## Jaguar – DFT Optimizations and Transition State Searches

Density Functional Theory (DFT) is a quantum mechanical (QM) method that gives results superior to Hartree-Fock (HF) in less computational time. A large amount of information can be obtained from the molecular wave function including the energies of reactants, products, intermediates and transition states. As you work with these programs, you will start to get a sense of what is feasible but be aware that some calculations can take hours or days.

Jaguar is a QM program optimized for larger molecules that a synthetic organic or organometallic chemist might want to study. Input and output files for this program are mostly text-based so they can be analyzed or edited in a text editor. The graphical user interface **Maestro** can also be used to set up, submit and analyze the results of calculations. In this tutorial we will examine the energetics of the simple S_N2 reaction of Br^- with H_3CCl, although these procedures are applicable to more complicated systems.

Step 1. Building Reactant:

Figure 1
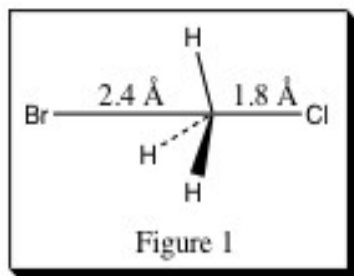
Start **Maestro**. Under the **Maestro** menu, select **Preferences** and then **Builder-Behavior** . Un-check "**Adjust number of hydrogens following build operations**". This will allow a hypervalent carbon when building.

Select **Fragments** from the Edit menu. Click on the **CH₄ icon** in the toolbar (or Edit-Build-Fragments menu) and click in the workspace. Click-hold on the **Atom Properties** icon (-A-) to activate the pulldown and select Cl (or Edit-Build-Fragments menu). Click on one of the H atoms of the methane molecule in the black workspace. Next, click on ✎ (check the **Edit-Build-Build Toolbars** box if you can't see the pencil icon). Then click on the methyl carbon and then in space where you want to place the Br. Re-click the pencil tool to end the drawing action. Change the new atom to Br with the **Atom Properties** icon. Click/hold on the label 🏷 icon and choose **Element** to label your molecule.

Click/hold ✗ and choose **Angle** from the pulldown. We need to set the bond lengths and angles to match those in the figure. The order in which you select atoms to define an angles and distances matters. To select the Cl-C-Br bond angle angle, **first click on Cl, then C and then Br**. If you select the atoms in the other order, the Cl will move and the H atoms will not be correctly situated. Once the angle is selected, set the angle to 180° with a click/hold on the left mouse button and movement of the mouse. Next, click/hold ✗ and choose **Distance** from the pulldown. Alter the C-Cl and C-Br bond lengths to the values in Figure 1. [If you have trouble getting these exactly as specified, try the menu: **Edit-Adjust-Distance**. You can type in the desired value in the Current box and then Enter. You can do the angles this way too.] Select **Symmetrize Workspace** from the Edit menu. **C3v** should be displayed as the **Point Group**. Click **Symmetrize**, then **Close**. [If you see **Cs**, just close the panel. As long as the structure is reasonably symmetric, the calculation will be fine.] Click the **Create Entry** icon and name the entry **reactant**.

Step 2. Minimizing Reactant:

Select the menu: **Applications-Jaguar-Optimization**. Set the **Molecular charge** to **-1** and then the enter key (warning about charge and multiplicity should go away). If you find that the C-Br bond has been deleted, don't worry. Drawn bonds mean nothing to a QM calculation. Next to **Basis set**, change 6-31G to **LACVP** and **Polarization** to *****. Under the **Theory** tab, note that the default setup is **Level of theory**: **DFT**, **Functionals**: **Hybrid**: **B3LYP**. [Basis set and functional choices are **very** dependent on the elements in your molecule, functional groups, charge, spin state, and desired level of accuracy. When you are doing your own work, you should ask for help and not blindly apply these settings.] Under the **Optimization** tab, set **Convergence criteria** to **Loose** (only for this exercise). Under the **Properties** tab, mark the boxes next to **Vibrational frequencies** and **Use available Hessian** (note that this does not give accurate frequencies and should not be used for final results). Click **Start**, and in the Start window select **Incorporate**: **Append new entries as a new group**. Click **Start**. [localhost is okay for this step since it should be less than 5 minutes. Normally jaguar_debug is best for short runs (less than 20 minutes), otherwise choose jaguar_dino].

When it finishes, note the thermodynamic data in the **Project Table**. If the columns are narrow, choose **Fit To Header + Data** from the ⟷ Columns menu on the **Project Table**. The **Gas Phase Energy** is the electronic energy in the atomic unit hartree.

Step 3. Building/Minimizing Product:

With the optimized **reactant** in the workspace, **Create Entry** and name the new entry: **product**. Set the

Figure 2

bond lengths in the **product** as in Fig 2. To get the H atoms in the right place, set the Cl-C-H angles to 72°. Remember, the order in which you select atoms matters. These steps change the reactant into the product without taking the shortcut of switching the Cl and Br. This will be important for transition state searching later on.
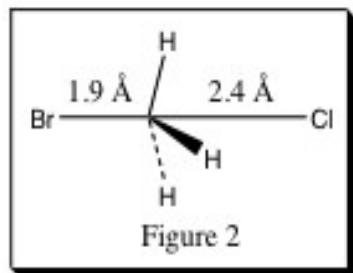
Re-open the **Jaguar Optimization** panel. Verify the settings are unchanged, and then optimize the structure as before. When the calculation completes, subtract the **reactant** Gas Phase Energy from the **product** (use all of the digits present in the field). Multiply the result by 627.51 to convert to kcal/mol. Which complex is more stable?

You may find it convenient at this point to delete the unoptimized reactant and product from the project table so you don't confuse the unoptimized and optimized structures later.

Step 4. Transition State Search – LST Method:

Under the **Applications** menu, select **Jaguar**, **Transition State Search**. Most settings should still be current. Under the **Optimization** tab, select **Convergence criteria**: **Default**. In the **Transition State** tab, click on **Search method**: **LST**. Then click the **Choose** button next to the **Reactant** field, change **Choose entry from** to **All**, and select **reactant** then click **Choose**. Do the same for **product** in the **Product** field. For this calculation, go with the default Initial LST guess of 0.50. Click on the squares next to the Structures (on the Transition State tab window) to display the two structures simultaneously.

Transition state searches require matching atom numbers in the reactant and product. This is why we built the product by inverting from the reactant. Verify that the numbers match using the menu: **Workspace-Atom Labels**. Under the **Atom Properties** section, highlight **Atom number by entry**, unhighlight other options, then click **All**. [This option is unavailable under the Label icon]. Do the numbers match?

Now, unclick the square next to the product (to undisplay it) in the Transition State tab of the Jaguar panel. Only one molecule can be in the workspace when you submit a calculation. Submit the calculation with the **Job Name** set to **ts1**. The program will identify a reaction coordinate between the **reactant** and **product** and generate a transition state guess, in this case 0.50 of the way along the reaction coordinate. The program then minimizes most coordinates while maximizing the reaction pathway coordinate.

Once the calculation is finished, change the title of the new entry in the **Project Table** to **ts1**. In that same title box, click on the blue button labeled *V* to view the results of the frequency calculation. The first frequency should be negative, indicating it is imaginary. Movement along this coordinate results in a reaction. The presence of exactly one imaginary frequency confirms that the structure is a transition state.

Click on the **Animate** button. Does this imaginary frequency correspond to the S_N2 reaction coordinate? Inspect the vibrational frequencies of the **reactant** and **product** structures. Frequency calculations are also important for confirming energy minima, which should possess no imaginary frequencies.

Record the Gas Phase Energy of **ts1**. What is the activation energy (in kcal/mol) of this reaction? What is the activation energy for the reverse reaction?

You can optimize the overlay of **ts1** with the **reactant** and **product** by displaying all three in the workspace. Select **Superposition** under the **Tools** menu. Set **Entries to superimpose** to **Included entries**. In the **ASL tab** click **All**. [Order matters – a structure lower in the table is moved relative to one higher, or if picking atom pairs, the second picked structure moves relative to the first.]

Step 5. TS Search - Relaxed Coordinate Scan Method:
We found a transition state in step 4 but that easy method often fails!! If that happens, you can manually search for a transition state. One way to do that is to generate a series of structures along the reaction coordinate. We will do that by adjusting the distance between the C and Br, driving the Br toward the C in each step. At each step, the C-Br distance will be fixed but the rest of the structure will be optimized.

Make sure only **reactant** is in the Workspace. Select the menu: **Applications-Jaguar-Relaxed Coordinate Scan**. Open the **Scan** tab. Verify the **Type:** is **Distance** and then click on the C then the Br in the Workspace structure. In the **Selected coordinate** box, enter **Starting value: 3.6**; **Final value: 1.9**; **Increment: 0.1**. The Number of steps field should now read 18. ****Turn off the frequencies option* by un-checking the Vibrational frequencies box in the **Properties** tab. Submit this calculation with the job name: **scan1**. It will take about 10 minutes.

When the scan finishes, the entries for the results should be "selected" (highlighted in yellow in the Project Table). Select the menu: **Tools**-**Measurements**-**Distances**. Check the **Create property for selected entries** box at the bottom of the panel. Click on the C and Br in the Workspace structure. The Project Table will now have a column titled **Distance 1-6**. To animate the reaction, select the **ePlayer**-**Play forward** menu option.

In the main window, select the menu: **Tools**-**Plot Coordinate Scan**-**One Coordinate**. Click **Open** and choose the file **scan1.grd**. Find the point on the chart closest to where the S_N2 transition state should be located, find that structure in the Project Table, and display it in the Workspace. How does it compare with the transition state you calculated using the LST method? How do the minima found in the scan compare with your optimized structures? What do you think is the significance of the "tails" on either end of the plot?

Note: You have not actually found a transition state in this scan! You have just mapped out a reaction profile which indicates roughly where the transition state is. From this data, you would typically take the structure closest to the top of the profile and perform a transition state optimization with a frequency calculation to test for the transition state. In that case, you would do a (full) frequency calculation on the TS guess, then read in its "restart" file (see below) and set up the following calculation: Applications/Jaguar/Transition State Search/Search Method = Standard (not LST); Properties = Vibrational Frequencies.

****If you are doing this for a class session you can stop here****

Step 6. TS verification - Intrinsic Reaction Coordinate Search:
Sometimes neither of the above approaches seems suitable or maybe you just want a shortcut? Often one can find a transition state by simply starting with a guess of what the structure might be. For example a Diels-Alder TS might be guessed by starting with the product in a chair conformation and stretching the bonds out by 0.5A or so. This would be followed by a transition state optimization and frequency calculation (same process as in the last sentence of the prior section). If you get lucky and locate a transition state from a guess you must confirm that your transition state really connects your reactant and product and is not just some other saddle point on the PES. In this case, you would start with the transition state you found and look along the reaction coordinate a few steps in either direction.

Open the **Jaguar** panel (it doesn't matter which subtask) and click on **Read** at the bottom. Select **ts1.01.in**. This is an output file from the earlier LST transition state search. It contains the job options, transition state geometry (and reactant and product geometries), the molecular orbitals, and information about the reaction coordinate. Such a file is often called a "restart" file (see above). Close the Jaguar panel and re-open it with the **Reaction Coordinate** task.

In the **IRC** tab, change **Number of IRC points** to **20**, **IRC step size** to **0.50**, and check the box next to **Use mass weighted coordinates**. At the bottom of the Jaguar panel, click **Write**, and name the file **irc1**. In this example, we're going to run the calculation on our server which is where most Jaguar calculations should be run. We will also do some manual edits on the Jaguar input file. To to this, open a new terminal window and type **gedit irc1.in**. Near the top of the file you should see a keyword section that looks like this:

MAEFILE:irc1.mae

&gen
basis=lacvp*
ircstep=0.5
molchg=-1
dftname=b3lyp
ifreq=-1
ircmax=20
irc=2
&

This section contains all of the non-default settings for the job and are things you often set by selecting in the Maestro/Jaguar menus. You can also make changes directly to the input file if you get familiar with a few common keywords. In this case, we forgot to deselect frequencies during job setup, so we will **delete** the line **ifreq=-1**. **Save** the file (overwrite filename) and **close gedit**. Editing the input files may seem a little strange at first but if you are doing calculations on a series of molecules, it is often easiest to be sure all have the same keywords by using copy/paste directly on the input files. It is a good idea regardless to view the input file to make sure the basis set and other keywords are really what you want.

On the command line, type **run_jaguar irc1**. The job has now been submitted to the server. Type **qstat** (or **qstat -u loginname**) and also **tail irc1.log** to monitor the job progress, which will take about 20 minutes. If you want to get fancy, try typing **tail -f irc1.log** (and ctrl+C to exit). The job is done when **Job irc1 completed on compute-0-##.local** is displayed at the end of the log file.

In **Maestro**, select **Import Structures** from the **Project** menu and **import irc1.01.mae**. You can view the calculated structures and create a scatter plot of C-Br distance (or rxn coordinate) as the x-axis vs. Gas Phase Energy as the y-axis. You would first need to measure the C-Br distance property for this entry group like you did in Step 5. Since this is not a Coordinate Scan though you will need to use the Project Table's menu: Table-Manage Plots-New Scatter Plot.

We had requested 20 structures in each direction from the transition state structure. Do you have 40 new structures? If not, search through the **irc1.log** file to investigate why not.

Note1: In these exercises, we set **Use available Hessian** in the calculation of **Vibrational frequencies**. This shortcut does not give very accurate frequencies and should not be used for publication-quality results.
Note2: The LACVP* basis set actually uses an **effective core potential** on heavy atoms like Br, and the all-electron 6-31G* basis set on lighter atoms. If your molecule does not contain anything heavier than Cl, then just use 6-31G* (often called 6-31G(d)) instead.