

In-class Practical 3

Today we'll be getting used to a data analysis program called Grace, and we'll be fitting approximate energy functions for three model problems. The quantum mechanical data for the three problems has been previously calculated and is available on the class web site.

1. The bond in N_2 molecules
Energy data stored in gezelterlab.org/data/N2.dat
2. The torsional potential in ethane hindered rotations
Energy data stored in gezelterlab.org/data/eth.dat
3. Non-bonded interatomic (dispersion) interaction in an Argon dimer
Energy data stored in gezelterlab.org/data/Ar2.dat

The first few sections of the exercise are to get you working with the plotting software. Note that Grace has a somewhat steep and sometimes frustrating learning curve, but it is a *very* powerful tool for extracting information from data. Because of this, it is one of the most widely used scientific tools.

Preliminaries:

1. First, make sure you have downloaded a copy of **qtgrace** to your laptop. To get the software, go to:
<https://sourceforge.net/projects/qtgrace/>
and click on the Download button.
2. Unpack the file that comes down and install it somewhere you can easily get to it: On a Mac, drag the **qtgrace** program to your Applications directory. On Windows 10, you can drag the qtgrace folder to your desktop - the qtgrace program itself is inside the bin directory.
3. There's a setup wizard the first time you run **qtgrace**. You'll want to activate the "Undo" feature, but you can leave all of the other defaults alone.
4. Download the three data files listed above using your web browser (see the table below). Save the files to your Desktop as **N2.dat**, **eth.dat**, and **Ar2.dat**. These are simple text files, but *don't* use the **.txt** extension your browser will want to append.

Browser	How to save the file	Save Format
Chrome	File → Save Page As...	text (but don't use the .txt file extension)
Firefox	File → Save Page As...	Plain text document
Safari	File → Save As...	Page Source (but don't append .txt)
Edge	Use another browser	
IE	Gear → File → Save As...	Text file

5. Make sure you can use `qtgrace` to plot some data: `Data` → `Import` → `ASCII...` and navigate until you reach your desktop directory. On a Mac this will be in:
`/Users/username/Desktop` On Windows, this is often in `C:\Home\Desktop`
 If you downloaded the data files to somewhere else like your Downloads directory, you'll have to find the correct path to the files before you can proceed. If you need help finding the files, ask!
6. Select the "`N2.dat`" file and then click the "OK" button to import the data file, and then "Cancel" to get rid of the import window. Your window should now have an intermolecular potential plotted in it. This is the electronic energy as the N_2 molecule is stretched and compressed. The units along the interatomic (x) axis are Angstroms, and along the energy (y) axis are Atomic Units of energy (Hartree).

Scaling and Shifting data in QtGrace:

1. First we need to change the energy units to something more common (kcal / mol), and shift the curve so that the zero of energy is at the *bottom of the well*. With the N_2 data still on screen, go to `Data` → `Transformations` → `Evaluate expression...`
2. Select the Source to be Graph: G0, Set: G0.S0 and the Destination to Graph: G0, Set: G0.S0. In the formula box, type:
 $y = y * 627.509$
 Then, click `Apply`
3. Click the Autoscale `AS` button to replot the data on a better scale.
4. Use the magnifying glass tool to zoom in on the minimum of the potential, which should be at around -68749.4. Follow the procedure in point 2, but *shift (not scale)* the potential up by 68749.4 kcal / mol. Click Autoscale and verify that your potential has a minimum energy of 0.

Fitting data in QtGrace:

1. Go to `Data` → `Non-linear curve fitting...`
2. Select the Source to be Graph: G0, Set: G0.S0 and leave the Destination set *unselected*. In the formula box, type:
 $y = 0.5 * A0 * (x-A1)^2$
 (i.e. a harmonic fit) and set Parameters to 2.
 Pick an initial value of 1.1 for A1, and 100 for A0. Click `Apply`. You should see a terrible fit.
3. Change the formula in the box to:
 $y = A0 * (1 - \exp(-A2 * (x-A1)))^2$
 (i.e. a Morse oscillator fit) and set Parameters to 3.
 Pick an initial value of 1.1 for A1. Click `Apply`. You should see a much better fit. In the qtGrace Console window, you should be able to find the best fitting bond length (A1) and dissociation energy (A0).

Limiting the region for a fit:

1. We'd like to tailor our fits to only the region around the minimum. With the N_2 data still on screen, go to `Edit` → `Regions` → `Define...` Click the `Define` button, and start drawing a

box around the minimum. Use the right mouse (or Ctrl-click) to close the region. This has now defined region 0 for the fit.

2. Go back to the fit window, click the Advanced tab and restrict the fit to region 0. Re-do the morse oscillator fit. You should have a much better fit near the minimum.
3. Change the formula back to $y = 0.5 * A0 * (x-A1)^2$ with Parameters set to 2, and re-do the harmonic fit. Zoom and tighten the region if necessary until you get a reasonable fit near the bottom of the well. What's the best fitting bond length (A1) and force constant (A0)?

Trigonometric functions in fits:

1. Start up `qtgrace` and plot the `eth.dat` file that you previously downloaded to your desktop.
2. Shift the y axis so that the 0° torsion is at the zero of energy ($y = y + 79.8561900875$)
3. Scale the y axis to so that you are using kcal / mol units instead of Hartree.
4. Scale the x axis so that we are in units of radians, not degrees.
5. Fit the data to the functional form $y = A0 * (1 - \cos(A1 * x + A2))$

Difficult fits:

1. Start up `qtgrace` and plot the `Ar2.dat` file that you previously downloaded to your desktop.
2. Shift the y axis so that the infinitely separated dimer is the zero of energy:
 $y = y + 1053.61385084$
3. Scale the y axis to so that you are using kcal / mol units instead of Hartree.
4. Zoom in and find the well.
5. Fit the data to the functional form $y = 4 * A0 * ((A1/x)^{12} - (A1/x)^6)$
This is a function called the “Lennard Jones” potential that is widely used to understand intermolecular interactions.
6. Fix the problem with the fit you get.
7. The standard form for the Lennard-Jones potential for Argon has $A0 = 0.2381$ kcal / mol and $A1 = 3.41$ angstroms. We'll create this function as follows:
 - a. `Edit → Data Sets...`
 - b. Within this window do: `Edit → Create new → By formula`
 - c. `Start at: 2.9, Stop at: 10, Length: 100,`
 $y = 4 * 0.2381 * ((3.41/x)^{12} - (3.41/x)^6)$

Homework questions:

1. What is the dissociation energy (in kcal / mol) for the best fitting Morse potential for N₂? How does this compare to the experimental value?
2. Based on your fit, what is the energy barrier for hindered rotation in the ethane torsion?
3. For the Lennard-Jones potential for intermolecular interactions,

$$V(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right)$$

there are 2 parameters, σ , and ϵ . In terms of these two parameters, answer the following questions (no fitting or plotting required, but Mathematica may come in helpful).

- a. What is the distance r to the location of the energy minimum?
 - b. What is the energy at the energy minimum?
 - c. What is the dissociation energy (i.e. what is the difference in energy between the infinitely separated atoms and those at the minimum)?
 - d. What is the distance of closest approach before the energy becomes repulsive (or greater than zero)?
4. Using **qtgrace**, create publication-ready plots of your fits for the N₂ bond, ethane torsion, and Argon dimer potentials comparing them to the raw data. A publication-ready plot is a plot you would be proud to show at a scientific conference. This means your axes should be *labeled* and have *units*, raw data should be distinguished from the fits using a *legend* and different symbols or line styles, the plot should be *titled*. In **qtgrace**, most of these can be done using the Plot menu (or by double clicking on the relevant regions of your plot). Add your plots to your solutions to problem set 5.