Week 2: Molecules, Potentials and Forces

2MMN40: Introduction to Molecular Modeling and Simulation
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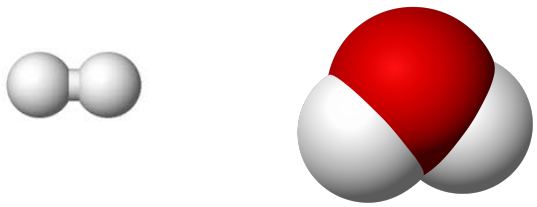
Contents

1 The Assignment

This weeks assignment consists of four parts

- Calculate bond lengths,
- Calculate angles and
- Calculate forces resulting from the two.

You should calculate these quantities for two molecules: hydrogen, which has only one bond, and water, which has one angle and two bonds (see Figure 1, .xyz files can be found at the end of this document). It is worth your while to write out the formulas for the angles and forces on paper before you try to implement them. Moreover for the bond in hydrogen it is very easy to check your implementation by hand. For the water molecule it is also possible, but it is a bit harder so we provide you with the solution at the end of this document so you can check your implementation.



(a) H_2 **(b)** H_2O

Figure 1. These are the molecules that we will be working with today. (a) A diatomic molecule, where we only have a single covalent bond - basically a spring. (b) A molecule of three atoms. Here we've got two bonds and an angle.

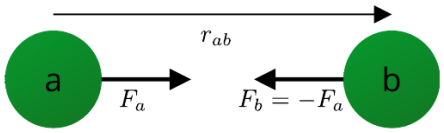


Figure 2. Attractive force for a bond between two atoms.

2 Potentials and Forces

In week 1 you have seen that the state of a molecular system is determined by the positions of the atoms and their velocity. The time evolution of a single atom i is given by Newton's equation

$$\mathbf{F}_i = m_i \cdot \ddot{\mathbf{q}}_i, \tag{1}$$

where $\mathbf{F}_i$ is the force acting on atom i and m_i the mass of the atom. To use this equation we need the force. Since all forces are conservative in MD (and actually in all of life) we can write them as the gradient (derivative) of some scalar potential,

$$\mathbf{F}_i = -\nabla_{\mathbf{q}_i} V(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N). \tag{2}$$

Note that the derivative is with respect to the atom (particle) of interest i, while the potential itself is for the whole system and depends on all particle positions. To simplify this a bit, the potential is generally taken to be the sum of many smaller potentials that describe specific parts of the system (e.g. a bond). The collection of all potentials used in a simulation is called the *force-field*.

In this week and weeks five and six we will build up a force field for our simulation. We can divide the forces and potentials in two categories, the so called *intra*-molecular (within a molecule) potentials and the *inter*-molecular (between molecules) potentials. This week we start with two intra-molecular potentials, describing the bonds and angles within a molecule.

2.1 Bond Potential

In a chemical bond two electrons are shared between two atoms. This sharing results in a force that is attractive most of the time (see Figure 2), but repulsive if the atoms get close together. This implies there should be some equilibrium position of the bond length where the force is zero, neither attractive nor repulsive. In physical terms, the potential energy has a minimum.

Every minimum (or maximum) of a potential can be approximated by a quadratic term (think of a taylor expansion where the zeroth and first derivative are zero, why can we take the zeroth derivative as zero?). This is exactly what is typically done in MD. This approximation results in the *harmonic bond potential*

$$V_{\text{bond}}(r) = \frac{1}{2} k (r - r_0)^2 \tag{3}$$

where k is the bond strength and r_0 the equilibrium length of the bond with current length r. To get the total bond energy E_{bond} you simply sum over all bonds

$$E_{\text{bond}} = \sum_{\text{all bonded i,j}} V_{\text{bond}}(|\mathbf{r}_i - \mathbf{r}_j|). \tag{4}$$

To arrive at a force we need to take the derivative with respect to the atom we want the force on. This is in most cases quite complicated, an easier approach is to find the magnitude of the force in its original variables (in this case bond length),

$$F_{\text{bond}} = -\frac{dV_{\text{bond}}}{dr}, \tag{5}$$

and then convert it to the correct 3D vector by multiplying it with the (unit) vector that points in the correct direction. As an example the force on atom a in Figure 2 is

$$\mathbf{F}_a = F_{\text{bond}} \cdot \frac{\mathbf{r}_{ab}}{\|\mathbf{r}_{ab}\|}. \tag{6}$$

From Newton's third law (action is minus reaction) we immediately have the force on particle b,

$$\mathbf{F}_b = -\mathbf{F}_a \tag{7}$$

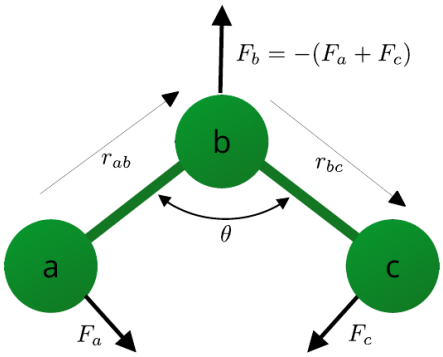


Figure 3. Forces due to the angular potential.

2.2 Angular Potential

The angular potential we use is also harmonic,

$$V_{\text{angle}}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2, \tag{8}$$

where k_θ is the strength of the angle and θ_0 the equilibrium position. How this potential acts on a molecule is depicted in Figure 3. How this potential should be converted to a force is left to you as part of this assignment (work this out on paper first). What follows are tips you can use to make it a bit easier.

2.2.1 Forces from potentials

You can take two approaches when computing a force from a potential

1. Compute the derivatives of the potential in the x, y and z directions for the correct atom position. This involves a lot of calculus since potentials are usually not defined in terms of xyz, but in what is convenient for that potential.
2. Figure out the magnitude of the forces first and then multiply them with a unit vector that gives the force the right direction (this is what I did in the bonds example above). Now the problem is divided into two problems, but both problems are easy and very straightforward to implement in a programming language. Don't get too excited though; for the angular potential you still need to do a bit of calculus to go from the angle to positions. (You can't simply take the derivative with respect to θ and multiply it with a direction vector. The force is given by $\mathbf{F}_i = -\nabla_{\mathbf{q}_i} V(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$ and hence we need to take the derivative of $V_{\text{angle}}(\theta)$ with respect to $\mathbf{q}_i$. Try to use the chain rule.)

2.2.2 Geometric tricks with vectors

In Figure 3 you see a schematic drawing of a triatomic molecule. It is drawn in the plane of the paper, but in reality it can be rotated in any direction. This makes finding out the direction of forces with respect to the xyz axes challenging. But we can use some basic vector tricks.

- To get a normal vector to the plane of the molecule you can use the cross product $\mathbf{n} = r_{ab} \times r_{bc}$ (or $\mathbf{n} = r_{ba} \times r_{bc}$?).
- To get a vector pointing in the direction of F_a, for example, you can use another cross product.
- To get θ you can use a dot product. But beware! Which numerical problems can occur? Is there a more stable approach?

2.2.3 Generalizing Newton's third law

We can generalize Newton's third law. We have seen the most basic case in the bond example,

$$\mathbf{F}_a + \mathbf{F}_b = 0. \tag{9}$$

It simply states that the forces within a closed system should sum to zero (Newton: for every action, there is an equal and opposite reaction). Generalizing this we have

$$\sum_i \mathbf{F}_i = 0. \tag{10}$$

2.3 Combining Forces

Forces are additive, to compute the total force acting on an atom we can simply sum all the forces acting on that atom.

$$\mathbf{F}_i = \mathbf{F}_{\text{bond},i} + \mathbf{F}_{\text{angle},i} \tag{11}$$

Note that in large molecules $\mathbf{F}_{\text{bond},i}$ or $\mathbf{F}_{\text{angle},i}$ might be sums of forces themselves, since there could be more than one bond to an atom and an atom can be part of more than one angle.

3 Quick Check (Solution)

3.1 Hydrogen

The hydrogen molecule can be checked by hand. Use the following parameters if you want to do explicit calculations $k = 24531\text{kJ mol}^{-1}\text{nm}^{-2}$ and $r_0 = 0.74\text{Å}$, check your units! The symbol Å stands for the unit Ångström, it is the standard unit for distance in molecular simulations and is equal to 10^{-10}m.

The xyz file

```
2
Hydrogen
H 0.0 0.0 -0.367
H 0.0 0.0  0.367
```

3.2 Water: parameters

r_o (nm)	k_b (kJ mol^{-1} nm^{-2})
0.09572	502416

Table 1. H_2O bonds.

θ_o (^{o})	k_θ (kJ mol^{-1} rad^{-2})
104.52	628.02

Table 2. H_2O Angles.

3.3 Water: xyz

```
3
Water
O          1.93617934      2.31884508      1.72261570
H          1.78931374      3.24075634      1.51114298
H          2.30448689      1.98045541      0.90160232
```

3.4 Water: Solution

When I did the calculations I got what follows, if you got something else, but you are absolutely sure it is right, let us know, maybe there is a mistake here. (Probably not though)

Every row is the total force vector for the corresponding atom in the xyz file. The first line is the Oxygen atom the second the first hydrogen etc.

```
[[ 16.    13.66 -55.08]
 [-10.08   4.37  25.81]
 [ -5.92 -18.04  29.28]]
```

Once again check the units, I used a particularly strange system of units where the unit energy is kJ/mol, the length is Å, the mass is amu, and the time is 0.1 ps. Which implies that the forces above are given in units of $\frac{\text{amu·Å}}{(0.1\text{ps})^2}$.

4 A note about units

You might be wondering why I used such strange units in the solution above. The short answer: computers are bad with very small numbers (you get rounding errors). If you pick a system of units such that your problem has mainly variables with a magnitude around 1 (or larger), you can workaround that issue. More about this next week.