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

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

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

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 $v^\dagger$:

$$\begin{aligned} v^\dagger \cdot A \cdot v &= \sum_{ij} v_i^* A_{ij} v_j = \sum_i v_i^* \lambda v_i = \lambda |v|^2 \\ &= \sum_{ij} v_i^* A_{ji}^* v_j = \sum_{ij} v_j A_{ji}^* v_i^* = \left(\sum_{ij} v_j^* A_{ji} v_i\right)^* = \lambda^* |v|^2 \end{aligned}$$

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

- 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

Matrix of rotation
start /home/jiri/vyuka/maple/mmpc1.mw

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:

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

because the trace

$$\operatorname{Tr} A = \sum_i A_{ii}$$

is invariant under basis change.

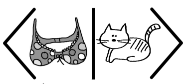
$$\begin{vmatrix} \cos\alpha - \lambda & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha-\lambda & 0 \\ 0 & 0 & 1-\lambda \end{vmatrix} = 0$$

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

Proof:

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

Bra-ket notation



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

Co-vector = "bra" = Hermitean conjugate:
$|v\rangle^\dagger = \langle v|$, $\langle v|_i = v_i^*$ ("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 $A|v\rangle$ or $|A|v\rangle$; $|Av\rangle_i = \sum_j A_{ij} v_j$

Operator acting on a bra (def.): $\langle uA|$ = 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: $\langle uA|_j = \sum_i u_i^* A_{ij} = (\sum_i u_i A_{ij}^*)^* = (\sum_i A_{ij}^* u_i)^* = (\sum_i A_{ji}^\dagger u_i)^* = |A^\dagger u\rangle_j^*$

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:

$$\begin{aligned} \langle v^{(2)}|A|v^{(1)}\rangle &= \langle v^{(2)}|Av^{(1)}\rangle = \langle v^{(2)}|\lambda_1 v^{(1)}\rangle = \lambda_1\langle v^{(2)}|v^{(1)}\rangle \\ &= \langle v^{(1)}|A|v^{(2)}\rangle^* = [\lambda_2\langle v^{(1)}|v^{(2)}\rangle]^* = \lambda_2^*\langle v^{(2)}|v^{(1)}\rangle = \lambda_2\langle v^{(2)}|v^{(1)}\rangle \end{aligned}$$

which can hold (for $\lambda_1 \ne \lambda_2$), 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:

$$\begin{aligned} \sum_{ij} v_i^{(2)*} A_{ij} v_j^{(1)} &= \sum_i v_i^{(2)*} \sum_j A_{ij} v_j^{(1)} = \sum_i v_i^{(2)*}\lambda_1 v_i^{(1)} = \lambda_1 \sum_i v_i^{(2)*} v_i^{(1)} \\ &= \sum_{ij} v_j^{(1)} A_{ji}^* v_i^{(2)*} = \sum_j v_j^{(1)} \lambda_2^* v_j^{(2)*} = \lambda_2^* \sum_i v_i^{(1)} v_i^{(2)*} = \lambda_2 \sum_i v_i^{(2)*} v_i^{(1)} \end{aligned}$$

Examples see `mmpc2.mw`

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:

- $\operatorname{diag}\{1, 1/4, 1/9, \dots\}$ is compact self-adjoint
- Identity $\delta = \operatorname{diag}\{1,1,1,\dots\}$ in an ∞-dimensional space is not compact
- $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$ is self-adjoint but not compact (proof: per partes, watch * and order!)

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 $b^{(j)\mathsf{T}} \cdot b^{(k)} = \delta_{jk}$ ⇒ 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

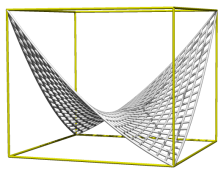
$$x^\mathsf{T}\cdot A\cdot x = u^\mathsf{T}\cdot U^\mathsf{T}\cdot A\cdot U\cdot u = u^\mathsf{T}\cdot\Lambda\cdot u = \sum_i \lambda_i u_i^2$$

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:

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

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

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

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

And normalized eigenvectors → basis:

rotation by 45°

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

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 $f(x_i)$ "countinuous enough", the condition for an extreme is:

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

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

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

- If the signature of A is $(n,0,0) = (++++\dots)$, the form is **positive definite** and f has a local minimum at x^0.
- If the signature of A is $(0,n,0) = (----\dots)$, 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 $(n_+, n_-, n_0) = (1, -1, 0)$

Sylvestr criterion (removed)

We calculate the subdeterminants.

$$\det|A_{ij}|_{i,j=1}$$

$$\det|A_{ij}|_{i,j=1..2}$$

$$\det|A_{ij}|_{i,j=1..3}$$

- All are positive at point x^0: minimum.
- Alternating signs at point x^0 $(-,+,-,\dots)$: maximum.

The proof uses the spectral theorem and the Cholesky decomposition of a Hermitean matrix $A = L^*\cdot L$, where L is a triangular matrix.

Fundamental vibrations

Let PES be $U_{\rm pot}(\boldsymbol{\tau})$, $\boldsymbol{\tau} = \{\vec r_1, \ldots, \vec r_N, \}$, with a (local) minimum at $\boldsymbol{\tau}_{\rm min}$; def. $\Delta\boldsymbol{\tau} = \boldsymbol{\tau} - \boldsymbol{\tau}_{\rm min}$.

Taylor expansion to the 2nd order:

$$U_{\rm pot}(\boldsymbol{\tau}) = U_{\rm pot}(\boldsymbol{\tau}_{\rm min}) + \underbrace{\sum_i \frac{\partial U_{\rm pot}}{\partial \vec r_i}(\boldsymbol{\tau}_{\rm min}) \cdot \Delta \vec r_i}_{=0} + \frac{1}{2}\sum_{i,j} \Delta \vec r_i \cdot \frac{\partial^2 U_{\rm pot}}{\partial \vec r_i \partial \vec r_j}(\boldsymbol{\tau}) \cdot \Delta \vec r_j$$

Newton's equations of motion:

$$m_i \Delta \ddot{\vec r}_i \equiv m_i \frac{d^2 \Delta \vec r_i}{dt^2} = \vec f_i = -\sum_j A_{ij} \Delta \vec r_j$$

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

$$A_{ij} = \frac{\partial^2 U_{\rm pot}}{\partial \vec r_i \partial \vec r_j}(\boldsymbol{\tau}_{\rm min}), \quad \Delta \vec r_i = \vec r_i - \vec r_{i,\rm min}$$

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

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

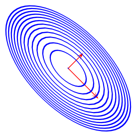
[b]by Ludwig Otto Hesse (1811–1874), German mathematician (differential geometry, group theory); the Hess law of thermochemistry is by Germain Henri Hess (1802–1850), Swiss-Russian chemist and doctor

Fundamental vibrations

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

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 $\boldsymbol{U}^{-1} \cdot \boldsymbol{M}^{-1/2} \cdot$:

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

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
$n_{\rm vibr} = 3N - n_0$

Fundamental vibrations – diatomic molecule

Two atoms connected by a spring:

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

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

The frequences are

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

Unnormalized eigenvectors:

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

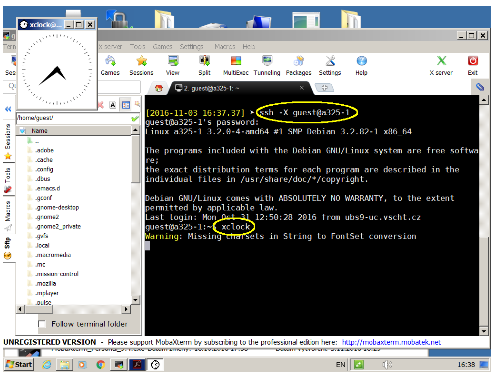
$\rightarrow\leftarrow \qquad \rightarrow\rightarrow$

Try vibrations by yourself – connect to a linux computer

computer:
403-a325-05 (4 cores)

- Check S:\pocitacova_chemie\Connect = pyr.vscht.cz/scratch/pocitacova_chemie/Connect
  or
  Find on the web "MobaXterm Home Edition – Portable"
  (Unzip and) run (skip paranoic messages)
- Click `+ Start local terminal`
- Write the chosen relation; e.g., :
  `[2019-11-11 11:11.11] ssh -X guest@403-a325-05.vscht.cz`
  Enter PASSWD given (no response while writing PASSWD)
- Alternatively, use dialog windows and select X-window forwarding
- See also PuTTY + XMing (sometimes installed)

Connect by MobaxTerm

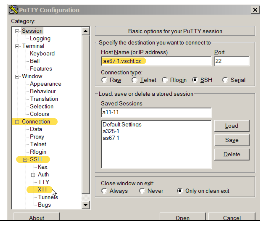


If MobaXTerm does not work: Connect by PuTTY + XMing

Terminal PuTTY

computer:
403-a325-05 (4 cores)

- Windows Start → Search → `putty` → Open
  or S:pocitacova chemie/Connect/putty64bit.exe
- 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
  S:pocitacova chemie/Connect/XLaunch.exe - Shortcut.lnk
- You should see the following icon in the bottom panel: X

Try vibrations by yourself

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.

- Start Midnight Commander by:
  `guest@403-a324-01:~/CHE$ CHE=2 mc`
- Check that you are in directory `~/CHE` (is a symlink)
- Click a che-file. First, MM program `blend` starts:
  - Right-clicking a `button` shows context help.
  - Check that the molecule is optimized by clicking `CG` (also hot key `,`)
    In case of problems, try editing: click an atom, `move` + mid button, `CG`, or `rand` etc.
  - Click `finish` or `.` to save and quit (do not use `quit` = not saved).
- 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`

Homogeneous linear differential equations of the 1st order

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

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

One of n linearly independent solutions:

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

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.

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

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

see `mmpc2.mw`

Example

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

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

General solution:

$$C_i v_i e^{it} + C_{-i} v_{-i} e^{-it} \quad \begin{cases} x = iC_i e^{it} + C_{-i} e^{-it} \\ y = C_i e^{it} + iC_{-i} e^{-it} \end{cases}$$

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

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

Equivalent differential equation of the 2nd order:

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

see `mmpc2.mw`