Chemistry 60641 — Spring 2011
Professor J. Daniel Gezelter — Due Fri. 2/4/2011

Problem Set 1

1. Derive Lagrange's equations of motion for N independent harmonic oscillators with:

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

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 Lagrangian

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

Derive the Hamiltonian for this system.

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 is 2-dimensional 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 $p(0) = p_0$, $q(0) = q_0$.
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:

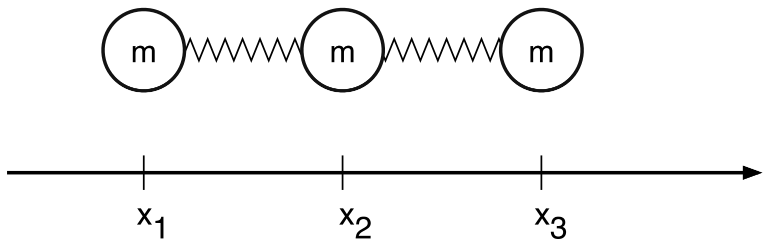
$$q = \sqrt{\frac{2J}{m\omega}}\sin\theta$$
$$p = \sqrt{2m\omega J}\cos\theta$$

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.