MATH 728B, WATER MOLECULE, HOMEWORK PROBLEMS I

Normal Modes. From the CHARMM22 all hydrogen force field we find that the potential energy for a single water molecule is

$$V(l_1, l_2, \theta) = k_{l_1}(l_1 - l_1^0) + k_{l_2}(l_2 - l_2^0) + k_\theta(\theta - \theta^0),$$

where $k_{l_1} = k_{l_2} = 450$ kcal/mole/angstrom^2, $l_1^0 = l_2^0 = 0.9572$ angstrom, $k_\theta = 55$ kcal/mole/radian^2, and $\theta_0 = 104.52°$. Also, in regard to the kinetic energy of a water molecule with zero linear momentum and zero angular momentum we have that $T = \frac{1}{2}p^T\tau(q)^{-1}p$, where $q = \langle l_1, l_2, \theta\rangle, \dot{q} = \langle \dot{l}_1, \dot{l}_2, \dot{\theta}\rangle = \tau(q)^{-1}p$, and where

$$\tau(q)^{-1} = \begin{pmatrix} \frac{1}{M_0} + \frac{1}{M_1} & \frac{\cos\theta}{M_0} & -\frac{\sin\theta}{M_0 l_2} \\ \frac{\cos\theta}{M_0} & \frac{1}{M_0} + \frac{1}{M_2} & -\frac{\sin\theta}{M_0 l_1} \\ -\frac{\sin\theta}{M_0 l_2} & -\frac{\sin\theta}{M_0 l_1} & \frac{M_0(M_1 l_1^2 + M_2 l_2^2) + M_1 M_2 l_{12}^2}{M_0 M_1 M_2 l_1^2 l_2^2} \end{pmatrix}.$$

In the above we use the abbreviation $l_{12}^2 = l_1^2 + l_2^2 - 2l_1 l_2 \cos\theta$. From the CHARMM22 all hydrogen topology file we find $M_1 = M_2 = 1.008$ amu (atomic mass unit), and $M_0 = 15.9994$ amu. From standard chemistry references we find that 1 amu $= 1.66054 \cdot 10^{-27}$ kilogram, 1 angstrom $= 10^{-10}$ meter, and 1 kcal/mole $= 4.184$ kJ/$(6.02214 \cdot 10^{23})$, where 1 J = 1 kg m^2 sec^{-2}. Show that 1 kJ/mole $= 10^{-4}$ amu angstrom^2 fs^{-2}, where 1 fs $= 10^{-15}$second (fs stands for femtosecond).

Define

$$K = \begin{pmatrix} 2k_{l_1} & 0 & 0 \\ 0 & 2k_{l_2} & 0 \\ 0 & 0 & 2k_\theta \end{pmatrix}.$$

Find a matrix B and a diagonal matrix μ^{-1} such that $B^T K B = K$ and $B^T\tau(q_0)^{-1}B = \mu^{-1}$, being careful about units. Here $q_0 = \langle l_1^0, l_2^0, \theta_0\rangle$. *Hint:* Diagonalize the matrix $K^{-1/2}\tau(q_0)^{-1}K^{-1/2}$ using an orthogonal matrix.

Approximate the Hamiltonian $h = \frac{1}{2}p^T\tau(q)^{-1}p + \frac{1}{2}(q - q_0)^T K(q - q_0)$ by the quadratic hamiltonian $h_0(p, q - q_0) = \frac{1}{2}p^T\tau(q_0)^{-1}p + \frac{1}{2}(q - q_0)^T K(q - q_0)$. Define $\tilde{q}, \tilde{p}$ by the relations $q - q_0 = B\tilde{q}, p = B\tilde{p}$, where B was found in the previous paragraph. Define $\tilde{h}_0(\tilde{q}, \tilde{p}) = \frac{1}{2}\tilde{p}^T\mu^{-1}\tilde{p} + \frac{1}{2}\tilde{q}^T K\tilde{q}$, where μ^{-1} is the diagonal matrix found in the previous paragraph. Write down Hamilton's equations of motion for the Hamiltonian $\tilde{h}_0$ and solve them explicitly (since they are uncoupled). Solutions of these equations with two of the three components of $\tilde{q}, \tilde{p}$ equal to zero are called *normal modes*. Give a geometric description of the three different normal modes for the water molecule.

Symmetric Water Molecules. Show that if $q(t), p(t)$ are solutions of Hamilton's equations $\dot{q} = \nabla_p h, \dot{p} = -\nabla_q h$ and if $q^1(0) = q^2(0)$ and $p_1(0) = p_2(0)$ then the equalities $q^1(t) = q^2(t)$ and $p_1(t) = p_2(t)$ hold for all t. Define $h_s(l, \theta, p_l, p_\theta) = h(l, l, \theta, p_l, p_l, p_\theta)$ to

be the Hamiltonian restricted to this type of trajectory. Compute the normal modes of h_s (i.e. symmetric normal modes) around the equilibrium values $l_0 = l_1^0, \theta_0$ as in the previous section. Relate the symmetric normal modes computed here to the general normal modes computed before.

Consider the three dimensional manifold $h_s(l, \theta, p_l, p_\theta) = E$ in the four dimensional space whose coordinates are $(l, \theta, p_l, p_\theta)$. If a trajectory of Hamilton's equations for h_s starts on this manifold, it stays on this manifold for all time. Note that if the three quantities l, θ, p_l are given, then the two possible values of p_θ can be determined by solving a quadratic equation. One way to visualize how the trajectories of Hamilton's equations move around in this three dimensional space is to use a *Poincaré surface of section*, i.e. we look at the intersections of a single trajectory with the two dimensional surface $\theta = \theta_0$ lying in the three dimensional constant energy manifold. Such pictures can be generated in Maple using DEtools,poincare. Using your explicit formulae for the symmetric normal modes describe what a Poincaré diagram for a symmetric normal mode looks like. Then use Maple to plot some Poincaré diagrams for the Hamiltonian h_s with different values of the energy E. Can you detect any differences between the normal mode case and the actual case? Describe them.