

1D Photochemical Models on a Computer

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A photochemical model consists of solving the the continuity equation for a set of molecular species. The continuity equation can be written as

$$\frac{\partial N_i}{\partial t} = P_i - L_i - \vec{\nabla} \cdot \vec{\Phi}_i \quad (1)$$

where P_i and L_i are the chemical production and loss rates and $\vec{\Phi}_i$ the flux. For a steady-state model, the usual approach is to integrate equation 1 forward in time until $\partial N_i / \partial t \sim 0$. Alternatively, equation 1 can be used to solve to calculate the time evolution of the system, i.e. the values of N_i at time $t + \Delta t$ give the values at time t .

Chemical Production and Loss

In general numerous chemical reactions as well as photon- and electron-induced dissociation processes contribute to the chemical production and loss terms. The chemical production terms can be written as

$$P_i = \sum_p J_p(j \rightarrow i) N_j + \sum_r k_r(j + k \rightarrow i) N_j N_k \quad (2)$$

$$L_i = \left(\sum_p J_p(i \rightarrow j) + \sum_r k_r(i + j \rightarrow k) N_j \right) N_i \quad (3)$$

where the first sums represents photon and supra-thermal electron induced reactions and the second sums chemical reactions. The notation $J_p(j \rightarrow i)$ means that photolysis process p destroys species j and creates species i . Similarly $k_r(j + k \rightarrow i)$ means that in chemical reaction r species j and k are destroyed and species i is created. For the production rates the sums are over all processes that produce species i , while for the loss rates the sums are over all processes that destroy species i . The net loss rate is proportional to N_i . The chemistry terms couple densities of chemical species at a specific altitude but the flux divergence term couples densities of a specific species at different altitudes.

Discretization of the Flux Divergence

In a 1D model we are concerned only with vertical variations and

$$\vec{\nabla} \cdot \vec{\Phi}_i = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \Phi_i \quad (4)$$

Also, in a 1D model there is no net vertical velocity for the atmosphere as a whole, but there is still a diffusive flux for individual species. This can be written as

$$\Phi_i = -D_i \left[\frac{dN_i}{dr} + N_i \left(\frac{1}{H_i} + \frac{1}{T} \frac{dT}{dr} \right) \right] - K \left[\frac{dN_i}{dr} + N_i \left(\frac{1}{H} + \frac{1}{T} \frac{dT}{dr} \right) \right] \quad (5)$$

where N_i is the density, Φ_i the flux, H_i the scale height, and D_i the molecular diffusion coefficient of the i th species. The temperature T , eddy diffusion coefficient K , and scale height H apply to all species in the atmosphere.

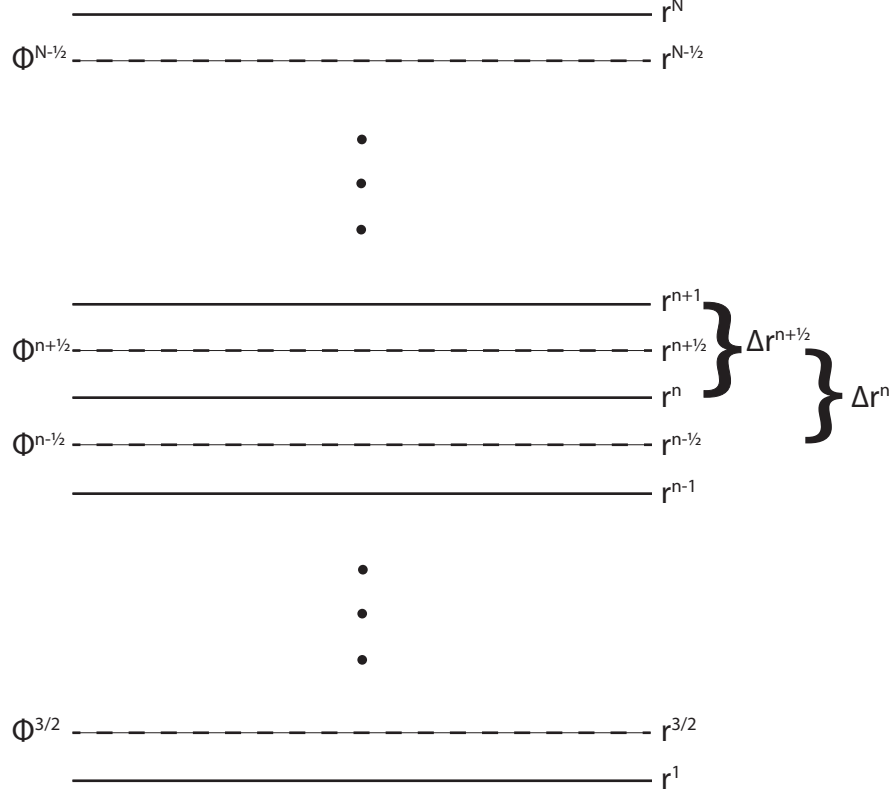


Figure 1: Discretization of the altitude scale for solution of the diffusion equation

Consider a discrete altitude grid where r^n denotes the radial distance to the n th boundary of the grid and $r_{n+\frac{1}{2}}$ represents the radial distance to the mid-point of the n th layer, halfway between r_n and r_{n+1} . The superscript on all other variables is used to denote their values at these locations. Replacing derivatives by differences we get the following expression for the flux in the n th layer.

$$\Phi_i^{n+\frac{1}{2}} = -\alpha_i^{n+\frac{1}{2}} (N_i^{n+1} - N_i^n) - \beta_i^{n+\frac{1}{2}} (N_i^{n+1} + N_i^n) \quad (6)$$

where

$$\alpha_i^{n+\frac{1}{2}} = \left[\frac{D_i^{n+\frac{1}{2}} + K^{n+\frac{1}{2}}}{\Delta r^{n+\frac{1}{2}}} \right] \quad (7)$$

$$\beta_i^{n+\frac{1}{2}} = \frac{1}{2} \left[\frac{D_i^{n+\frac{1}{2}}}{H_i^{n+\frac{1}{2}}} + \frac{K^{n+\frac{1}{2}}}{H^{n+\frac{1}{2}}} + \frac{D_i^{n+\frac{1}{2}} + K^{n+\frac{1}{2}}}{T^{n+\frac{1}{2}}} \left(\frac{T^{n+1} - T^n}{\Delta r^{n+\frac{1}{2}}} \right) \right]$$

The equation for the flux divergence (2) becomes in discrete form

$$\left(\vec{\nabla} \cdot \vec{\Phi}_i\right)^n = \frac{1}{\Delta r^n} \left[\left(\frac{r^{n+\frac{1}{2}}}{r^n} \right)^2 \Phi^{n+\frac{1}{2}} - \left(\frac{r^{n-\frac{1}{2}}}{r^n} \right)^2 \Phi^{n-\frac{1}{2}} \right] \quad (8)$$

Substituting equation 6 into equation 8 gives

$$\left(\vec{\nabla} \cdot \vec{\Phi}_i\right)^n = a_i^n N_i^{n-1} + b_i^n N_i^n + c_i^n N_i^{n+1} \quad (9)$$

where

$$a_i^n = -\frac{1}{\Delta r^n} \left(\frac{r^{n-\frac{1}{2}}}{r^n} \right)^2 \left(\alpha_i^{n-\frac{1}{2}} - \beta_i^{n-\frac{1}{2}} \right) \quad (10a)$$

$$b_i^n = \frac{1}{\Delta r^n} \left(\frac{r^{n-\frac{1}{2}}}{r^n} \right)^2 \left(\alpha_i^{n-\frac{1}{2}} + \beta_i^{n-\frac{1}{2}} \right) + \frac{1}{\Delta r^n} \left(\frac{r^{n+\frac{1}{2}}}{r^n} \right)^2 \left(\alpha_i^{n+\frac{1}{2}} - \beta_i^{n+\frac{1}{2}} \right) \quad (10b)$$

$$c_i^n = -\frac{1}{\Delta r^n} \left(\frac{r^{n+\frac{1}{2}}}{r^n} \right)^2 \left(\alpha_i^{n+\frac{1}{2}} + \beta_i^{n+\frac{1}{2}} \right) \quad (10c)$$

The only connection in the flux divergence between the diffusing species and other atmospheric species occurs through the molecular diffusion coefficient D_i . For the situation of the minor species diffusing through a chemically inert background atmosphere, the flux divergence is independent of the densities of other chemically active constituents.

Advancing in Time

We solve for densities by integrating the coupled continuity equations in time until a steady state is reached. An implicit technique is used for the time integration because this allows for large time steps while maintaining stability. Implicit in this context means that the time derivative is evaluated using densities at the current time step. Explicit techniques rely on the densities at the previous time step and are limited to small time step. Although implicit techniques are more complicated the time step can often be two orders or more larger than for explicit techniques.

To advance the equations to the next time step using an implicit technique, we define the function:

$$F(N_i) = P_i - L_i - \vec{\nabla} \cdot \vec{\Phi}_i - \frac{\partial N_i}{\partial t} \quad (11)$$

and find the values of N_i^n that make $F(N_i^n) = 0$. We solve for the N_i^n using Newton's method. Let ${}^m N_i^n$ and ${}^{m+1} N_i^n$ be the densities at the m and $m+1$ time step. In order to cut down on the number of indices that we need to write, I will use bold font to represent a vector of the altitude values of the variable, i.e. ${}^m \mathbf{N}_i$ in place of ${}^m N_i^n$. Using Newton's method, I calculate new densities from

$${}^{m+1} \mathbf{N}_i = {}^m \mathbf{N}_i - \mathbf{T}^{-1} \mathbf{F}({}^m \mathbf{N}_i) \quad (12)$$

where \mathbf{T} is the Jacobian matrix defined by

$$T_{i,j}^{n,m} = \frac{\partial F_i^n}{\partial N_j^m} \quad (13)$$

The Jacobian contains terms due to chemical production and loss and to the flux divergence:

$$T_{i,j}^{n,n-1} = \delta_{i,j} a_i^n \quad (14a)$$

$$T_{i,j}^{n,n} = \sum_r k_r(j+k \rightarrow i) N_k^n - \sum_p J_p(i \rightarrow j) - \sum_r k_r(i+j \rightarrow k) N_i + \delta_{i,j} \left(b_i^n + \frac{1}{\Delta t} \right) \quad (14b)$$

$$T_{i,j}^{n,n-1} = \delta_{i,j} c_i^n \quad (14c)$$

where $\delta_{i,j}$ is the Kronecker delta function. The Jacobian has block tridiagonal structure

$$\mathbf{T} = \begin{pmatrix} \mathbf{B}_1 & \mathbf{C}_1 & 0 & \cdots & 0 & 0 & 0 \\ \mathbf{A}_2 & \mathbf{B}_2 & \mathbf{C}_2 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & \mathbf{A}_{N-1} & \mathbf{B}_{N-1} & \mathbf{C}_{N-1} \\ 0 & 0 & 0 & \cdots & 0 & \mathbf{A}_N & \mathbf{B}_N \end{pmatrix} \quad (15)$$

where A , B , and C are $I \times I$ matrices that contain the derivatives of F with respect to set of chemical species, i.e.

$$A_{i,j}^k = T_{i,j}^{k,k-1} \quad (16a)$$

$$B_{i,j}^k = T_{i,j}^{k,k} \quad (16b)$$

$$C_{i,j}^k = T_{i,j}^{k,k+1} \quad (16c)$$

The virtue of writing \mathbf{T} in block tridiagonal fashion is that the highly efficient techniques for solution of tridigaonal systems may be adapted.

Boundary Conditions

Fixed Density at Lower Boundary

If, through measurements or some other means we know the density of an atmospheric constituent at the lower boundary then it might make sense to hold that density fixed during the calculation

$$N_i(r^1) = N_i^\circ \quad (17)$$

This implies that $F_i^1 = 0$ and $T_i, i^1, 1 = 1$, with all other elements of \mathbf{T} equal to zero. It is important to remember that if the density is fixed, the velocity is unconstrained and that this may affect the chemical balance in the calculational domain.

Photochemical Equilibrium at Lower Boundary

In this case we set the divergence of the flux equal to zero so that

$$\mathbf{F}_i = \mathbf{P}_i - \mathbf{L}_i - \frac{^{m+1}\mathbf{N}_i - ^m\mathbf{N}_i}{\Delta t} \quad (18)$$

and for the Jacobian we include only those terms due to chemical production and loss

$$T_{i,j}^{n,m} = \delta_{n,m} \left(\sum_r k_r(j+k \rightarrow i) N_k^n - \sum_p J_p(i \rightarrow j) - \sum_r k_r(i+j \rightarrow k) N_i + \delta_{i,j} \frac{1}{\Delta t} \right) \quad (19)$$

Fixed Diffusion Velocity at Lower Boundary

To implement this boundary conditions we rely on equation 6 for the flux rather than equation 8 for the flux divergence. One complication is that the fluxes are defined at the mid-points of atmospheric layers so the velocity condition must be applied at $r^{\frac{3}{2}}$ rather than r^1 . Rewriting equation 6 for the bottom layer we have

$$w_i^1 \frac{1}{2} (N_i^1 + N_i^2) = -\alpha_i^{\frac{3}{2}} (N_i^2 - N_i^1) - \beta_i^{\frac{3}{2}} (N_i^2 + N_i^1). \quad (20)$$

Collecting coefficients of the densities gives

$$\left(\frac{w_i^1}{2} - \alpha_i^{\frac{3}{2}} + \beta_i^{\frac{3}{2}} \right) N_i^1 + \left(\frac{w_i^1}{2} + \alpha_i^{\frac{3}{2}} + \beta_i^{\frac{3}{2}} \right) N_i^2 = 0 \quad (21)$$

or

$$b_i^1 = \frac{w_i^1}{2} - \alpha_i^{\frac{3}{2}} + \beta_i^{\frac{3}{2}} \quad (22a)$$

$$c_i^1 = \frac{w_i^1}{2} + \alpha_i^{\frac{3}{2}} + \beta_i^{\frac{3}{2}} \quad (22b)$$

Fixed Diffusion Velocity at Upper Boundary

This is similar to the case above but the velocity condition must be applied at $r^{N-\frac{1}{2}}$. We have

$$w_i^N \frac{1}{2} (N_i^{N-1} + N_i^N) = -\alpha_i^{N-\frac{1}{2}} (N_i^N - N_i^{N-1}) - \beta_i^{N-\frac{1}{2}} (N_i^N + N_i^{N-1}). \quad (23)$$

Collecting coefficients of the densities gives

$$\left(\frac{w_i^N}{2} - \alpha_i^{N-\frac{1}{2}} + \beta_i^{N-\frac{1}{2}} \right) N_i^{N-1} + \left(\frac{w_i^N}{2} + \alpha_i^{N-\frac{1}{2}} + \beta_i^{N-\frac{1}{2}} \right) N_i^N = 0 \quad (24)$$

or

$$a_i^N = \frac{w_i^N}{2} - \alpha_i^{N-\frac{1}{2}} + \beta_i^{N-\frac{1}{2}} \quad (25a)$$

$$b_i^N = \frac{w_i^N}{2} + \alpha_i^{N-\frac{1}{2}} + \beta_i^{N-\frac{1}{2}} \quad (25b)$$

Diffusive Equilibrium at Upper Boundary

Diffusive equilibrium means that the diffusion velocity is zero so implementation of the boundary conditions is identical to that for a fixed diffusion velocity which is set to zero.