

# Chemistry 4010 Fall 2019 Assignment 7

**Due:** Dec. 3, 6:00 p.m.

**Total marks:** 32

The Morse potential is often used as a model for the potential energy of a chemical bond. It is given by the formula

$$V(x) = D_e \left( e^{-2a(x-x_e)} - 2e^{-a(x-x_e)} \right),$$

where  $x$  is the bond length,  $x_e$  is the equilibrium bond length,  $a$  is a constant related to the stiffness of the bond, and  $D_e$  is the classical dissociation energy.

1. Write down the Hamiltonian and derive the equations of motion. **4 marks**

Note: Treat this case as if you had a single particle experiencing the Morse potential. Other than replacing the mass by a reduced mass, this is essentially correct if the molecule isn't rotating.

2. Orbits in the phase plane can be drawn without integrating the equations, using the fact that the Hamiltonian is constant. Draw orbits for the following parameters, roughly inspired by the HCl molecule: **4 marks**

$$m = 1.6 \times 10^{-27} \text{ kg}$$

$$D_e = 9 \times 10^{-19} \text{ J}$$

$$a = 2 \times 10^{10} \text{ m}^{-1}$$

$$x_e = 1 \times 10^{-10} \text{ m}$$

Try the following values of  $H$ :  $-7 \times 10^{-19} \text{ J}$ , and  $-2 \times 10^{-19} \text{ J}$ .

Hints: The easiest way to do this that I can think of is to use the MAPLE `implicitplot()` function. To use this, you need an estimate of the minimum and maximum values of  $x$  and  $p$ . The minimum and maximum values of  $x$  will be reached when  $p = 0$ . Conversely, the minimum and maximum values of  $p$  will be reached when  $x = x_e$ . You can find these minima and maxima using `solve()`.

3. The frequency of oscillation (in Hz) can be estimated from the harmonic-oscillator formula **4 marks**

$$\nu = \frac{1}{2\pi} \sqrt{k/m}.$$

For an anharmonic oscillator like the Morse oscillator, the “spring constant”  $k$  is related to the potential as follows:

$$k = \left. \frac{d^2V}{dx^2} \right|_{x=x_e}.$$

Using the parameters given above, estimate the frequency of the oscillator.

4. Implement the semi-implicit Euler method for this problem. Choose a sensible initial conditions using the  $H = -2 \times 10^{-19}$  J orbit from question 2. (It is not necessary to be extremely precise. Just read your graph as best you can. This will have a small effect on your initial energy, but I’m not too worried about that for this question.) Use the frequency calculated above to determine reasonable values of the step size and total integration time. Note that you will want to observe several dozen oscillations. Verify that the energy is constant on average. (The MATLAB function `mean()` may be useful for this purpose.) Determine the vibrational frequency from your simulation results. Comment on its agreement (or lack thereof) with your analytic calculation. Plot the computed orbit in phase space, and compare this result to the exact result from question 2. **15 marks**
5. You wouldn’t expect to get good results if you use a step size that is about the same as the oscillation period. Try this anyway. What happens? If you gradually decrease the step size (e.g. reducing it by a factor of 2 at each new attempt), how do things change? **5 marks**