Exercise 2

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Hand-in: 06.03.2024 HCI D267.1 or `meghna.manae@phys.chem.ethz.ch`

In this exercise you will write a program to simulate the dynamics of the harmonic oscillator. You will start by writing an algorithm that propagates the classical trajectory from an initial state at time $t = 0$ to a later time $t = t_e$. Afterwards you will combine this algorithm with the knowledge about distribution functions you acquired in Exercise 1 to calculate correlation functions for both the classical and quantum harmonic oscillator. The plots you are creating in this exercise not only serve the purpose of illustrating your results, but should also be used to check whether your program works properly. At each step of the exercise you should therefore ask yourself whether the results of your calculations agree with your expectations. You can use the skeleton code provided for your solution, see `skeleton02.py`.

NOTE: We request you to please change the extension of your solution codes from .py to .txt before mailing them to us, to ensure that the file is transferred correctly.

Problem 1: Dynamics of the harmonic oscillator

The time evolution of a classical harmonic oscillator is given by

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{\mathrm{d}T}{\mathrm{d}p} = \frac{p}{m}\,, \\ \frac{\mathrm{d}p}{\mathrm{d}t} &= -\frac{\mathrm{d}V}{\mathrm{d}x} = F(x) = -m\omega^2 x\,, \end{aligned} \tag{1.1}$$

where $F(x)$ is the force at position x.

The velocity Verlet algorithm can be used to numerically solve this set of differential equations. Given the state at time t, $(x(t), p(t))$, the state $(x(t+\Delta t), p(t+\Delta t))$ is calculated as follows:

$$p\left(t + \frac{\Delta t}{2}\right) = p(t) + F(x(t)) \cdot \frac{\Delta t}{2}\,, \tag{1.2}$$

$$x(t+\Delta t) = x(t) + \frac{p(t+\frac{\Delta t}{2})}{m} \cdot \Delta t\,, \tag{1.3}$$

$$p(t+\Delta t) = p\left(t + \frac{\Delta t}{2}\right) + F(x(t+\Delta t)) \cdot \frac{\Delta t}{2}\,. \tag{1.4}$$

(This can be obtained by replacing the derivatives in (1.1) by difference quotients, $\frac{\mathrm{d}f}{\mathrm{d}t} \to \frac{f(t+\Delta t)-f(t)}{\Delta t}$. Further, an additional halfstep of $\frac{\Delta t}{2}$ is taken in p. Intuitively, this can be understood as taking the average velocity (average velocity between $p(t)$ and $p(t+\Delta t)$ is $p(t+\frac{\Delta t}{2})$) between distance steps $x(t)$ and $x(t+\Delta t)$. This additional half step in p optimizes the convergence rate of the algorithm.)

a) Write a function `trajectory_cl` that takes the initial state, (x_0, p_0), the force function F and the time step Δt as well as the total number of steps N_t as inputs and computes the trajectory $\boldsymbol{x} = (x_0, x_1, ..., x_{N_t})$, $\boldsymbol{p} = (p_0, p_1, ..., p_{N_t})$ where $x_i = x(i \cdot \Delta t)$, $p_i = p(i \cdot \Delta t)$.
Remark: Passing the force function as an input makes your trajectory simulation more generally applicable. This will help you in future exercises where we will look at systems other than the harmonic oscillator.

b) Obtain the analytical solution for the dynamics ($x(t)$ and $p(t)$) of the harmonic oscillator.

c) For $m = 0.1$, $\omega = 2\pi$, $x_0 = 1$ and $p_0 = 0$, calculate $\boldsymbol{x}$ and $\boldsymbol{p}$ and plot your results as a function of time ($\boldsymbol{t} = (0, \Delta t, 2\Delta t, ..., N_t\Delta t)$) in the same figure. Choose N_t and Δt so that you see at least two periods of the oscillation. What is the observed frequency and amplitude of the oscillation? Compare your plots to the analytical solution calculated in part (b).

If your plots don't look as expected, then go back to part (a) and rework your code.

In the same figure, plot the total energy $E(t) = \frac{1}{2}\frac{p(t)^2}{m} + \frac{1}{2}m\omega^2 x(t)^2$. How small do you need to take Δt to observe energy conservation? Use this value for the following exercises.

d) In the lectures, we saw that vibrational states of molecules have significant quantum character even at room temperatures. Let us evaluate that statement by calculating thermal averages using classical and quantum (Wigner) distributions introduced in Exercise 1.

Calculate the correlation functions $\langle x(0)x(t)\rangle$ and $\langle p(0)p(t)\rangle$ for $t = 0, \Delta t, 2\Delta t, ..., N_t\Delta t$ using $m = 0.1$ and $\omega = 2\pi$ and compare the cases $\beta = 0.1, 1.0, 10$ for the classical and the Wigner distribution. Plot $\langle x(0)x(t)\rangle$ and $\langle p(0)p(t)\rangle$ for the different values of β. What value do you expect for $\langle x(0)x(t)\rangle$ at $t = 0$, and does this match the value in your plot? What differences do you observe between the classical and the Wigner case? Explore results for further values of β if necessary.

In the same way, calculate $\langle E(t)\rangle$ for $\beta = 0.1, 1.0, 10, ...$ in the classical and the Wigner case. Plot the energy in units of $\hbar\omega$. What energy do you observe for $\beta \to \infty$ in each case? Do you think the numerical result for $\langle E(t)\rangle$ makes sense?

Hint 1: To calculate the correlation functions, start by sampling the initial states using the appropriate distribution functions. For each initial state, calculate the trajectory and compute the arrays $x_0 \cdot \boldsymbol{x}$ and $p_0 \cdot \boldsymbol{p}$. Take the average over all trajectories at each time step $i\Delta t$. See the skeleton code for more hints.

Hint 2: Depending on your machine and the efficiency of your program, a full-blown simulation may take a while. Use a small number of samples ($N_s < 500$) while you are testing your program, and only increase sampling after your have debugged your code.

e*) Bonus: Consider the low temperature limit you found in (d) for the Wigner distribution. Can you find a β^* so that the classical correlation functions reproduce the results of the Wigner case for $\beta \to \infty$? Plot $\langle x(0)x(t)\rangle$, $\langle p(0)p(t)\rangle$ and $\langle E(t)\rangle$ for β^* in the classical case and compare. Is it true that we can always replace a quantum simulation with a classical one by transforming $\beta \to \beta^*$?

Hint: Think about a molecule as many different oscillators.