

# Mathematical Determination of Diatomic Molecule Properties

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## 1 Introductory Reading

### 1.1 Background

The goal of this lab activity is to use data from a quantum chemical calculation to determine the properties of a series of simple diatomic (two-atom) molecules. Although several of the values to be determined in this activity are done automatically by the software, one of the goals of this activity is to give you some sense of the mathematics involved in these calculations. The computer should not be seen as a *black box*;

All molecules have energy. One of most important quantum chemical calculations we can perform is to determine the energy of a molecule. Indeed, the Schrodinger equation explicitly determines the energy of a molecule:

$$H\Psi = E\Psi \quad (1)$$

In this equation,  $\Psi$  is the wavefunction, and  $E$  is the energy of the molecule, typically expressed in units of Hartrees ( $E_h$ ).  $H$  is a mathematical operator that can take a variety of forms. One form is as follows:

$$H_{elec} = -\frac{1}{2} \sum^{elec} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \sum_i \sum_I \left( \frac{Z_I}{R_I - r_i} \right) + \sum_i \sum_{j < i}^{elec} \left( \frac{1}{r_i - r_j} \right) + \sum_J \sum_{J < I}^{nucl} \left( \frac{Z_I Z_J}{R_I - R_J} \right) \quad (2)$$

Molecules have different types of energy. All molecules vibrate, so it can be said that molecules have *vibrational energy*. Vibrations occur because the molecule absorbs infrared (IR) radiation. In other words, infrared light will hit the molecule and cause it to vibrate. This infrared light happens at a specific frequency on the electromagnetic spectra.

Molecules can also rotate, and, to no surprise, we call this *rotational energy*. Rotational energy is usually due to energy in the microwave region of the electromagnetic spectra. Finally, the electrons in a molecule move, resulting in energy, and we call this *electronic energy*. Electronic energy comes from light typically in the visible region of the electromagnetic spectra:

Energy type:	Associated behavior:	Typical source of energy
Rotational	Rotation of the whole molecule	Microwaves
Vibrational	Vibration of chemical bonds within the molecule	Infrared radiation
Electronic	Energy associated with the molecule's electrons	Visible light

Imagine, if you will, two weights connected by a spring. Each weight has mass. If I pull the weights apart (stretching the spring), we can say that there is a lot of *potential energy* in the spring. If I let the weights go, that energy gets converted to *kinetic energy*. Most of the time, the spring will vibrate, or *oscillate*, until it reaches equilibrium, with all of the energy dissipated. If you have taken physics, we would say that the spring exhibits *harmonic oscillations*. It is a *harmonic oscillator*.

Figure 1 below looks to show this oscillation. If you can imagine the graph as showing one pulling the weights apart – the *internuclear separation* – the energy increases (energy is getting higher from bottom to top in this graph). Once we let go of the weights, the energy decreases until the energy is at its lowest point – an energy *minima*. This energy minima is identified as  $E_0$ .

In quantum chemistry, one difference is that there is not a spring between atoms, and the change in energy doesn't decrease smoothly. Energy in quantum systems decreases in energy levels, represented by the letter  $n$ . In your introductory class, you should have been exposed to this idea of a *principal quantum number*. As such, the released spring jumps from  $n=4$  to  $n=3$  to  $n=2$  to  $n=1$  to, and finally,  $n=0$ . When  $n=0$ , this is the *equilibrium level*.

How do we determine the amount of energy between these various energy levels? One way is to calculate the *rotational constant*,  $B$ . This quantum mechanical value can be determined computationally, and is typically a standard quantity determined almost any time you perform some quantum chemical calculation. Figure 2 shows a screensnap of the rotational constant output from WebMO. Notice that it reports the value in units of GHz (gigahertz) and wavenumber ( $1/\text{cm}$ ).

Once we have calculated the rotational constant ( $B$ ), we can *derive* other important characteristics of the molecule. Primarily, we can determine the *equilibrium bond length*,  $r_e$ , one of the goals of this lab. It is indeed the case that the computer determines this value, but for purposes of this lab we will ask you to calculate the value of  $r_e$  by hand.

Another property we wish to determine is the *bond force constant*, a measure of the strength of a bond. This unit is measured in units of Newtons per meter. Newtons (N)

Figure 1: Potential energy chart for a diatomic molecule

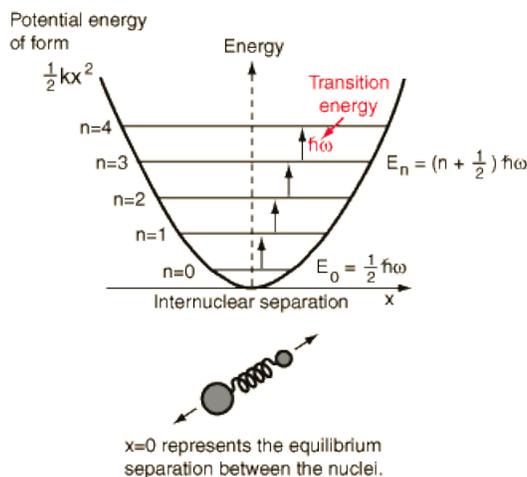


Figure 2: WebMO screensnap showing rotational constant

Rotational Constants		
Constant	Frequency (GHz)	Frequency ( $\text{cm}^{-1}$ )
a	0.0000000	0.000000000000
b	321.7703541	10.73310370270
c	321.7703541	10.73310370270

is a measure of force, and has an energy equivalence of one Joule per meter (J/m). The larger the bond force constant, the stronger the bond between the two atoms.

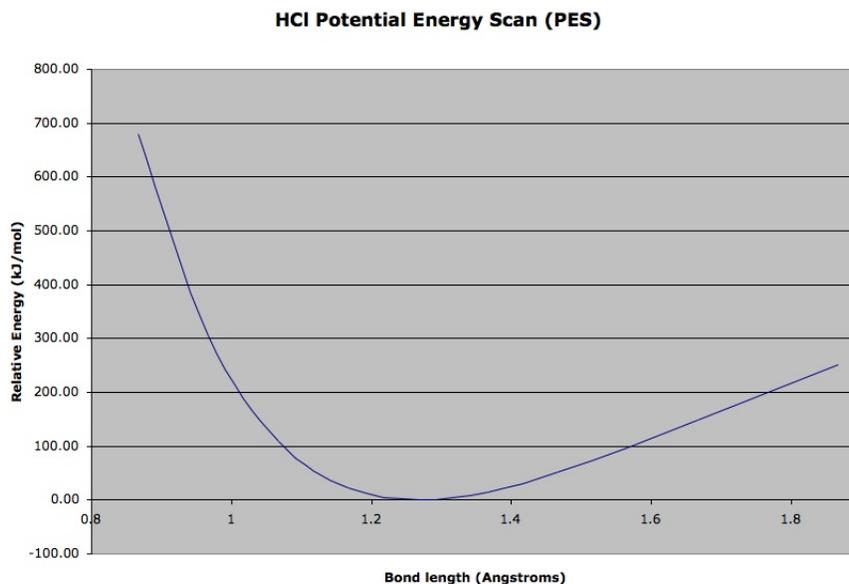
Another critically important value is the *zero-point energy*, typically referred to as the *ZPE*. This is the energy value at the bottom of the curve, that energy value when  $n=0$ .

Another important calculation in computational chemistry is the *potential energy scan*, or *PES*. PES calculations are conducted to help understand the variation in energy values at points below and above the equilibrium bond length. A typical PES plot is shown in Figure 3. On PES plots, we plot the bond radius (in Angstroms) on the x-axis and the energy or relative energy (in kJ/mol) on the y-axis.

## 1.2 Relevant Mathematics

This section describes the relevant mathematics needed to do the computations and calculations for this lab.

Figure 3: Potential energy scan (PES) for HCl (relative energies)



### 1.2.1 Constants

The following constants will come in handy for this computational exercise:

Planck's constant ( $h$ )	$6.63 \times 10^{-34} \text{ kg} \cdot \text{m}^2 / \text{s}$
Avogadro's number	$6.02 \times 10^{23} \text{ mol}^{-1}$
Speed of light ( $c$ )	$3.00 \times 10^{10} \text{ cm/s}$
Hartree/kJ conversion	$1 \text{ Hartree} = 2.6255 \times 10^{03} \text{ kJ/mol}$

### 1.2.2 Reduced Mass ( $\mu$ )

To calculate the value of the equilibrium bond length ( $r_e$ ), we must first calculate the *reduced mass*, or  $\mu$ , of the diatomic molecule. This is done with the equation:

$$\mu = \frac{m_A + m_B}{m_A m_B} \quad (3)$$

where  $m_A$  and  $m_B$  are the masses (in units of atomic mass units, or *amu*, of the most abundant isotope of the element. For this calculation, we need the masses in units of kilograms (kg). You can use the data below, or you can convert the amu mass values to kg mass values with the conversion factor  $\frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}}$ .

Most Abundant Isotope	Mass (amu)	Mass (kg)
H	1.00783	1.6735E-27
Li	7.01600	1.1650E-26
C	12.00000	1.9927E-26
N	14.00307	2.3253E-26
O	15.99491	2.6560E-26
F	18.99840	3.1548E-26
Na	22.98977	3.8175E-26
Cl	34.96885	5.8067E-26
K	38.96371	6.4701E-26
Br	78.91834	1.3105E-25

### 1.2.3 Equilibrium Radius ( $r_e$ )

The equilibrium radius ( $r_e$ ) is measured in units of Angstroms ( $\frac{1\text{Angstrom}}{1 \times 10^{10}\text{m}}$ ) using the formula:

$$r_e = \sqrt{\frac{h}{8\pi^2 B \mu}} \quad (4)$$

where  $B$  is the rotational constant (in units of GHz, or gigahertz, or  $1 \times 10^9$  Hz, or  $1 \times 10^9$  cycles/sec<sup>-1</sup>). The value for  $B$  is found in the **Calculated Quantities** page of your Gaussian computational run. **NOTE:** you have to be very careful with units here. It is up to you to determine how to ensure that you end up with the value of the bond radius in units of Angstroms.

### 1.2.4 Force Constant ( $k$ )

As before, the force constant or *bond force constant*,  $k$  is a measure of the strength of a bond. The larger the value of  $k$ , the stronger the bond. The units of the bond force constant are Newton/m.

$$k = (2\pi\nu_0)^2 \mu \quad (5)$$

## 2 Computational Approach

In this activity, your group will be assigned three diatomic molecules, as is shown in the table below:

Example	HF	HCl	HBr
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Your task is to perform a **HF/6-31(d) geometry optimization and vibrational frequency determination** to compute three values:

- Rotational constant ( $B$ , in units of GHz)
- Energy of the molecule ( $E_h$ , in units of Hartrees)
- Fundamental vibrational frequency ( $\nu_0$ , in units of  $cm^{-1}$ )

Once you have determined these quantum mechanical quantities for each of the three molecules, construct a spreadsheet that calculates the **derived values** listed below:

- the equilibrium radius ( $r_e$ , in units of Angstroms)
- the bond force constant ( $\mu_0$ , in units of N/m)

Figure 4 shows a sample screensnap for the example molecules of HF, HCl, and HBr. You might want to consider using these values to build and validate your spreadsheet. If your spreadsheet is correct, then simply replacing the computed quantities with the data from your runs should yield an accurate spreadsheet.

**NOTE: you do not have to include all of the values on the isotope datatable, only those atoms that pertain to your molecules.**

Once you have completed your spreadsheet analysis, you should also conduct a potential energy scan of each molecule. To do this in Gaussian, follow these steps:

- Build your molecule as usual
- Select Gaussian as the computational engine
- Select "Coordinate Scan" as your method, and 6-31G(d) as your basis set
- In the Job Options window, click on the **Preview** tab
- Generate the input file by clicking on the **Generate** button. You now see the actual Gaussian input file. You are modifying this **by hand** rather than having WebMO do it for you!
- For HCl as the example, you should have a file that looks like Figure 5.
- Change the first line to read: N HCl/6-31(d) Scan. The **Scan** keyword tells Gaussian to do a potential energy scan (PES), sometimes called a **coordinate scan**.
- The notation "B1 1.2662310" says that the bond length of the hydrogen to the chlorine is 1.26 angstroms. This number **should be** close to your calculated equilibrium bond length ( $r_e$ ).

- Change the bond length number as follows: subtract ABOUT 0.6 angstroms from this number. That is your starting point for the scan. Then type in 11 with no decimal points. That says you want to run the job 11 times. Then type the number 0.1. This is the increment number. What you are doing is calculating the molecular energy (SPE) at EACH of those 11 geometries, starting (in this case) at 0.7 angstroms, each time incremented by 0.1.
- When you are done, click on the submit arrow, it will ask you to submit the edited file, and that's what you want to do.
- Once your job runs, open the job. Click on "Raw Output" on the left window. This is the file that Gaussian actually produces. Some of this data is displayed as WebMO output.
- Scroll down to where you find your scan. You should see two columns of data, the first being the bond length in angstroms, the second the energy in units of Hartrees.
- Copy this data into a new worksheet in Excel (you can do this using whatever graphing program you want). Convert the energy values in Hartrees to energy values in kJ/mole with the conversion factor: 1 Hartree = 2725.5 kJ/mole
- Calculate the **relative energies** by subtracting the **lowest energy value – the minima** – from all of the other energies.
- Plot the bond length in angstroms versus the **relative energies**.
- Copy this data into your spreadsheet, and plot the potential energy scan. Your chart might look like Figure 7 (I used slightly different starting values for my bond lengths).

Your group should choose one of the sets of data in the data table **except Dataset 5** (the set used in the example).

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	CO	NO	O <sub>2</sub>

Figure 4: Screen snapshot of spreadsheet analysis for sample dataset

A	B	C	D
<b>DATA AND CALCULATIONS</b>			
<b>Constants:</b>			
Planck's constant	6.63E-34	kg m <sup>2</sup> /s	
Avogadros	6.022E+23	mol <sup>-1</sup>	
Speed of light	2.998E+10	cm/s	
Hartree/kJ conversion	2625.50	kJ/mol	
<b>Data from Gaussian</b>			
	<b>HF</b>	<b>HCl</b>	<b>HBr</b>
Rotational Constant B GHz =	636.2822356	321.7703541	252.1209116
Fundamental freq (cm <sup>-1</sup> ) =	4357.1959	2924.7696	2799.7343
Energy (Hartrees) =	-100.002907	-460.0599763	-2570.465551
<b>Calculated Quantities:</b>			
Reduced Mass (u, kg) =	6.2925E+26	6.1477E+26	6.0518E+26
re (angstroms) =	0.91127	1.26662	1.41971
Energy (kJ/mol) =	-262557.63229	-1207887.46777	-6748757.30426
Frequency (Hz) =	1.30624E+14	8.76817E+13	8.39332E+13
k (N m <sup>-1</sup> ) =	1070.50	493.70	459.56
	<b>Most Abundant Isotope</b>	<b>Mass (amu)</b>	<b>Mass (kg)</b>
	H	1.00783	1.6735E-27
	Li	7.01600	1.1650E-26
	C	12.00000	1.9927E-26
	N	14.00307	2.3253E-26
	O	15.99491	2.6560E-26
	F	18.99840	3.1548E-26
	Na	22.98977	3.8175E-26
	Cl	34.96885	5.8067E-26
	K	38.96371	6.4701E-26
	Br	78.91834	1.3105E-25

### 3 Analysis and Discussion

#### 3.1 Analysis

Your group should do a complete analysis for each of the three molecules. A complete analysis includes a HF/6-31G(d) optimization/frequency calculation and a potential energy scan (PES). Your spreadsheet should have a complete analysis for all three molecules on one worksheet, a worksheet to determine the relative energies (for each of the three molecules) and plots of relative energies for each of the three molecules.

Figure 5: Screen snapshot of Gaussian coordinate scan preview

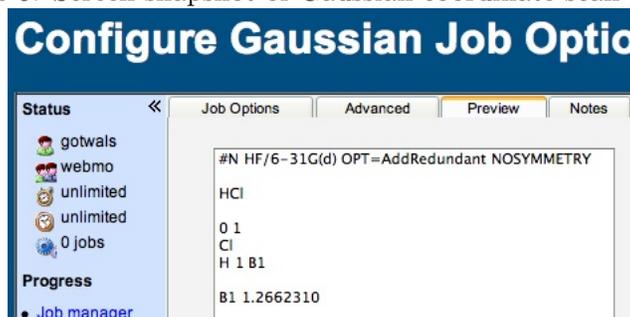
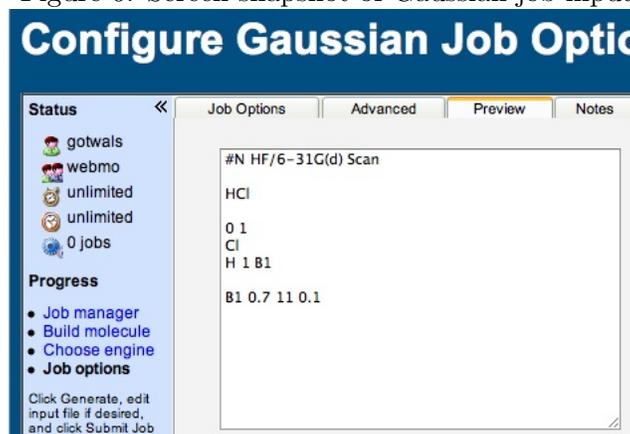


Figure 6: Screen snapshot of Gaussian job input



## 3.2 Discussion

Observe your data for the three molecules. What observations can you make about your molecules? Do you observe any trends or patterns? What does the PES data/graphs tell you?

To submit this graph, you need to include:

- A 250-300 word lab abstract describing purpose, computational method, sample data, results and discussion, and potential errors
- A printout of your spreadsheet with all three molecules (similar to Figure 4).
- A printout of the PES graph for **one** of your molecules.

Figure 7: Screen snapshot of spreadsheet PES data for HCl

	A	B	C	D
1	HCl Energies			
2	Bond Length	Calc Energy (Hartrees)	Calc Energy (kJ/mol)	Relative Energy (kJ.mol)
3	0.8666	-459.81065	-1253213.92658	679.55
4	0.9666	-459.94857	-1253589.82754	303.65
5	1.0666	-460.02013	-1253784.86432	108.61
6	1.1666	-460.05189	-1253871.42620	22.05
7	<b>1.2666</b>	<b>-460.05998</b>	<b>-1253893.47549</b>	0.00
8	1.3666	-460.05435	-1253878.13093	15.34
9	1.4666	-460.04115	-1253842.15433	51.32
10	1.5666	-460.02412	-1253795.73906	97.74
11	1.6666	-460.00546	-1253744.88123	148.59
12	1.7666	-459.9864	-1253692.93320	200.54
13	1.8666	-459.96761	-1253641.72106	251.75

Figure 8: Screen snapshot of HCl PES calculation

