032CM - 2025

PROGRAMMING FOR COMPUTATIONAL CHEMISTRY

Fourier analysis

Gianluca Levi

gianluca.levi@units.it, giale@hi.is

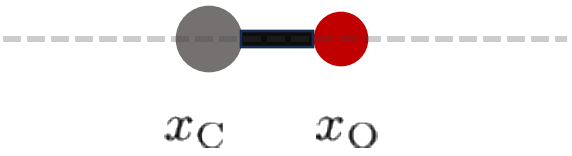
Office: Building C11, 3rd floor, Room 329

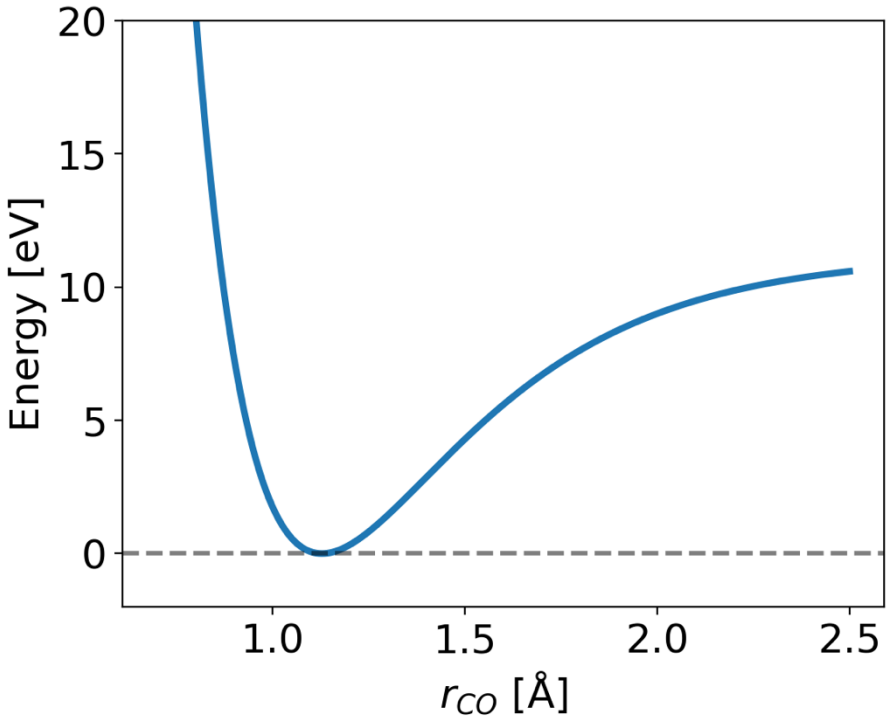
Fall 2025

Vibrational dynamics of the CO molecule (Assignment 6)

Morse potential

$$V_{\mathrm{CO}}(r) = D_{\mathrm{e}}\left(1 - e^{-\alpha(r-r_e)}\right)^2$$

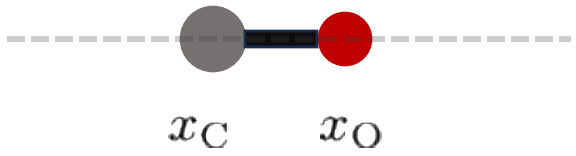


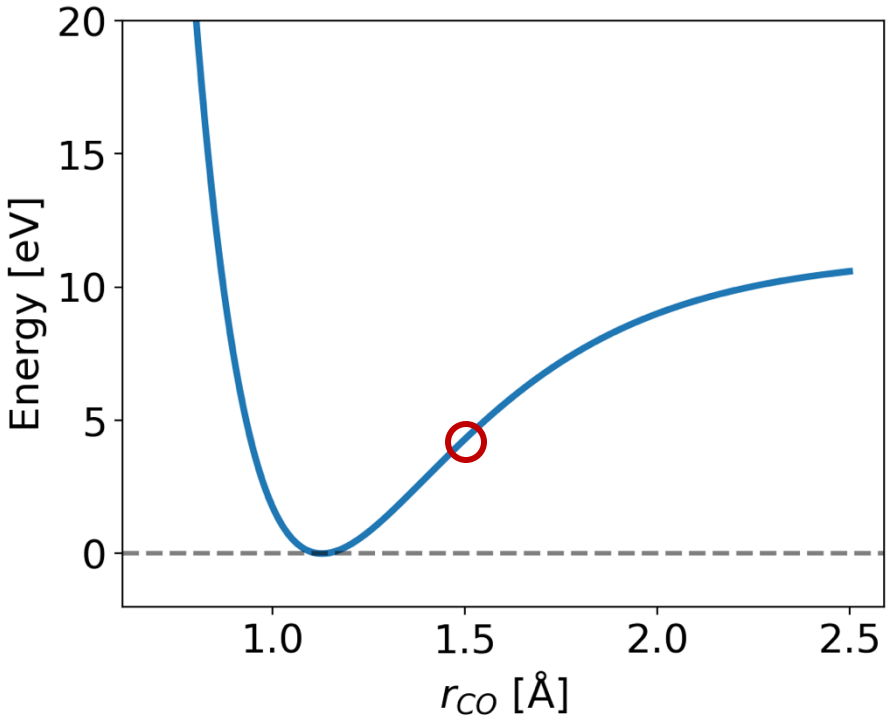


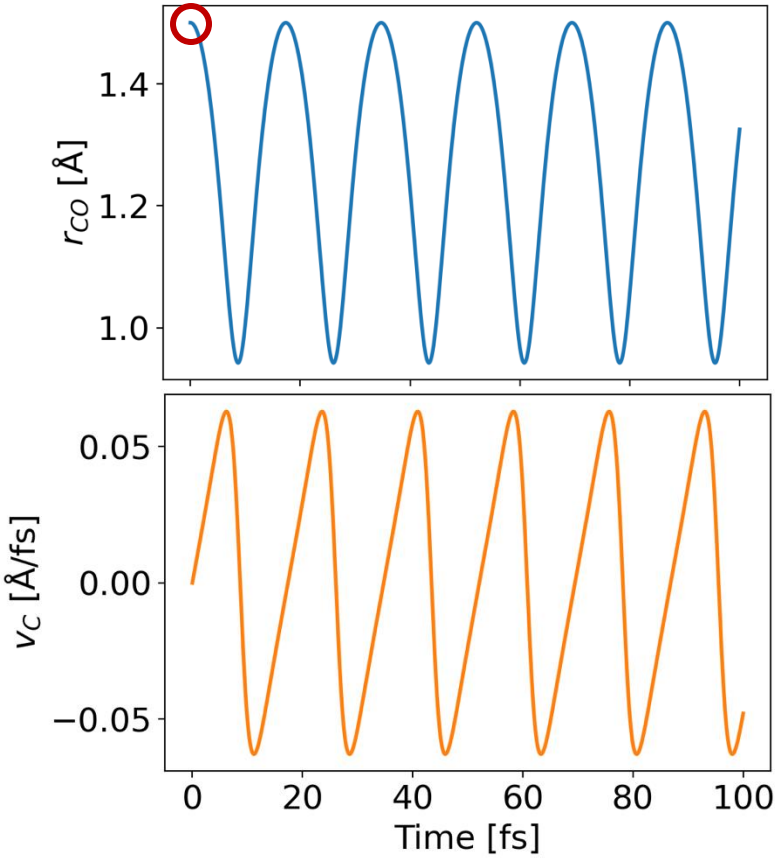
Vibrational dynamics of the CO molecule (Assignment 6)

Morse potential

$$V_{\mathrm{CO}}(r) = D_{\mathrm{e}}\left(1 - e^{-\alpha(r-r_e)}\right)^2$$



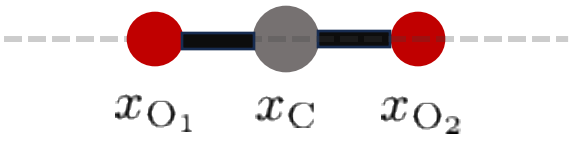




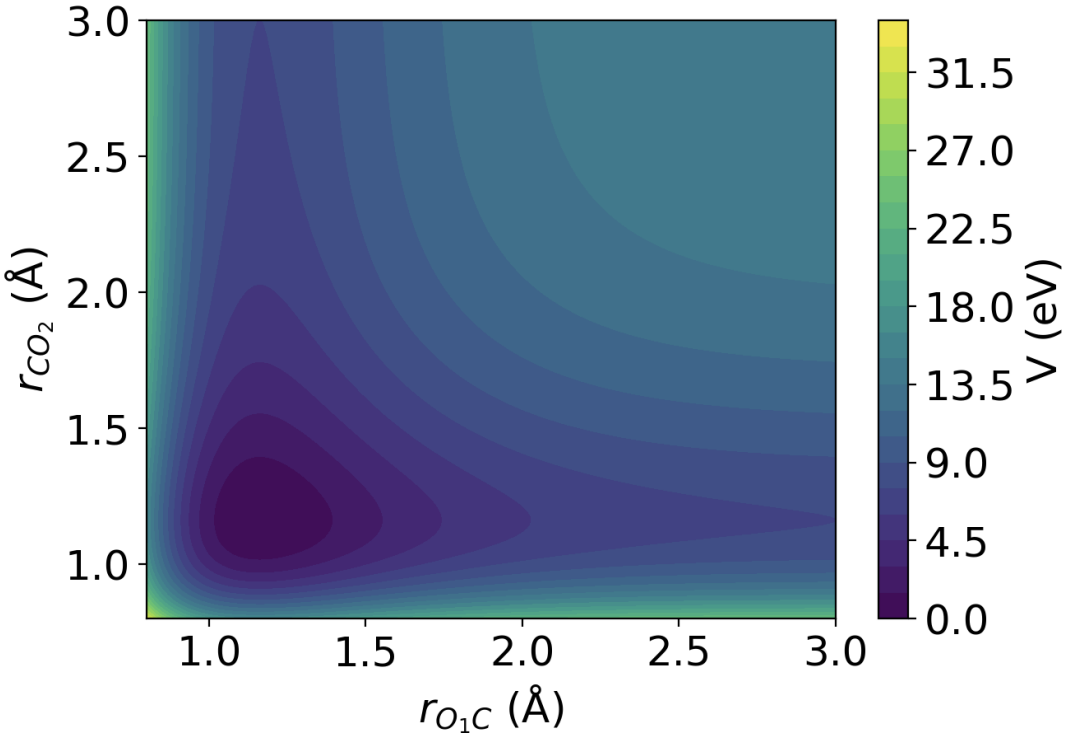
Vibrational dynamics of the CO2 molecule (Assignment 7)

Morse potential

$$V_{\mathrm{CO}}(r) = D_{\mathrm{e}}\left(1 - e^{-\alpha(r-r_e)}\right)^2$$

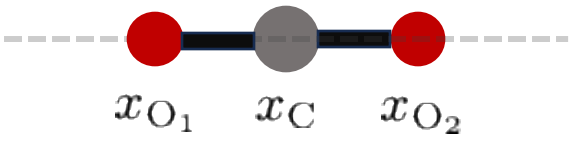


$$V(r_{O_1C}, r_{CO_2}) = V_{\mathrm{CO}}(r_{O_1C}) + V_{\mathrm{CO}}(r_{CO_2})$$



Vibrational dynamics of the CO2 molecule (Assignment 7)

Morse potential



$$V_{CO}(r) = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2$$

$$V(r_{O_1C}, r_{CO_2}) = V_{CO}(r_{O_1C}) + V_{CO}(r_{CO_2})$$

$$F_{O_1} = -\frac{\partial V}{\partial x_{O_1}} = -\frac{\partial V}{\partial r_{O_1C}} \frac{\partial r_{O_1C}}{\partial x_{O_1}}$$

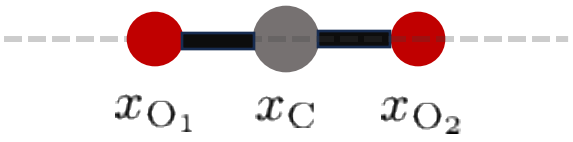
$$F_C = -\frac{\partial V}{\partial x_C} = -\frac{\partial V}{\partial r_{O_1C}} \frac{\partial r_{O_1C}}{\partial x_C} - \frac{\partial V}{\partial r_{CO_2}} \frac{\partial r_{CO_2}}{\partial x_C} = -\frac{\partial V}{\partial r_{O_1C}} + \frac{\partial V}{\partial r_{CO_2}}$$

$$F_{O_2} = -\frac{\partial V}{\partial x_{O_2}} = -\frac{\partial V}{\partial r_{CO_2}} \frac{\partial r_{CO_2}}{\partial x_{O_2}}$$

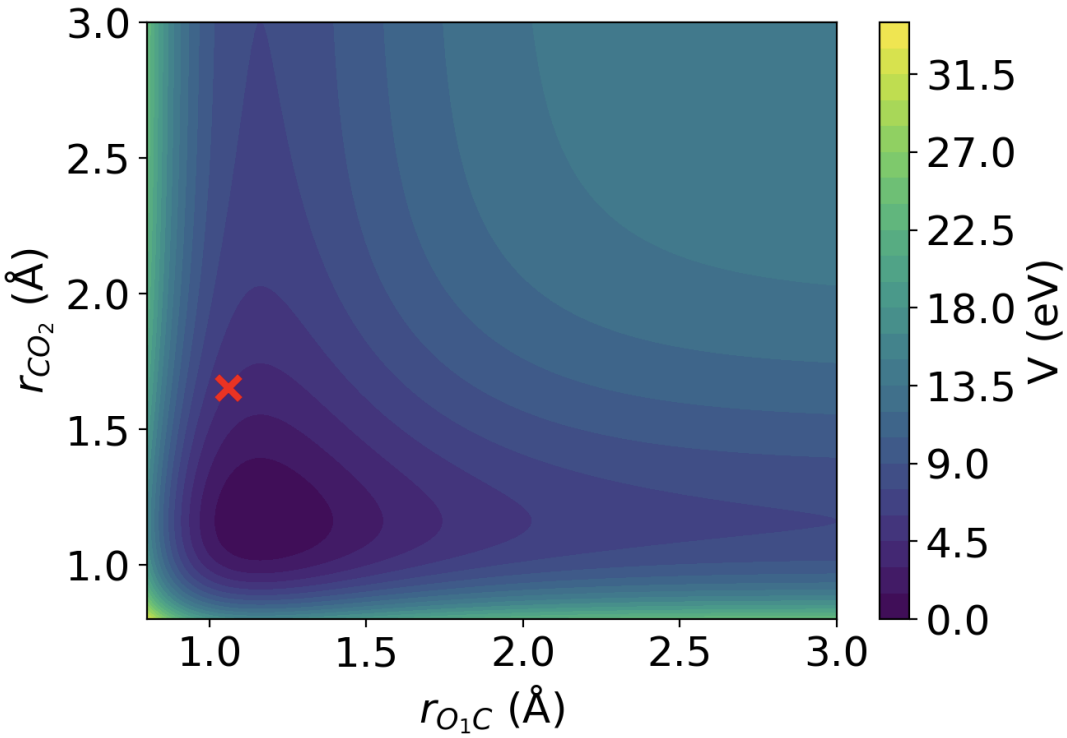
Vibrational dynamics of the CO2 molecule (Assignment 7)

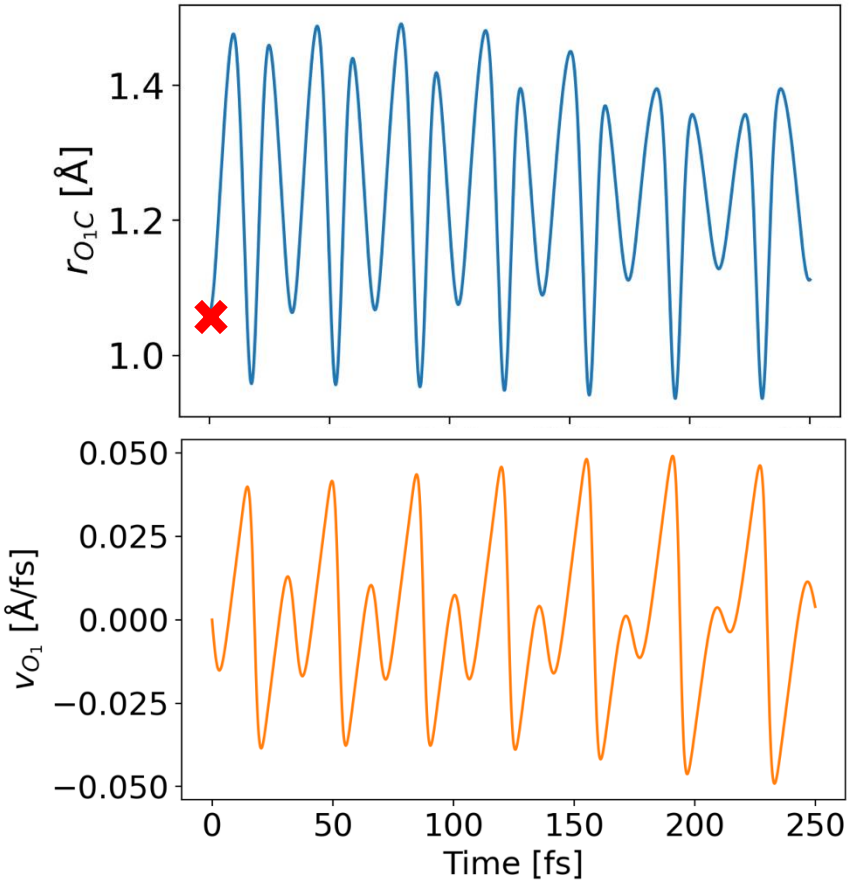
Morse potential

$$V_{\mathrm{CO}}(r) = D_{\mathrm{e}}\left(1 - e^{-\alpha(r-r_e)}\right)^2$$



$$V(r_{O_1C}, r_{CO_2}) = V_{\mathrm{CO}}(r_{O_1C}) + V_{\mathrm{CO}}(r_{CO_2})$$



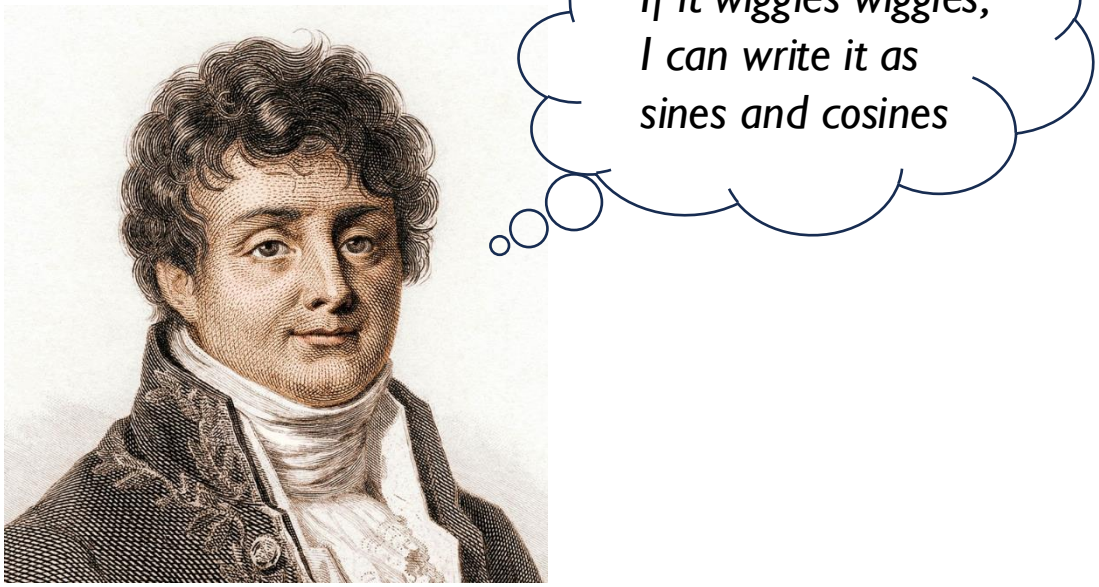


Fourier analysis

Decompose **periodic** and **aperiodic** functions into **sum of sinusoidal functions**

Fourier series → periodic functions
Fourier transform → aperiodic (non-periodic) functions

Widely used in physics, chemistry, biology, engineering, medicine, signal and image processing, and more...



Joseph Fourier
turning messy signals into
neat sinusoidals since 1822

Periodic function

Periodic function

$$T > 0 \qquad f(x+T) = f(x) \quad \text{for all } x$$

Periodic function

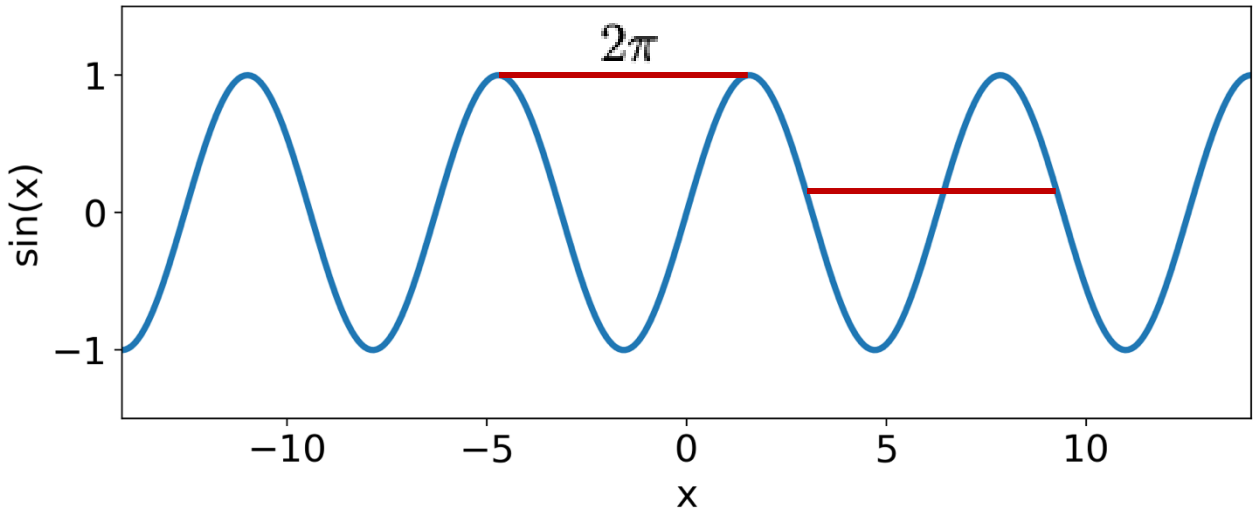
Periodic function

$$T > 0 \qquad f(x+T) = f(x) \quad \text{for all } x$$

2π-periodic function

$$f(x+2\pi) = f(x)$$

For example: $\sin(x+2\pi) = \sin x$



Fourier series

Fourier series on $[-L, L]$ period $T = 2L$

$$f(x) = a_0 + \sum_{n=1}^{\infty} \left(a_n \cos\left(\frac{n\pi x}{L}\right) + b_n \sin\left(\frac{n\pi x}{L}\right) \right)$$

Fourier series

Fourier series on $[-L, L]$ period $T = 2L$

$$f(x) = a_0 + \sum_{n=1}^{\infty} \left(a_n \cos\left(\frac{n\pi x}{L}\right) + b_n \sin\left(\frac{n\pi x}{L}\right) \right)$$

$$a_0 = \frac{1}{2L} \int_{-L}^{L} f(x)\, dx$$

$$a_n = \frac{1}{L} \int_{-L}^{L} f(x) \cos\left(\frac{n\pi x}{L}\right)\, dx \qquad n \geq 1$$

$$b_n = \frac{1}{L} \int_{-L}^{L} f(x) \sin\left(\frac{n\pi x}{L}\right)\, dx \qquad n \geq 1$$

Fourier coefficients

Fourier series of a 2π-periodic function

Fourier series on $[-\pi, \pi]$ period $T = 2\pi$

$$f(x) = a_0 + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx)$$

$$a_0 = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x)\, dx$$

$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx)\, dx \qquad n \geq 1$$

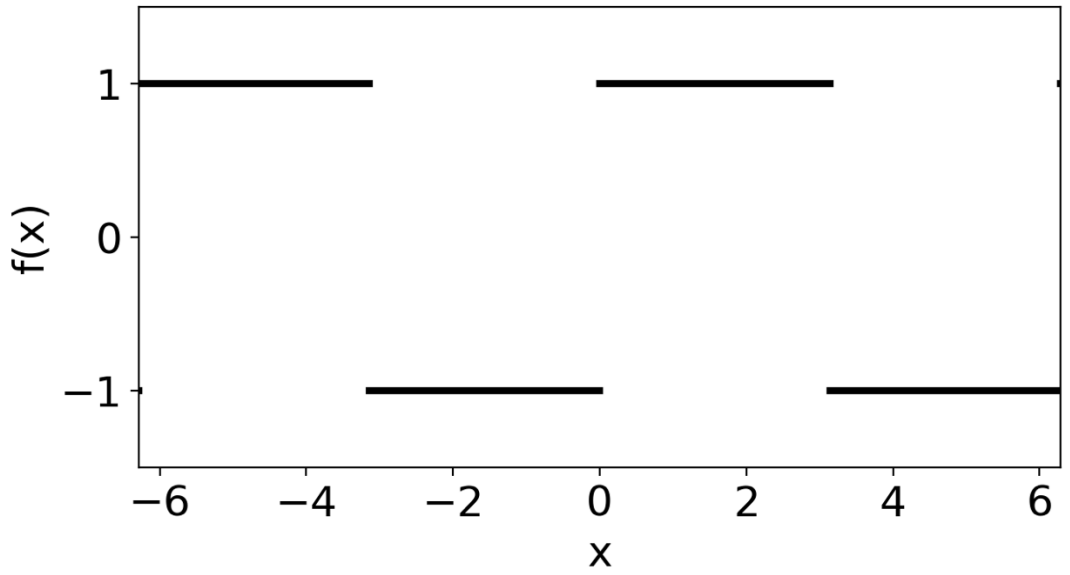
$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx)\, dx \qquad n \geq 1$$

Fourier coefficients

Fourier series of a 2π-periodic function

Example

$$f(x) = \begin{cases} 1, & n\pi < x < (n+1)\pi, \quad n = \ldots, -2, 0, 2, \ldots \\ -1, & n\pi < x < (n+1)\pi, \quad n = \ldots, -1, 1, \ldots. \end{cases}$$



Fourier series of a 2π-periodic function

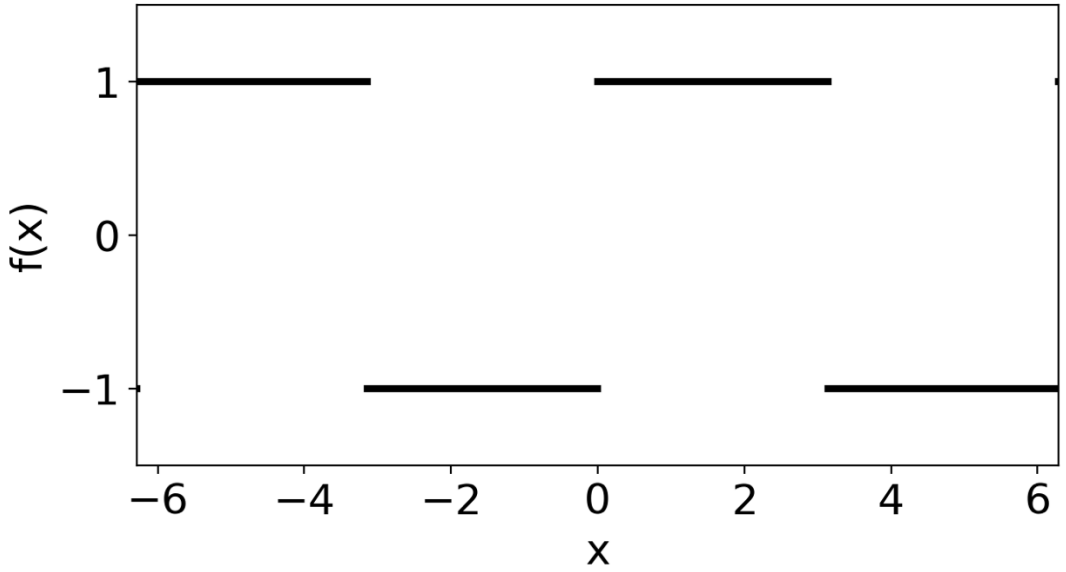
Example

$$f(x) = \begin{cases} 1, & n\pi < x < (n+1)\pi, \quad n = \ldots, -2, 0, 2, \ldots \\ -1, & n\pi < x < (n+1)\pi, \quad n = \ldots, -1, 1, \ldots. \end{cases}$$

$$a_0 = 0$$

$$a_n = 0$$

$$b_n = \frac{2}{\pi n}\left(1 - \cos(n\pi)\right)$$

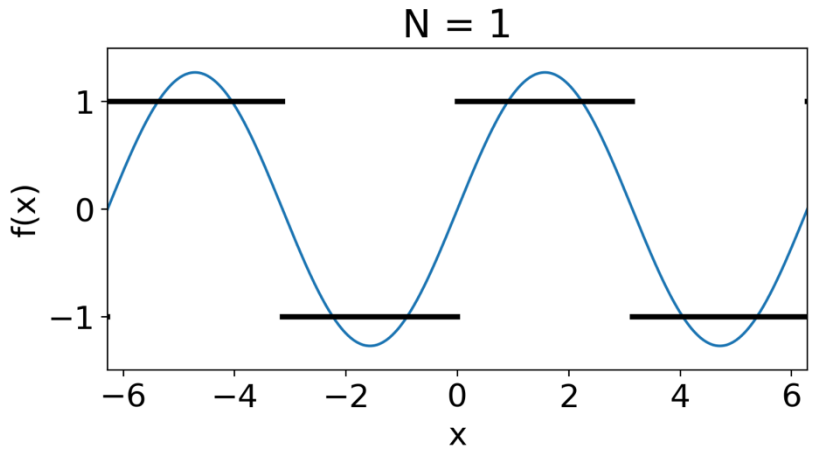


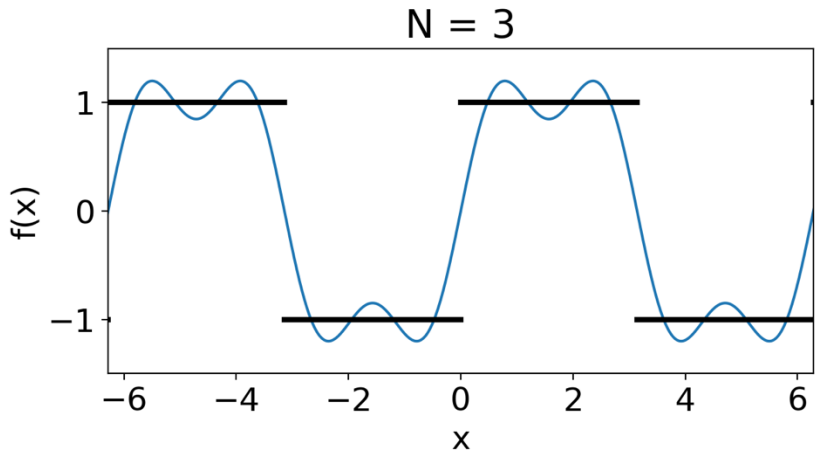
$$f(x) = \sum_{n=1}^{\infty} b_n \sin(nx) = \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} \frac{4}{\pi n} \sin(nx)$$

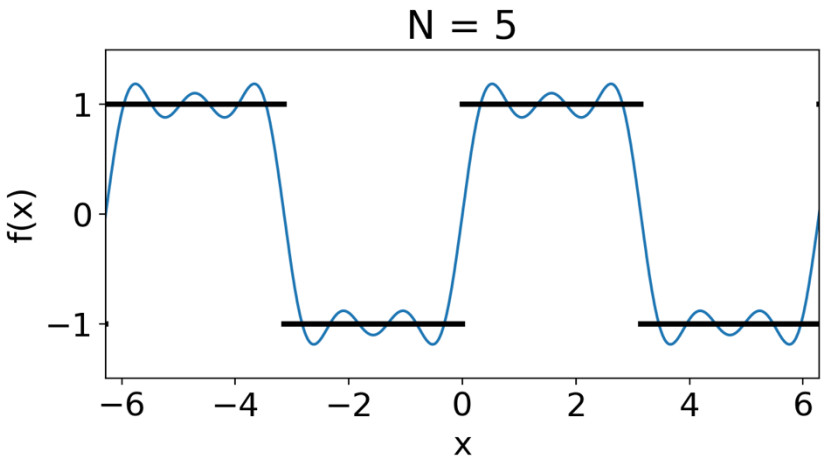
Fourier series of a 2π-periodic function

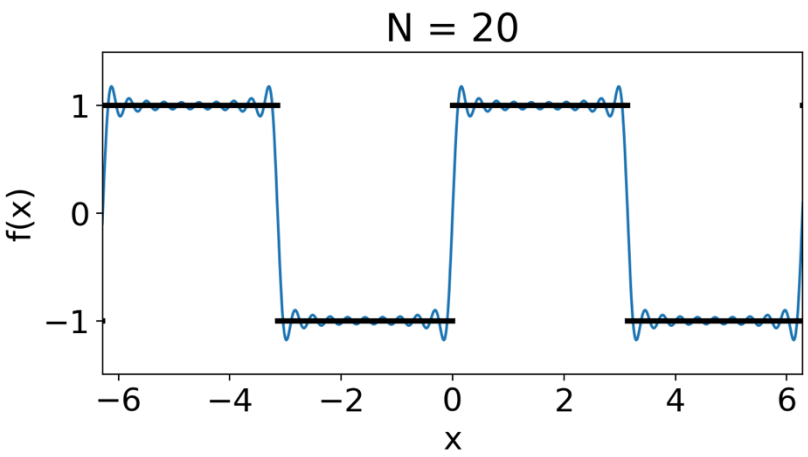
Example

$$f(x) = \begin{cases} 1, & n\pi < x < (n+1)\pi, \quad n = \ldots, -2, 0, 2, \ldots \\ -1, & n\pi < x < (n+1)\pi, \quad n = \ldots, -1, 1, \ldots. \end{cases}$$









Fourier transform

Use Euler's formula:

$$e^{ix} = \cos x + i \sin x \qquad \cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right) \qquad \sin x = \frac{1}{2i}\left(e^{ix} - e^{-ix}\right)$$

Fourier series in **complex form**:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\omega x}, \qquad c_n = \frac{1}{2L}\int_{-L}^{L} f(x) e^{-in\omega x}\, dx, \qquad \omega = \frac{2\pi}{T}$$

Fourier transform

Use Euler's formula:

$$e^{ix} = \cos x + i \sin x \qquad \cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right) \qquad \sin x = \frac{1}{2i}\left(e^{ix} - e^{-ix}\right)$$

Fourier series in **complex form**:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\omega x}, \qquad c_n = \frac{1}{2L}\int_{-L}^{L} f(x) e^{-in\omega x}\, dx, \qquad \omega = \frac{2\pi}{T}$$

$$2Lc_n = \int_{-L}^{L} f(x) e^{-ikx}\, dx \qquad k = n\omega$$

Fourier transform

Use Euler's formula:

$$e^{ix} = \cos x + i \sin x \qquad \cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right) \qquad \sin x = \frac{1}{2i}\left(e^{ix} - e^{-ix}\right)$$

Fourier series in **complex form**:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\omega x}, \qquad c_n = \frac{1}{2L}\int_{-L}^{L} f(x) e^{-in\omega x}\, dx, \qquad \omega = \frac{2\pi}{T}$$

$$2Lc_n = \int_{-L}^{L} f(x) e^{-ikx}\, dx \qquad k = n\omega$$

Fourier transform of *f*

$$\lim_{L\to\infty} 2Lc_n = \int_{-\infty}^{\infty} f(x)\, e^{-ikx}\, dx \qquad \hat{f}(k) = \int_{-\infty}^{\infty} f(x)\, e^{-ikx}\, dx$$

Fourier transform

Rewriting:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\omega x}$$

as:

$$f(x) = \frac{1}{2\pi} \sum_{k} \frac{\pi}{L} \left(2Lc_n\right) e^{ikx} \qquad \Delta k = \frac{\pi}{L} = \frac{2\pi}{T}$$

Suggests that for $L \to \infty$:

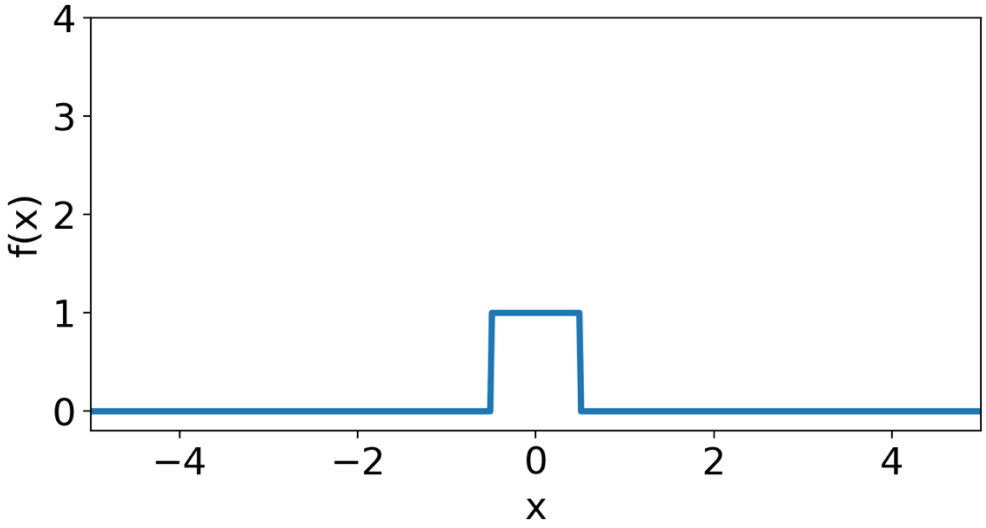
$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{f}(k)\, e^{ikx}\, dk$$

Inverse Fourier transform

Fourier transform of a rectangular function

Example

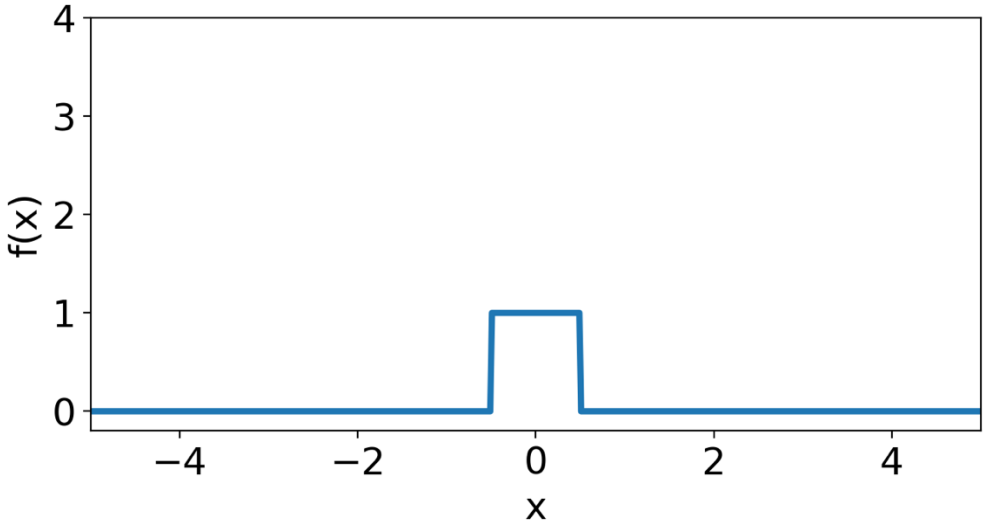
$$f(x) = \begin{cases} 1, & -\frac{1}{2} < x < \frac{1}{2} \\ 0, & x \leq -\frac{1}{2} \text{ or } x \geq \frac{1}{2} \end{cases}$$



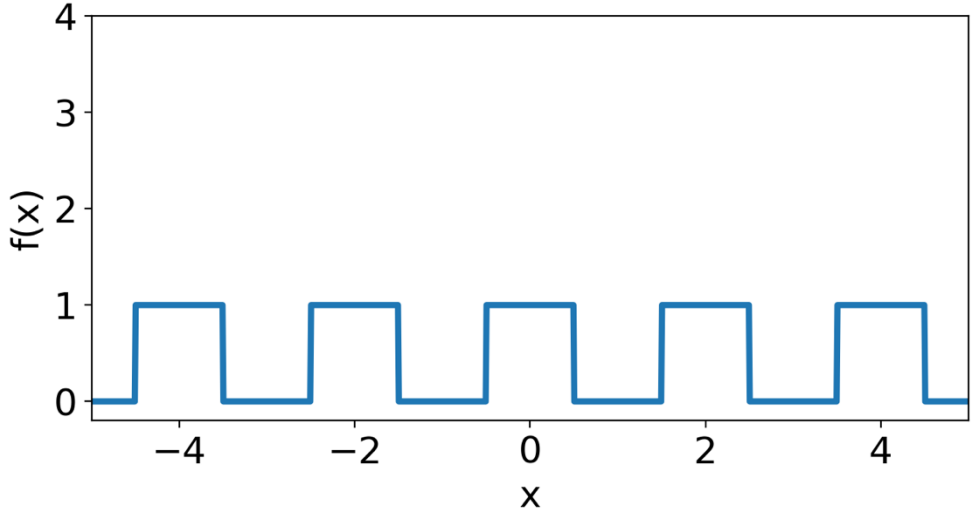
Fourier transform of a rectangular function

Example

$$f(x) = \begin{cases} 1, & -\frac{1}{2} < x < \frac{1}{2} \\ 0, & x \leq -\frac{1}{2} \text{ or } x \geq \frac{1}{2} \end{cases}$$



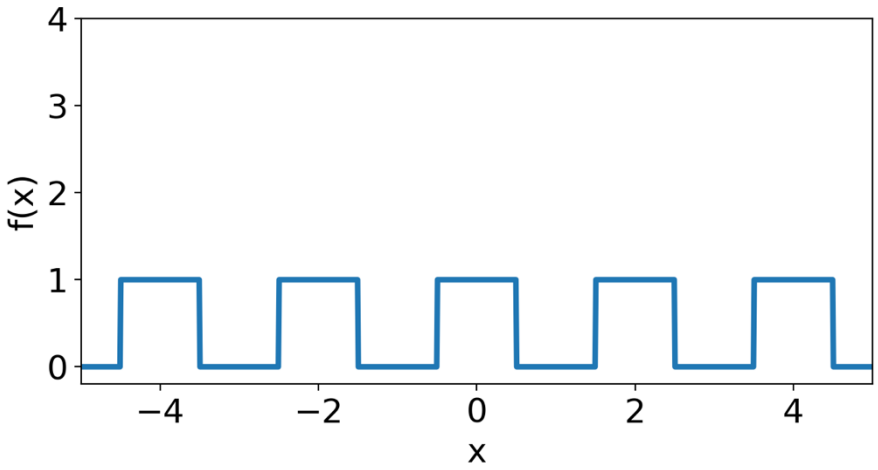
Make periodized version:

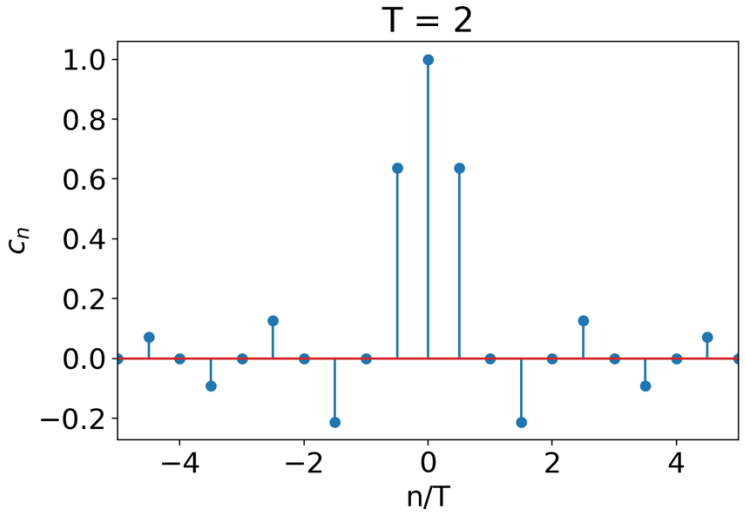


Fourier transform of a rectangular function

$$c_n = \frac{1}{T}\int_{-1/2}^{1/2} e^{-in\omega x}\,dx = \frac{1}{\pi n}\sin\left(\frac{n\omega}{2}\right)$$

Fourier coefficients

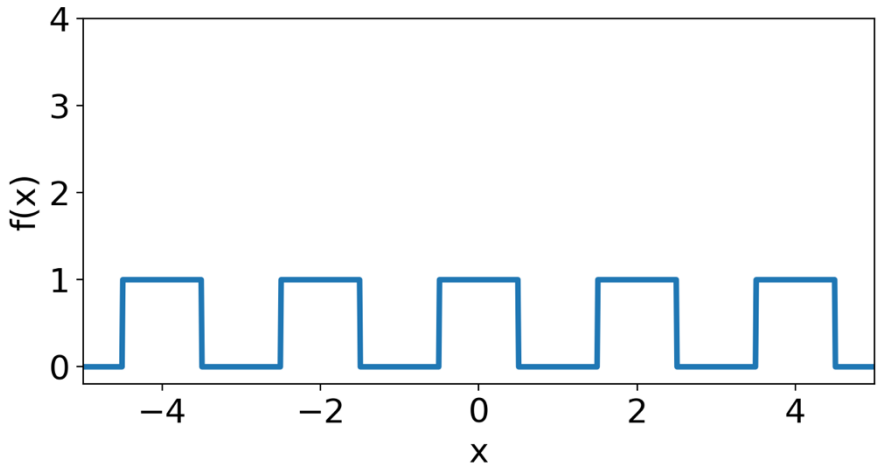


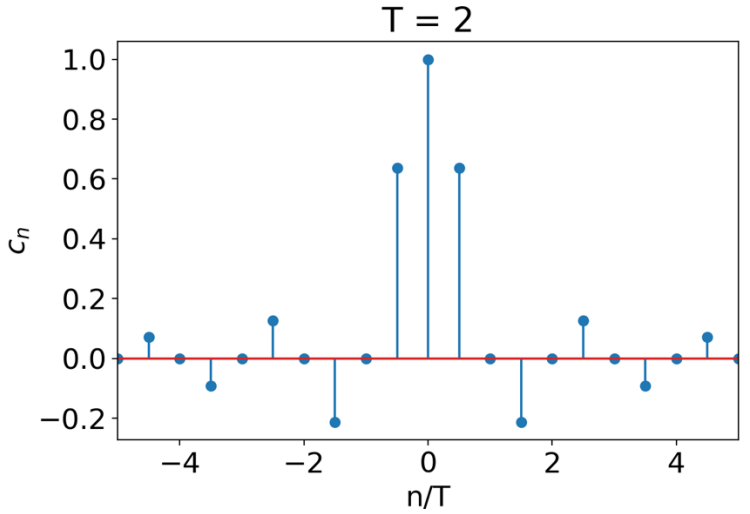


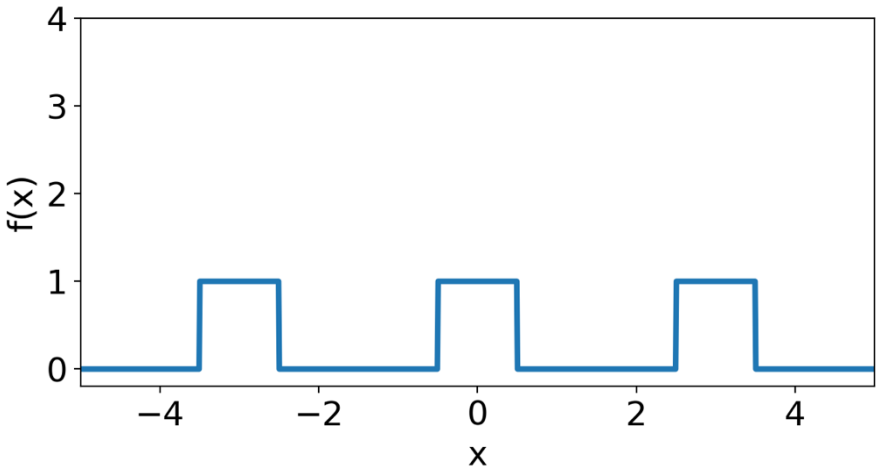
Fourier transform of a rectangular function

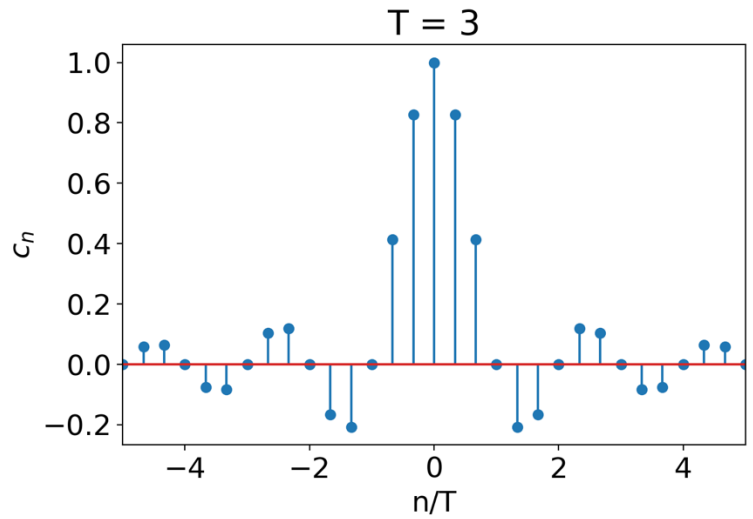
$$c_n = \frac{1}{T}\int_{-1/2}^{1/2} e^{-in\omega x}\,dx = \frac{1}{\pi n}\sin\left(\frac{n\omega}{2}\right)$$

Fourier coefficients





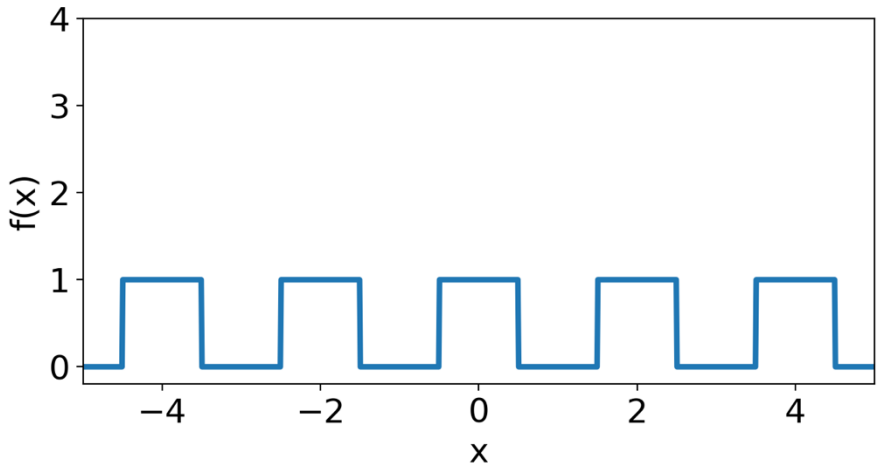


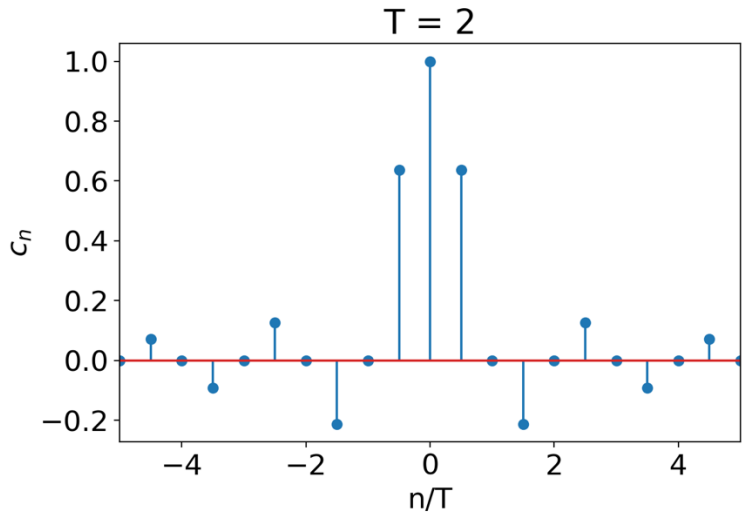


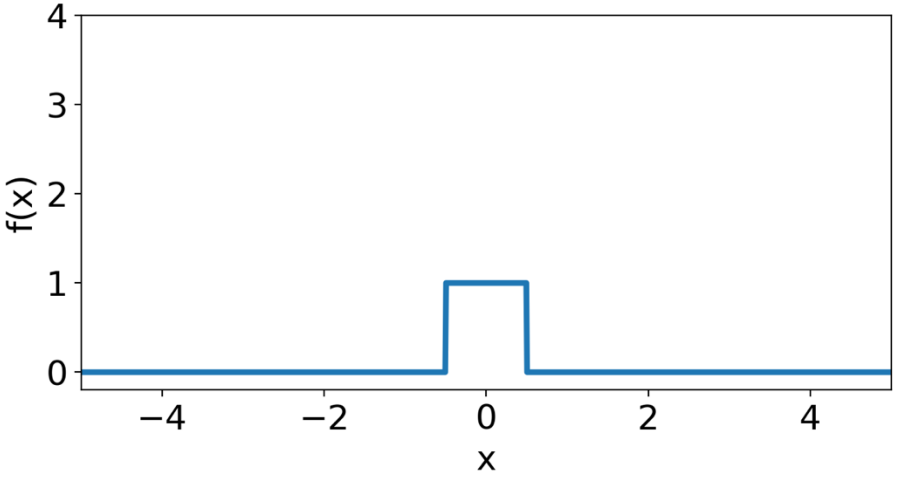
Fourier transform of a rectangular function

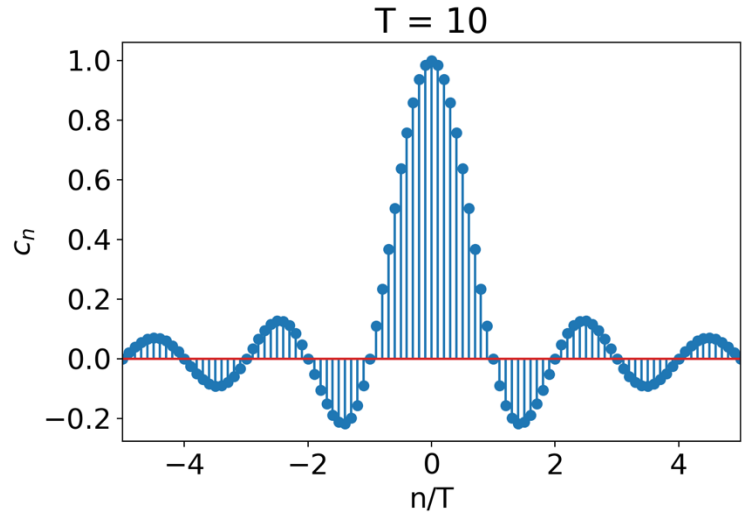
$$c_n = \frac{1}{T}\int_{-1/2}^{1/2} e^{-in\omega x}\,dx = \frac{1}{\pi n}\sin\left(\frac{n\omega}{2}\right)$$

Fourier coefficients





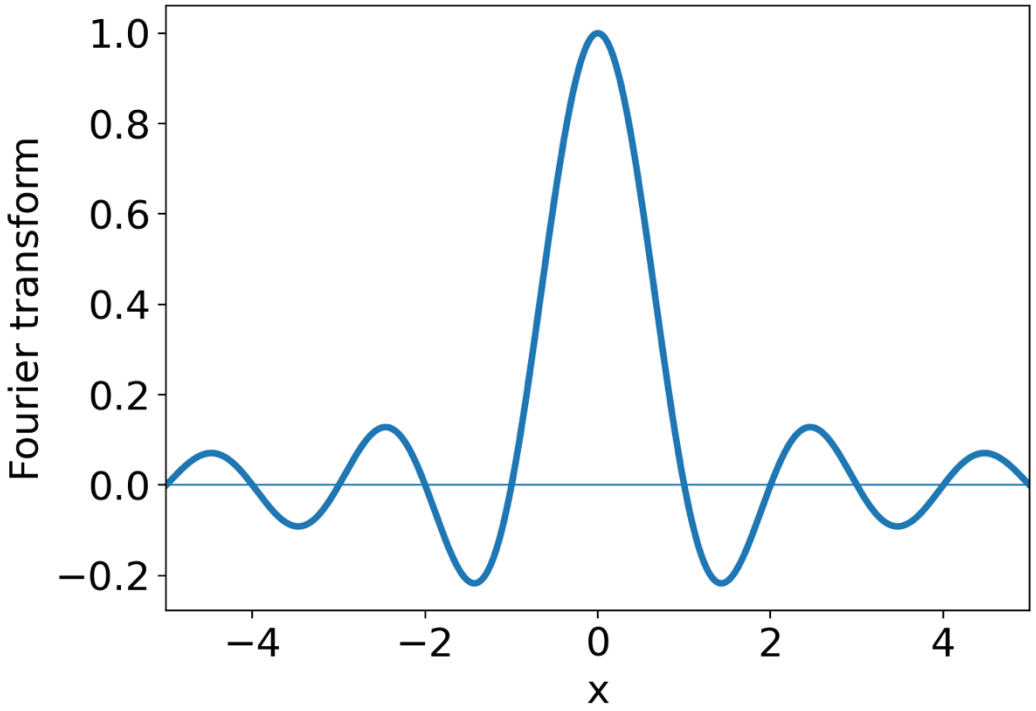




Fourier transform of a rectangular function

$T \to \infty$ has the effect of replacing the discrete variable $2\pi n/T$ by the continuous variable k:

$$c_n = \frac{1}{T}\int_{-T/2}^{T/2} f(x)\, e^{-i\frac{2\pi n}{T}x}\, dx \qquad \hat{f}(k) = \int_{-\infty}^{\infty} f(x)\, e^{-ikx}\, dx$$



Fourier transform of a time series

$$t = 0,\ \Delta t,\ 2\Delta t,\ 3\Delta t,\ \ldots,\ N\Delta t \qquad\qquad T = N\Delta t$$

$$\omega = \omega_1, \omega_2, \ldots, \omega_N = 0,\ \Delta\omega,\ 2\Delta\omega,\ \ldots,\ N\Delta\omega$$

Fourier transform of a time series

$$t = 0,\ \Delta t,\ 2\Delta t,\ 3\Delta t,\ \ldots,\ N\Delta t \qquad T = N\Delta t$$

$$\omega = \omega_1, \omega_2, \ldots, \omega_N = 0,\ \Delta\omega,\ 2\Delta\omega,\ \ldots,\ N\Delta\omega$$

Angular frequency corresponding to harmonic component *n*:

$$\omega_n = n\,\Delta\omega \qquad \Delta\omega = \frac{2\pi}{T}$$

Smallest non-zero angular frequency

Frequency corresponding to harmonic component *n*:

$$\nu_n = \frac{\omega_n}{2\pi} = \frac{n}{T}$$

Assignment 7

Problem 1

In this problem, you will extend the CO model from Problems 1–2 to describe the vibrations of a linear carbon dioxide (CO_2) molecule. For simplicity, consider the molecule to be constrained to move along the x-axis. The three atoms, O_1, C, and O_2, have positions x_{O_1}, x_C, x_{O_2} such that $x_{O_1} < x_C < x_{O_2}$. The two C–O bond lengths are

$$r_{O_1C} = x_C - x_{O_1}, \qquad r_{CO_2} = x_{O_2} - x_C.$$

The potential energy of the molecule is described as the sum of two identical Morse potentials, one for each C–O bond,

$$V(r_{O_1C}, r_{CO_2}) = V_{\mathrm{CO}}(r_{O_1C}) + V_{\mathrm{CO}}(r_{CO_2}),$$

with

$$V_{\mathrm{CO}}(r) = D_{\mathrm{e}} \left(1 - e^{-\alpha(r-r_e)}\right)^2,$$

where $D_{\mathrm{e}} = 7.65$ eV is the well depth, $r_e = 1.162$ Å is the equilibrium C–O bond length and $\alpha = 2.5$ Å^{-1} controls the curvature of the potential. Assume atomic masses (in atomic mass units) $m_{\mathrm{O}} = 16.00$ and $m_{\mathrm{C}} = 12.01$.

You should reuse your `model_potential.py` and `molecular_dynamics.py` modules from Problems 1–2 of Assignment 6 and extend them where necessary.

(a) Extend your `model_potential.py` module with a new class `CO2_morse` that models the CO_2 molecule. The class should include a method that computes the total potential energy and the forces on each atom along the x-axis (use analytical derivatives of the Morse potential as in Assignment 6, Problem 1), and a method that calculates the total kinetic energy.

(b) At the end of your `model_potential.py` module, add a test block (inside `if __name__ == '__main__'`) that performs sanity checks for the CO_2 model: When the atoms are at the equilibrium geometry ($r_{O_1C} = r_{CO_2} = r_{\mathrm{e}}$), all atomic forces are (approximately) zero; for a random configuration, the total force on the molecule (approximately) vanishes, i.e. $F_{O_1} + F_C + F_{O_2} \approx 0$. Run `model_potential.py` as a script and verify that these tests pass.

(c) In a Jupyter notebook, import your updated `model_potential` and `molecular_dynamics` modules. Use the `MD` class from Problem 2 of Assignment 6 together with the new `CO2_morse` calculator to run a classical simulation of CO_2 with the velocity Verlet algorithm. Choose initial positions corresponding to $x_{O_1} = -1.342$ Å, $x_C = -0.28$ Å, $x_{O_2} = 1.372$ Å and set the initial velocities to zero. Select a time step `dt=0.05` fs and number of steps `nsteps` such that the total simulation time is 1 ps. From the trajectory, store $r_{O_1C}(t)$ and $r_{CO_2}(t)$, as well as the velocities of the atoms, $v_{\mathrm{O1}}(t)$, $v_{\mathrm{C}}(t)$ and $v_{\mathrm{O2}}(t)$. Plot the trajectory $(r_{O_1C}(t), r_{CO_2}(t))$ as a line on top of the 2D potential energy contour plot of $V(r_{AB}, r_{BC})$ (see Assignment 4, Problem 3). Comment briefly on the trajectory.

(d) Using the same simulation as in part (c), plot $v_{\mathrm{O1}}(t)$ as a function of time. Then, compute the Fourier transform of the velocity of the first oxygen atom using the NumPy function `np.fft.rfft`. Plot the corresponding power spectrum $|\hat{f}(\omega)|^2$.

(e) From the spectrum obtained in part (d), estimate the vibrational frequencies (in cm^{-1}) corresponding to the dominant peaks. Report the values of the main vibrational peaks and comment on how many vibrational frequencies you can resolve.

Hint: Use that the total simulation time is $T = N_{\mathrm{steps}} \cdot dt$ and that the discrete frequencies of the Fourier transform are given by

$$\nu_n = \frac{n}{T}, \qquad n = 0, 1, 2, \ldots \text{max. harmonic component}$$