Homework H2 Solution

1. A spring has restoring force F=-kx, where k is the spring constant. x=0 when the spring is not stretched or compressed. Assume that x(t=0) = 0 and v(t=0)=0 initially. Plug into the Verlet algorithm to show that x(t=Δt) = 0 also. If the spring is initially unstretched and not moving, it will remain still and do nothing!

Solution: Starting with the Verlet algorithm

$$x(t+\Delta t) = x(t) + v(t)\Delta t + \frac{F(x,t)}{m}\Delta t^2 \tag{1}$$

and substituting the given force expression along with initial conditions for t=0 into (1) we have

$$x(\Delta t) = x(0) + v(0)\Delta t - \frac{kx(0)}{m}\Delta t^2$$

$$x(\Delta t) = 0 + 0\Delta t - \frac{k\cdot 0}{m}\Delta t^2 = 0 \tag{2}$$

It is worth noting that the time dependence of the force in (1) is parametric as defined through the equation F=-kx because x is a function of t. You could have calculated the force for a spring also from $F=-\partial V/\partial x = \partial/\partial x\,[(k/2)\,x^2] = -kx$ again. The potential energy for a spring is $V(x) = (k/2)\,x^2$.

Turn in: 2. Now do the same, but let $x(t=0) = x_0 > 0$, and v(t=0) = 0. What is x(t=Δt)? Is x(t) bigger or smaller than x(t=0), and why?

Solution: We proceed in the same manner as Problem 1, only now our initial conditions have changed so we get

$$x(\Delta t) = x_0 + v(0)\Delta t - \frac{kx_0}{m}\Delta t^2 = x_0 - \frac{kx_0}{m}\Delta t^2 \tag{3}$$

We observe that $x(\Delta t) < x(0)$ given (3). This makes sense intuitively because of the nature of the restoring force of a spring (F=-kx indicates that the force is always in the opposite direction of the displacement. As such, if you have a positive displacement x_0, the next time step after that displacement will be less than x_0). Basically, you have stretched the spring, and when you let go, the spring will contract.

3. Starting with V(r) for the Lennard-Jones potential, calculate F(r)=-∂V/∂x. Show that F approaches 0 as r approaches ∞: when two argon atoms are far apart, they do not exert a force on one another.

Solution: The Lennard-Jones potential is given by

$$V(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right] \tag{4}$$

Taking -∂V/∂r of (4) yields (remember, $\partial x^{-n}/\partial x = -nx^{-(n+1)}$)

$$-\frac{\partial V}{\partial r} = -4\varepsilon\left[-\frac{12}{r_0}\left(\frac{r_0}{r}\right)^{13} + \frac{6}{r_0}\left(\frac{r_0}{r}\right)^{7}\right] = \frac{24\varepsilon}{r_0}\left[2\left(\frac{r_0}{r}\right)^{13} - \left(\frac{r_0}{r}\right)^{7}\right] \tag{5}$$

Now, take the limit

$$\lim_{r\to\infty} F(r) = \lim_{r\to\infty}\frac{24\varepsilon}{r_0}\left[2\left(\frac{r_0}{r}\right)^{13} - \left(\frac{r_0}{r}\right)^{7}\right] = \frac{24\varepsilon}{r_0}\left[2\left(\frac{r_0}{\infty}\right)^{13} - \left(\frac{r_0}{\infty}\right)^{7}\right] = 0 \tag{6}$$

where we arrived at the answer by direct substitution at the end of (6). Think about what happens: at long distance r, V(r) decays to zero. So the potential energy becomes independent of the distance between the two argon atoms. If the argon atoms no longer attract one another, no significant force is required to pull them apart yet further, so F approaches 0 also.

4. If I move two electrons closer to one another by a factor of 2 in distance, by what factor does the potential energy change? Does it go up or down? Draw a sketch of V(r) as a function of r and mark two distances consistent with the problem.

Solution: The Coulombic potential between two electrons is given by

$$V(r) = +\frac{e^2}{4\pi\varepsilon_0 r} \tag{7}$$

Note the plus sign: two electrons have the same charge and repel one another. If it were a proton and an electron making a hydrogen atom, they would attract one another. Denoting the new distance in (7) as $r' = \frac{r}{2}$ we get

$$V(r') = +\frac{e^2}{4\pi\varepsilon_0 r'} = +\frac{e^2}{4\pi\varepsilon_0 (\frac{r}{2})} = +\frac{2e^2}{4\pi\varepsilon_0 r} = 2V(r) \tag{8}$$

As you can see, the *magnitude* of the potential energy increases by a factor of two when the distance between electrons decreases by a factor of two. See plot below.

Note that the repulsive potential between two electrons shown in the plot below is **very important in chemistry** because most atoms (except hydrogen or some ions) and molecules (except H_2^+ and other 'weird' molecules) have more than one electron. Such electron repulsion weakens chemical bonds and makes the ionization potential of atoms lower than it would have been without the extra repulsion. It is actually what creates the properties of the elements in the periodic table!

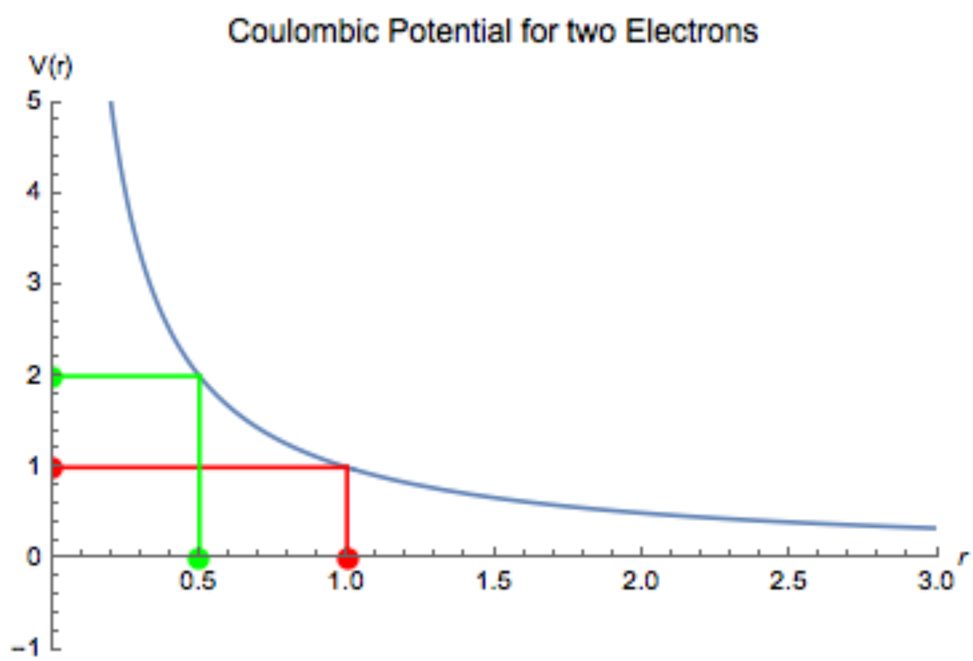

Figure 1. Plot of V(r) ~ +1/r (leaving out the other constants for simplicity). As you can see, starting at r=1 the potential is +1, and brining the electrons closer together by a factor of two to r=0.5 doubles the magnitude of the potential, bringing it to +2.