It is important to determine if a set of vectors is linearly dependent or independent.

Consider a set of vectors $\vec{A}$, $\vec{B}$, and $\vec{C}$. If we can find $a$, $b$, and $c$ such that,

\[ a\vec{A} + b\vec{B} + c\vec{C} = 0 \]

Then this set of vectors is linearly dependent.

More generally, if we have $N$ vectors $v_n$, and we can find a set of coefficients $c_n$,

\[ \sum_{n=1}^{N} c_n v_n = 0 \]

Then the vectors are linearly dependent. (Note that we don’t count the case where $c_n = 0$ for all $n$).
Linear dependence and independence continued, and homogeneous equations

For example, think of vectors $\vec{A}$, $\vec{B}$, and $\vec{C}$ in 3 dimensions that all lie in the same plane. Since we only need two vectors to define a plane, these vectors must be linearly dependent.

- We can take the condition $\sum_{n=1}^{N} c_n v_n = 0$ and write a matrix $A$ whose columns are the vectors $v_n$, and a column vector $c$ whose elements are the $c_n$,
- Then we solve the *homogeneous equations*

$$Ac = 0$$
Homogeneous equations, continued

• Trivial solution $c = 0$ always exists
• If we have $n$ equations and $n$ unknowns, only a non-trivial solution exists if the number of linearly independent equations (rows) is less than the number of unknowns
• Think of row reduction; at least one row must be reduced to zero
• In elementary row reduction, combining rows does not change determinant
• If we have $n$ equations and $n$ unknowns, a non-trivial solution exists only if $\det A = 0$
• If we have more vectors than the dimension of the vectors, they are always dependent
Connection to Cramer’s rule

\[ a_1x + b_1y = c_1 \]
\[ a_2x + b_2y = c_2 \]

Using row-reduction, we find

\[
x = \frac{\begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}
\]
\[
y = \frac{\begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}
\]

• Thus \( x = 0, y = 0 \) if \( c_1 = c_2 = 0 \), unless \( \det A \neq 0 \).
Eigenvalues and eigenvectors; diagonalization

- We have described linear operators acting on vectors in some space to yield new vectors

\[ Mr = k \]

- A special case occurs when \( k = \lambda r \), where \( \lambda \) is just a number called an eigenvalue

\[ Mr = \lambda r \]

- We can write this in index notation as,

\[ \sum_j M_{ij} r_j = \lambda r_i \]

- The vector \( r \) in this case is the eigenvector corresponding to the eigenvalue \( \lambda \)

- For a square \( n \times n \) matrix, there can be \( n \) eigenvalues and \( n \) corresponding eigenvectors
Once we have found all the eigenvectors and eigenvalues, we can *diagonalize* the matrix. Consider the simple $2 \times 2$ matrix $\sigma_x$

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]

If we want the eigenvectors and eigenvalues, we want to solve

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \lambda \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} \]

First write the homogeneous equation

\[ \begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0 \]
Matrix diagonalization, continued

- We know that nontrivial solutions exist when
  \[ \begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = 0 \]

- In this case, the two rows are linearly dependent, and an infinite number of solutions exist
- Taking the determinant, we get
  \[ \lambda^2 - 1 = 0 \]

- We find eigenvalues \( \lambda_1 = 1 \), and \( \lambda_2 = -1 \)
Finding the eigenvectors

• For $\lambda_1 = 1$, the eigenvector is found from

$$\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$$

• We find $v_1 = v_2$. Usually we normalize to make a unit vector, so for $\lambda_1 = 1$ we have eigenvector

$$\begin{pmatrix} v_1 \\ v_2 \end{pmatrix}_1 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$$

• For $\lambda_1 = -1$, the eigenvector is found from

$$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$$

• We find $v_1 = -v_2$, so for $\lambda_2 = -1$ we have eigenvector

$$\begin{pmatrix} v_1 \\ v_2 \end{pmatrix}_2 = \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$$
Properties of the eigenvalues and eigenvectors

- Notice that in the last case, \( \lambda_1 \) and \( \lambda_2 \) were real.
- Also, notice that the eigenvectors are orthonormal.

\[
\begin{pmatrix}
1/\sqrt{2} & -1/\sqrt{2}
\end{pmatrix}
\begin{pmatrix}
1/\sqrt{2} \\
1/\sqrt{2}
\end{pmatrix} = 0
\]

\[
\begin{pmatrix}
1/\sqrt{2} & -1/\sqrt{2}
\end{pmatrix}
\begin{pmatrix}
1/\sqrt{2} \\
-1/\sqrt{2}
\end{pmatrix} = \begin{pmatrix}
1/\sqrt{2} & 1/\sqrt{2}
\end{pmatrix}
\begin{pmatrix}
1/\sqrt{2} \\
1/\sqrt{2}
\end{pmatrix} = 1
\]
Matrix diagonalization

- We can diagonalize a matrix $M$ by making a matrix $U$ with columns as the eigenvectors of $A$
- We can find $U^{-1}$
- Then we have $U^{-1}MU = D$, where $D$ is a matrix of the eigenvalues
- Called a similarity transformation
Hermitian matrices

• Take $A^\dagger$ as the adjoint, and define it as

$$A^\dagger = (A^*)^T$$

• If $A^\dagger = A$, the matrix is said to be Hermitian
• The eigenvalues of a Hermitian matrix are real, and the eigenvectors are orthogonal (and can be made orthonormal)
• Proof:

$$Hr = \lambda r$$

• Take the adjoint of both sides to get equation

$$r^\dagger H = \lambda^* r^\dagger$$
Proof, continued

• Multiply first equation by $r^\dagger$ on left, second equation by $r$ on right, and combine them

$$(\lambda^* - \lambda)r^\dagger r = 0$$

• Now take two vectors $r_1$, $r_2$, with $Hr_1 = \lambda_1 r_1$ and $Hr_2 = \lambda_2 r_2$

• We can multiply first equation on left by $r_2^\dagger$

$$r_2^\dagger Hr_1 = \lambda_1 r_2^\dagger r_1$$

• Multiply second equation on left by $r_1^\dagger$

$$r_1^\dagger Hr_2 = \lambda_2 r_1^\dagger r_2$$
• Take adjoint of second equation, and use $H^\dagger = H$

$$(r_1^\dagger H r_2)^\dagger = r_2^\dagger H r_1 = \lambda_1 r_2^\dagger r_1 = (\lambda_2 r_1^\dagger r_2)^\dagger = \lambda_2 r_2^\dagger r_1$$

• So finally we have, using $\lambda_2^* = \lambda_2$

$$(\lambda_1 - \lambda_2) r_2^\dagger r_1 = 0$$

• So then $r_i^\dagger r_j = \delta_{i,j}$ for normalized vectors
Applications of diagonalization; normal vibrational modes

- Consider a simple model of a linear triatomic molecule (see Fig. 12.2 in text)
- Take a specific case (for fun), of CO$_2$, so $\frac{m}{M} = \frac{16}{12} = \frac{4}{3}$.
- Hence, $M = \frac{3}{4} m$, and $m = 16$ amu
- We can find the equations of motion:

  \begin{align*}
  m\ddot{x} &= -k(x - y) \\
  M\ddot{y} &= -k(y - x) - k(y - z) \\
  m\ddot{z} &= -k(z - y)
  \end{align*}

- Now we assume a solution of the form

  \[
  \begin{pmatrix}
  x(t) \\
  y(t) \\
  z(t)
  \end{pmatrix}
  =
  \begin{pmatrix}
  x_0 \\
  y_0 \\
  z_0
  \end{pmatrix}
  e^{i\omega t}
  \]
• We can write the equations of motion then as a matrix equation

\[-\omega^2 \begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} = \begin{pmatrix} -k & k & 0 \\ k & -2k & k \\ 0 & k & -k \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} \]

• We can easily invert the matrix of the masses, and then write the homogeneous equation

\[
\begin{pmatrix} \omega^2 - \frac{k}{m} & \frac{k}{m} & 0 \\ \frac{k}{M} & \omega^2 - \frac{2k}{M} & \frac{k}{M} \\ 0 & \frac{k}{m} & \omega^2 - \frac{k}{m} \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} = 0
\]

• We find from this \( \omega_1 = \sqrt{\dfrac{k}{m}} \) and \( \omega_2 = \sqrt{\left(\dfrac{k}{m}\right)(1 + \dfrac{2m}{M})} \)
Eigenvectors for linear triatomic molecule

• For $\omega_1 = \sqrt{\frac{k}{m}}$, we find the eigenvector from

$$
\begin{pmatrix}
0 & \frac{k}{m} & 0 \\
\frac{k}{M} & \frac{k}{m} - \frac{2k}{M} & \frac{k}{M} \\
0 & \frac{k}{m} & 0
\end{pmatrix}
\begin{pmatrix}
x_0 \\
y_0 \\
z_0
\end{pmatrix}
= 0
$$

We find then the symmetric stretch mode

$$
\begin{pmatrix}
x_0 \\
y_0 \\
z_0
\end{pmatrix}
_1
= \begin{pmatrix}
\frac{1}{\sqrt{2}} \\
0 \\
-\frac{1}{\sqrt{2}}
\end{pmatrix}
$$
Eigenvectors continued

- For $\omega_2 = \sqrt{\left(\frac{k}{m}\right)(1 + \frac{2m}{M})}$, we find the eigenvector from

$$
\begin{pmatrix}
\frac{2k}{M} & \frac{k}{m} & 0 \\
\frac{k}{M} & \frac{k}{m} & \frac{k}{M} \\
0 & \frac{k}{m} & \frac{2k}{M}
\end{pmatrix}
\begin{pmatrix}
x_0 \\
y_0 \\
z_0
\end{pmatrix}
= 0
$$

- We find $x_0 = z_0$, and $y_0 = -\frac{2m}{M}x_0 = -\frac{2m}{M}z_0$, or if we normalize the asymmetric stretch mode

$$
\begin{pmatrix}
x_0 \\
y_0 \\
z_0
\end{pmatrix}_2
= \begin{pmatrix}
2^{-1/2}(1 + \frac{2m^2}{M^2})^{-1/2} \\
-2^{1/2}(2 + \frac{M^2}{m^2})^{-1/2} \\
2^{-1/2}(1 + \frac{2m^2}{M^2})^{-1/2}
\end{pmatrix}
$$
A particular case... CO₂

- Take a specific case (for fun), of CO₂, so \( \frac{m}{M} = \frac{16}{12} = \frac{4}{3} \).
- Hence, \( M = \frac{3}{4} m \), and \( m = 16 \text{amu} \).
- In experiment, the two frequencies are found 1388 cm\(^{-1}\) and 2349 cm\(^{-1}\), so

\[
\nu_1 = (3 \times 10^{10} \text{cm/s})(1388 \text{cm}^{-1}) = 4.16 \times 10^{13} \text{s}^{-1} = 41.6 \text{THz}
\]

\[
\nu_2 = (3 \times 10^{10} \text{cm/s})(2349 \text{cm}^{-1}) = 7.05 \times 10^{13} \text{s}^{-1} = 70.5 \text{THz}
\]

- We find \( \frac{\nu_2}{\nu_1} \approx 1.69 \).
• We expect from our simple theory that

\[ \frac{\nu_2}{\nu_1} = \sqrt{1 + \frac{2m}{M}} \]

• We have here \( \frac{m}{M} = \frac{4}{3} \) so,

\[ \frac{\nu_2}{\nu_1} = \sqrt{1 + \frac{8}{3}} = \sqrt{\frac{11}{3}} \approx 1.91 \]

• Comparison to experiment \( \frac{70.5}{41.6} \approx 1.69 \ldots \) not too bad
• We could estimate \( k \) (for example using the symmetric stretch mode \( \nu_1 = 41.6\ THz \) and \( m = 12\ amu \)), \( k = m\omega_1^2 \)

\[ k = \left[ \frac{(16\ g/mol)(10^{-3}\ kg/g)}{6.022 \times 10^{23}\ mol^{-1}} \right] (2\pi)^2 (41.6 \times 10^{12}\ s^{-1})^2 \approx 1814\ J/m^2 \]

• Might be better expressed as \( k \approx 113.3\ \frac{eV}{A^2} \)