A.1 \textit{Summary of Matrices}

A column vector is indicated by
\[ f = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \\ f_N \end{pmatrix}. \]

A matrix consisting of M rows and N columns is defined by
\[
A = \begin{pmatrix}
A_{11} & A_{12} & \ldots & A_{1N} \\
A_{21} & A_{22} & \ldots & A_{2N} \\
A_{31} & A_{32} & \ldots & A_{3N} \\
\vdots & \vdots & \ddots & \vdots \\
A_{M1} & A_{M2} & \ldots & A_{MN}
\end{pmatrix}.
\]

A is said to be an M x N matrix which is denoted by A_{ij}. The vector f is considered as a M x 1 matrix.

The product of a M x N matrix with a N x K matrix gives a M x K matrix. It is obvious that matrix multiplication is not commutative, that is AB is not equal to BA. When C = AB we have
\[
C_{ik} = \Sigma A_{ij} B_{jk}.
\]

Matrix products are associative so that A(BC) = (AB)C.

On the basis of the rule of matrix multiplication, the product of a row vector (1 x N) and a column vector (N x 1) gives a (1 x 1) matrix, or the scalar product
\[
f^t f = f_1 f_1 + f_2 f_2 + \ldots + f_N f_N.
\]

But the product of a column vector (N x 1) and a row vector (1 x N) gives a (N x N) matrix, or a vector product
\[
f f^t = \begin{pmatrix} f_1 f_1 & f_1 f_2 & \ldots & f_1 f_N \\
f_2 f_1 & f_2 f_2 & \ldots & f_2 f_N \\
\vdots & \vdots & \ddots & \vdots \\
f_N f_1 & f_N f_2 & \ldots & f_N f_N
\end{pmatrix}.
\]
To summarize these few properties of matrix multiplication: (a) matrix multiplication is not commutative, (b) the $ji$ element of $AB$ is the sum of products of elements from the $j$th row of $A$ and $i$th column of $B$, and (c) the number of columns in $A$ must equal the number of rows in $B$ if the product $AB$ is to make sense.

There are several matrices that are related to $A$. They are:

(a) $A^t$ which is the transpose of $A$ so that $[A^t]_{ij} = [A]_{ji}$,

(b) $A^*$ which is the complex conjugate of $A$ so that $[A^*]_{ij} = [A]_{ij}^*$,

(c) $A^+$ which is the adjoint of $A$ so that $[A^+]_{ij} = [A]^*_{ji}$, and

(d) $A^{-1}$ which is the inverse of $A$ so that $A^{-1}A = AA^{-1} = I$, where $I$ denotes the identity matrix.

A few definitions follow:

(a) $A$ is real if $A^* = A$,

(b) $A$ is symmetric if $A^t = A$,

(c) $A$ is antisymmetric if $A^t = -A$,

(d) $A$ is Hermitian if $A^+ = A$,

(e) $A$ is orthogonal if $A^{-1} = A^t$, and

(f) $A$ is unitary if $A^{-1} = A^*$.

### A.2 Eigenvalue Problems

To understand some of the techniques for solving the radiative transfer equation it is necessary to review solutions to eigenvalue problems. When a operator $A$ acts on a vector $x$, the resulting vector $Ax$ is in general distinct from $x$. However there may exist certain non-zero vectors for which $Ax$ is just a multiple of $x$. That is

$$Ax = \lambda x$$

or written out explicitly

$$\sum A_{ij} x_j = \lambda x_i \quad l=1,...,n .$$

Such a vector is called an eigenvector of the operator $A$, and the constant $\lambda$ is called an eigenvalue. The eigenvector is said to belong to the eigenvalue. Consider an example where the operator $A$ is given by
So we are trying to solve

\[ \begin{align*}
  x_1 + 2x_2 + 3x_3 &= \lambda x_1 \\
  4x_1 + 5x_2 + 6x_3 &= \lambda x_2 \\
  7x_1 + 8x_2 + 9x_3 &= \lambda x_3 
\end{align*} \]

For a nontrivial solution the determinant of coefficients must vanish

\[ \begin{vmatrix}
  1 - \lambda & 2 & 3 \\
  4 & 5 - \lambda & 6 \\
  7 & 8 & 9 - \lambda 
\end{vmatrix} = 0 \]

This produces a third order polynomial in \( \lambda \) whose three roots are the eigenvalues \( \lambda_i \).

There are several characteristics of the operator \( A \) that determine the character of the eigenvalue. Briefly summarized they are (a) if \( A \) is hermitian, then the eigenvalues are real and the eigenvectors are orthogonal (eigenvectors of identical or degenerate eigenvalues can be made orthogonal through the Gram Schmidt process) and (b) if \( A \) is a linear operator, then the eigenvalues and eigenvectors are independent of the coordinate system. A proof of (b) is quickly apparent.

\[ A x = \lambda x \]

Let \( Q \) represent an arbitrary coordinate transformation, then

\[ \gamma^{-1} A x = \lambda \gamma^{-1} x \]

\[ \gamma^{-1} A \gamma \gamma^{-1} x = \lambda \gamma^{-1} x \]

\[ A' x' = \lambda x' \]

Thus if \( x \) is an eigenvector of the linear operator \( A \), its transform

\[ x' = \gamma^{-1} x \]

is an eigenvector of the transformed matrix.
\[ A' = \gamma^{-1} A \gamma, \]
and the eigenvalues are the same.

It is often desirable to make a transformation to a coordinate system in which \( A' \) is a diagonal matrix and the diagonal elements are the eigenvalues. The desired transformation matrix consists of the eigenvectors of the original matrix \( A \).

\[
\gamma = \begin{bmatrix} e_1 & e_2 & \cdots & e_n \end{bmatrix}
\]

where the \( j^{th} \) col consists of components of eigenvector \( e_j \). For the transformation to be unitary, the eigenvectors must be orthonormal (orthogonal and normalized).

### A.3 \( \text{CO}_2 \) Vibration Example

Consider the problem of molecular vibrations in \( \text{CO}_2 \), which is shown schematically as a simple linear triatomic molecule system consisting of three masses connected by springs of spring constant \( k \). Let \( x_i \) represent deviations from the equilibrium position.

\[
x_1 \quad x_2 \quad x_3
\]

\[
m \quad M \quad m
\]

\[
O \quad C \quad O
\]

The kinetic energy of this system can be written

\[
T = \frac{1}{2} \sum_{i} m_i v_i^2 = \frac{1}{2} v^T M v
\]

where \( v \) represents \( dx/dt \). The potential energy is given by

\[
P = \frac{1}{2} \sum_{ij} P_{ij} x_i x_j = \frac{1}{2} x^T P x
\]

where

\[
P = P_o + \sum_i \left( \frac{\partial P}{\partial x_i} \right)_o x_i + \frac{1}{2} \sum_{ij} \left( \frac{\partial^2 P}{\partial x_i \partial x_j} \right)_o x_i x_j
\]

and without loss of generality let \( P_o = 0 \) and use the fact that \( \partial P/\partial x = 0 \) at equilibrium. Then Lagrange's equation:

\[
d \frac{\partial T}{\partial \dot{x}} + \frac{\partial P}{\partial x} = 0
\]
\[
\frac{\partial}{\partial t} \frac{\partial}{\partial x} \mathbf{v}
\]
with
\[
T = \frac{1}{2} m v^2 \text{ and } P = \frac{1}{2} kx^2,
\]
becomes
\[
m v = -kx.
\]
This suggests a solution of the form \( x_i = a_i \sin (\omega t + \delta_i) \), so that
\[
\sum_P a_i - \omega^2 T a_i = 0.
\]
Now the potential energy is written
\[
P = \frac{1}{2} k (x_2 - x_1)^2 + \frac{1}{2} k (x_3 - x_2)^2
\]
\[
= \frac{1}{2} k (x_1^2 + 2x_2^2 + x_3^2 - 2x_1x_2 - 2x_2x_3),
\]
so the matrix operator is,
\[
P = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}
\]
which is real and symmetric. And the kinetic energy is written
\[
T = \frac{1}{2} m (x_1^2 + x_3^2) + \frac{1}{2} Mx_2^2,
\]
so the matrix operator is
\[
T = \begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}
\]
which is diagonal. So, we find \(| P - \omega^2 T | = 0 \) implies
\[
\det A = \begin{vmatrix} k - \omega^2 m & -k & 0 \\ -k & 2k - \omega^2 M & -k \end{vmatrix} = 0
\]
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o  -k  k-ω²m

and direct evaluation of the determinant leads to the cubic equation

\[ \omega^2(k-\omega^2m)(kM + 2km - \omega^2Mm) = 0. \]

This yields the three roots

\[ \omega_1 = 0, \ \omega_2 = [k/m]^{1/2}, \ \omega_3 = [(k/m)(1+2m/M)]^{1/2}. \]

Now solve for the eigenvectors. For \( \omega_1 = 0 \)

\[
\begin{array}{ccc}
  k & -k & 0 & a_{11} \\
  -k & 2k & -k & a_{12} \\
  0 & -k & k & a_{13}
\end{array} = 0 \Rightarrow a_{11} = a_{12} = a_{13}
\]

which represents a translation since the centre of mass doesn't move \( mx_1 + Mx_2 + mx_3 = 0 \).

For \( \omega_2 = [k/m]^{1/2} \)

\[
\begin{array}{ccc}
  0 & -k & 0 & a_{21} \\
  -k & 2k-kM/m & -k & a_{22} \\
  0 & -k & 0 & a_{23}
\end{array} = 0 \Rightarrow a_{22} = 0, a_{21} = -a_{23}
\]

which represents a vibration in the breathing mode with the carbon molecule stationary and the oxygen molecules moving in opposite directions.

For \( \omega_3 = [(k/m)(1+2m/M)]^{1/2} \)

\[
\begin{array}{ccc}
  -2mk/M & -k & 0 & a_{31} \\
  -k & -kM/m & -k & a_{32} \\
  0 & -k & -2mk/M & a_{33}
\end{array} = 0 \Rightarrow a_{31} = a_{33}, a_{32} = -(2m/M)a_{31}
\]

which represents the carbon molecule motion offset by the combined motion of the oxygen molecules.

Recalling that the mass of the proton is given by \( m_p = 1.67 \times 10^{-27} \text{Kg} \), that the spring constant for the \( \text{CO}_2 \) is roughly \( k \sim 1.4 \times 10^3 \text{J/m}^2 \) (from the second derivative of the potential curves), and that \( m = 16m_p \) while \( M = 12m_p \), then

\[
\omega_3 = \left[ \frac{1.4 \times 10^3}{16 \times 1.67 \times 10^{-27}} \left( 1 + \frac{32}{12} \right) \right]^{1/2} = [0.192 \times 10^{30}]^{1/2} = 0.438 \times 10^{15},
\]
and

\[ \lambda = \frac{2\pi c}{\omega} = \frac{2\pi \times 10^8}{4.38 \times 10^{15}} \approx 4.3 \times 10^{-6} \text{ m} = 4.3 \mu\text{m} \]

This simple one dimensional model of the CO₂ molecular motions yields the absorption wavelength of 4.3 micron observed in the spectra. Considering two dimensional vibrations yields the solution at 15 micron.