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:

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

$\Rightarrow$ 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

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

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

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

Matrix of rotation

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.

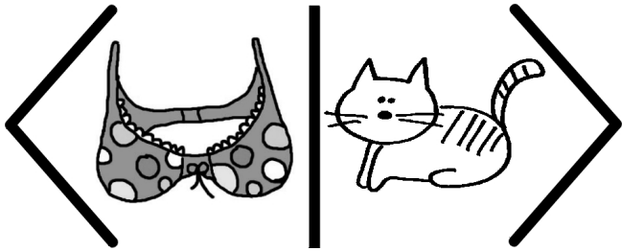
$$\begin{vmatrix} \cos\alpha - \lambda & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha - \lambda & 0 \\ 0 & 0 & 1-\lambda \end{vmatrix} = 0$$

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

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:
$|v\rangle^\dagger = \langle v|$, $\langle v|_i = v_i^*$ (“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: $\langle v|A|v\rangle = \langle v|\lambda v\rangle = \lambda \langle v|v\rangle \stackrel{!}{=} \langle v|A|v\rangle^* = \lambda^* \langle v|v\rangle$

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 $\lambda_1 \neq \lambda_2$), 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:

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

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:

- $\mathrm{diag}\{1, 1/4, 1/9, \ldots\}$ is compact self-adjoint
- Identity $\delta = \mathrm{diag}\{1, 1, 1, \ldots\}$ in an ∞-dimensional space is not compact
- $\hat{p}_x = -\mathrm{i}\hbar\frac{\partial}{\partial x}$ 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 ${b^{(j)}}^{\mathsf{T}} \cdot b^{(k)} = \delta_{jk} \quad \Rightarrow \quad U$ 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

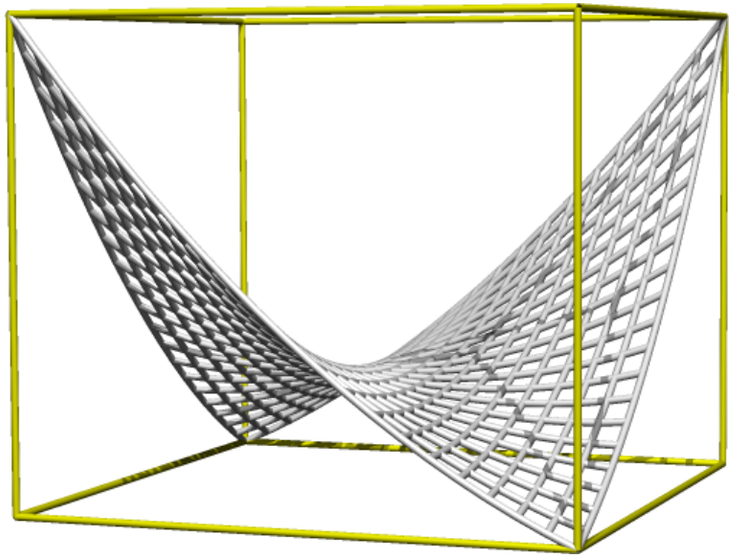
$$x^{\mathsf{T}} \cdot A \cdot x = u^{\mathsf{T}} \cdot U^{\mathsf{T}} \cdot A \cdot U \cdot u = u^{\mathsf{T}} \cdot \Lambda \cdot u = \sum_i \lambda_i u_i^2$$

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

Thus “diagonalization = calculating eigenvectors and eigenvalues”.

Example – quadratic form

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



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:

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

rotation by 45°

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:

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

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 $(n_+, n_-, n_0) = (1, -1, 0)$

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 $(-,+,-,\ldots)$: 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 $U_{\mathrm{pot}}(\boldsymbol{\tau})$, $\boldsymbol{\tau} = \{\vec{r}_1, \ldots, \vec{r}_N, \}$, with a (local) minimum at $\boldsymbol{\tau}_{\mathrm{min}}$; def. $\Delta\boldsymbol{\tau} = \boldsymbol{\tau} - \boldsymbol{\tau}_{\mathrm{min}}$.

Taylor expansion to the 2nd order:

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

Newton's equations of motion:

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

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

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

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

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

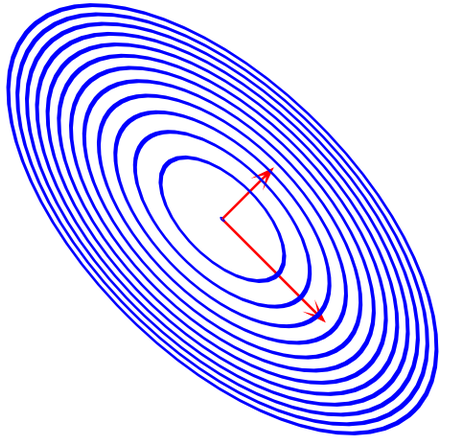
[b] by Ludwig Otto Hesse (1811–1874), German mathematician (differential geometry, group theory);
the Hess law of thermochemistry is by Germain Henri Hess (1802–1850), Swiss-Russian chemist and doctor

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

Fundamental vibrations – diatomic molecule

Two atoms connected by a spring:

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

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

The frequences are

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

Unnormalized eigenvectors:

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

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

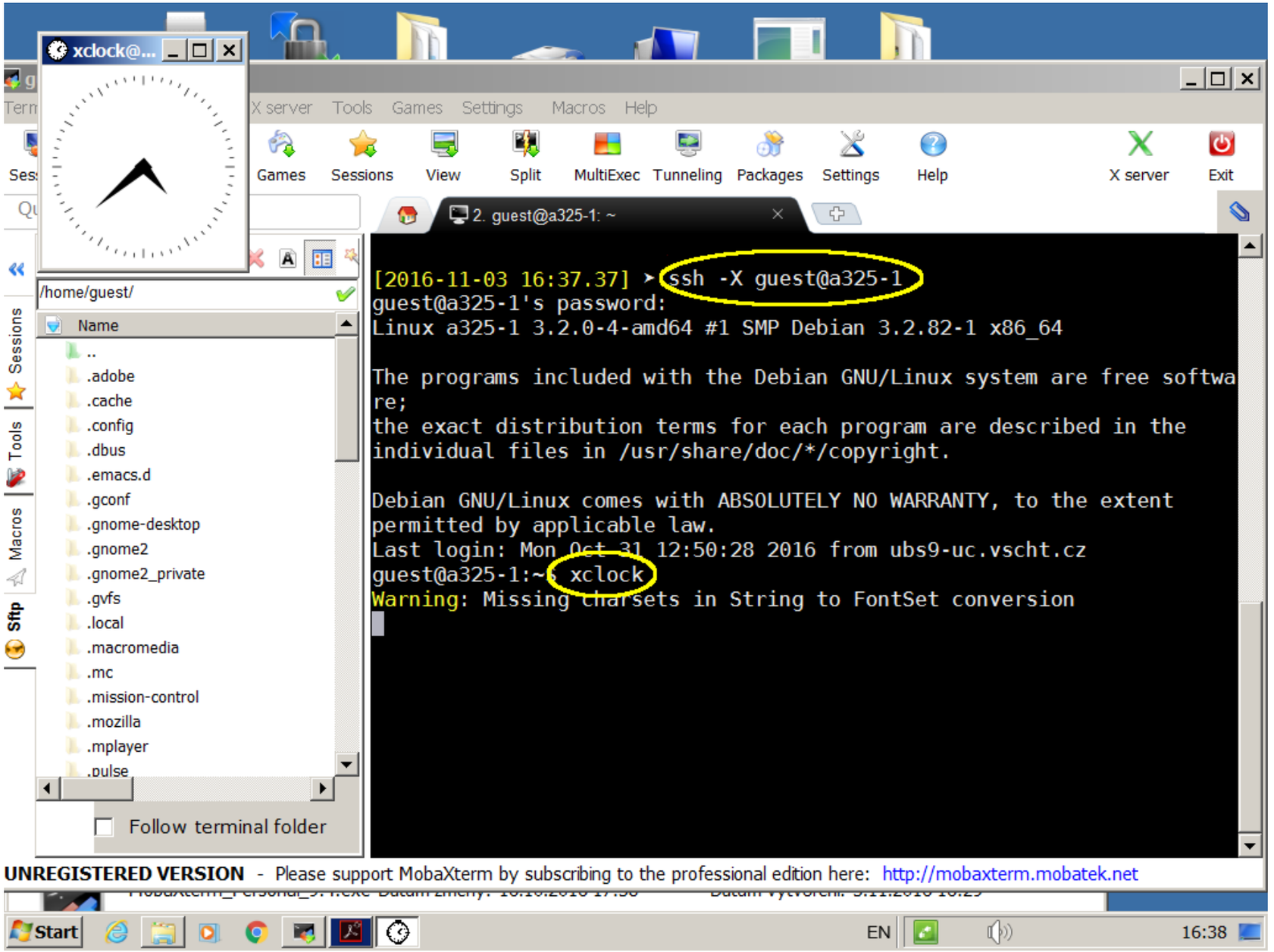
Try vibrations by yourself – connect to a linux computer

- 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)

computer:
403-a325-05 (4 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`
  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

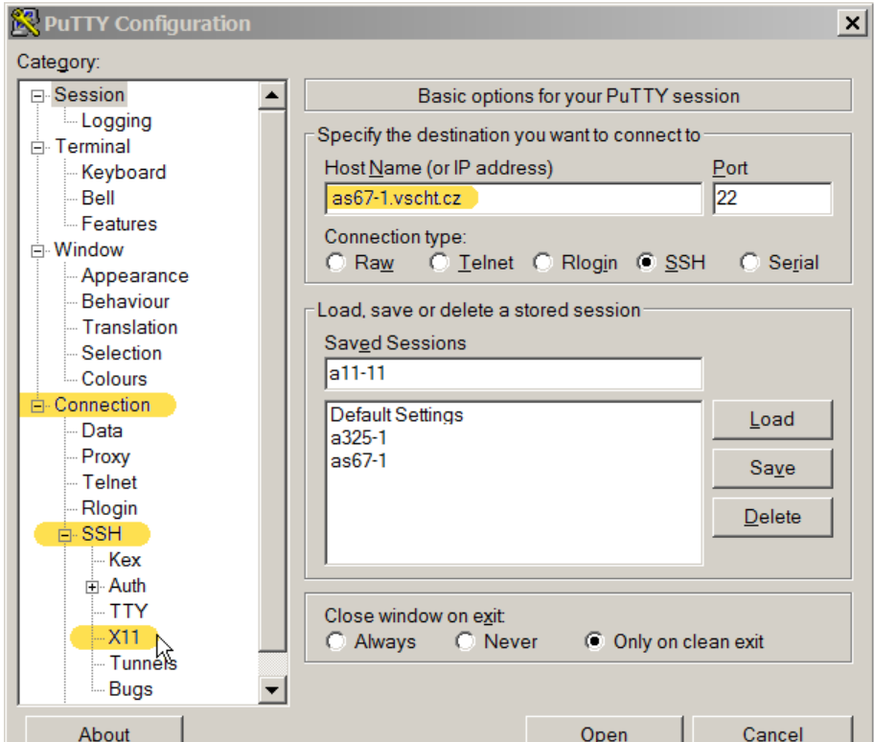


If MobaxTerm does not work: Connect by PuTTY + XMing

Terminal PuTTY

- Windows Start → Search → `putty` → Open
  or S:pocitacova chemie/Connect/putty64bit.exe
- Host name → 403-a325-05 or other computer
- Connection → [+] SSH → Tunnels → X11
  → [X] Enable X11 forwarding
- back to Session → Open
- Login as: guest
- Password: PASSWD

computer:
403-a325-05 (4 cores)



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:

Try vibrations by yourself

- 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`

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.

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:

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

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

General solution if all λ's are diferent:

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

where C_λ's are determined from the initial conditions.

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

The set is always equivalent to one homogeneous linear differential equations of the n-th order.
see `mmpc2.mw`

Example

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

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

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

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

Equivalent differential equation of the 2nd order:

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

see `mmpc2.mw`