Assignment #1 – MM & FF

Date Assigned: 1/11/06; Date Due: 1/18/06

Note: Assignments are to be performed either individually or in groups of two. Students working together should turn in one joint copy of their solutions for grading.

1. The Morse representation of a stretch energy can be written in the form:

\[ E_{str}(r) = D \{ 1 - \exp[-\alpha(r-r_0)] \}^2 \]  

1-1

A polynomial expansion of \( E_{str}(r) \) might be written as:

\[ E_{str}(r) = \frac{1}{2} [ k + k^{(3)}(r-r_0) + k^{(4)}(r-r_0)^2 ](r-r_0)^2 \]  

1-2

Using this notation, the result of expanding the Morse potential to 4th order is:

\[ E_{str}(r) = D[\alpha^2 - \alpha^3(r-r_0) + \frac{2}{15} \alpha^4 (r-r_0)^2 ](r-r_0)^2 \]  

1-3

(a) Use these results to express the force constants \( k, k^{(3)}, k^{(4)} \) in the polynomial expansion Eq. 1-2 in terms of the Morse potential parameters \( D, \alpha, \) and \( r_0. \)

(b) Use a numerical program such as Excel to compute and plot the Morse function for the diatomic molecule HX whose parameters in atomic units are:

\[ D = 0.225 \, E_h \quad r_0 = 1.732 \, a_0, \quad \alpha = 1.381 \, a_0^{-1} \]

\( (E_h = 1 \text{ Hartree}, \ a_0 = 1 \text{ Bohr radius}; \ \text{see Cramer Ch. 1 on atomic units.}) \)

Try to make a high-quality plot. The axes should be properly labeled with units and you should chose a range of values that provides a good depiction of the well region of the potential. [Hint: Computations in the range of \( r/a_0 = 1-5 \) are sufficient.]

(c) Calculate the 2nd, 3rd, and 4th order polynomial approximations to this Morse function and plot them together with the original Morse representation. (Note that the 4th order representation includes all terms up to \( r^4 \), not just the \( r^4 \) term itself.)

(d) In a classical world, the average energy contained in a vibrational mode such as this stretch is \( k_B T \).

At room temperature, how large is \( k_B T \) in atomic units? Plot this energy on your graph from part (c).

(e) Discuss the quality of these polynomial representations in light of your comparisons.

(f) Express the quantities \( D, \alpha, \) and \( r_0 \) in SI units.

(g) What is the molecule HX? (How do you know?)

2. In Chapter 1 of Stone, pair potential well depths \( \epsilon \) are discussed in terms of temperatures, i.e. described as “typically in the region … 100-2000 K”.

(a) In what sense is a temperature “equivalent” to an energy?

(b) Convert the well depths provided by Stone in Table 1.1 (the \( \epsilon_{exp} \) values) to units of kJ/mol and compare them to typical values for bond energies and for conformational barriers.

(c) Why might it be convenient to discuss all of these energies in terms of temperatures?