Review

Generating Potential Energy Surfaces

We have discussed two ways of generating a PES: 1) electronic structure methods and 2) empirical potential. We will generate PESs using both of these general classes of methods throughout this class. Below is a chart summarizing these methods. Fill out this chart with the information you have learned so far in this course:

<table>
<thead>
<tr>
<th>Method for generating a PES</th>
<th>Which method is more accurate?</th>
<th>Which method is more computationally efficient?</th>
<th>What software have we used with this method?</th>
<th>Give an example of how this type of potential can be generated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Potentials</td>
<td>x</td>
<td>Python modules ASE/TSASE (introduced in Lab 3)</td>
<td>Lennard Jones or Morse Potentials</td>
<td></td>
</tr>
<tr>
<td>Electronic Structure Methods</td>
<td>X</td>
<td>VASP (Lab 1- Part 2)</td>
<td>Density Functional Theory</td>
<td></td>
</tr>
</tbody>
</table>

We have introduced a few examples of potential energy surfaces for simple 1D systems (See figure 1 below). Next, we will build on these examples by raising the dimensionality of our chemical system.

a) Diatomic molecule

b) Noble gas

Figure 1. Two examples of 1D PES are shown above one of which is a diatomic molecule (a) and the other is two noble atoms interacting (b). The locations on these plots where the force is very close to zero is the blue point for (a) and configurations with bond lengths greater than the red points for both (a) and (b).
The L-J Potential Energy for Chemical Systems with >2 atoms

The L-J potential can be used for chemical systems with more than two atoms. In order to do this we will need to sum over all pairs of atoms. Let’s first look at a three atom system:

In this chemical system with three atoms of the same type, we can take the sum of the L-J potential energy resulting from all pairs of atoms in the chemical system. The total potential energy for this system would be,

\[ V(\vec{r}) = V_{LJ}(r_{ij}) + V_{LJ}(r_{ik}) + V_{LJ}(r_{jk}) \]

where \( \vec{r} \) contains information on where atoms i, j and k are located and \( V_{LJ}(r) \) is the Lennard Jones potential used in lab 2 part2 (equation is on the next page).

Note that in the example given for the triatomic molecule with all three atoms constrained to a line (on the next page of this worksheet), we replaced \( r_{ik} \) with \( r_{ij} + r_{jk} \).

In general, for an LJ system with N atoms the total potential energy is:

\[ V_{Total}(\vec{r}) = \sum_{i=1}^{N} \sum_{j=i}^{N} V_{LJ}(r_{ij}) \]

where \( r_{ij} \) is the bond length between atoms i and j.

**Problem.** Write down an expression of the potential energy for a LJ system with 4 atoms. Draw a picture of the 4 atom chemical systems and define the variables used in your expression for the potential energy.

\[ V(\vec{r}) = V_{LJ}(r_{12}) + V_{LJ}(r_{13}) + V_{LJ}(r_{14}) + V_{LJ}(r_{23}) + V_{LJ}(r_{24}) + V_{LJ}(r_{34}) \]

On the next page, you will look at two example PES for triatomic systems.
2D Potential Energy Surfaces: Contour Plots

Below are two 2D contour surfaces representing the PES for two different triatomic molecules constrained to a line. The plot on the left is the 2D LJ potential and the plot on the right is a 2D potential known as the LEPS potential (named after four people whose names began with L, E, P, and S). The “ideal” bond length in LJ is 1.12 and the “ideal” bond length in LEPS is 0.75.

<table>
<thead>
<tr>
<th>Atomic Configuration</th>
<th>Draw a picture of the configuration of the chemical system.</th>
<th>Is the force ~ equal to 0 on the LJ PES?</th>
<th>Is force ~ equal to 0 on LEPS PES?</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{AB}=1.12 ) ( r_{BC}=1.12 )</td>
<td>A---B---C</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>( r_{AB}=1.12 ) ( r_{BC}=10.0 )</td>
<td>A---B-------------C</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>( r_{AB}=10.0 ) ( r_{BC}=0.75 )</td>
<td>A-------------B--C</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>( r_{AB}=1.0 ) ( r_{BC}=1.0 )</td>
<td>A--B--C</td>
<td>No</td>
<td>Yes, but it is not a local minima; it is a saddle point</td>
</tr>
</tbody>
</table>

What is the key difference between these two potential energy surfaces in terms of stability of the triatomic molecule?
Left: Triatomic molecule is the most stable configuration.
Right: The diatomic molecule is most stable. The triatomic molecule is not stable and represents a transition state between forming molecules AB----C and A-----BC.

\[
V(r_{AB}, r_{BC}) = V_{LJ}(r_{AB}) + V_{LJ}(r_{AB} + r_{BC}) + V_{LEPS}(r_{BC})
\]

Where \( V_{LJ}(r) = 4\epsilon \left( \frac{\delta}{r} \right)^{12} - \left( \frac{\delta}{r} \right)^{6} \)

I will leave this equation out. You can find it in a paper called *Location of Energy Barriers. II. Correlation with Barrier Height* published in the Journal of Chemical Physics by M. H. Mok and J. C. Polanyi.

In the contour plots shown here, dark blue is low energy, and light brown is high energy.
1) Suppose you have a vector, \( \vec{v} = (-1, 1) \). Find the ending point of the vector if the initial point is at (0,0), (2,1), and (-3,-2). Draw each vector on the plot below.

![Plot of vectors with points and vector additions](image)

2) Let vectors \( \vec{v} = (-1, 1) \), \( \vec{u} = (2, 1) \) and \( \vec{w} = (3, -1) \). Compute the following:
   a. \( \vec{v} + \vec{u} \) (Illustrate the vector addition in the graph below)
      \[
      \vec{v} + \vec{u} = (-1, 1) + (2, 1) = (-1 + 2, 1 + 1) = (1, 2)
      \]

![Graph with vectors and vector addition](image)

   b. \( 2\vec{v} + 0.5\vec{w} \)
      \[
      2\vec{v} + 0.5\vec{w} = 2(-1, 1) + 0.5(3, -1) = (-2, 2) + (1.5, -0.5) = (-0.5, 1.5)
      \]

3) Let \( \vec{v} = (-3, 4) \). Compute the magnitude (\( \|\vec{v}\| \)) and unit vector (\( \hat{v} \)). Then, find a new vector, \( \vec{w} \), that is in the same direction as \( \vec{v} \) but has a magnitude of 2.
   \[
   \|\vec{v}\| = \sqrt{(-3)^2 + 4^2} = 5
   \]
   \[
   \hat{v} = \frac{\vec{v}}{\|\vec{v}\|} = \frac{\langle -3, 4 \rangle}{5} = \langle -\frac{3}{5}, \frac{4}{5} \rangle
   \]
   \[
   \vec{w} = 2\hat{v} = 2\langle -\frac{3}{5}, \frac{4}{5} \rangle = \langle -\frac{6}{5}, \frac{8}{5} \rangle
   \]
Gradients

In the 1D example where you have a PES, \( V(r) \), the definition of the force was as follows:
\[
\vec{F} = -\frac{dV}{dr}
\]

For higher dimensional systems, the PES is dependent on more than one dimension. Below is the force for a 2D PES, \( V(x,y) \):
\[
\vec{F} = -\left( \frac{\partial}{\partial x} V(x,y), \frac{\partial}{\partial y} V(x,y) \right) = \left( F_x, F_y \right)
\]
where \( \frac{\partial}{\partial x} \) represents the partial derivative with respect to the coordinate \( x \) or \( y \). With the extra dimension, our gradient descent equation becomes:
\[
\langle x, y \rangle_{n+1} = \langle x, y \rangle_n + \alpha \langle F_x, F_y \rangle_n
\]
Next, let’s try going through an example for a simple 2D potential:
\[
V(x,y) = x^2 + y^2
\]
where the force vector is as follows:
\[
\vec{F} = -(2x, 2y)
\]
Below is the contour plot of \( V(x,y) \). Let’s try writing out the first few steps of the gradient descent algorithm. Set \( \alpha \) equal to 0.25. Add a point on the contour plot below for each step number listed in the table. Also, add the direction of the force at each configuration sampled.

<table>
<thead>
<tr>
<th>Step #((n))</th>
<th>( \langle x, y \rangle_n )</th>
<th>( \langle F_x, F_y \rangle_n )</th>
<th>( \alpha \langle F_x, F_y \rangle_n )</th>
<th>( \langle x, y \rangle_{n+1} = \langle x, y \rangle_n + \alpha \langle F_x, F_y \rangle_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \langle 4, 2 \rangle_1 )</td>
<td>( \langle -8, -4 \rangle_1 )</td>
<td>0.25 ( \langle -8, -4 \rangle_1 ) = ( \langle -2, -1 \rangle_1 )</td>
<td>( \langle 4, 2 \rangle_1 + \langle -2, -1 \rangle_1 = \langle 2, 1 \rangle_2 )</td>
</tr>
<tr>
<td>2</td>
<td>( \langle 2, 1 \rangle_2 )</td>
<td>( \langle -4, -2 \rangle_2 )</td>
<td>( \langle -1, -0.5 \rangle_2 )</td>
<td>( \langle 2, 1 \rangle_2 + \langle -1, 0.5 \rangle_2 = \langle 1, 0.5 \rangle_3 )</td>
</tr>
<tr>
<td>3</td>
<td>( \langle 1, 0.5 \rangle_3 )</td>
<td>( \langle -2, -1 \rangle_3 )</td>
<td>( \langle -0.5, -0.25 \rangle_3 )</td>
<td>( \langle 1, 0.5 \rangle_3 + \langle -0.5, -0.25 \rangle_3 = \langle 0.5, 0.25 \rangle_4 )</td>
</tr>
</tbody>
</table>
Diatomic

Qualitatively draw the force each atom feels based on the geometry drawn below for the diatomic molecules. The PES of each diatomic molecule is the Lennard Jones potential with $\sigma$ and $\epsilon$ equal to 1.
Three Atom System

In step 3 below is a picture of a three atom system. Complete the following exercises based on this system:

1. Write down a general expression for the potential energy of the 3 atom chemical system visually shown in step 3 in terms of the expression for the following pairwise interaction: 
   \[ V(r_{ij}) = (r_{ij} - 2)^2 \] 
   where \( r_{ij} \) represents the bondlength between two atom numbers where \( i \neq j \). Calculate the potential energy at the configuration shown in step 3 where \( r_{12} = 1.6 \), \( r_{13} = 2.8 \), and \( r_{23} = 1.9 \).

   \[ V_{3\text{atom}} = V(r_{12}) + V(r_{13}) + V(r_{23}) \]
   \[ V_{3\text{atom}} = (r_{12} - 2)^2 + (r_{13} - 2)^2 + (r_{23} - 2)^2 \]
   \[ V_{3\text{atom}} = (1.6 - 2)^2 + (2.8 - 2)^2 + (1.9 - 2)^2 \]

2. Write down a general expression for the force of a pairwise interaction. Calculate the pairwise forces for each pairwise interaction (\( r_{12}, r_{13}, r_{23} \)).

   \[ \vec{F}(r_{ij}) = -\frac{dV}{dr_{ij}} = -2(r_{ij} - 2) \]
   \[ \vec{F}(r_{12}) = -2(1.6 - 2) = +0.8 \]
   \[ \vec{F}(r_{13}) = -2(2.8 - 2) = -1.6 \]
   \[ \vec{F}(r_{23}) = -2(1.9 - 2) = +0.2 \]

3. Next draw an approximate force vector that the atoms feels based on each pairwise interaction (there should be two force vectors acting on each atom; so atom 1 should feel a force from both atom 2 and 3, atom 2 should feel a force from atom 1 and 3, etc.).

   ![Diagram showing pairwise forces and overall forces](image)

   Note: Pairwise force vectors and overall force vectors are approximate.

4. Lastly approximately sum the force vectors on each atom to visually show the overall force on each atom based on its current configuration.