Exercise 01

Force fields

Deadline: Please hand in your protocol in pdf format by Thursday, the 3rd of May 2018, 10 am to jan.joswig@fu-berlin.de. The protocol should contain analytical solutions, short discussions, Python-code and plots.

1.1 Lennard-Jones potential (30 points)

Non-binding interactions are often modelled with a Lennard-Jones potential according to following equation:

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \varepsilon\left[\left(\frac{r_{\mathrm{m}}}{r}\right)^{12} - 2\left(\frac{r_{\mathrm{m}}}{r}\right)^{6}\right] \tag{1}$$

where r is the distance between two atoms and the constants σ and ε depend on the given atome types.

1. What is the relation between σ and r_{m}?
2. Sketch the potential. Explain the mathematical and physical implications of such a plot. Discuss σ and r_{m}.
3. Approximate the Lennard-Jones potential with the first three terms of a Taylor series for $r = r_{\mathrm{m}}$. What is the value of the second derivative of the potential $U''(r = r_{\mathrm{m}})$
4. How can one construct a harmonic oscillator potential in order to approximate $U(r)$? What is the value of the respective force constant?

1.2 Water force field (30 points)

Consider a typical modelling of a water dimer in terms of a classical force field representation. Atoms are annotated as follows: $H_1-O_2-H_3$ and $H_4-O_5-H_6$.

1. Provide all the terms of a typical force field representing the bonding interactions within water molecules.
2. Provide all the terms of a typical force field representing the bonding interactions between two water molecules.
3. In which energy range would you place the different force field terms ($1\,\mathrm{kJ\,mol^{-1}}$, $10\,\mathrm{kJ\,mol^{-1}}$, $100\,\mathrm{kJ\,mol^{-1}}$)
4. How would you model the tetrahedral coordination between water molecules?

5. How does the number of binding and non-binding interactions increase with the increasing number N of the water molecules in a system? What are the difficulties in computation of the interactions for a very large number N? What is the solution to this problem?

1.3 Critical points of the potential energy surface (40 points)

Consider the following function in 2D space:

$$U(r) = \left(r_x^2 - 1\right)^2 + \frac{5}{4}\left(r_y - \frac{1}{2}r_x\right)^2 \tag{2}$$

1. Calculate the gradient and the Hessian matrix of the function $U(r)$.
2. Provide the location of all the critical points.
3. Characterise the critical points as minima, maxima or saddle points.
4. Write a Python-script which plots this function as a 3D potential energy surface. Provide a 2D projection of the 3D potential surface as contour plot and mark all the critical points.