An Analytical Method for Solving Systems of Linear n^{th}-order ODEs

(an entirely self-contained lecture)

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I. Derivation of the analytical method for solving a single first-order linear ODE

In its most general form, a single first-order linear ODE can be written as:

$$\frac{dy}{dx} + a(x)y = b(x) \tag{I.1}$$

and we have an initial condition of the form:

$$y(x = x_o) = y_o \tag{I.2}$$

A. Method of the integrating factor
We solve this problem by using an integrating factor, namely:

$$I.F. = e^{\int a(x)dx} \tag{I.3}$$

Multiply both side of equation (I.1) by our integrating factor yields:

$$\left[\frac{dy}{dx} + a(x)y\right]e^{\int a(x)dx} = b(x)e^{\int a(x)dx} \tag{I.4}$$

We must recognize that the L.H.S. of the equation can be rearranged as

$$\left[\frac{dy}{dx} + a(x)y\right]e^{\int a(x)dx} = \frac{d\left(ye^{\int a(x)dx}\right)}{dx} \tag{I.5}$$

so that equation (I.3) becomes:

$$\frac{d\left(ye^{\int a(x)dx}\right)}{dx} = b(x)e^{\int a(x)dx} \tag{I.6}$$

Then, we separate variables:

$$d\left(ye^{\int a(x)dx}\right) = b(x)e^{\int a(x)dx}dx \tag{I.7}$$

and integrate

$$\int_{y=y_o}^{y} d\left(ye^{\int a(x)dx}\right) = \int_{x=x_o}^{x} b(x)e^{\int a(x)dx}dx \tag{I.8}$$

$$ye^{\int a(x)dx} - \left[ye^{\int a(x)dx}\right]_{x=x_o} = \int_{x=x_o}^{x} b(x)e^{\int a(x)dx}dx \tag{I.9}$$

We can rearrange this as:

$$y(x) = \left\{\left[ye^{\int a(x)dx}\right]_{x=x_o} + \int_{x=x_o}^{x} b(x)e^{\int a(x)dx}dx\right\}e^{-\int a(x)dx} \tag{I.10}$$

This is the general solution to a single first-order linear ODE.

Example. Integrating Factor

As an example, consider the case where a = 2 and b(x) = 3x with the initial condition $y(x=4)=5$. We have an integrating factor:

$$\text{I.F.} = e^{\int a(x)dx} = e^{2x} \tag{I.11}$$

The integral on the R.H.S. of equation (I.10) is

$$\int_{x=x_o}^{x} b(x)e^{\int a(x)dx}dx = \int_{x=4}^{x} 3xe^{2x}dx = 3\left[\frac{e^{2x}}{2}\left(x-\frac{1}{2}\right)\right]_{x=4}^{x} \tag{I.12}$$

$$\int_{x=x_o}^{x} b(x)e^{\int a(x)dx}dx = 3\left[\frac{e^{2x}}{2}\left(x-\frac{1}{2}\right) - \frac{e^{8}}{2}\left(\frac{7}{2}\right)\right] \tag{I.13}$$

$$\left[ye^{\int a(x)dx}\right]_{x=x_o} = y_o e^{2x_o} = 5e^{8} \tag{I.14}$$

so that our solution (equation (I.10)) becomes:

$$y(x) = \left\{5e^{8} + \frac{3}{4}\left[e^{2x}(2x-1) - 7e^{8}\right]\right\}e^{-2x} \tag{I.15}$$

B. Homogeneous and Particular solutions

The ODE

$$\frac{dy}{dx} + a(x)y = b(x) \tag{I.1}$$

is called homogeneous when $b(x) = 0$. Otherwise it is non-homogeneous. We can solve this problem in a way that is algorithmically different than the integrating factor. It is useful to do so because it is this second method that we will eventually extend to solve systems of linear ODEs.

The general solution of this nonhomogeneous equation, $y_{nh}(x)$, is the sum of the solution to the homogeneous equation, $y_h(x)$, and a particular solution, $y_p(x)$.

$$y_{nh}(x) = y_h(x) + y_p(x) \tag{I.16}$$

We obtain the homogeneous solution by solving:

$$\frac{dy}{dx} + a(x)y = 0 \tag{I.17}$$

This is easily shown, (using separation of variables) to yield a solution

$$y_h(x) = ce^{-\int a(x)dx} = cy_{id}(x) \tag{I.18}$$

where c is a constant that satisfies the non-homogeneous problem and the initial conditions and $y_{id}(x)$ is the indefinite homogeneous solution, which does not take into account the initial conditions. Note that you cannot solve for c until you have both $y_h(x)$ and $y_p(x)$.

The theory of ODEs tells us that we ought to search for a solution to the particular equation with the form:

$$y_p(x) = u(x)y_{id}(x) \tag{I.19}$$

Another way to look at the non-homogeneous solution is then

$$y_{nh}(x) = [c + u(x)]y_{id}(x) \tag{I.20}$$

To derive the functional form of $u(x)$, we simply plug our solution $y_{nh}(x)$ into our ODE, as given in equation (I.1).

$$\frac{du}{dx}y_{id}+[c+u]\frac{dy_{id}}{dx}+a(x)[c+u]y_{id}=b(x) \tag{I.21}$$

$$c\left(\frac{dy_{id}}{dx}+a(x)y_{id}\right)+u\left(\frac{dy_{id}}{dx}+a(x)y_{id}\right)+\frac{du}{dx}y_{id}=b(x) \tag{I.22}$$

$$c(0)+u(0)+\frac{du}{dx}y_{id}=b(x) \tag{I.23}$$

$$u=\int\frac{b(x)}{y_{id}}dx \tag{I.24}$$

Once we have $u(x)$, we can obtain c

$$y_{nh}(x=x_o)=y_o=[c+u(x=x_o)]y_{id}(x=x_o) \tag{I.25}$$

$$c=\frac{y_o}{y_{id}(x=x_o)}-u(x=x_o) \tag{I.26}$$

so that our final solution becomes

$$y_{nh}(x)=\left[\frac{y_o}{y_{id}(x=x_o)}-\left[\int\frac{b(x)}{y_{id}}dx\right]_{x=x_o}+\int\frac{b(x)}{y_{id}}dx\right]y_{id}(x) \tag{I.27}$$

$$y_{nh}(x)=\left[\left[\frac{y_o}{e^{-\int a(x)dx}}\right]_{x=x_o}-\left[\int\frac{b(x)}{e^{-\int a(x)dx}}dx\right]_{x=x_o}+\int\frac{b(x)}{e^{-\int a(x)dx}}dx\right]e^{-\int a(x)dx} \tag{I.28a}$$

It is worthwhile pointing out here that we could write this solution as:

$$y_{nh}(x)=\left[y_o\left[\frac{1}{e^{-\int a(x)dx}}\right]_{x=x_o}-u(x_o)+u(x)\right]e^{-\int a(x)dx} \tag{I.28b}$$

Example. Homogeneous and particular solutions

As an example, consider the case where a = 2 and b(x) = 3x with the initial condition $y(x=4)=5$.

$$y_h(x) = ce^{-\int a(x)dx} = ce^{-2x} \tag{I.29}$$

$$y_{id}(x) = e^{-2x} \tag{I.30}$$

$$u = \int \frac{b(x)}{y_{id}} dx = \int \frac{3x}{e^{-2x}} dx = \frac{3}{2} e^{2x}\left(x - \frac{1}{2}\right) \tag{I.31}$$

$$c = y_o e^{2x_o} - \frac{3}{2} e^{2x_o}\left(x_o - \frac{1}{2}\right) \tag{I.32}$$

$$y_{nh}(x) = \left[y_o e^{2x_o} - \frac{3}{2} e^{2x_o}\left(x_o - \frac{1}{2}\right) + \frac{3}{2} e^{2x}\left(x - \frac{1}{2}\right)\right] e^{-2x} \tag{I.33}$$

$$y_{nh}(x) = \left[5e^{8} - \frac{3}{2} e^{8}\left(\frac{7}{2}\right) + \frac{3}{2} e^{2x}\left(x - \frac{1}{2}\right)\right] e^{-2x} \tag{I.34}$$

which is the same result we obtained from using the integrating factor method.

This has shown us how we can solve any single first-order linear ODE. What if we have a single higher-order linear ODE. We can reduce a single nth-order linear ODE to a system of n first-order linear ODEs. (Refer to ChE 301 notes for a refresher on this process.) Therefore, if we know how to solve a system of n first-order linear ODEs, we know how to solve any single linear ODE of arbitrary order.

II. Extension of the analytical method to systems of first-order linear ODEs

In its most general form, a system of n first-order linear ODEs can be written as:

$$\frac{dy_i}{dx} + \sum_{j=1}^{n} a_{i,j}(x) y_j = b_i(x) \tag{II.1}$$

where we have n of these equations and we have n initial conditions of the form:

$$y_i(x = x_o) = y_{o,i} \tag{II.2}$$

We can write this system in matrix notation as:

$$\frac{d\underline{y}}{dx} + \underline{\underline{A}}(x)\underline{y} = \underline{b}(x) \tag{II.3}$$

$$\underline{y}(x = x_o) = \underline{y}_o \tag{II.4}$$

Things get ugly pretty fast in this case. We will limit ourselves to the case where $\underline{\underline{A}}$ is a matrix of constants and not a function of x. (If we want to solve the case where $\underline{\underline{A}}$ is a function of x, then we had better turn to a numerical solution.)

Example 1. Homogeneous Case $\underline{b}(x) = \underline{0}$

When $\underline{b}(x) = \underline{0}$, mathematicians refer to the problem as homogeneous. The terminology isn't important, only that we can obtain the solutoin.

Our system has the form:

$$\frac{d\underline{y}}{dx} = \underline{\underline{A}}(x)\underline{y} \tag{1.1}$$

$$\underline{y}(x = x_o) = \underline{y}_o \tag{1.2}$$

In order to obtain the general analytical solution, we need to recall a good amount of linear algebra theory.

The adjoint (complex conjugate of the transpose) of the matrix $\underline{\underline{A}}$, is designated $\underline{\underline{A}}^*$. For a real matrix, the adjoint of $\underline{\underline{A}}$ is the transpose so

$$\underline{\underline{A}}^* = \underline{\underline{A}}^T. \tag{1.3}$$

The matrix $\underline{\underline{A}}$ has eigenvalues, $\lambda_1, \lambda_2, \lambda_3 \ldots \lambda_{n-1}, \lambda_n$ and eigenvectors, $\underline{w}_{c,1}, \underline{w}_{c,2}, \underline{w}_{c,3} \cdots \underline{w}_{c,n-1}, \underline{w}_{c,n}$.

The eigenvalues of its adjoint $\underline{\underline{A}}^*$ are identical to the eigenvalues of $\underline{\underline{A}}$: $\lambda_1, \lambda_2, \lambda_3$. The eigenvectors of $\underline{\underline{A}}^*$ are known as the eigenrows of $\underline{\underline{A}}$: $\underline{w}_{r,1}, \underline{w}_{r,2}, \underline{w}_{r,3}$.

The most general solution to

$$\frac{d\underline{y}}{dx} = \underline{\underline{A}}(x)\underline{y} \tag{1.4}$$

$$\underline{y}(x = x_o) = \underline{y}_o \tag{1.5}$$

is going to be of a form

$$\underline{y}_h(x) = \sum_{i=1}^{n} \left\{ c_i \underline{w}_{c,i} \exp\left[\lambda_i (x - x_o)\right] \right\} \tag{1.6}$$

which can be written in matrix notation as

$$\underline{y}_h(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x - x_o)\right]\underline{c} \tag{1.6}$$

where $\underline{\underline{W}}_c$ is the matrix of eigenvectors

$$\underline{\underline{W}}_c = \left[\underline{w}_{c,1}, \cdots, \underline{w}_{c,n}\right] \tag{1.7}$$

and $\underline{\underline{\Lambda}}$ is the diagonal matrix of eigenvalues

$$\underline{\underline{\Lambda}} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \lambda_n \end{bmatrix} \tag{1.8}$$

such that

$$\exp\left[\underline{\underline{\Lambda}}(x-x_o)\right] = \begin{bmatrix} \exp\left[\lambda_1(x-x_o)\right] & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \exp\left[\lambda_n(x-x_o)\right] \end{bmatrix} \tag{1.9}$$

In this case:

$$\exp\left[\underline{\underline{\Lambda}}(x-x_o)\right]\underline{c} = \begin{bmatrix} \exp\left[\lambda_1(x-x_o)\right] c_1 \\ \vdots \\ \exp\left[\lambda_n(x-x_o)\right] c_n \end{bmatrix} \tag{1.10}$$

and

$$\underline{y}_h(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x-x_o)\right]\underline{c} = \begin{bmatrix} \sum_{i=1}^{n} w_{c_{1,i}} \exp\left[\lambda_i(x-x_o)\right] c_i \\ \vdots \\ \sum_{i=1}^{n} w_{c_{n,i}} \exp\left[\lambda_i(x-x_o)\right] c_i \end{bmatrix} \tag{1.11}$$

So we see that the matrix formulation is equivalent to the summation formulation.
The constant $\underline{c}$ can then be determined from the initial condition.

$$\underline{y}_h(x_o) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x_o-x_o)\right]\underline{c} = \underline{y}_o \tag{1.12}$$

$$\underline{c} = \underline{\underline{W}}_c^{-1}\underline{y}_o \tag{1.13}$$

so that the homogeneous solution becomes

$$\underline{y}_h(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x-x_o)\right]\underline{\underline{W}}_c^{-1}\underline{y}_o \tag{1.14}$$

Now, this form of the solution is perfectly legitimate. However, there is another form that is often presented as the solution and we will derive that too. Consider that

$$\left(\underline{\underline{W}}_r{}^T \underline{\underline{W}}_c\right)^{-1} = \underline{\underline{W}}_r{}^{T^{-1}} \underline{\underline{W}}_c{}^{-1} \tag{1.15}$$

then

$$\underline{\underline{W}}_c{}^{-1} = \underline{\underline{W}}_r{}^T \left(\underline{\underline{W}}_r{}^T \underline{\underline{W}}_c\right)^{-1} \tag{1.16}$$

We need to recognize that

$$\left(\underline{\underline{W}}_r{}^T \underline{\underline{W}}_c\right)^{-1} = \begin{bmatrix} \dfrac{1}{\left(\underline{w}_{r,1} \cdot \underline{w}_{c,1}\right)} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \dfrac{1}{\left(\underline{w}_{r,n} \cdot \underline{w}_{c,n}\right)} \end{bmatrix} \tag{1.17}$$

This allows us to write the solution as

$$\underline{y}_h(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x - x_o)\right] \underline{\underline{W}}_r{}^T \left(\underline{\underline{W}}_r{}^T \underline{\underline{W}}_c\right)^{-1} \underline{y}_o \tag{1.18}$$

$$\underline{y}_h(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x - x_o)\right] \begin{bmatrix} \dfrac{\left(\underline{w}_{r,1} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,1} \cdot \underline{w}_{c,1}\right)} \\ \vdots \\ \dfrac{\left(\underline{w}_{r,n} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,n} \cdot \underline{w}_{c,n}\right)} \end{bmatrix} \tag{1.19}$$

$$\underline{y}_h(x) = \underline{\underline{W}}_c \begin{bmatrix} \dfrac{\left(\underline{w}_{r,1} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,1} \cdot \underline{w}_{c,1}\right)} \exp\left[\lambda_1(x - x_o)\right] \\ \vdots \\ \dfrac{\left(\underline{w}_{r,n} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,n} \cdot \underline{w}_{c,n}\right)} \exp\left[\lambda_n(x - x_o)\right] \end{bmatrix} \tag{1.20}$$

$$\underline{y}_h(x) = \begin{bmatrix} \sum_{i=1}^{n} w_{c_{1,i}} \dfrac{\left(\underline{w}_{r,1} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,1} \cdot \underline{w}_{c,1}\right)} \exp\left[\lambda_i (x - x_o)\right] \\ \vdots \\ \sum_{i=1}^{n} w_{c_{n,i}} \dfrac{\left(\underline{w}_{r,n} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,n} \cdot \underline{w}_{c,n}\right)} \exp\left[\lambda_i (x - x_o)\right] \end{bmatrix} \tag{1.21}$$

$$\underline{y}(x) = \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o)\right] \right\} \tag{1.22}$$

In the case where n =1, the eigenvector and eigenrow are scalars with the value of unity and we have only a single equation. We see that we obtain the single equation solution:

$$y(x) = y_o \cdot \exp\left[\lambda_i (x - x_o)\right] \tag{1.23}$$

PROOF: (by substitution)

$$\frac{d\underline{y}}{dx} = \underline{\underline{A}}(x)\underline{y} \tag{1.24}$$

$$\frac{d\sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o)\right] \right\}}{dt} = \underline{\underline{A}} \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o)\right] \right\} \tag{1.25}$$

$$\sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \frac{d\exp\left[\lambda_i (x - x_o)\right]}{dt} \right\} = \underline{\underline{A}} \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o)\right] \right\} \tag{1.26}$$

$$\sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o)\right] \lambda_i \right\} = \underline{\underline{A}} \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o)\right] \right\} \tag{1.27}$$

Let the matrix of eigenvectors (an nxn matrix) be defined:

$$\underline{\underline{W}}_c = \left[\underline{w}_{c,1}, \cdots, \underline{w}_{c,n}\right] \tag{1.28}$$

and let the matrix of eigenvalues (a diagonal nxn matrix) be defined:

$$\underline{\underline{\Lambda}} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \lambda_n \end{bmatrix} \tag{1.29}$$

$$\underline{c} = \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \exp\left[\lambda_i \left(x - x_o\right)\right] \right\} \tag{1.30}$$

and let

$$\underline{d} = \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \exp\left[\lambda_i \left(x - x_o\right)\right] \lambda_i \right\} \tag{1.31}$$

which means that

$$\underline{d} = \underline{\underline{\Lambda}}\,\underline{c} \tag{1.32}$$

then substituting into the ODE in equation (1.8) we have:

$$\underline{\underline{W}}_c \underline{d} = \underline{\underline{A}}\,\underline{\underline{W}}_c \underline{c} \tag{1.33}$$

$$\underline{\underline{W}}_c^{-1} \underline{\underline{W}}_c \underline{d} = \underline{\underline{W}}_c^{-1} \underline{\underline{A}}\,\underline{\underline{W}}_c \underline{c} \tag{1.34}$$

$$\left(\underline{\underline{W}}_c^{-1} \underline{\underline{W}}_c\right) \underline{d} = \left(\underline{\underline{W}}_c^{-1} \underline{\underline{A}}\,\underline{\underline{W}}_c\right) \underline{c} \tag{1.35}$$

$$\underline{\underline{I}}\,\underline{d} = \underline{\underline{\Lambda}}\,\underline{c} \tag{1.36}$$

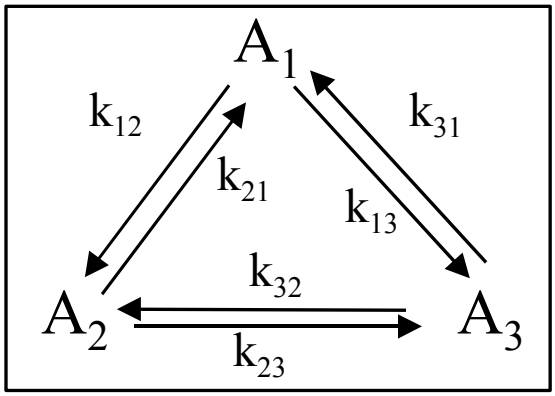
$$\underline{d} = \underline{d} \tag{1.37}$$

Q.E.D.

Example 2. Chemical Reaction Equilibria ($\underline{b}(x) = \underline{0}$)

One very famous example of a scientific application of a system of linear ODEs is the analysis of chemical equilibria in a reactor, where all the reactions are reversible and first-order.

Consider that you have a three-component reactive mixture, all undergoing reversible reactions, as pictured below:



In this picture, the A's are concentrations of the three species and the k's are rate constants. An example of this system is the kinetic equilibrium between para-, meta-, and ortho-xylene.

Now suppose we want to know what the concentration is as a function of time. We can write the mass balances for each component. There are no in and out terms (the reactor is a batch reactor). There is only the accumulation term and the reaction terms. Also, assume each reaction is first order in concentration.

$$\begin{aligned}
\frac{dA_1}{dt} &= -k_{12}A_1 + k_{21}A_2 - k_{13}A_1 + k_{31}A_3 \\
\frac{dA_2}{dt} &= -k_{21}A_2 + k_{12}A_1 - k_{23}A_2 + k_{32}A_3 \\
\frac{dA_3}{dt} &= -k_{31}A_3 + k_{13}A_1 - k_{32}A_3 + k_{23}A_2
\end{aligned} \tag{2.1}$$

We can gather like terms and rearrange the right hand side:

$$\begin{aligned}
\frac{dA_1}{dt} &= -(k_{12} + k_{13})A_1 + k_{21}A_2 + k_{31}A_3 \\
\frac{dA_2}{dt} &= k_{12}A_1 - (k_{21} + k_{23})A_2 + k_{32}A_3 \\
\frac{dA_3}{dt} &= k_{13}A_1 + k_{23}A_2 - (k_{31} + k_{32})A_3
\end{aligned} \tag{2.2}$$

and we change this system of equations into matrix & vector form:

$$\frac{d\underline{A}}{dt} = \underline{\underline{X}}\,\underline{A} \tag{2.3}$$

where

$$\underline{\underline{X}} = \begin{bmatrix} -(k_{12}+k_{13}) & k_{21} & k_{31} \\ k_{12} & -(k_{21}+k_{23}) & k_{32} \\ k_{13} & k_{23} & -(k_{31}+k_{32}) \end{bmatrix}$$
$$\underline{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \tag{2.4}$$

The matrix $\underline{\underline{X}}$ is singular. It has a determinant of zero and a rank of 2. Therefore, it has one zero value eigenvalue. Nevertheless, the matrix has three distinct real eigenvalues, $\lambda_1, \lambda_2, \lambda_3$. Corresponding to each of these eigenvalues is a real, distinct eigenvector, $\underline{w}_{c,1}, \underline{w}_{c,2}, \underline{w}_{c,3}$. The eigenvectors of $\underline{\underline{X}}^*$ are known as the eigenrows of $\underline{\underline{X}}$: $\underline{w}_{r,1}, \underline{w}_{r,2}, \underline{w}_{r,3}$.

The solution is then:

$$\underline{A}(t) = \sum_{i=1}^{n} \left\{ \frac{(\underline{w}_{r,i} \cdot \underline{A}_o)}{(\underline{w}_{r,i} \cdot \underline{w}_{c,i})} \cdot \underline{w}_{c,i} \cdot \exp[\lambda_i (t - t_o)] \right\} \tag{2.5}$$

In order to obtain numerical values for this problem, we would have to first obtain the eigenvalues, eigenvectors, and eigenrows. This can be done numerically, using routines discussed in the section on numerical methods for solving systems of linear algebraic equations.

Example 3. $\underline{b}(x) \neq \underline{0}$

When $\underline{b}(x) \neq \underline{0}$, mathematicians refer to the problem as nonhomogeneous. The terminology isn't important, only that we can obtain the solution. (Still there is no x-dependence in $\underline{\underline{A}}$.)

Our system has the form:

$$\frac{d\underline{y}}{dx} = \underline{\underline{A}}\underline{y} + \underline{b}(x) \tag{3.1}$$

$$\underline{y}(x = x_o) = \underline{y}_o \tag{3.2}$$

The general solution of this nonhomogeneous equation, $\underline{y}_{nh}(x)$, is the sum of the solution to the homogeneous equation, $\underline{y}_h(x)$, and a particular solution, $\underline{y}_p(x)$.

$$\underline{y}_{nh}(x) = \underline{y}_h(x) + \underline{y}_p(x) \tag{3.3}$$

In order to obtain the general analytical solution, we need to recall a good amount of linear algebra theory and single equation ODE theory. We know that the solution to the problem where $\underline{b}(x) = \underline{0}$ is given by

$$\underline{y}_h(x) = \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (x - x_o) \right] \right\} \tag{3.4}$$

We are going to rewrite this solution in a way that will make the following work easier. This summation can be expressed in matrix form as

$$\underline{y}_h(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \underline{c} \tag{3.5}$$

where the individual elements of the vector $\underline{c}$ are given by

$$c_i = \frac{\left(\underline{w}_{r,i} \cdot \underline{y}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \exp\left[\lambda_i (x_o) \right] \tag{3.6}$$

and where

$$\exp\left[\underline{\underline{\Lambda}}(x)\right] = \begin{bmatrix} \exp\left[\lambda_1(x)\right] & 0 & 0 \\ 0 & \exp\left[\lambda_2(x)\right] & 0 \\ 0 & 0 & \exp\left[\lambda_3(x)\right] \end{bmatrix} \tag{3.7}$$

Perform the matrix multiplication and dot product as indicated in equation (3.5) to see that equation (3.5) is equivalent to equation (3.4). We need to remember that the value of c as given by (3.7) is only the value of c for the homogeneous case. It will be different for the nonhomogeneous case.

By analogy with the single equation case, the particular solution can be expressed as

$$\underline{y}_p(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x)\right] \underline{u}(x) \tag{3.8}$$

and the nonhomogeneous solution as

$$\underline{y}_{nh}(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x)\right] \left[\underline{c} + \underline{u}(x)\right] \tag{3.9}$$

If we substitute $\underline{y}_{nh}$ into the original ODE, we have:

$$\frac{d\underline{y}_{nh}}{dx} = \underline{\underline{A}}\underline{y}_{nh} + \underline{b}(x) \tag{3.10}$$

$$\frac{d\underline{y}_h}{dx} + \frac{d\underline{y}_p}{dx} = \underline{\underline{A}}\underline{y}_h + \underline{\underline{A}}\underline{y}_p + \underline{b}(x) \tag{3.11}$$

$$\frac{d\underline{y}_p}{dx} = \underline{\underline{A}}\underline{y}_p + \underline{b}(x) \tag{3.12}$$

$$\frac{d\left\{\underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x)\right] \underline{u}(x)\right\}}{dx} = \underline{\underline{A}}\left\{\underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x)\right] \underline{u}(x)\right\} + \underline{b}(x) \tag{3.13}$$

Evaluate left hand side of equation (3.13)

$$\frac{d\left\{ \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \underline{u}(x)\right\}}{dx} = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \frac{d\underline{u}}{dx} + \underline{\underline{W}}_c \underline{\underline{\Lambda}} \exp\left[\underline{\underline{\Lambda}}(x) \right] \underline{u} \tag{3.14}$$

One can manually check and confirm that $\underline{\underline{\Lambda}}$ must appear after $\underline{\underline{W}}_c$ and not before.
Subsitute (3.14) back into (3.13)

$$\underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \frac{d\underline{u}}{dx} + \underline{\underline{W}}_c \underline{\underline{\Lambda}} \exp\left[\underline{\underline{\Lambda}}(x) \right] \underline{u} = \underline{\underline{A}}\left\{ \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \underline{u}\right\} + \underline{b}(x) \tag{3.15}$$

Rearrange

$$\left(\underline{\underline{A}}\underline{\underline{W}}_c - \underline{\underline{W}}_c \underline{\underline{\Lambda}}\right)\left(\exp\left[\underline{\underline{\Lambda}}(x) \right] \underline{u}\right) + \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \frac{d\underline{u}}{dx} = \underline{b}(x) \tag{3.16}$$

$$\underline{\underline{W}}_c^{-1} \underline{\underline{A}} \underline{\underline{W}}_c - \underline{\underline{\Lambda}} = \underline{\underline{0}} \tag{3.17}$$

This is the definition of the diagonalization of the matrix $\underline{\underline{A}}$ into its matrix of eigenvalues.

This results in two terms dropping out of equation (3.15) which leaves us with

$$\underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \frac{d\underline{u}}{dx} = \underline{b}(x) \tag{3.19}$$

which is satisfyingly analogous to the single equation constraint on the derivative of u.

Solving equation (3.19) we find

$$\frac{d\underline{u}}{dx} = \left\{ \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \right\}^{-1} \underline{b}(x) \tag{3.20}$$

$$\underline{u} = \int \left\{ \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x) \right] \right\}^{-1} \underline{b}(x)\, dx \tag{3.21}$$

$$\underline{u} = \int \exp\left[\underline{\underline{\Lambda}}(x) \right]^{-1} \underline{\underline{W}}_c^{-1} \underline{b}(x)\, dx \tag{3.22}$$

$$\underline{u} = \int \exp\left[-\underline{\underline{\Lambda}}(x)\right] \underline{\underline{W}}_c^{-1} \underline{b}(x)\, dx \tag{3.23}$$

This leaves the determination of c which will satisfy the initial conditions.

$$\underline{y}_{nh}(x_o) = \underline{y}_o = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x_o)\right] [\underline{c} + \underline{u}(x_o)] \tag{3.24}$$

$$\underline{c} = \exp\left[\underline{\underline{\Lambda}}(x_o)\right]^{-1} \underline{\underline{W}}_c^{-1} \underline{y}_o - \underline{u}(x_o) \tag{3.25}$$

Thus we can rewrite our nonhomogeneous solution as

$$\underline{y}_{nh}(x) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(x)\right] \left[\exp\left[\underline{\underline{\Lambda}}(x_o)\right]^{-1} \underline{\underline{W}}_c^{-1} \underline{y}_o - \underline{u}(x_o) + \underline{u}(x) \right] \tag{3.26}$$

To check our solution we can first make sure that equation (3.26) reduces to the nonhomogeneous solution for a single equation

$$y_{nh}(x) = e^{-\int a(x)dx} \left[y_o \left[\frac{1}{e^{-\int a(x)dx}} \right]_{x=x_o} - u(x_o) + u(x) \right] \tag{I.28b}$$

This solution checks because the eigenvector of a single equation is unity and the eigenvalue is $-a$.

A second check of our solution is to make sure that equation (3.26) reduces to the homogeneous solution when $\underline{u}(x) = \underline{0}$. We can see that it does by comparing equation (3.26) with equation (1.14)

$$\underline{y}_h(x_o) = \underline{\underline{W}}_c \exp[\underline{\underline{\Lambda}}(x - x_o)] \underline{\underline{W}}_c^{-1} \underline{y}_o \tag{1.14}$$

Example 4. Chemical Reaction Equilibria with addition/deletion of components $\underline{b}(x) \neq \underline{0}$

We can add constant flowrates to our system by adding a constant term to the ODEs.

$$\begin{aligned}
\frac{dA_1}{dt} &= -(k_{12}+k_{13})A_1 + k_{21}A_2 + k_{31}A_3 + F_1 \\
\frac{dA_2}{dt} &= k_{12}A_1 - (k_{21}+k_{23})A_2 + k_{32}A_3 + F_2 \\
\frac{dA_3}{dt} &= k_{13}A_1 + k_{23}A_2 - (k_{31}+k_{32})A_3 + F_3
\end{aligned} \tag{4.1}$$

The flowrates can either be feed or effluent, depending upon the sign. To keep the problem simple, let's enforce conservation of volume by stipulating that

$$\sum_{i=1}^{3} F_i = 0 \tag{4.2}$$

and we change this system of equations into matrix & vector form:

$$\frac{d\underline{A}}{dt} = \underline{\underline{X}}\,\underline{A} + \underline{F} \tag{4.3}$$

We know the solution to the nonhomogeneous equation is

$$\underline{A}_{nh}(t) = \underline{\underline{W}}_c \exp\left[\,\underline{\underline{\Lambda}}(t)\,\right]\left[\exp\left[\underline{\underline{\Lambda}}(t_o)\,\right]^{-1}\underline{\underline{W}}_c{}^{-1}\underline{A}_o - \underline{u}(t_o) + \underline{u}(t)\right] \tag{4.4}$$

The only question is the form of u.

$$\underline{u} = \int \exp\left[-\,\underline{\underline{\Lambda}}(x)\,\right]\underline{\underline{W}}_c{}^{-1}\underline{b}(x)\,dx \tag{3.23}$$

Since, for this problem, b is a constant, all the x functionality lies in $\exp\left[-\,\underline{\underline{\Lambda}}(x)\,\right]$

$$\underline{u}(t) = \left[\int_0^t \exp\left[-\,\underline{\underline{\Lambda}}(x)\,\right]dx\right]\underline{\underline{W}}_c{}^{-1}\underline{b} \tag{4.5}$$

$$\underline{u}(t) = -\left[\underline{\underline{\Lambda}}^{-1} \exp\left[-\underline{\underline{\Lambda}}(t)\right]\right]\underline{\underline{W}}_c^{-1}\underline{b} \tag{4.6}$$

Plugging back into the solution we find

$$\underline{A}_{nh}(t) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(t)\right]\begin{bmatrix} \exp\left[\underline{\underline{\Lambda}}(t_o)\right]^{-1}\underline{\underline{W}}_c^{-1}\underline{A}_o + \left[\underline{\underline{\Lambda}}^{-1}\exp\left[-\underline{\underline{\Lambda}}(t_o)\right]\right]\underline{\underline{W}}_c^{-1}\underline{b} \\ -\left[\underline{\underline{\Lambda}}^{-1}\exp\left[-\underline{\underline{\Lambda}}(t)\right]\right]\underline{\underline{W}}_c^{-1}\underline{b} \end{bmatrix} \tag{4.7}$$

A complication arises because one of the eigenvalues is zero. Thus there is no x-dependency in the exponential because there is no exponential. Then we would have a term of the form

$$\underline{u}(t) = [t]\underline{\underline{W}}_c^{-1}\underline{b} \tag{4.8}$$

so that we would have

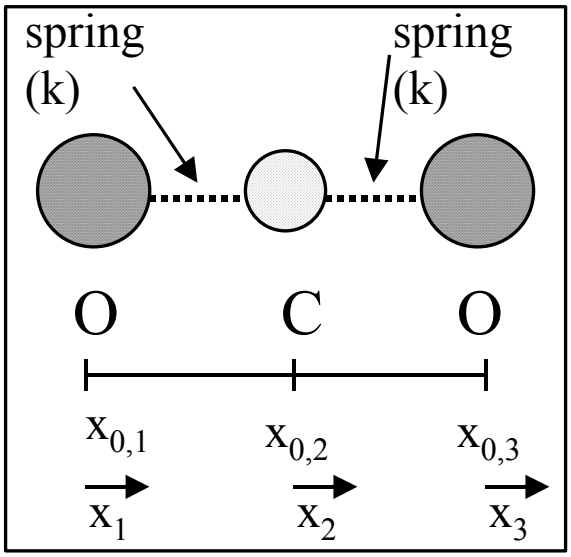
$$\underline{u}(t) = \underline{\underline{U}}\underline{\underline{W}}_c^{-1}\underline{b} \tag{4.9}$$

$$\underline{\underline{U}} = \begin{bmatrix} -\dfrac{\exp\left[-\lambda_1(t)\right]}{\lambda_1} & 0 & 0 \\ 0 & -\dfrac{\exp\left[-\lambda_2(t)\right]}{\lambda_2} & 0 \\ 0 & 0 & t \end{bmatrix} \tag{4.10}$$

for the case where we had three eigenvalues, the first two of which are non-zero.

B. Normal Mode Analysis of the Vibrational Spectrum of a Molecule

Consider that we want to investigate the vibrational properties of carbon dioxide, CO_2. Our model of the molecule looks like this:



We model the interaction between molecules as Hookian springs. For a Hookian spring, the potential energy, U, is

$$U = \frac{k}{2}(x - x_0)^2 \tag{5.1}$$

and the force, F, is

$$F = -k(x - x_0) \tag{5.2}$$

where k is the spring constant (units of kg/s^2), x_0 is the equilibrium displacement, and x is the actual displacement.

When both ends of the spring are mobile we can write, for the spring that connects mass 1 and 2:

$$U_{12} = \frac{k}{2}((x_2 - x_1) - x_{120})^2 \tag{5.3}$$

and we can write, for the spring that connects mass 2 and 3:

$$U_{32} = \frac{k}{2}((x_3 - x_2) - x_{320})^2 \tag{5.4}$$

The forces are then:

$$F_1 \equiv -\frac{\partial U}{\partial x_1} = k((x_2 - x_1) - x_{120})$$
$$F_2 \equiv -\frac{\partial U}{\partial x_2} = -k((x_2 - x_1) - x_{120}) + k((x_3 - x_2) - x_{320}) \quad (5.5)$$
$$F_3 \equiv -\frac{\partial U}{\partial x_3} = -k((x_3 - x_2) - x_{320})$$

With only a slight sleight of hand, we redefine our variables to be:

$$x_1 = x_1 + x_{120}$$
$$x_2 = x_2 \quad (5.6)$$
$$x_3 = x_3 - x_{320}$$

This eliminates the equilibrium bond distances from the calculation. So, with this definition,

$$x_1 = x_2 = x_3 \quad (5.7)$$

at equilibrium. This does not affect our equations of motion because the derivatives of our variables before and after the transformation of the variables are the same. Our forces become:

$$F_1 \equiv -\frac{\partial U}{\partial x_1} = k(x_2 - x_1)$$
$$F_2 \equiv -\frac{\partial U}{\partial x_2} = -k(x_2 - x_1) + k(x_3 - x_2) \quad (5.8)$$
$$F_3 \equiv -\frac{\partial U}{\partial x_3} = -k(x_3 - x_2)$$

We can write Newton's equations of motion for the three molecules:

$$m_O a_1 = F_1 = k(x_2 - x_1)$$
$$m_C a_2 = F_2 = -k(x_2 - x_1) + k(x_3 - x_2) \quad (5.9)$$
$$m_O a_3 = F_3 = -k(x_3 - x_2)$$

We can generalized this to a non-symmetric linear tri-atomic molecule by writing:

$$\begin{aligned} m_1 a_1 &= F_1 = k_{12}(x_2 - x_1) \\ m_2 a_2 &= F_2 = -k_{12}(x_2 - x_1) + k_{13}(x_3 - x_2) \\ m_3 a_3 &= F_3 = -k_{13}(x_3 - x_2) \end{aligned} \tag{5.10}$$

Knowing that the acceleration is the second derivative of the position, we can rewrite the above equations in matrix form as (first divide both side of all of the equations by the masses)

$$\frac{d^2\underline{x}}{dt^2} = \underline{\underline{A}}\,\underline{x} \tag{5.11}$$

where

$$\underline{\underline{A}} = \begin{bmatrix} -k_{12}/m_1 & k_{12}/m_1 & 0 \\ k_{12}/m_2 & -k_{12}-k_{13}/m_2 & k_{13}/m_2 \\ 0 & k_{13}/m_3 & -k_{13}/m_3 \end{bmatrix} \tag{5.12}$$

$$\underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}$$

Solving this system of second order linear differential equations yields the integrated equations of motion for carbon dioxide.

We can convert the three second order ODEs into six first order ODEs as shown below. Take atom number one.

$$m_1 a_1 = F_1 = k_{12}(x_2 - x_1) \tag{5.13}$$

which we write as

$$m_1 \frac{d^2 x_1}{dt^2} = k_{12}(x_2 - x_1) \tag{5.14}$$

Now we can rewrite that second order ODE as two first order ODEs.

$$\frac{dx_1}{dt} = x_4 \tag{5.15}$$

$$m_1 \frac{dx_4}{dt} = k_{12}(x_2 - x_1) \tag{5.16}$$

We can write analogous equation for the other two atoms, to come with ODEs for variables 5 and 6. Of course, variables 1, 2, and 3 are still the positions of the atoms. Variables 4, 5, and 6 are now the velocities of the atoms.

All of these equations are homogeneous.

Our 3x3 A matrix becomes a 6x6 matrix:

$$\underline{\underline{A}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -k_{12}/m_1 & k_{12}/m_1 & 0 & 0 & 0 & 0 \\ k_{12}/m_2 & -k_{12}-k_{13}/m_2 & k_{13}/m_2 & 0 & 0 & 0 \\ 0 & k_{13}/m_3 & -k_{13}/m_3 & 0 & 0 & 0 \end{bmatrix} \tag{5.17}$$

where the solution vector, x, is now defined as:

$$\underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} \tag{5.18}$$

Now, clearly, we can solve this problem exactly as we solve any system of homogeneous linear first order ODEs. The solution will be given as

$$\underline{x}_h(t) = \underline{\underline{W}}_c \exp[\underline{\underline{\Lambda}}(t - t_o)] \underline{\underline{W}}_c^{-1} \underline{x}_o \tag{1.14}$$

or

$$\underline{x}_h(t) = \sum_{i=1}^{n} \left\{ \frac{(\underline{w}_{r,i} \cdot \underline{x}_o)}{(\underline{w}_{r,i} \cdot \underline{w}_{c,i})} \cdot \underline{w}_{c,i} \cdot \exp[\lambda_i(t - t_o)] \right\} \tag{1.22}$$

In this problem the eigenvalues and eigenvectors are complex. They have real and imaginary components. The solution in equation (1.14) is purely real. The imaginary contributions have been transformed into real components via the Euler identities. If we have a software that can handle complex algebra then we can simply obtain the solution as given in equation (1.14). Matlab can handle this sort of thing. However, do to round-off error, the imaginary component of the solution won't cancel to be precisely zero. Rather we will obtain imaginary components on the order of 10^{-15} (since the computer only keeps sixteen significant figures). Therefore, we need to realize that these very small imaginary components have no mathematical basis. They are simply the results of truncation errors.

Well we might think we have solved this problem, and we have. However, it is worthwhile to investigate this problem further because some of the eigenvalues of a vibrational problem are complex. They have to be; how else would be obtain the periodic trigonometric functions from this solution? If we want to derive the analytical formula in terms of sines and cosines we can proceed further.

From this point on, our derivation is based upon existing knowledge of the problem. We will consider one broad subcase. In this subcase,

- the six eigenvalues constitute purely complex conjugate pairs (two of which are zero)
- each complex conjugate pair of eigenvalues necessarily has complex conjugate eigenvectors.

Knowing this, we can proceed to write .

$$\underline{x}(t) = \sum_{j=1}^{2n} \left\{ \frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \cdot \exp\left[\lambda_j (t - t_o)\right] \right\} \tag{1.22}$$

The pre-exponential factor can very well have both real and imaginary parts

$$\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} = \text{real}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] + \text{imag}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] i \tag{5.19}$$

which allows us to write:

$$\begin{aligned} \underline{x}(t) = & \sum_{j=1}^{2n} \left\{ \text{real}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] \cdot \exp\left[\lambda_j (t - t_o)\right] \right\} \\ & + \sum_{j=1}^{2n} \left\{ \text{imag}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] \cdot \exp\left[\lambda_j (t - t_o)\right] \right\} i \end{aligned} \tag{5.20}$$

Because (i) our pre-exponential factors are complex conjugates and (ii) the eigenvalues are complex conjugates, the summations can be transformed into summations over n molecules rather than 2n variables:

$$\underline{x}(t) = \sum_{j=1}^{n} \left\{ \text{real}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] \cdot \left(\exp\left[|\lambda_j| i(t-t_o) \right] + \exp\left[-|\lambda_j| i(t-t_o) \right] \right) \right\}$$
$$+ \sum_{j=1}^{n} \left\{ \text{imag}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] \cdot \left(\exp\left[|\lambda_j| i(t-t_o) \right] - \exp\left[-|\lambda_j| i(t-t_o) \right] \right) \right\} i \tag{5.21}$$

We must recognize Euler's identities. For the summation with the real pre-exponential factors:

$$\exp\left[|\lambda_j| i(t-t_o) \right] + \exp\left[-|\lambda_j| i(t-t_o) \right] = 2\cos\left[|\lambda_j| (t-t_o) \right] \tag{5.22}$$

and for the summation with the imaginary pre-exponential factors:

$$\left(\exp\left[|\lambda_j| i(t-t_o) \right] - \exp\left[-|\lambda_j| i(t-t_o) \right] \right) i = -2\sin\left[|\lambda_j| (t-t_o) \right] \tag{5.23}$$

so that we see:

$$\underline{x}(t) = \sum_{j=1}^{n} \left\{ \text{real}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] \cdot 2\cos\left[|\lambda_j| (t-t_o) \right] \right\}$$
$$- \sum_{j=1}^{n} \left\{ \text{imag}\left[\frac{\left(\underline{w}_{r,j} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,j} \cdot \underline{w}_{c,j}\right)} \cdot \underline{w}_{c,j} \right] \cdot 2\sin\left[|\lambda_j| (t-t_o) \right] \right\} \tag{5.24}$$

Well, we have the solution. You think we are done. There are two catches.

First, because of the nature of the system, the eigenvectors don't form an orthonormal basis set. Two of the eigenvectors have zeros through all of the velocity entries. Two of the eigenrows have zeros through all of the position entries. The dot product of those vectors, as needed in the denominator of the pre-exponential factor, is zero, so that exponential prefactor blows up. This happens for only one of the three exponential prefactors. That problem can be remedied by

selecting the pre-exponential factor corresponding to the problematic eigenvector,eigenrow dot product to satisfy the initial positions conditions. This works fine.

Second, these equations for $\underline{x}(t)$ as we have written them are indeed solutions to

$$\frac{d^2\underline{x}}{dt^2} = \underline{\underline{A}}\underline{x} \tag{5.25}$$

However, they may not provide the solution to certain types of initial conditions. There is another family of solutions given by

$$\underline{x}(t) = \underline{x}(t) + \underline{k}_1 t + \underline{k}_0$$

where the k's are vectors of constants. These additional terms will be needed to satisfy the initial conditions when the total momentum of the molecule is non-zero, i.e. in addition to the vibration, there is a non-zero translational component to the motion.

$\underline{k}_0$ and $\underline{k}_1$ are going to turn out to be non-zero only if the initial velocities of the atoms are specified such that the total momentum of the molecule is non-zero. The initial momentum of the molecule is

$$\sum_{j=1}^{n} m_j \dot{x}_j(t = t_o) = mom_o$$

By the conservation of momentum the total momentum won't change. This total momentum translates into a uniform center of mass motion:

$$\dot{x}_{cm} \sum_{j=1}^{n} m_j = mom_o = \sum_{j=1}^{n} m_j \dot{x}_j(t = t_o)$$

$$\dot{x}_{cm} = \frac{\sum_{j=1}^{n} m_j \dot{x}_j(t = t_o)}{\sum_{j=1}^{n} m_j}$$

It can be shown that the value for $\underline{k}_0$ is given by

$$\underline{k}_0 = \begin{bmatrix} k_{0,1} \\ k_{0,2} \\ k_{0,3} \\ k_{0,4} \\ k_{0,5} \\ k_{0,6} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \dot{x}_{cm} \\ \dot{x}_{cm} \\ \dot{x}_{cm} \end{bmatrix}$$

It can be shown that our value for $\underline{k}_1$ is given by

$$\underline{k}_1 = \begin{bmatrix} k_{1,1} \\ k_{1,2} \\ k_{1,3} \\ k_{1,4} \\ k_{1,5} \\ k_{1,6} \end{bmatrix} = \begin{bmatrix} \dot{x}_{cm} \\ \dot{x}_{cm} \\ \dot{x}_{cm} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Why didn't these two additional terms enter naturally in our formulation, instead of being added in as an afterthought? My guess is because we are engineers who patch things up better than we know how to design flawlessly a priori.

III. Codification of the analytical method for numerical solution

These gruesome derivations given above are truly unnecessary. A simple Runge-Kutta algorithm will yield the solution with only a few minutes work. However, the Runge-Kutta method would not have given us the functional form of the solution, which is often times all that we are after.

The analytical solution techniques given above can be coded up as written.

The purpose in giving two forms of the solution, for example, for the system of linear homogeneous equations,

$$\underline{x}_h(t) = \underline{\underline{W}}_c \exp\left[\underline{\underline{\Lambda}}(t - t_o)\right] \underline{\underline{W}}_c^{-1} \underline{x}_o \tag{1.14}$$

and

$$\underline{x}_h(t) = \sum_{i=1}^{n} \left\{ \frac{\left(\underline{w}_{r,i} \cdot \underline{x}_o\right)}{\left(\underline{w}_{r,i} \cdot \underline{w}_{c,i}\right)} \cdot \underline{w}_{c,i} \cdot \exp\left[\lambda_i (t - t_o)\right] \right\} \tag{1.22}$$

is to make codification of the solutions simple for any type of software platform. A language like FORTRAN is going to favor the use of equation (1.22). However, a platform like MATLAB, which can handle matrix multiplication implicitly would be much easily solved using equation (1.14). In fact, here is an example of solving the chemical reaction equilibria problem above using MATLAB. The code is less than a page long and completely solves and plots the problem.

```
% input
k12 = 0.50;
k21 = 0.25;
k13 = 0.20;
k31 = 0.05;
k23 = 0.30;
k32 = 0.15;
A = [ (-k13-k12), k21, k31; k12, (-k21-k23), k32; k13, k23, (-
k31-k32)];
yo = [1.0/3.0;  1.0/3.0; 1.0/3.0];
to = 0.0;
tf = 10.0;
n = max(size(A));
% compute eigenvalues and eigenvectors
[wcol,lambdac] = eig(A);
wcolinv = inv(wcol);
% set up discretized solution grid
npoints = 1000;
dt = (tf-to)/npoints;
for i = 1:1:npoints+1
   tp(i) = (i-1)*dt +to;
end
% calculate solution
explambda = zeros(n,n);
yp = zeros(n,npoints);
for i = 1:1:npoints+1
   for j = 1:n
      explambda(j,j) = exp(lambdac(j,j)*(tp(i) - to) );
   end
   yp(:,i) = wcol*explambda*wcolinv*yo;
end
%plot
for j = 1:1:n
  if (j==1)
     plot (tp,yp(j,:),'g-'), xlabel( 't' ), ylabel ( 'y' )
  elseif (j==2)
     plot (tp,yp(j,:),'r-'), xlabel( 't' ), ylabel ( 'y' )
  elseif (j==3)
     plot (tp,yp(j,:),'b-'), xlabel( 't' ), ylabel ( 'y' )
  end
  hold on
end
hold off
```