Chemistry 60641 | Spring 2025
Professor J. Daniel Gezelter | Due Friday, January 31, 2025

Problem Set 1

1. Start by writing down the total Lagrangian for N independent harmonic oscillators that have the following total potential energy:

$$V(\mathbf{q}) = \frac{1}{2}\sum_i k_i q_i^2.$$

   Using the total Lagrangian, derive the N Lagrangian *equations of motion* to get differential equations for $\ddot{q}_i$. (Hint: the equations of motion are all identical).

   Solve these equations of motion assuming the initial velocities are $\mathbf{v}_i$ and the initial positions $\mathbf{x}_i$.

2. A system has the total Lagrangian

$$L = a\dot{q}_1^2 + b\frac{\dot{q}_2}{q_1} + c\dot{q}_1\dot{q}_2 + fq_1^2\dot{q}_1 q_3 + g\dot{q}_2 - k\sqrt{q_1^2 + q_2^2}$$

   Find expressions for the conjugate momenta, p_1, p_2, and p_3. Derive the Hamiltonian for this system. If you have done it correctly, your expression for the Hamiltonian should be expressed only in terms of the position variables and their conjugate momenta (and a few constants).

3. A one-dimensional simple harmonic oscillator is described by a Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

   Thus, the phase space has 2-dimensions consisting only of the momentum p and the coordinate q.

   a. Sketch the constant energy curves in this two-dimensional space corresponding to the condition $H = E$ for different values of E.
   b. Derive Hamilton's equations for this sytem.
   c. Solve the equations $p(t)$ and $q(t)$ subject to the general initial condition $p(0) = p_0$, $q(0) = q_0$. There are a couple of ways of doing this, and to get yourself comfortable using matrices, you might want to do this part using two coupled linear equations in matrix-vector form.
   d. By explicitly substituting the solutions back into the expression for the Hamiltonian, show that energy is conserved, i.e., that

$$H(p(t), q(t)) = H(p(0), q(0))$$

e. Next, consider the change of variables:

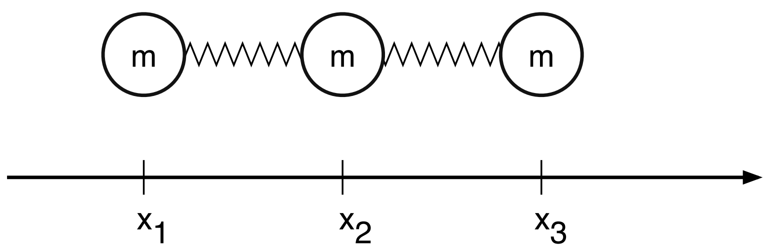
$$
\begin{aligned}
q &= \sqrt{\frac{2J}{m\omega}}\sin\theta \\
p &= \sqrt{2m\omega J}\cos\theta
\end{aligned}
$$

where J and θ are called the *action* and *angle* variables, respectively. Derive the new harmonic oscillator Hamiltonian in terms of J and θ.

f. Sketch the constant energy curves in the $J-\theta$ phase space.

g. Derive Hamilton's equations for these new variables and solve for the motion of the system in terms of J and θ, and explain how the phase space of part f is mapped onto the phase space of part a.

4. Consider a triatomic model for Ozone that lives in Lineland (i.e. a one-dimensional world): That is, there are three identical masses (all with mass m) that each have one



coordinate (x_1, x_2, and x_3) to describe their positions.

a. Write down an expression for the kinetic energy in terms of the momenta of the three particles, $T(p_1, p_2, p_3)$

b. Harmonic bonds between atoms are usually described in terms of a spring constant k and an equilibrium bond distance r_0. For two bound atoms at a distance r from each other, the bond potential would be:

$$V(r) = \frac{1}{2}k\left(r - r_0\right)^2$$

Write down an expression for the *total* potential energy for the triatomic molecule in terms of the atomic positions, $V(x_1, x_2, x_3)$.

c. The problem of the linear triatomic molecule can be reduced to one of two degrees of freedom by introducing coordinates $u = x_2 - x_1 - r_0$, $v = x_3 - x_2 - r_0$, and eliminating x_2 by requiring that the center of mass ($w = (x_1 + x_2 + x_3)/3$) remain at rest. Make these substitutions and rewrite both the potential and kinetic energies.

d. Can you find a different set of coordinates that would allow you to rewrite the Hamiltonian as a sum of two *uncoupled* harmonic oscillators?

5. Extra Credit: Develop a perturbation theory to study the action-angle variables of the Henon-Heiles problem,

$$H = \frac{1}{2}\left(p_1^2 + p_2^2 + q_1^2 + q_2^2\right) + q_1 q_2^2 - \frac{1}{3}q_1^3$$

Begin by using the normal canonical transformation for Harmonic oscillator action-angle variables and write H in the form,

$$H = H_0(J_1, J_2) + gV(J_1, J_2, O_1, O_2)$$

Assuming gV is small, find the new action-angle variables to first order in g. Explain the conditions under which the perturbation theory fails and relate this to the ergodic behavior of the system.