1. What is meant by “molecular structure”? How is this concept related to the potential energy surface of a molecule?

2. Electrons aren’t explicitly included when we discuss molecular structure. Why not?

3. How many coordinates are required to completely describe the nuclear positions of a triatomic molecule?

4. How many coordinates are required to describe the potential energy surface of such a molecule? If your answer differs from that of #3 explain why.
5. Use the area provided below to sketch a contour plot of the potential energy surface of HCN similar to the one in Fig. 1 of the Born-Oppenheimer handout. Use a reduced representation in which the H-C-N angle is assumed to be 180° and the coordinates are the H-C and C-N bond lengths. Define the zero of energy to be separated H, C, and N atoms. Relevant data are:

\begin{align*}
\text{H-C bond length} & \sim 1.0 \, \text{Å} & \text{H-C bond energy} & \sim 413 \, \text{kJ mol}^{-1} \\
\text{C≡N bond length} & \sim 1.2 \, \text{Å} & \text{C≡N bond energy} & \sim 891 \, \text{kJ mol}^{-1}
\end{align*}

Be as quantitative as possible and indicate maxima and minima on the plot as well as their energies.

6. What information is missing from the PES of HCN in #5? How might this missing information be depicted?
7. At the right are shown nine isomers of molecular formula C₄H₆. Given that all of these structures consist of the same numbers of H and C nuclei and electrons, from a fundamental viewpoint they all represent the same electronic structure problem: these isomers are all merely particular points on the PES of C₄H₆. Yet we give these species individual chemical names (butadiene, dimethylacetylene, etc.) and talk about the distinctive physical and chemical properties of each of these species.

(a) What is special about these particular locations on the PES that enables us to think in this fashion?

(b) How is the situation different when we consider trans versus gauche butane? Is temperature important?
8. Below is a flow chart classifying some of the various types of isomerism common in molecular systems.

Use this scheme to classify the following pairs of molecules.

1. HOOC–C–COOH
2. HOOC–C–CH(CH₃)–H
3. H₃C–C=CH=CH(CH₃)
4. C≡C–C(CH₃)=H
5. H₃C–C=CH(CH₃)
6. H₃C–C=CH
7. H₃C–C–Cl
8. H₃C–C–Cl
9. H₃C–C–Cl
10. H₃C–C–Cl
9. The classifications of isomers into those whose interconversion requires only rotations about single bonds and those requiring rotation about double bonds or breaking and reforming of single bonds is especially important for how we view chemical species. The reason lies in the differences in the energy barriers separating these types of interconversions. In the case of C-C bonds, barriers to rotation about single bonds typically fall in the range 10-80 kJ/mol, whereas rotation about double bonds requires 260 kJ/mol and (single) bond breaking 350 kJ/mol. Use these estimates and the data tabulated below (T=298 K) to discuss isomer interconversion at room temperature. (Recall that the transition theory rate constant for a unimolecular process is approximately given by \( (k_B T / h)e^{-\Delta H^*/RT} \), where \( \Delta H^* \) is the activation energy.)

<table>
<thead>
<tr>
<th>( \Delta H^* / kJ \text{ mol}^{-1} )</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H^*/RT )</td>
<td>0.4</td>
<td>0.8</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>20</td>
<td>40</td>
<td>81</td>
<td>202</td>
</tr>
<tr>
<td>( \frac{k_B T}{h}e^{-\Delta H^*/RT} / s^{-1} )</td>
<td>( 10^{12.6} )</td>
<td>( 10^{12.4} )</td>
<td>( 10^{11.9} )</td>
<td>( 10^{11.0} )</td>
<td>( 10^{9.3} )</td>
<td>( 10^{4.0} )</td>
<td>( 10^{4.7} )</td>
<td>( 10^{22.3} )</td>
<td>( 10^{74.9} )</td>
</tr>
</tbody>
</table>
10. Define the terms “molecular mechanics” (MM) and “force-field” (FF).

11. The use of FFs in MM requires that the properties of atoms or small groups of atoms be nearly the same in different molecular environments so that the parameters specifying these properties are “transferable” among different molecules. (For example, all of the CH3 groups in the C4H6 isomers from #7 have nearly the same properties.) Give several examples of properties that are transferable and one or more properties that are not transferable in this sense.

12. Jensen describes the energy computed from a FF calculation using the expression (Eq. 2.1):

$$E_{FF} = E_{str} + E_{bnd} + E_{tors} + E_{vdw} + E_{el} + E_{cross}$$

(a) Briefly state the meaning of each of these components of the energy.
(b) Which of these terms would be identically zero when describing a diatomic molecule?

13. Shown at the right is a schematic plot of $E_{str}(R_{CH})$ in HCN. How does this curve relate to the PES you sketched in #5?

14. A very good first approximation to the molecular potential of a diatomic molecule is the Morse function, $E_{str}(R) = D\{1 - \exp[\alpha(R - R_0)]\}^2$.

(a) Instead of this function, most force-fields use a polynomial expansion about $R=R_0$, which is much less accurate. Why is this practice adopted?

(b) Many force fields stop at a harmonic representation for the bond stretching energy, $E_{str}(r) = k(R - R_0)^2$. Why is this form acceptable for strong but not weak bonds?
15. On the grids below, sketch the torsional potentials expected for (i) ethane and (ii) 1,2-dichloroethane. Indicate the molecular structures at key points on the potential.
16. On the grids below, sketch the torsional potentials expected for (i) ethene and (ii) 1,2-dichloroethene. Indicate the molecular structures at key points on the potential.
17. If the torsional potentials for the molecules of questions 10 & 11 were expressed in terms of the standard form:

\[ 2E_{\text{tors}}(\omega) = V_1 \{1 + \cos(\omega)\} + V_2 \{1 + \cos(2\omega)\} + V_3 \{1 + \cos(3\omega)\} \]

which of the parameters \( V_1, V_2, V_3 \) would be identically zero?

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( V_1 )</th>
<th>( V_2 )</th>
<th>( V_3 )</th>
</tr>
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<tbody>
<tr>
<td>ethane</td>
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<td></td>
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<tr>
<td>1,2-dichloroethane</td>
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<tr>
<td>ethene</td>
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<tr>
<td>1,2-dichloroethene</td>
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</table>

18. Why are “extra” out-of-plane terms needed for describing formaldehyde (H\(_2\)CO)?