Eigenvalues and eigenvectors

Eigenvector, v_λ, and **eigenvalue**, λ, of square matrix A are defined by

$$A\cdot v_\lambda = \lambda v_\lambda \quad \text{or} \quad (A-\lambda\delta)\cdot v_\lambda = 0$$

δ = unit matrix

The second equation can hold (for nonzero vector v_λ) only if matrix $A-\lambda\delta$ is singular, i.e:

$$\det(A-\lambda\delta)=0$$

⇒ algebraic equation of the n-th degree, with n roots (multiplicity included).

Examples: The weighted matrix of the 2nd derivatives of a potential in a calculation of fundamental frequencies, heat (conduction) equation, wave equation, Schrödinger equation, stochastic matrix, system of linear differential equations, simultaneous 1st order kinetic equations . . .

Example. Calculate eigenvalues and eigenvectors of matrix

mmpc2.mw
mmpc2/2a-eigenC2.py

$$\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$$

$$(1-\lambda)^2-(-1\times 1)=0 \Rightarrow \lambda=\{1+i,1-i\},\quad \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\cdot\begin{pmatrix} x \\ y \end{pmatrix}=(1+i)\begin{pmatrix} x \\ y \end{pmatrix} \Rightarrow v_\lambda=\left\{\begin{pmatrix} i \\ 1 \end{pmatrix},\begin{pmatrix} -i \\ 1 \end{pmatrix}\right\}$$

Eigenvalues

A **symmetric** matrix (in $\mathbb{R}$): $A=A^{\mathsf{T}}$

A **self-adjoint** (Hermitian, Hermitean) matrix (in $\mathbb{C}$): $A=A^\dagger$, $A^\dagger\equiv(A^*)^{\mathsf{T}}$

Eigenvalues of a self-adjoint (symmetric in $\mathbb{R}$) matrix are real.

Proof: Left-multiply $A\cdot v=\lambda v$ by $v^\dagger$:

$$v^\dagger\cdot A\cdot v = \sum_{ij} v_i^* A_{ij} v_j = \sum_i v_i^*\lambda v_i = \lambda|v|^2$$

$$= \sum_{ij} v_i^* A_{ji}^* v_j = \sum_{ij} v_j A_{ji}^* v_i^* = \left(\sum_{ij} v_j^* A_{ji} v_i\right)^* = \lambda^*|v|^2$$

$\Rightarrow \lambda=\lambda^* \Rightarrow \lambda\in\mathbb{R}$.

- The proof for symmetric matrices in $\mathbb{R}$ uses a (richer) complex Hilbert space.
- Matrices in $\mathbb{R}$ have real eigenvalues or pairs of complex conjugate ones.

The eigenvectors of a regular (invertible) matrix A are the same, the eigenvalues are reciprocal. The eigenvectors of A^n, $n=2,3\ldots$, are the same, the eigenvalues are ^{n}.

Matrix of rotation again

An orthogonal matrix R in 3D (rotation or improper rotation by α around an axis) has 3 eigenvalues:

$$\{1,\cos\alpha+i\sin\alpha,\cos\alpha-i\sin\alpha\}$$

Proof: It is enough to consider matrix of rotation by α around axis $\hat{z}$ ↘; cf. mmpc1.mw (general).

The eigenvector corresponding to eigenvalue of 1 is the axis of rotation (this vector does not change by applying the rotation). For the angle of rotation, it holds:

$$2\cos\alpha+1=\mathrm{Tr}\,R$$

because the trace

$$\mathrm{Tr}\,A=\sum_i A_{ii}$$

is invariant under basis change.

$$\begin{vmatrix} \cos\alpha-\lambda & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha-\lambda & 0 \\ 0 & 0 & 1-\lambda \end{vmatrix}=0$$

$$[(\cos\alpha-\lambda)^2+\sin^2\alpha](1-\lambda)=0$$

$$[\lambda^2-2\lambda\cos\alpha+1](1-\lambda)=0$$

Proof:

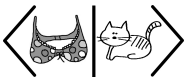
- $\mathrm{Tr}(ABC)=\mathrm{Tr}(BCA)=\mathrm{Tr}(CAB)=\sum_{ijk}A_{ij}B_{jk}C_{ki}$
- $\mathrm{Tr}(X^{-1}AX)=\mathrm{Tr}(AXX^{-1})=\mathrm{Tr}\,A$ (basis change)

Bra-ket notation

Vector = "ket" = $|v\rangle$, $|v\rangle_i=v_i$ ("column vector")

Co-vector = "bra" = Hermitean conjugate:

$$|v\rangle^\dagger=\langle v|,\ \langle v|_i=v_i^*\ \text{("row vector")}$$



Scalar product: $\langle u|v\rangle=\sum_i u_i^* v_i=\sum_i\langle u|_i|v\rangle_i=\sum_i|u\rangle_i^*\langle v|_i^*=\sum_i\langle v|_i^*|u\rangle_i^*=\langle v|u\rangle^*$

Operator: A or $\hat{A}$: $|Av\rangle$, in some context also $A|v\rangle$; $|Av\rangle_i=\sum_j A_{ij}v_j$

Definition: Operator acting on a bra: $\langle uA|=$ bra such that $\langle uA|v\rangle=\langle u|Av\rangle\equiv\langle u|A|v\rangle\ \forall v$;

Hence, we can write a matrix element as: $\langle u|A|v\rangle=\sum_{ij}u_i^*A_{ij}v_j$

In coordinates: $\langle uA|_j=\sum_i u_i^*A_{ij}=(\sum_i u_iA_{ij}^*)^*=(\sum_i A_{ij}^\dagger u_i)^*=(A^\dagger u)_j^*$

Any matrix: $\langle u|A^\dagger|v\rangle=\langle v|A|u\rangle^*$

Distinguish: $\langle Au|$ and $\langle uA|$: $\langle Au|_j=(|Au\rangle^\dagger)_j=\sum_i A_{ji}^*u_i^*$

For a Hermitean (self-adjoint) matrix: $A^\dagger=A\Rightarrow\langle u|A|v\rangle=\langle v|A|u\rangle^*$ (it is also scalar product)

Proving $\lambda\in\mathbb{R}$ again: $\langle v|A|v\rangle=\langle v|\lambda v\rangle=\lambda\langle v|v\rangle\overset{!}{=}\langle v|A|v\rangle^*=\lambda^*\langle v|v\rangle$

credit: http://backreaction.blogspot.cz/2006/07/bra-cat.html

Orthogonality of eigenvectors

Eigenvectors (of different eigenvalues) of a self-adjoint matrix are perpendicular.

Proof:

$$\langle v^{(2)}|A|v^{(1)}\rangle = \langle v^{(2)}|Av^{(1)}\rangle=\langle v^{(2)}|\lambda_1 v^{(1)}\rangle=\lambda_1\langle v^{(2)}|v^{(1)}\rangle$$

$$= \langle v^{(1)}|A|v^{(2)}\rangle^*=[\lambda_2\langle v^{(1)}|v^{(2)}\rangle]^*=\lambda_2^*\langle v^{(2)}|v^{(1)}\rangle=\lambda_2\langle v^{(2)}|v^{(1)}\rangle$$

which can hold (for $\lambda_1\neq\lambda_2$), only if $\langle v^{(1)}|v^{(2)}\rangle=0$. We can always orthonormalize a subspace of degenerate eigenvalues, hence **a self-adjoint matrix generates an orthogonal basis**.

In coordinates:

mmpc2.mw, mmpc2/2b-eigenR3.py

$$\sum_{ij}v_i^{(2)*}A_{ij}v_j^{(1)} = \sum_i v_i^{(2)*}\sum_j A_{ij}v_j^{(1)}=\sum_i v_i^{(2)*}\lambda_1 v_i^{(1)}=\lambda_1\sum_i v_i^{(2)*}v_i^{(1)}$$

$$= \sum_{ij}v_j^{(1)}A_{ji}^*v_i^{(2)*}=\sum_j v_j^{(1)}\lambda_2^*v_j^{(2)*}=\lambda_2^*\sum_i v_i^{(1)}v_i^{(2)*}=\lambda_2\sum_i v_i^{(2)*}v_i^{(1)}$$

Spectral theorem

A similar statement ("spectral theorem") holds for **compact** self-adjoint operators in ∞-dimensional Hilbert spaces. Various generalizations exist.

Hermitean in physics = self-adjoint, in mathematics there are subtleties: the generated basis may not span the entire Hilbert space.

Compact operator:
A map of an infinite sequence in a 1-ball contains a Cauchy subsequence (which converges).
An operator is compact if it is bounded and it maps a compact (= closed + bounded) set to a set whose closure space is compact (closure = set + boundary).
Loosely: An image of a 1-ball shrinks enough ("in higher dimensions").

Compact set X:
Every sequence in X has a convergent subsequence whose limit is in X.
Every open cover of X has a finite subcover.
Loosely (Peter Lax): A compact city can be guarded by finitely many near-sighted policemen.

Examples:

- Operator diag$\{1,1/4,1/9,\ldots\}$ is compact self-adjoint.
- Identity $\delta=$ diag$\{1,1,1,\ldots\}$ in an ∞-dimensional space is not compact.
- Operator $\hat{p}_x=-i\hbar\frac{\partial}{\partial x}$ in L^2 is self-adjoint (proof: per partes, watch * and order!) but not compact (proof: $g_n=e^{inx}f(x)\in L^2$ is Cauchy, $\hat{p}_x g_n(x)$ is not).

Diagonalization of a symmetric matrix

Let $A\in\mathbb{R}^n\times\mathbb{R}^n$ be a symmetric matrix and $b^{(j)}$ be its eigenvectors, $|b^{(j)}|=1$.
Let matrix U be composed of column vectors $b^{(j)}$; i.e., $U_{ij}=b_i^{(j)}$.
Then $b^{(j)\top}\cdot b^{(k)}=\delta_{jk}\ \Rightarrow\ U$ is orthogonal, $U^{\mathsf{T}}\cdot U=\delta$.
The eigenvector condition becomes:

$$b^{(i)\mathsf{T}}\cdot A\cdot b^{(j)}=b^{(i)\mathsf{T}}\cdot\lambda_j b^{(j)}=\lambda_j\delta_{ij} \quad\Rightarrow\quad U^{\mathsf{T}}\cdot A\cdot U=\begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_n \end{pmatrix}=\Lambda\ \text{(diagonal matrix)}$$

For $x=U\cdot u$ or $u=U^{-1}\cdot x\equiv U^{\mathsf{T}}\cdot x$, we get a diagonal quadratic form

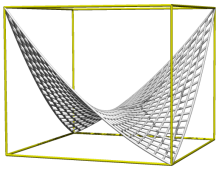
$$x^{\mathsf{T}}\cdot A\cdot x=u^{\mathsf{T}}\cdot U^{\mathsf{T}}\cdot A\cdot U\cdot u=u^{\mathsf{T}}\cdot\Lambda\cdot u=\sum_i\lambda_i u_i^2$$

Similarly in $\mathbb{C}$ for self-adjoint matrices ($^{\mathsf{T}}$ replaced by †)

Thus "diagonalization = calculating eigenvectors and eigenvalues".

Example – quadratic form

pic/qform.sh



$$x^2-4xy+y^2$$

Matrix:

$$A=\begin{pmatrix} 1 & -2 \\ -2 & 1 \end{pmatrix}$$

Characteristic equation:

$$\det\begin{pmatrix} 1-\lambda & -2 \\ -2 & 1-\lambda \end{pmatrix}=(1-\lambda)^2-4=\lambda^2-2\lambda-3$$

roots: $\lambda_1=-1,\lambda_2=3$. Equations for the eigenvectors:

$$Av_1=-v_1\ \Rightarrow\ v_1=\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$Av_2=3v_2\ \Rightarrow\ v_2=\begin{pmatrix} -1 \\ 1 \end{pmatrix}$$

And normalized eigenvectors → basis:

rotation by 45°

$$U=\begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}$$

Signature of a quadratic form

The signature = number of (positive,negative,zero) eigenvalues.

Example: the signature of $x^2-4xy+y^2$ is (+−)[a].

For function $f(x_i)$ in $\mathbb{R}^n$ "countinuous enough", the condition for an extreme is:

$$\frac{\partial f}{\partial x_i}=0,\ i=1,\ldots,n$$

If this holds true for x^0, the Taylor expansion at the minimum is ($A=$ Hessian):

$$f(x)=f(x^0)+\frac{1}{2}\sum_{ij}(x_i-x_i^0)A_{ij}(x_j-x_j^0),\quad A_{ij}=\frac{\partial f^2}{\partial x_i\partial x_j|_{x_i=x_i^0,x_j=x_j^0}}$$

- If the signature of A is $(n,0,0)=(++++\ldots)$, the form is **positive definite** and f has a local minimum at x^0.
- If the signature of A is $(0,n,0)=(----\ldots)$, then the form is **negative definite**, and f has a local maximum at x^0.
- If the signature contains pluses and minuses, it is **indefinite**, and f has a saddle point at x^0.

[a] Often written in form $(n_+,n_-,n_0)=(1,-1,0)$

Fundamental vibrations

Let PES be $U_{\mathrm{pot}}(\boldsymbol{\tau})$, $\boldsymbol{\tau}=\{\vec{r}_1,\ldots,\vec{r}_N,\}$, with a (local) minimum at $\boldsymbol{\tau}_{\min}$; def. $\Delta\boldsymbol{\tau}=\boldsymbol{\tau}-\boldsymbol{\tau}_{\min}$.
Taylor expansion to the 2nd order:

$$U_{\mathrm{pot}}(\boldsymbol{\tau})=U_{\mathrm{pot}}(\boldsymbol{\tau}_{\min})+\sum_i\underbrace{\frac{\partial U_{\mathrm{pot}}}{\partial\vec{r}_i}(\boldsymbol{\tau}_{\min})}_{=0}\cdot\Delta\vec{r}_i+\frac{1}{2}\sum_{i,j}\Delta\vec{r}_i\cdot\frac{\partial^2U_{\mathrm{pot}}}{\partial\vec{r}_i\partial\vec{r}_j}(\boldsymbol{\tau})\cdot\Delta\vec{r}_j+\cdots$$

Newton's equations of motion:

$$m_i\Delta\ddot{\vec{r}}_i\equiv m_i\frac{\mathrm{d}^2\Delta\vec{r}_i}{\mathrm{d}t^2}=\vec{f}_i=-\frac{\partial}{\partial\Delta\vec{r}_i}U_{\mathrm{pot}}\approx-\sum_j A_{ij}\Delta\vec{r}_j$$

where the so called **Hessian matrix** is[b]

$$A_{ij}=\frac{\partial^2U_{\mathrm{pot}}}{\partial\vec{r}_i\partial\vec{r}_j}(\boldsymbol{\tau}_{\min}),\quad\Delta\vec{r}_i=\vec{r}_i-\vec{r}_{i,\min}$$

In the matrix form (vector = $3N$ numbers, matrix = $3N\times 3N$):

$$\boldsymbol{M}\cdot\Delta\ddot{\boldsymbol{\tau}}=-\boldsymbol{A}\cdot\Delta\boldsymbol{\tau},\ \text{where}\ \boldsymbol{M}=\mathrm{diag}(m_1,m_1,m_1,\ldots,m_N,m_N,m_N)$$

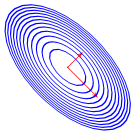
[b] by Ludwig Otto Hesse (1811–1874), German mathematician (differential geometry, group theory);
the Hess law of thermochemistry is by Germain Henri Hess (1802–1850), Swiss-Russian chemist and doctor

Fundamental vibrations

$$\boldsymbol{M}\cdot\Delta\ddot{\boldsymbol{\tau}} = -\boldsymbol{A}\cdot\Delta\boldsymbol{\tau},\ \text{where}\ \boldsymbol{M} = \text{diag}(m_1, m_1, m_1, \ldots, m_N, m_N, m_N)$$

We are looking for a transformation (basis) in the form

$$\Delta\boldsymbol{\tau} = \boldsymbol{M}^{-1/2}\cdot\boldsymbol{U}\cdot\boldsymbol{u}$$



where $\boldsymbol{U}$ is orthogonal. By inserting:

$$\boldsymbol{M}\cdot\boldsymbol{M}^{-1/2}\cdot\boldsymbol{U}\cdot\ddot{\boldsymbol{u}} = -\boldsymbol{A}\cdot\boldsymbol{M}^{-1/2}\cdot\boldsymbol{U}\cdot\boldsymbol{u}$$

Left-multiplied by $\boldsymbol{U}^{-1}\cdot\boldsymbol{M}^{-1/2}$. :

$$\ddot{\boldsymbol{u}} = -\boldsymbol{\Lambda}\cdot\boldsymbol{u},\quad \boldsymbol{\Lambda} = \boldsymbol{U}^{-1}\cdot\boldsymbol{M}^{-1/2}\cdot\boldsymbol{A}\cdot\boldsymbol{M}^{-1/2}\cdot\boldsymbol{U}$$

There exists an orthogonal matrix $\boldsymbol{U}$ so that $\boldsymbol{\Lambda} = \boldsymbol{U}^{-1}\cdot\boldsymbol{M}^{-1/2}\cdot\boldsymbol{A}\cdot\boldsymbol{M}^{-1/2}\cdot\boldsymbol{U}$ is diagonal, in other words, we diagonalize the symmetric matrix $\boldsymbol{A'}$:

$$\boldsymbol{A'} = \boldsymbol{M}^{-1/2}\cdot\boldsymbol{A}\cdot\boldsymbol{M}^{-1/2}$$

The Newton equations separate into $3N$ independent harmonic oscillators:

$$\ddot{u}_\alpha = -\Lambda_{\alpha\alpha}u_\alpha,\quad \alpha = 1, \ldots, 3N$$

The frequences are

$$\nu_\alpha = \frac{\sqrt{\Lambda_{\alpha\alpha}}}{2\pi}$$

# of zero frequencies n_0:
6 for general molecules
5 for linear molecules
3 for atoms
$n_{\text{vibr}} = 3N - n_0$

Fundamental vibrations – diatomic molecule

Two atoms connected by a spring:

$$U_{\text{pot}} = \frac{K}{2}(x-y)^2 \ \Rightarrow\ \boldsymbol{A'} = \begin{pmatrix} K/m & -K/m \\ -K/m & K/m \end{pmatrix}$$

$$\left(\frac{K}{m}-\lambda\right)^2 = \left(\frac{K}{m}\right)^2 \ \Rightarrow\ \frac{K}{m}-\lambda = \pm\frac{K}{m} \ \Rightarrow\ \lambda \in \{2K/m, 0\}$$

The frequences are

$$\nu_1 = \frac{\sqrt{2K/m}}{2\pi}\ \text{(sym. stretch)},\quad \nu_2 = 0\ \text{(translation)}$$

Unnormalized eigenvectors:

$$\boldsymbol{\psi}_1 = \begin{pmatrix} 1 \\ -1 \end{pmatrix},\ \boldsymbol{\psi}_2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$\boldsymbol{\psi}_1$: →← $\boldsymbol{\psi}_2$: →→

Try vibrations yourself – connect to a linux computer

- On disk S: = pyr.vscht.cz/scratch: Find subdirectory KOLAFA → Connect → MobaXterm and run MobaXterm_Personal_26.6.exe.

  Or find on the web "MobaXterm Home Edition – Portable".

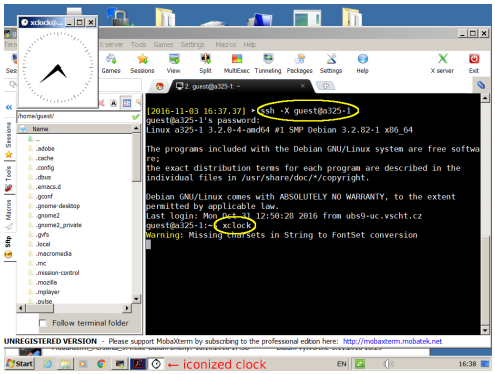
computers:
403-a325-05 (4 cores)
403-a324-01 (Argon, 6 cores)

- Click + Start local terminal.
- Write the chosen relation; e.g., :
  `[2019-11-11 11:11.11] ssh -X guest@403-a325-05.vscht.cz`
  NB: -X = X11 forwarding (graphics will be available) with extended security control.
  Enter PASSWD given (no response while writing PASSWD).

  If there are problems, try:
  `[2019-11-11 11:11.11] ssh -Y guest@403-a325-05.vscht.cz`
  NB: -Y = X11 forwarding without extended security control.

  Alternatively, use menu and select X-window forwarding.
- See also PuTTY + XMing (sometimes installed).
- To test, type xclock to the terminal – a clock should appear. If it does not and you do not see any error message, it may be iconized: find it in the bottom bar.

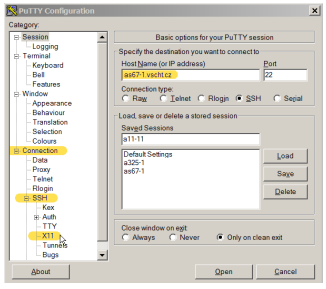
Connect by MobaXterm



If MobaXterm does not work: Connect by PuTTY + XMing

Terminal PuTTY

- Windows Start → Search → putty → Open
  or find on the net the executable version
- Host name → 403-a325-05 or other computer
- Connection → ⊞ SSH → Tunnels → X11
  → ☒ Enable X11 forwarding
- back to Session → Open
- Login as: guest
- Password: PASSWD



X server to show graphics (Xming)

- Windows Start → Search → xming → Open
  or find on the net the executable version
- You should see the following icon in the bottom panel:

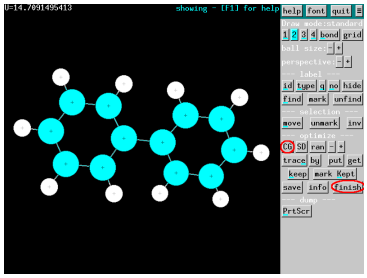
Try vibrations yourself

- Start Midnight Commander by:
  `guest@403-a324-01:~/CHE$ CHE=2 mc`
- Check that you are in directory ~/CHE (is a symlink)
- Double-click a che-file. First, MM program blend starts:
  - Click finish or . to minimize, and calculate vibrations (do not use quit = not saved).
  - In case of problems, check whether the molecule is optimized by CG (also hot key ,),
    and/or try editing: click an atom, move + mid button, CG, or rand etc.
  - Right-clicking any button shows context help.
- Then, molecule viewer show starts (if not, type Ctrl-O in the Midnight Commander window and check a possible message). Watch vibrations:
  - Use < / > (bottom of the control panel) or PgUp / PgDn to switch vibrational modes.
    NB: modes 0..5 (0..4 for a linear molecule) correspond to translations and rotations ($\nu \approx 0$).
  - Use 1 .. 7 etc. to change showing style, NFF to raytrace, zbuf for a stereogram, . . .
  - If needed, control speed by - + (bottom of the control panel) or s S

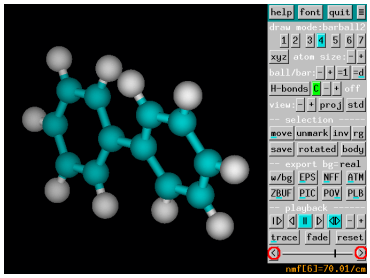
Environment variable CHE=2 tells the script che.sh associated in Midnight Commander with che-files to start normal mode calculations and showing in a unique temporary directory.

Try vibrations yourself

blend



show



Homogeneous linear differential equations of the 1st order

The system of homogeneous linear differential equations of the 1st order:

$$\left.\begin{aligned} \dot{x}_1 &= A_{11}x_1 + A_{12}x_2 + \cdots + A_{1n}x_n \\ &\vdots \\ \dot{x}_n &= A_{n1}x_1 + A_{n2}x_2 + \cdots + A_{nn}x_n \end{aligned}\right\}\quad \dot{x} = A\cdot x$$

mmpc2.mw
mmpc2/2d-consecutive.py
mmpc2/2d-cons-dsolve.py

One of n linearly independent solutions:

$$x = e^{\lambda t}v\ \Rightarrow\ A\cdot v = \lambda v$$

For real A, λ are real or complex conjugate pairs.

General solution if all λ's are diferent:

$$x = \sum_\lambda C_\lambda e^{\lambda t}v_\lambda$$

where C_λ's are determined from the initial conditions.

In case of multiple eigenvalues (roots of the characteristic equation), we have $e^{\lambda t}$, $te^{\lambda t}$, $t^2e^{\lambda t}$, etc.

The set is always equivalent to one homogeneous linear differential equations of the n-th order.

Example

$$\dot{x} = y,\ \dot{y} = -x$$

$$A = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\ \Rightarrow\ \lambda = \pm i,\ \ v_i = \begin{pmatrix} i \\ 1 \end{pmatrix}, v_{-i} = \begin{pmatrix} 1 \\ i \end{pmatrix}$$

General solution:

$$C_iv_ie^{it} + C_{-i}v_{-i}e^{-it}\quad \left\{\begin{aligned} x &= iC_ie^{it} + C_{-i}e^{-it} \\ y &= C_ie^{it} + iC_{-i}e^{-it} \end{aligned}\right.$$

With initial conditions $x(0) = 1, y(0) = 0$: $\left\{\begin{aligned} 1 &= iC_i + C_{-i} \\ 0 &= C_i + iC_{-i} \end{aligned}\right.\ \Rightarrow\ C_i = -\frac{i}{2}, C_{-i} = \frac{1}{2}$

$$x = \frac{1}{2}e^{it} + \frac{1}{2}e^{-it} = \cos t,\quad y = -\frac{i}{2}e^{it} + \frac{i}{2}e^{-it} = -\sin t$$

Equivalent differential equation of the 2nd order:

$$\ddot{x} = -x\ \ \text{(harmonic oscillator)}$$