Exercise 03

Equations of motion

Deadline: Please hand in your protocol by Thursday, the 16th of May 2019, 10 am to jan.joswig@fu-berlin.de and marco.manni@fu-berlin.de. If your solution includes Python-code, you should submit executable files (or even better a jupyter notebook). Pen and paper solutions can be also submitted in paper form.

3.1 Harmonic oscillator

Consider the following harmonic stretching vibrations:

1. C−H: Wavenumber $\tilde{\nu} = 3000\,\mathrm{cm}^{-1}$
2. C−D: $\tilde{\nu} = 2100\,\mathrm{cm}^{-1}$
3. C−C: $\tilde{\nu} = 1000\,\mathrm{cm}^{-1}$
4. C=C: $\tilde{\nu} = 1700\,\mathrm{cm}^{-1}$
5. C≡C: $\tilde{\nu} = 2200\,\mathrm{cm}^{-1}$

1. Look up the definition of *wavenumber* and convert the values above to frequencies f, angular frequency ω and vibration periods T.
2. Calculate the reduced mass μ and force constant k for the examples above.
3. Discuss the influence of μ and chemical bond strength on the vibrational frequencies for the given examples.

3.2 Integration of the equation of motion

In this task you should solve the equation of motion for a harmonic diatomic vibration analytically and numerically. Write a commented python script for the numeric solution. Both ways should be compared. The harmonic potential is given as:

$$U(q) = \frac{k}{2}(q - q_0)^2 \tag{1}$$

Assume a reduced mass of $\mu = 6.00\,\mathrm{u}$, a force constant of $k = 6.15 \times 10^5\,\mathrm{kJ\,mol^{-1}\,nm^{-2}}$ and an equilibrium bond distance of $q_0 = 0.134\,\mathrm{nm}$ (corresponding to a C=C bond). Use molecular units throughout your calculations (compare script p. 190).

1. Give the equation of motion for the harmonic oscillation and derive the analytical solution $q(t)$.
2. Let the bond distance at time $t = 0$ be $q(0) = 0.187\,\mathrm{nm}$ and the velocity $v(0) = \dot{q}(0) = 0\,\mathrm{nm\,ps^{-1}}$. Draw a curve for the analytical solutions to $q(t)$ and $\dot{q}(t)$.

3. What would be an appropriate time step τ for the numerical solution?
4. Write a script that solves the equation of motion by a) an Euler algorithm and b) an Verlet algorithm. Calculate $q(t+\tau)$ and $\dot{q}(t+\tau)$ starting from $t=0$, $q(0) = 0.187\,\mathrm{nm}$ and $v(0) = 0\,\mathrm{nm\,ps^{-1}}$. The result should be visualised graphically.
5. Let the program run for an appropriate number of timesteps (at least 100 fs) and variate τ (at constant simulation lengths), so that the difference between the two algorithms and between (nearly) exact and completely wrong behaviour becomes obvious.
6. Discuss shortly the difference between analytical and numerical solution.