

# *An Introduction to Computational Chemistry*

## *Introduction*

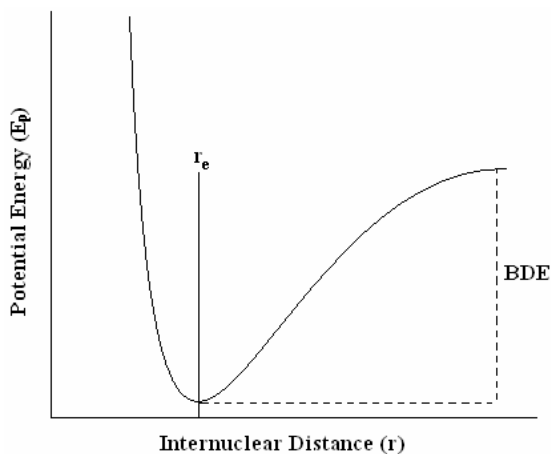
Quantum mechanics is an increasingly popular tool used by a variety of chemists who wish to study many different kinds of chemical systems. The advantage is that computers can be used to simulate species and/or reactions that can be very difficult or even impossible to observe in experiment. In particular, computational chemistry has become an important tool in the pharmaceutical industry. In many cases, computational results have led to significant time and cost savings, due to a more guided approach to drug development.

While the systems that you will be studying today are readily observable by conventional spectroscopic means, you will learn how to use research grade software (Gaussian 03) to compute physical properties of molecules.

The importance of learning about the value of a powerful research tool such as quantum mechanics is perhaps matched by the importance of learning the limitations of such a tool. By the end of today you should have some familiarity about what can and can't be done in chemistry using basic computational methods.

The energy of a diatomic molecule is directly related to the distance between the two atoms,  $r_{AB}$ . When the system is in its lowest energy state the two atoms, A and B, are separated by a distance known as the equilibrium bond distance,  $r_e$ . If we bring the atoms closer together there is an unfavorable repulsion between them and the energy of the system rises sharply. If we separate the two atoms, there will be an attractive force and the energy of the system will also rise until you reach a point at which the bond

breaks. The amount of energy it takes to do this is called the bond dissociation energy or BDE. This is shown schematically in Figure 1.



**Figure 1:** Potential energy curve of a diatomic molecule highlighting the equilibrium bond distance and the bond dissociation energy (BDE).

In today's experiment you will generate a potential energy plot like the one above. To do this you will first find  $r_e$ . This can be accomplished by considering rotational spectroscopy.

As you will remember from your class notes on *Rotation*, the frequency ( $\nu$ ) of a particular rotational quantum state,  $J$ , using the rigid rotor approximation can be represented by:

$$\nu = \frac{2h(J+1)}{8\pi^2 I} \quad (1)$$

where  $h$  is Planck's constant,  $I$  is the moment of inertia, and the fraction  $h/8\pi^2 I$ , is referred to as the rotational constant,  $B$  (in units of Hz or  $s^{-1}$ ), such that:

$$B = \frac{h}{8\pi^2 I} \quad (2)$$

If  $B$  is known, the moment of inertia can be calculated and from the definition of  $I$  for a diatomic molecule we need only know the masses of the two atoms ( $A$  and  $B$ ), and the equilibrium bond distance ( $r_e$ ) can be determined:

$$I = \frac{m_A m_B}{(m_A + m_B)} r_e^2 = \frac{h}{8\pi^2 B} \quad (3)$$

where  $m_A m_B / (m_A + m_B)$  is defined as the reduced mass,  $\mu$ , and has units of kg. The resulting bond distance will be in units of meters and can be calculated by rearranging equation (2).

$$r_e = \sqrt{\frac{h}{8\pi^2 B} \times \frac{m_A + m_B}{m_A m_B}} \quad (4)$$

Once  $r_e$  is known you can calculate the energy of the system at a series of internuclear distances both shorter and longer using the Gaussian 03 software package.

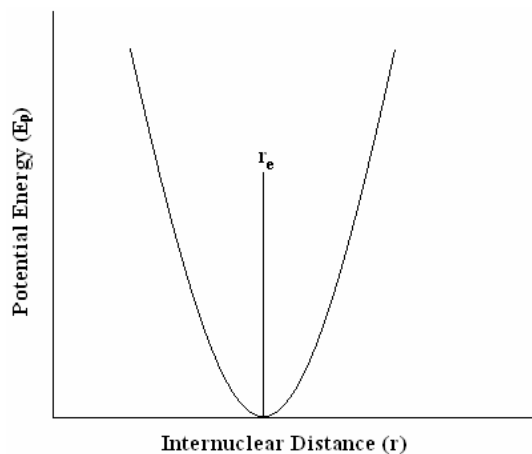
The energy of a molecule with respect to bond length is often approximated using a harmonic oscillator potential derived from Hooke's Law.

$$E_p = \frac{k(r - r_e)^2}{2} \quad (5)$$

Basically, this states that the potential energy will be a minimum at the equilibrium bond length ( $r = r_e$ ) and will behave in a parabolic fashion as we change the internuclear distance,  $r$  (See Figure 2). In the above equation,  $k$  is a force constant (usually in units of  $\text{Nm}^{-1}$ ), which describes the strength of the bond between atoms  $A$  and  $B$  and reflects the steepness of the potential energy well.

Of course, the harmonic approximation is not entirely correct but it generally does provide a fairly good description near the equilibrium bond length. You will plot the

harmonic oscillator potential along with your calculated potential energy curve to highlight the differences.



**Figure 2:** Harmonic approximation to a potential energy curve of a diatomic molecule with the equilibrium bond length highlighted.

To obtain the force constant needed in the above equation you will use Gaussian 03 to perform a frequency calculation. This calculation will yield what is called the fundamental frequency,  $\nu_0$ , as output in units of  $\text{cm}^{-1}$ . This fundamental frequency describes the energy needed to vibrate the A-B bond. This fundamental vibrational frequency is related to  $k$  and the reduced mass,  $\mu$ , by

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (6)$$

where  $\nu_0$  is in units of hertz or  $\text{s}^{-1}$  if  $k$  is in units of  $\text{Nm}^{-1}$  and  $\mu$  is in units of kg.

Finally, you will calculate the energy of the  $v = 0$  vibrational energy level and include it in your plot. For *Vibrations*, the total energy of a molecule vibrating in a particular quantum state,  $v$ , is given by the following equation:

$$E_v = h\nu_0(v + 1/2) \quad (7)$$

In today's lab, you will study rotational and vibrational properties of one series of three diatomic molecules taken from Table 1.

**Table 1:** The molecular systems to be investigated in this lab. Each group will be responsible for one of the nine series of molecules here.

Series	Molecule		
	1	2	3
1	LiF	LiCl	LiBr
2	NaBr	NaCl	NaF
3	KF	KCl	KBr
4	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>
5	HF	LiF	NaF
6	KBr	NaBr	LiBr
7	N <sub>2</sub>	F <sub>2</sub>	O <sub>2</sub>
8	HF	HCl	HBr
9	CO	NO	O <sub>2</sub>

### ***Procedure***

For this lab you will be using Gaussian 03. To begin calculations click the *File* menu and then click *New*. This will open the job entry screen as shown in Figure 3. To perform the calculations required for this lab, data will need to be entered in 4 of the five fields in the job entry screen.

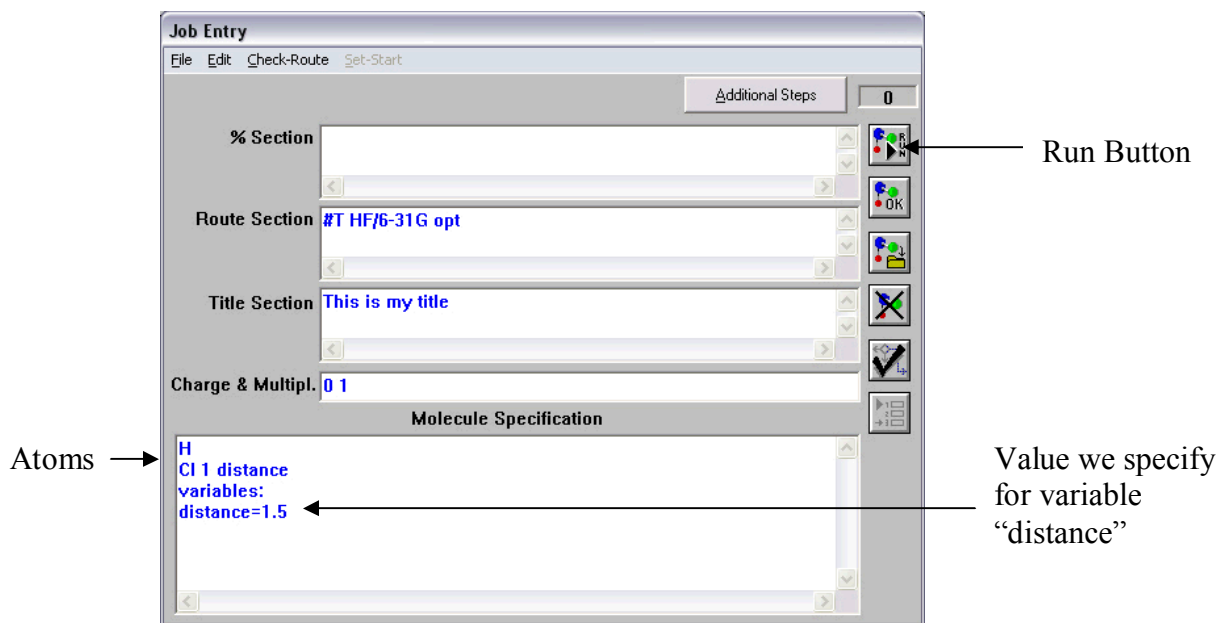
The *% Section* is where you might specify the amount of memory you would like the software to use or where to store various files that may be important to a particular user. You will not use this section in today's lab.

The *Route Section* describes the type of calculation you would like to perform and how the software is to perform it (i.e. an energy calculation or a vibrational frequency calculation).

The *Title Section* is where you can give your job a title. It doesn't matter what is typed in this space, as it will have no effect on the calculation.

The *Charge & Multiplicity* section is where we specify the charge of the molecule as well as the multiplicity (the charge and multiplicity of all molecules you will look at today is 0 and 1, respectively) separated by a single space.

Finally, the *Molecule Specification* section is where we describe our molecule to the program. Today you will be describing your molecule using what is called a simple z-matrix. In the sample input for HCl shown in Figure 3 you can see exactly how your z-matrix will be constructed. On the first line you type the symbol of the first atom, in this case it is “H” for hydrogen. The second line begins with the symbol for the second atom, in this case “Cl” for chlorine. In order to specify that it is bonded to the first atom, we then type the number 1. To specify the bond length (or our guess at the bond length), we use a variable, which in this case is the word “distance” although we could have used any letter or word. The value of “distance” is specified by typing the word “variables:” on the next line, and then on the line below that we type “distance=1.5”. Here, 1.5 angstroms is our guess at the distance between the hydrogen and chlorine atoms. That is how a simple z-matrix for a diatomic is constructed.



**Figure 3:** Sample input for the HCl molecule.

Once your job is ready for processing you can click the *Run* button and specify a location for the output file.

*Step 1; Finding the Rotational Constant, B.* To find B you will need to modify the *Route Section* of your job to resemble that of Figure 3. Every *Route Section* begins with the number sign (#). A “T” follows it in this case because that is the keyword to limit the amount of output in our output file. The “HF” stands for “Hartree-Fock” and that describes the method by which the computer will try and calculate the rotational constants. The code “6-31G” describes what is called the “basis set”. This is the specific set of functions to be used by the computer to calculate what you are asking for. The more functions we use, the more accurate our results should get, but it may also take the computer longer to solve. In step 5 of today’s lab, you will experiment with different basis sets. Finally, the “opt” keyword tells the computer the type of data you want as output. This is the keyword needed for it to find rotational constants. For this command it is not necessary that the bond length you specify be exactly correct. Just start with a value of about 1.5 angstroms (Å). Run the job and scan the output file when it completes. The output for any calculation usually contains much more data than you require and this is no exception. When you open the file scroll directly to the bottom. Now as you scroll up you are looking for something similar to the following:

```

Standard orientation:
-----
Center      Atomic   Atomic   Coordinates (Angstroms)
Number      Number   Type      X           Y           Z
-----
   1         17        0      0.000000    0.000000    0.071949
   2          1        0      0.000000    0.000000   -1.223134
-----
Rotational constants (GHZ):      0.0000000    307.5928986    307.5928986

```

As you can see, the rotational constants are output clearly. Note that there are two but they are identical. You will only need to use one in your calculations. Use equation (4)

to calculate  $r_e$ . Also, make a note of the time it took to complete this calculation. You will need it for step 5.

*Step 2; Generating the Potential Energy Curve.* From B you can calculate the equilibrium bond length,  $r_e$ . You must now calculate the energy of your molecule at a total of 11 different bond lengths. Start your calculations 0.5 Å below  $r_e$ , and then increment that value by 0.1 Å each time until you get to a bond length 0.5 Å above  $r_e$ . So if your optimum bond length was 1.29508332 Å, then you would calculate the energy from 0.79508332 Å to 1.79508332 Å. Go to the *File* menu and click *Modify*. This will allow you to adjust the commands as necessary. To calculate the energy, remove the “opt” command from the *Route Section*. Run the calculation using at least four decimal places in the bond length. When the output file is ready scroll to the bottom of it again. Now you are looking for the following:

```
SCF DONE:  E(RHF) = -460.032043460      A.U. AFTER      5 CYCLES
             CONVG  =   0.1061D-04      -V/T = 2.0000
             S**2   =   0.0000

*****
                POPULATION ANALYSIS USING THE SCF DENSITY.
*****
```

Where the output says “SCF DONE” is where you can find the energy and it is highlighted above. This energy value is in units of Hartrees. Your plot should be a relative energy plot in units of kJ / mol. The conversion from Hartrees to kJ / mol requires the following conversion factor: 1 Hartree = 2625.5 kJ / mol. To make the plot a *relative* energy diagram, first make a table with bond length in one column and the calculated energy (in kJ / mol) in the next column. For the third and final column, find the energy in the second column that is the lowest. Now for each entry in the third



column it will be the energy from the second column minus the lowest energy from the second column. This will make the lowest energy value 0 and the rest should be positive numbers. Plot the third column on the  $y$  axis and the bond length on the  $x$  axis.

Bond Length, $r$ (Å)	Calculated Energy (kJ/mol)	Relative Energy (kJ/mol), (i.e. calc. energy minus lowest from column 2)

*Step 3; Calculating the Force Constant,  $k$ .* To plot the harmonic oscillator potential along with your potential energy curve you will need the force constant of the bond. To do this, use the “freq” command in the *Route Section* and for the molecule specification use the equilibrium bond length that you found in step 1.

In this job, the fundamental frequency,  $\nu_0$ , is being calculated. It will appear in the output in the following way:

Harmonic frequencies ( $\text{cm}^{-1}$ ), IR intensities (KM/Mole), Raman scattering activities ( $\text{Å}^4/\text{AMU}$ ), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/Å), and normal coordinates:

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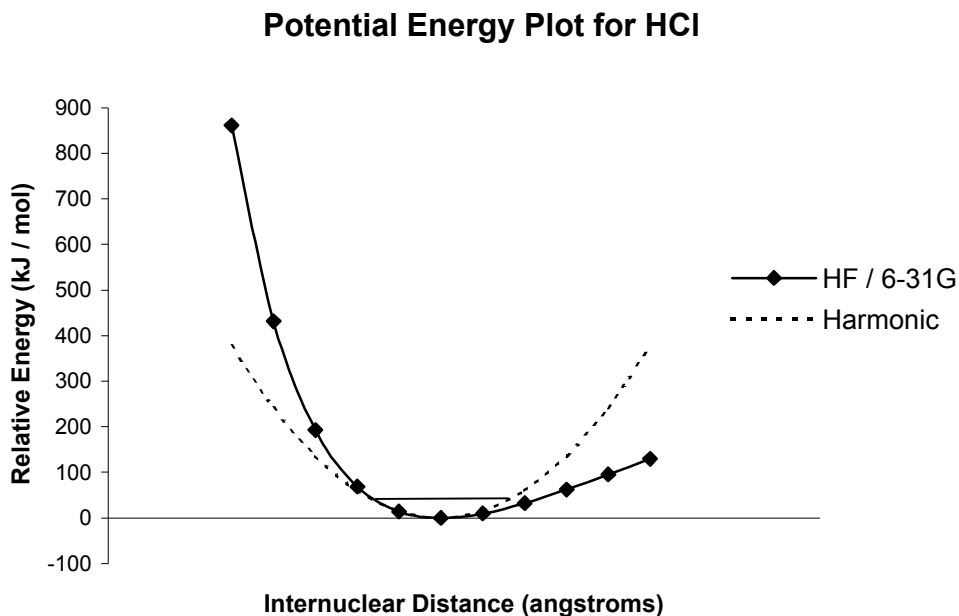
          1
          SG
Frequencies -- 2947.7445
Red. masses  --  1.0360
Frc consts   --  5.3039
IR Inten     -- 18.0237
Atom AN      X      Y      Z
  1   1      0.00   0.00   1.00
  2  17      0.00   0.00  -0.03

```

You will find  $\nu_0$  in units of wavenumbers, or  $\text{cm}^{-1}$ . Convert this value to Hertz and use it to calculate the force constant  $k$  (in units of  $\text{Nm}^{-1}$ ) with equation (6) and plot the harmonic oscillator potential (equation (5)) with your previous potential energy curve. In equation (5),  $r_e$  is constant and is what you calculated in step 1.  $k$  is constant and is what you calculated here.  $r$  is the bond length and you will use the 11 values you have from

your previous potential energy plot. Be sure to include both the potential energy curve and the harmonic oscillator potential on the same plot.

You can also use this frequency to calculate the zero-point vibrational energy ( $v=0$ ) using equation (7) and include it in your plot. To do this, use the fundamental frequency (in units of Hertz or  $s^{-1}$ ) in equation (7) with the vibrational quantum number equal to 0. This will give you the amount of energy the molecule has in its lowest vibrational energy state in units of Joules. Convert this value to units of kJ / mol and draw a straight line on your plot corresponding to that value.



**Figure 4:** Potential energy plot for HCl including the harmonic oscillator potential as well as the zero-point vibrational energy.

Figure 4 shows an example of how your plot should look. Notice the straight line running across the bottom of the well. This is the zero-point vibrational energy.

*Step 4; Bond Dissociation Energy Calculation.* To compute the BDE for each of your three molecules is relatively straightforward. The energy associated with the bond

between two atoms gives the system stability and thus the energy will be lower than if the two atoms were separated. Therefore the BDE can be defined as follows:

$$\text{BDE (A-B)} = E(\text{A}\cdot) + E(\text{B}\cdot) - E(\text{A-B}) \quad (8)$$

In other words, if we add the energies of the individual atoms (radicals) and subtract from that the energy of the molecule, what's leftover is the bond energy. You've already got  $E(\text{A-B})$ ; that's the equilibrium energy.

To calculate the energy of the two atomic radicals you must change the molecule specification so that only one atomic symbol is present and change the multiplicity to the required value because now you are dealing with a radical. To do this, add one to the bond order of your original molecule. Therefore if your original molecule had a single bond, the multiplicity of the atomic radical would be two. No need for "opt" or "freq" to be included in the *Route Section*. Perform the energy calculation on each radical and then calculate the BDE using equation (8).

Repeat these four steps for each of your molecules.

*Step 5; Method Comparison.* For this step you will only consider your third molecule and repeat step 1 using different basis sets. Remember, the number 6-31G in the *Route Section* is a code for the amount and types of mathematical functions used to calculate the properties that you need; it is called a basis set. Generally, the more functions you use the better. Replace the 6-31G with 3-21G and then with 6-311++G(d,p). Just like with the 6-31G basis set, keep track of the time each computation takes. You can report the time for each of the three computational methods. You must start with the same bond length in each case. For example if you chose 1.5

angstroms with the 6-31G case, you must choose 1.5 angstroms again for the other two basis sets.

***Write up:***

The write-up for this lab will be in the form of a formal lab report. In your report please include and/or discuss the following:

- Introduction and background information.
- Your methods.
- One set of sample calculations
- Excel spreadsheet with all data
- One potential energy curve plot for each of your molecules with the harmonic oscillator.
- Two additional potential energy curves corresponding to the different basis sets used on one of your molecules (Step 5).
- Comment on the quality of the harmonic oscillator approximation.
- In a table compare the equilibrium bond length, force constants (in units of  $\text{Nm}^{-1}$ ), and bond dissociation energies of your three molecules to the literature values. Discuss your results. (note: you may have trouble finding force constants in the literature but the other two parameters should be readily available)
- For the molecule that you performed additional calculations on, use a table to compare the equilibrium bond lengths calculated at each basis set (ie 3-21G, 6-31G, 6-311++G(d,p)) along with the average time (in seconds) that the energy calculations took.

Address the following questions:

1. Why is the absolute energy calculated with Gaussian 03 a negative number?
2. Which one of your molecules has the greatest force constant? Which has the smallest? Is it what you expected? Why or why not?
3. In the case of the molecule that you performed additional calculations on, which basis set took the longest to perform energy calculations? Which one yielded a bond length closest to the literature value?
4. What are some sources of error in this investigation?

<b>Most Abundant Isotopes of Selected Atoms</b>	<b>Mass (amu)</b>	<b>Mass (kg)</b>
<sup>1</sup> H	1.00783	$1.6735 \times 10^{-27}$
<sup>7</sup> Li	7.01600	$1.1650 \times 10^{-26}$
<sup>12</sup> C	12.00000	$1.9927 \times 10^{-26}$
<sup>14</sup> N	14.00307	$2.3253 \times 10^{-26}$
<sup>16</sup> O	15.99491	$2.6560 \times 10^{-26}$
<sup>19</sup> F	18.99840	$3.1548 \times 10^{-26}$
<sup>23</sup> Na	22.98977	$3.8175 \times 10^{-26}$
<sup>35</sup> Cl	34.96885	$5.8067 \times 10^{-26}$
<sup>39</sup> K	38.96371	$6.4701 \times 10^{-26}$
<sup>79</sup> Br	78.91834	$1.3105 \times 10^{-25}$

<b>Selected Physical Constants</b>	<b>Value</b>
Planck's Constant (h)	$6.626 \times 10^{-34} \text{ kg m}^2 / \text{s}$
Avogadro's Number (n)	$6.022 \times 10^{23} \text{ mol}^{-1}$
Speed of Light (c)	$2.9979 \times 10^{10} \text{ cm} / \text{s}$
Joule Definition	$1 \text{ J} = 1 \text{ kg m}^2 / \text{s}^2$
Newton Definition	$1 \text{ N} = 1 \text{ kg m} / \text{s}^2$