposed that will drastically reduce the number of calculation per time step, and thereby render a feasible numerical solution at the interesting times.

2. VARIABLE TRANSFORMATION

A new state variable is defined which is the ratio of the instantaneous to the equilibrium population

$$\xi(i) = n(i)/\bar{n}(i) \tag{2.1}$$

$$\xi(\epsilon) = n(\epsilon)/\bar{n}(\epsilon), \tag{2.2}$$

where $\bar{n}(i)$ and $\bar{n}(\epsilon)$ are the corresponding equilibrium population. At macroscopic equilibrium, we have the detailed balancing condition

$$W(i \mid j)\, \bar{n}(j) = W(j \mid i)\, \bar{n}(i) \tag{2.3}$$

$$\overline{W}(\epsilon \mid i)\, \bar{n}(i) = \overline{W}(i \mid \epsilon)\, \bar{n}^2(\epsilon). \tag{2.4}$$

Taking into account the variable transformation and the detailed balancing condition, equations (1.0) and (1.1) become

$$\frac{d\xi(i)}{dt} = [M] \sum_{j=0}^{m-1} W(j \mid i)[\xi(j) - \xi(i)] + [M]\, \overline{W}(\epsilon \mid i)[\xi^2(\epsilon) - \xi(i)] \tag{2.5}$$

and

$$\sum_{i=0}^{m-1} \tilde{n}(i)\, \xi(i) + 1/2\tilde{n}(\epsilon)\, \xi(\epsilon) = N. \tag{2.6}$$

Equation (2.5) may be written in a more compact form:

$$\frac{d}{dt}\left(\begin{array}{c} \vdots \\ \xi(i) \\ \vdots \\ \xi(m-1) \\ \hline 0 \end{array}\right) = \left(\begin{array}{c|c} \mathbf{A}_{00} & \mathbf{A}_{01} \\ \hline 0 & 0 \end{array}\right) \cdot \left(\begin{array}{c} \vdots \\ \xi(i) \\ \vdots \\ \xi(m-1) \\ \hline \xi^2(\epsilon) \end{array}\right) \tag{2.7}$$

where

$$a_{ij} = [M]\left\{W(j \mid i)(1 - \delta_{ij}) - \delta_{ij}\Big[\overline{W}(\epsilon \mid i) + \sum_{\substack{l=0 \\ l \neq i}}^{m-1} W(j \mid l)\Big]\right\} \qquad \text{for} \quad i, j < m$$

and

$$a_{im} = [M]\; \overline{W}(i \mid \epsilon).$$

It is obvious from (2.7) that $\sum_{j=0}^{m} a_{ij} = 0$ for all i. This implies that the steady state solution is

$$\tilde{\xi}(i) = 1 \qquad \text{for all } i.$$

3. SIMILARITY TRANSFORMATION

Before equation (2.7) is integrated, it is beneficial to perform a number of transformations on the A matrix. From the detailed balancing conditions, it is possible to symmetrize $\mathbf{A}_{00}$:

$$\left(\begin{array}{c|c} \mathbf{E}_{00} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{E}_{11} \end{array}\right) \cdot \left(\begin{array}{c|c} \mathbf{A}_{00} & \mathbf{A}_{01} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right) \cdot \left(\begin{array}{c|c} \mathbf{E}_{00}^{-1} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{E}_{11}^{-1} \end{array}\right) = \left(\begin{array}{c|c} \mathbf{B}_{00} & \mathbf{B}_{01} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right) \tag{3.1}$$

where

$$\mathbf{E}_{00} = \{\delta_{ij}\tilde{n}(i)^{1/2}\}, \qquad \mathbf{E}_{11} = \{\delta_{im}\tilde{n}(\epsilon)\}$$

and

$$\mathbf{B}_{00} = \mathbf{E}_{00}\mathbf{A}_{00}\mathbf{E}_{00}^{-1}, \qquad \mathbf{B}_{01} = \mathbf{E}_{00}\mathbf{A}_{01}\mathbf{E}_{11}^{-1}$$

In order to uncouple the discrete levels, the B matrix is partially diagonalized:

$$\left(\begin{array}{c|c} \tilde{\mathbf{S}}_0 & \mathbf{0} \\ \hline \mathbf{0} & 1 \end{array}\right)\left(\begin{array}{c|c} \mathbf{B}_{00} & \mathbf{B}_{01} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right)\left(\begin{array}{c|c} \mathbf{S}_0 & \mathbf{0} \\ \hline \mathbf{0} & 1 \end{array}\right) = \left(\begin{array}{c|c} \tilde{\mathbf{S}}_0\mathbf{B}_{00}\mathbf{S}_0 & \mathbf{S}_0\mathbf{B}_{01} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right). \tag{3.2}$$

By using this orthogonal transformation, the matrix $\tilde{\mathbf{S}}_0\mathbf{B}_{00}\mathbf{S}_0$ is a diagonal matrix $\mathbf{D}_{00}$ and $\tilde{\mathbf{S}}_0\mathbf{B}_{01} = \mathbf{D}_{01}$
where

$$\mathbf{D}_{00} = \{\delta_{ij}d_{ii}\}$$

and

$$\mathbf{D}_{01} = \{d_{im}\}.$$

$$\frac{d}{dt}\left[\begin{array}{c} \sum_{j=0}^{m-1} S_{j0}\tilde{n}^{1/2}(j)\,\xi(j) \\ \vdots \\ \sum_{j=0}^{m-1} S_{j,m-1}\tilde{n}^{1/2}(j)\,\xi(j) \\ \hline \mathbf{0} \end{array}\right] = \left[\begin{array}{c|c} \mathbf{D}_{00} & \mathbf{D}_{01} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right]\left[\begin{array}{c} \sum_{j=0}^{m-1} S_{j0}\tilde{n}^{1/2}(j)\,\xi(j) \\ \vdots \\ \sum_{j=0}^{m-1} S_{j,m-1}\tilde{n}^{1/2}(j)\,\xi(j) \\ \hline \tilde{n}(\epsilon)\,\xi^2(\epsilon) \end{array}\right] \tag{3.3}$$

Consequently, we define the new variable $y_i = \sum_{j=0}^{m-1} S_{ji}\tilde{n}^{1/2}(j)\,\xi(j)$ for $i = 1,\ldots, m-1$ and $y_m{}^2 = \tilde{n}(\epsilon)\,\xi^2(\epsilon)$. Equation (3.3) becomes

$$\dot{y}_i(t) = d_{ii}y_i(t) + d_{im}y_m{}^2(t)$$

with the corresponding integral equation

$$y_i(t) = e^{d_{ii}t}y_i(0) + d_{im}e^{d_{ii}t}\int_0^t e^{-d_{ii}t'}y_m{}^2(t')\,dt' \qquad \text{for} \quad i = 1,\ldots, m-1. \tag{3.4}$$

4. SOLUTION OF THE INTEGRAL EQUATION

The set of integral equations, along with the conservation condition, is the new system that must be solved. In order to facilitate matters, a recursive relationship can be obtained for equation (3.4):

$$y_i(t+h) = e^{d_{ii}(t+h)}\left\{y_i(0) + d_{im}\int_0^{t+h} e^{-d_{ii}t'}y_m{}^2(t')\,dt'\right\} \tag{4.1}$$

$$y_i(t+h) = e^{d_{ii}h}\left\{y_i(t) + d_{im}e^{d_{ii}t}\int_t^{t+h} e^{-d_{ii}t'}y_m{}^2(t')\,dt'\right\}. \tag{4.2}$$

Making the transformation $\alpha = t' - t$, we get

$$y_i(t+h) = e^{d_{ii}h}\left\{ y_i(t) + d_{im} \int_0^h e^{-\alpha d_{ii}} y_m^2(\alpha + t)\, d\alpha \right\}. \tag{4.3}$$

From the conservation condition, we have

$$\sum_{ij}^{m-1} n(i)^{1/2} S_{ij} y_j(t) + 1/2\tilde{n}^{-1/2}(\epsilon)\, y_m(t) = N. \tag{4.4}$$

Using a simple two-point closed quadrature and taking into account equations (4.3) and (4.4), the following quadratic equation evolves for $y_m(t+h)$.

$$\left[\sum_{ij}^{m-1} n(i)^{1/2} S_{ij} \frac{h}{2} d_{im}\right] y_m^2(t+h) + [\tfrac{1}{2}\tilde{n}^{-1/2}(\epsilon)]\, y_m(t+h)$$
$$+ \left\{ N - \sum_{i,j}^{m-1} n(i)^{1/2} S_{ij} \left[e^{d_{ii}h} y_i(t) + d_{im} \frac{h}{2} e^{d_{ii}h} y_m^2(t) \right] \right\} = 0. \tag{4.5}$$

Equation (4.3) becomes

$$y_i(t+h) = e^{d_{ii}h} y_i(t) + d_{im} \frac{h}{2} e^{d_{ii}h} y_m^2(t) + d_{im} \frac{h}{2} y_m^2(t+h). \tag{4.6}$$

Using equations (4.5) and (4.6), one can readily calculate the trajectories of $y_i(t)$. Consequently, using the transformation $\xi = \mathbf{E}^{-1}\mathbf{SY}$, the corresponding solution for $\xi(t)$ can be obtained. Solving the trajectory of y_i has the advantage that one just has to do one diagonalization rather than one for each cycle. Since the eigenvalue spectrum [1, 6] is usually a pathological one, namely from -10^{-3} to -10^{15}, in order to obtain numerical stability, the eigenvalues and eigenvectors must be improved e.g. by a Rayleigh–Quotient iteration. For a further discussion of the numerical results, the reader is referred to the author's previous work [6]. Another added feature is that in equation (4.5) the sums

$$\sum_{ij}^{m-1} n(i)^{1/2} S_{ij}\, d_{im} \qquad \text{and} \qquad \sum_{j}^{m-1} S_{ij}$$

are computed only once.

5. Error Propagation

The total error propagation of the numerical quadrature is

$$E_{\mathrm{TOT}}(t+h) = [-h^3/12]\,\tilde{n}(\epsilon) \sum_{i=0}^{m-1} e^{-|d_{ii}|h} d_{im}[4\,|\,d_{ii}\,|\,\xi_m(t+\theta)\,\xi_m{}'(t+\theta)$$
$$-\,2\xi_m(t+\theta)\,\xi_m''(t+\theta) - 2[\xi_m{}'(t+\theta)]^2 - d_{ii}^2\xi_m{}^2(t+\theta)], \qquad (5.1)$$

where $0 \leqslant \theta \leqslant h$.

It is necessary to estimate the error propagation in order to change an economical value for h in our calculation. In this particular case, it is not an easy problem since we know very little about θ or the value of the function and it first and second derivatives. The simplest method for checking whether or not the chosen value for h is reasonable, consists in recalculating some of the results with a new value of h and making a comparison. The function $\xi(t)$ is a monotonically increasing or decreasing depending on whether the case considered is a dissociation or recombination. At a very short time the error term may be approximated by

$$E_{\mathrm{TOT}}(t+h) \approx h^3/6\tilde{n}(\epsilon)[\xi_m{}'(t)]^2 \sum_{i=0}^{m-1} e^{-|d_{ii}|h} d_{im}\,. \qquad (5.2)$$

While at long time, we have

$$E_{\mathrm{TOT}}(t+h) \approx h^3/12\tilde{n}(\epsilon) \sum_{i=0}^{m-1} d_{ii}^2 d_{im} e^{-|d_{ii}|h}. \qquad (5.3)$$

At intermediate times one may use the equation (5.1). Knowing the total error criterion one may make a choice based on the knowledge of the function and its derivatives at the time t.

6. Example

In the actual case for the recombination and dissociation of a gas, the **A** matrix is quite large and the matrix elements have a wide range of numerical values. In this example, we consider the simplest of cases for illustrative purposes. Consider a three-level system in which the third level corresponds to the contimum, and the initial distribution is $(0, N, 0)$. The set of rate equations for this system is

$$\frac{dn_1}{dt} = +W_{11}n_1 + W_{12}n_2 + W_{13}n_3{}^2 \qquad (6.1)$$

$$\frac{dn_2}{dt} = W_{21}n_1 + W_{22}n_2 + W_{23}n_3{}^2 \qquad (6.2)$$

$$n_1 + n_2 + 1/2n_3 = N. \qquad (6.3)$$

Using the similarity transformations (3.1) and (3.2), one finds the eigenvalues for the discrete submatrix to be

$$d_{11,22} = 1/2\{-[|W_{11}| + |W_{22}|] \pm [(W_{11} + W_{22})^2 - 4(W_{11}W_{22} - W_{12}W_{21})]^{1/2}\}.$$

Since all W_{ij} for $i \neq j$ are positive, this implies that d_{11} and d_{22} are less than zero. In this model calculation one has the condition that

$$(W_{11} + W_{22})^2 \gg -4(W_{12}W_{21} - W_{11}W_{22}) \quad \text{and} \quad (W_{11} + W_{22})^2 \gg 0.$$

This implies that $d_{11} \gg d_{22}$. Since the eigenvalue spectrum of **A** is seminegative definite [1], and from the partitioning theorem we have the following bounds on the eigenvalues

$$d_{11} < \lambda_1(t) \leqslant 0, \qquad d_{22} < \lambda_2(t) < d_{11}, \qquad \text{and} \qquad \lambda_{33} < d_{22}.$$

Hence, a lower bound on the eigenvalue spectrum is the ratio of the largest eigenvalue to smallest which is d_{22}/d_{11}. It is this ratio that illustrates the pathological nature of the eigenvalue spectrum.

In the numerical example the initial condition is $(0, 1.105 \times 10^5, 0)$. The following set of equations was considered:

$$\frac{dn_1}{dt} = -1.1 \times 10^3 n_1(t) + 316.22278 n_2(t) + 106.833 n_3^2(t)$$

$$\frac{dn_2}{dt} = 31.622278 n_1(t) - 5.1 \times 10^4 n_2(t) + 506.838 n_3^2(t)$$

$$n_1 + n_2 + 1/2 n_3 = 1.105 \times 10^5.$$

Using the results from the previous sections one obtains Table I.

TABLE I

Time	$\xi_1(t)$	$\xi_2(t)$	$\xi_3(t)$	Error
0.0(+00)	0.000000(+00)	1.105000(+01)	0.000000(+00)	$<10^{-6}$
7.8(−08)	1.130191(−04)	1.100740(+01)	8.293247(−01)	
9.7(−07)	3.910230(−03)	1.086306(+01)	2.956560(+00)	
8.9(−06)	7.475054(−02)	1.015684(+01)	2.913144(+00)	
5.5(−05)	3.585504(−01)	7.340150(+00)	2.486894(+00)	
1.3(−04)	7.376431(−01)	3.585317(+00)	1.765040(+00)	
3.0(−04)	9.558909(−01)	1.432900(+00)	1.163815(+00)	
9.2(−04)	9.998982(−01)	1.001002(+00)	1.000321(+00)	↓
∞	1.000000(+00)	1.000000(+00)	1.000000(+00)	—

The equilibrium distribution is $(10^5, 10^4, 10^3)$.

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