3.   THE CHEMISTRY OPERATOR

The chemistry operator of the continuity equation involves the solution at every gridpoint of the chemical kinetic equation

$$\frac{dn}{dt} = P - L \tag{3.1}$$

For a chemical mechanism involving p chemically interacting species, we have a system of p coupled ODEs

$$\frac{dn_i}{dt} = P_i(\mathbf{n}) - L_i(\mathbf{n}) \tag{3.2}$$

where $\mathbf{n}$ is the vector of number densities n_j ($j = 1, \ldots p$). A general characteristic of atmospheric chemistry systems is that they are *stiff*, that is, the lifetimes of the species involved vary over many orders of magnitude. If τ_L and τ_S are the longest and shortest time scales over which the species vary (we will define these time scales below), then the stiffness can be defined as $s = \tau_L/\tau_S$. Numerical ODE solvers generally require time steps $\Delta t \sim \tau_S$, but we are interested in solutions integrated over time periods $\sim \tau_L$. Thus the number of time steps is of order s. A typical atmospheric chemistry problem will require solution for long-lived species over a time period of 1 year with a chemical mechanism involving species with lifetimes ~ 1 s; the corresponding stiffness is $s \sim 10^7$ and solution requires $\sim 10^7$ time steps, which quickly becomes a formidable problem on a 3-D model grid.

Stiff systems are not amenable to solution with *explicit* solvers, such as forward Euler or Runge-Kutta, where the concentration at time $t+\Delta t$ is calculated solely on the basis of concentrations at previous time steps. In these solvers, the time step needs to be kept shorter than the lifetime of the shortest-lived species in order to maintain stability. *Implicit* solvers, where the concentrations predicted at time $t+\Delta t$ are used to converge numerically to the solution, do not have this constraint and are much more stable. In this chapter we first examine linearization as a general approach for solving coupled non-linear problems, derive the time scales for the evolution of atmospheric chemical systems, describe the simple first-order implicit solver (*backward Euler*) that offers an efficient and flexible approach for integration of chemical mechanisms, and briefly describe the higher-order *Gear method* which is frequently used in 3-D models.

3.1   Linearization as a method for solving non-linear problems

Consider the problem of determining the value of a scalar function $f(x)$. If its value at point x_o is known, then its value at point x can be determined by Taylor expansion about x_o:

$$f(x) = f(x_o) + (x - x_o)f'(x_o) + O((x - x_o)^2) \tag{3.3}$$

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where the second-order term is negligible if x is sufficiently close to x_o. This is an important result; any non-linear function has a linear approximation to its solution for values sufficiently close to a value with known solution. Now consider the problem of determining the value of a vector function $\mathbf{f(x)}$ of vector $\mathbf{x}$ where the vector function has elements $f_1(\mathbf{x})$, $f_2(\mathbf{x})$, etc. that are independent scalar functions. If the value $\mathbf{f(x_o)}$ is known, then Taylor expansion about $\mathbf{x_o}$ gives for values of $\mathbf{x}$ sufficiently close to $\mathbf{x_o}$:

$$\mathbf{f(x)} = \mathbf{f(x_o)} + \mathbf{K(x - x_o)} \tag{3.4}$$

where $\mathbf{K}$ is the *Jacobian matrix* (sometimes called *sensitivity matrix*) with elements $k_{ij} = \partial f_i / \partial x_j$ evaluated at $\mathbf{x_o}$. This is an important result, similarly to scalar functions, in that it allows linear algebra to be applied to the solution of any non-linear problem involving coupled variables. We will apply it in what follows.

3.2 Characteristic time scales in atmospheric chemistry mechanisms

In a chemical mechanism involving p species with chemical kinetic equations of the form (3.2), one can define the *lifetime* τ_i of species i as the concentration divided by the loss rate:

$$\tau_i = \frac{n_i}{L_i(\mathbf{n})} \tag{3.5}$$

Considering that the mechanism is usually nonlinear and involves coupling between species, these lifetimes do not define the characteristic time scales for the evolution of the system (although they are acceptable as order-of-magnitude estimates). The formal way to derive the characteristic time scales is to examine the decay of a perturbation $\Delta\mathbf{n}$ applied to a steady-state solution $\mathbf{n_o}$ to the chemical mechanism. Taking the ensemble of p coupled ODEs (3.2) as a vector function $d\mathbf{n}/dt$, we apply the linearization (3.4) about $\mathbf{n_o}$ to obtain

$$\frac{d\Delta\mathbf{n}}{dt} = \mathbf{K}\Delta\mathbf{n} \tag{3.6}$$

where the Jacobian matrix $\mathbf{K}$ has elements $k_{ij} = \partial(P_i(\mathbf{n}_o) - L_i(\mathbf{n}_o))/\partial n_j$ that can usually be derived analytically from the rate formulations of P_i and L_i. Let us now consider the eigenvectors $\mathbf{a}_i$ of the Jacobian matrix, for which by definition

$$\mathbf{Ka_i} = \lambda_i \mathbf{a_i} \tag{3.7}$$

where λ_i is the eigenvalue corresponding to $\mathbf{a_i}$. The eigenvectors represent a base of dimension p, and any initial perturbation $\Delta\mathbf{n}$ can be decomposed over that base:

$$\Delta\mathbf{n} = \sum_p \alpha_i \mathbf{a_i} \tag{3.8}$$

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where the α_i are coefficients. Replacing (3.7) and (3.8) into (3.6), we obtain for the temporal evolution of the perturbation:

$$\Delta\mathbf{n}(t) = \sum_p \alpha_i \mathbf{a_i} e^{\lambda_i t} \tag{3.9}$$

If all eigenvalues λ_i are real and negative, then $\Delta\mathbf{n}$ will relax back to steady state over a suite of time scales $[-1/\lambda_1, ...-1/\lambda_p]$ which represent the *characteristic time scales* of the system; one can then define the stiffness of the system as the ratio of the largest to the smallest eigenvalue. If one of the λ_i is real and positive then the corresponding mode of the perturbation will amplify; the system is unstable. If one of the λ_i is a pure imaginary number then corresponding mode of the perturbation will oscillate without decaying. All evidence so far indicates that the eigenvalues for the mechanisms used in atmospheric chemistry models are real and negative, so that the systems are stable against perturbations. There has been quite a bit of recent research seeking conditions where atmospheric chemistry mechanisms would be unstable or oscillating, because these conditions would be very interesting! But all such conditions that have been identified so far are quite exotic and far from the conditions likely to be encountered in the real atmosphere.

Example. We illustrate the above idea with a trivial but instructive example. Consider the system of two species X_1 and X_2 converting between each other with rate constants k_1 and k_2 (s^{-1}):

$$X_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} X_2 \tag{3.10}$$

The lifetimes of X_1 and X_2 are $1/k_1$ and $1/k_2$ respectively, and the chemical kinetic equations are

$$\frac{dn_1}{dt} = -k_1 n_1 + k_2 n_2 \tag{3.11}$$

$$\frac{dn_2}{dt} = k_1 n_1 - k_2 n_2 \tag{3.12}$$

At steady state, n_1 and n_2 are related by $n_2(\infty) = (k_1 / k_2)n_1(\infty)$. Let us solve for the time-dependent system analytically; this can be done expeditiously by using the closure equation

$$n_T = n_1 + n_2 = \text{constant} \tag{3.13}$$

and replacing into (3.11):

$$\frac{dn_1}{dt} = k_2 n_T - (k_1 + k_2)n_1 \tag{3.14}$$

Integration then yields

$$n_1(t) = n_1(0)e^{-(k_1+k_2)t} + n_1(\infty)(1 - e^{-(k_1+k_2)t}) \tag{3.15}$$

where $n_1(\infty) = k_2 n_T /(k_1 + k_2)$ is the steady-state solution. Expressing (3.15) in terms of a perturbation $\Delta n_1(t) = n_1(t) - n_1(\infty)$ to steady state, we obtain a simple exponential decay for the perturbation:

$$\Delta n_1(t) = \Delta n_1(0)e^{-(k_1+k_2)t} \tag{3.16}$$

A similar equation applies to $\Delta n_2(t)$. Thus we see that the characteristic time for relaxation of the perturbation to steady state is $\tau=1/(k_1+k_2)$, and is faster than either of the species lifetimes $1/k_1$ and $1/k_2$. However, if the perturbation does not conserve n_T (that is, if $\Delta n_1(0) \neq -\Delta n_2(0)$), then the system will never recover to the original steady state; a second time scale in the system is thus $\tau \to \infty$.

Let us now derive this result from the eigenvector method. The Jacobian matrix $\mathbf{K}$ for the system is given by

$$\mathbf{K} = \begin{pmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{pmatrix} \tag{3.17}$$

which we recognize as degenerate (the second row is simply the opposite of the first). The rank of $\mathbf{K}$ is 1, so there is only one non-zero eigenvalue and corresponding eigenvector. Let us proceed, however, to obtain the eigenvectors by solution to

$$(\mathbf{K} - \lambda_i \mathbf{I})\mathbf{a}_i = \mathbf{0} \tag{3.18}$$

The system of equations (3.18) must be degenerate, since it must allow as solution all scalar multipliers of $\mathbf{a_i}$. Therefore we must have

$$\det(\mathbf{K} - \lambda_i \mathbf{I}) = 0 \tag{3.19}$$

The solutions of (3.19) are $\lambda_1 = 0$ and $\lambda_2 = -(k_1+ k_2)$, and the corresponding time scales are $\tau_1 \to \infty$ and $\tau_2 = 1/(k_1 + k_2)$, as was previously found from the analytical solution to the system. The eigenvector corresponding to $\lambda_1 = 0$ is $\mathbf{a_1} = (1, k_1/k_2)$ while that corresponding to $\lambda_2 = -(k_1+ k_2)$ is trivially $\mathbf{a_2} = (0,0)$. The physical meaning is evident; a perturbation applied to the steady state system such that $\Delta n_2 = (k_1 / k_2)\Delta n_1$ (multiple of $\mathbf{a_1}$) will not decay at all, since it will simply shift the system to a new steady state. In the general case of any perturbation applied to the system, the projection onto $\mathbf{a_1}$ will not decay while the residual will decay on a time scale $\tau_2 = 1/(k_1 + k_2)$, following (3.14).

3.3 Implicit finite difference solvers

In the first-order implicit finite difference solver (also called *backward Euler*), we express the terms on the right-hand side of (3.2) in terms of the concentrations at time $t+\Delta t$:

$$\frac{n_i(t + \Delta t) - n_i(t)}{\Delta t} = P_i(\mathbf{n}(t + \Delta t)) - L_i(\mathbf{n}(t + \Delta t) \tag{3.20}$$

resulting in a system of p algebraic equations with p unknowns $\mathbf{n}(t + \Delta t)$. We express this system as a vector $\mathbf{f}$ of functions f_i:

$$f_i(\mathbf{n}) = n_i(t + \Delta t) - n_i(t) - (P_i(\mathbf{n}(t + \Delta t)) - L_i(\mathbf{n}(t + \Delta t))\Delta t = 0 \tag{3.21}$$

and seek a solution $\mathbf{f(n)} = \mathbf{0}$. The solution can be obtained numerically by Newton's method. We write a first-order Taylor expansion of $\mathbf{f}$ about an initial guess $\mathbf{n^0}$:

$$\mathbf{f}(\mathbf{n}) = \mathbf{f}(\mathbf{n}^0) + \frac{\partial \mathbf{f}}{\partial \mathbf{n}}(\mathbf{n} - \mathbf{n}^0) + ... \tag{3.22}$$

where the matrix $\partial \mathbf{f} / \partial \mathbf{n}$ has as elements $\partial f_i / \partial n_j$ and can be expressed in terms of the previously defined Jacobian matrix $\mathbf{K^0}$ calculated for the ensemble of concentrations $\mathbf{n^0}$ (section 3.1) and the identity matrix $\mathbf{I}$:

$$\frac{\partial \mathbf{f}}{\partial \mathbf{n}} = \mathbf{I} - \mathbf{K}^0 \Delta t \tag{3.23}$$

From the Taylor expansion (3.22), we seek a solution $\mathbf{n^1}$ to $\mathbf{f(n^1)} = \mathbf{0}$:

$$\mathbf{n}^1 = \mathbf{n}^0 - (\mathbf{I} - \mathbf{K}^0 \Delta t)^{-1} \mathbf{f}(\mathbf{n}^0) \tag{3.24}$$

and iterate:

$$\mathbf{n}^{i+1} = \mathbf{n}^i - (\mathbf{I} - \mathbf{K}^i \Delta t)^{-1} \mathbf{f}(\mathbf{n}^i) \tag{3.25}$$

until convergence to the true solution within an acceptable error ε, which we define by an *absolute error criterion* $\mathbf{n^{i+1}}$-$\mathbf{n^i} < \varepsilon$ or a *relative error criterion* $(\mathbf{n^{i+1}}$-$\mathbf{n^i})/\mathbf{n^i} < \varepsilon$ or some combination of the two.

The implicit finite difference method is unconditionally stable and mass-conserving, and it can be made as accurate as desired by adjusting the size of the time step Δt (a good test of accuracy is to compare the solution obtained with time steps Δt to that obtained with time steps $\Delta t/2$). There is no constraint on stability associated with the shortest time scales of the system, since species with lifetimes $\tau_i \ll \Delta t$ will simply adjust to a *quasi steady state* at time $t+\Delta t$ defined by $P_i(\mathbf{n}(t+\Delta t) = L_i(\mathbf{n}(t+\Delta t)$:

$$\frac{n_i(t + \Delta t) - n_i(t)}{\Delta t} \ll P_i(\mathbf{n}(t + \Delta t)) - L_i(\mathbf{n}(t + \Delta t)) \Rightarrow f_i(\mathbf{n}) \approx L_i(\mathbf{n}(t + \Delta t)) - P_i(\mathbf{n}(t + \Delta t))$$

$$(3.26)$$

A particularly attractive feature of the implicit finite difference method when applied to chemical mechanisms is that the algebraic functions $f_i(\mathbf{n})$ used to define the

solution system do not necessarily need to be finite-difference forms of the chemical kinetic equation (3.1). For any species i in the mechanism one can replace the chemical kinetic equation by any alternate algebraic constraint. For example, one might want to impose chemical steady state for short-lived species:

$$f_i(\mathbf{n}) = L_i(\mathbf{n}(t + \Delta t)) - P_i(\mathbf{n}(t + \Delta t)) \tag{3.27}$$

Or one may want to impose conservation of the sum n_T of a chemical family of species $j=1,...q$:

$$f_i(\mathbf{n}) = n_T - n_i(t + \Delta t) - \sum_{\substack{j=1 \\ j \neq i}}^{q} n_j(t + \Delta t) \tag{3.28}$$

(A simple example of this would be imposing a fixed concentration of $NO_x = NO + NO_2$ while allowing the concentrations of NO and NO_2 to change; this can be done by replacing the chemical kinetic equation for either NO or NO_2 by the NO_x conservation equation). Yet other alternate constraints that one may want to impose on the system are chemical equilibria between species, charge balance, etc… The implicit finite difference system allows total flexibility in the choice of constraints.

The only drawback of the implicit finite difference method is that it is computationally expensive. At every time step and every iteration one needs to invert a matrix of dimension p (equation 3.22). One can save costs by not recalculating the Jacobian matrix at every iteration (keeping the same Jacobian once convergence is well on its way) and one can also use fast sparse-matrix inversion techniques to take advantage of the generally sparse nature of the Jacobian matrix (most of the off-diagonal terms are zero). In applications other than 3-D modeling, computational costs are generally not an issue and the implicit finite difference method is highly recommended.

For 3-D models the most popular and accurate chemical solver is the *Gear solver*, named after its inventor Charles Gear. The Gear solver is an implicit finite difference method of variable order s (up to $s = 6$) where the results at previous time steps back to $t-(s-1)\Delta t$ are used to optimize the finite difference expression of dn_i/dt at time $t+\Delta t$ on the left-hand side of equation (3.10):

$$\left. \frac{dn_i}{dt} \right|_{t+\Delta t} \approx \frac{n_i(t + \Delta t) - \sum_{k=1}^{s} \alpha_{s,k} n_i(t - (k-1)\Delta t)}{\beta_{s,k} \Delta t} \tag{3.29}$$

Gear solver codes include an efficient machinery to choose the time step and order of the method in order to optimize computational performance given user-specified error criteria. As in the first-order implicit finite difference method, the solution involves the inversion of the Jacobian matrix at every time step and iteration. But the higher order of the method, by providing a better definition of the trajectory towards the solution, allows for longer time steps and less frequent recalculations of the Jacobian.

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