

**Investigating the Effects that Dipole Moments, Atomic Partial
Charges, Vibrational Coupling, and the Potential Energy
Function have on the HNO Molecule (Nitroxyl)**

James Roger Smith III

Undergraduate Thesis

Research Professor: Dr. Robert Hinde

5/6/15

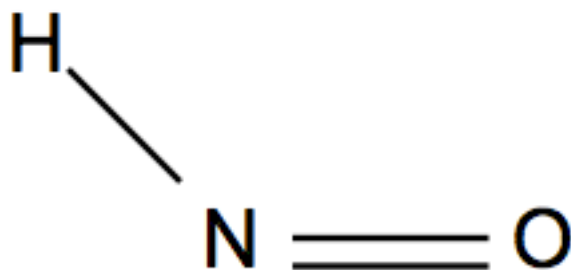
Table of Contents

Introduction	page 3
Dipole Moments and Atomic Partial Charges	page 6
Potential Energy Function and Vibrational Coupling.....	page 19
Potential Energy Function and Vibrational Coupling with SCS-MP2	page 33
Conclusion	page 43
Appendix.....	page 46
References.....	page 78

Introduction:

The HNO molecule, also known as nitroxyl¹, is a relatively unstudied molecule. The chemical structure of this molecule can be found in Figure 1. While some research has been done on the molecule¹, the molecule is largely unexplored due to the fact that the molecule is very reactive and the only way to realistically study it is by immobilizing it in low-temperature solids such as rare gases or H₂ matrices, an experimental technique called matrix isolation. A research group at the University of Wyoming is currently using the matrix isolation technique to conduct experimental research on the HNO molecule, with the hopes of understanding infrared (IR) spectrum for the molecule. Because the molecule is so difficult to make, the Wyoming research group needs to be sure that they are in fact creating the HNO molecule. While they are relatively confident that they are successfully creating the HNO molecule, they need theoretical data to confirm their assumptions.

Figure 1: Chemical Structure of Nitroxyl



IR spectroscopy can be used to identify molecules in a sample of an unknown solution or mixture. It does this by looking at the vibrations of the constituent atoms². When electromagnetic radiation passes through a substance, energy is either absorbed or transmitted². Absorbed energy depends on the radiation frequency and on the molecule's structure². Typically an IR spectrum will plot % Transmittance vs. Frequency (usually expressed in wavenumbers,

cm^{-1}). Different peaks in the spectrum will correspond to different vibrations of different covalent bonds that exist in the molecule. For example, a peak somewhere in the range of 3200-3600 cm^{-1} will indicate that there is an O-H bond present in the molecule². The intensity, or height, of a peak in an IR spectrum is proportional to the number of different molecules (concentration) in the sample, the path length that the IR light travels through the sample, and the square of the transition dipole moment for the vibration. This is expressed in Beer's Law, $A = \epsilon bc$, where A is absorbance, ϵ is the molar absorption constant, b is path length, and c is concentration.³ This means that different concentrations of the same solution will give two different IR spectra. If two unknown substances have identical IR spectra, it is safe to deduce that the two solutions are identical². The molar absorption constant, ϵ , is proportional to the square of the transition dipole moment for the vibration.⁹

The dipole moment function and the potential energy function of a molecule can both be linked to the IR spectroscopy of a molecule. Both of these are functions of a molecule's geometry. HNO has three distinct geometric coordinates: H-N bond length, N-O bond length, and the HNO angle. To simplify things, the H-N bond length will be referred to as r_{HN} and the N-O bond length will be referred to as r_{NO} . The bulk of this report will now be split into two parts. The first part will discuss theoretical data for the molecule's dipole moments and atomic partial charges. The second part will look at theoretical data for potential energy and coupling functions of the HNO molecule.

For HNO at the MP2 ACCT equilibrium geometry⁵, r_{HN} is 1.0506 Å, r_{NO} is 1.2217 Å, and the HNO bond angle is 107.64°. Experimental research¹¹ says that r_{HN} in ammonia (NH_3) is 1.008Å. It also says that the NO single bond in nitric acid (HNO_3) has a length of 1.41Å, while the NO double bond in nitric acid has a length of 1.22Å. While these lengths are not

specifically the MP2 ACCT values, they still allow one to compare the bond lengths in nitroxyl to more commonly studied molecules.

Dipole Moments and Atomic Partial Charges:

For practical purposes, the HNO molecule was assumed to be in an xy coordinate plane so data measurement can be simplified. The nitrogen atom was placed at the origin and the oxygen molecule was kept on the x-axis. This implied several things about the positioning of the molecule. The coordinates for the nitrogen atom would always be (0,0,0). The y and z coordinates for the oxygen atom would always be 0. The z coordinates for the hydrogen atom would always be zero. This means that the only three coordinates that could change location as the HNO geometry was manipulated were the x values for the oxygen atom and the x and y values for hydrogen atom. All other coordinate values were always assumed to be 0.

In order to look at the dipole moment as a function of geometry, it was necessary to find a way to calculate the dipole moment for a specific geometry. Dipole moment is the negative derivative of the energy with respect to applied electric field. The GAMESS⁴ program calculates the energy of a molecule for a specific geometry and a specific basis set of functions used to approximate the molecule's molecular orbitals. Using the GAMESS program, electric fields of varying strengths can be applied along the x-, y-, or z-axis, or any combination of these. The GAMESS program therefore allows one to put in any geometry for the HNO molecule and then manipulate the strength of the electric field. Once run, the program will then calculate the HNO molecule's energy at that field value. An example of a GAMESS input and GAMESS output can be found at the end of the report in the appendices (see Appendices 1 and 2). For the purpose of this experiment, the strength of the electric field was changed from the range -0.003 to 0.003 atomic units, with a test being done every 0.001 atomic units. This produced seven data points for each geometry's x-field values and seven data points for each geometry's y-field values. These values were entered into a Maple document that produced the derivative for the

data (see Appendix 3). As stated above, the dipole moment is the negative derivative of this data so the derivatives were multiplied by -1 and then these values were recorded as the x and y components of the dipole moments. These calculations were done using the ACCT atomic basis set that is built into GAMESS and the MP2 electronic structure method. The ACCT basis set is a “library” of three-dimensional mathematical functions that GAMESS uses to describe the HNO molecular orbitals. It includes s, p, and d orbitals for the H atom, and s, p, d, and f orbitals for the N and O atoms. The MP2 method is the simplest way to include the effects of electron correlation in a GAMESS calculation. Electron correlation refers to the instantaneous correlations between the motions of different electrons in a molecule and is a correction to the simple molecular orbital picture of a molecule’s electronic structure. It is important to note that for this section of the report, all reported energy values are the given MP2 values, not the SCS-MP2 values. The SCS-MP2 values will be discussed in a later section. All calculations in this section used the ACCT^{6,7} basis set for the H, N, and O atoms.

In order to have a starting point for manipulating the molecule’s geometry, the equilibrium geometry of HNO was used. The equilibrium geometry for a molecule can be defined as the geometry with minimum energy. For HNO at the MP2 ACCT equilibrium geometry⁵, rHN is 1.0506 Å, rNO is 1.2217 Å, and the HNO bond angle is 107.64°. Visual representation of the equilibrium geometry can be found in Figure 2. Using simple trigonometry and assuming the molecule is on a coordinate plane as mentioned above, the x and y values for hydrogen are -0.3183688 Å and 1.0012001 Å, respectively. Also, the x-value for oxygen is 1.2217 Å. All other values are assumed to be 0. These coordinates were the first ones input into the GAMESS program and all fourteen desired electric field values were found. These values were plugged into the Maple document and the dipole moments were found. The x-dipole (dx

HNO) for the molecule was found to be -0.339410714 atomic units and the y-dipole (μ_y HNO) for the molecule was found to be 0.576396429 atomic units.

Figure 2: Equilibrium Geometry of Nitroxyl

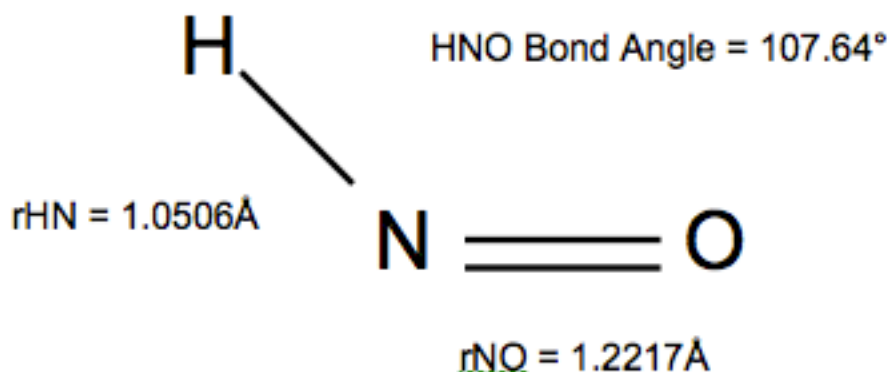


Figure 3: Coordinates for the Equilibrium Geometry of Nitroxyl (assuming nitrogen is at the origin)

			Hydrogen Coordinates			Nitrogen Coordinates			Oxygen Coordinates		
rNO (Å)	rHN (Å)	Bond Angle (°)	x	y	z	x	y	z	x	y	z
1.2217	1.0506	107.64	-0.318368849	1.001200098	0	0	0	0	1.2217	0	0

After finding the dipole moments for the equilibrium geometry, the geometry was manipulated for each of the three geometric coordinates. This was done to simulate the vibration of the molecule. For every new geometry, the dipole moment was calculated from the electric field values. For rNO, the dipole moments were found from $r_{\text{NO}} = 1.0917$ to $1.4917 \text{ \AA}$ in increments of $0.01 \text{ \AA}$. For rHN, the dipole moments were found from $r_{\text{HN}} = 0.8706$ to $1.3206 \text{ \AA}$ in increments of $0.01 \text{ \AA}$. For the HNO bond angle, the dipole moments were found from bond angles from 85.14 to 132.64° in increments of 2.5° . This gave a total of 104 more geometries tested with the GAMESS program. This information can be found in table form in Figure 4 and the MP2 energies for the equilibrium geometry can be found in Figure 5. Including the equilibrium geometry, a total of 105 different geometries were run in the GAMESS program.

Figure 4: Table Representing the 104 Different Geometries Tested with the GAMESS Program

Parameter	# of Tests	Range	Increments
rNO	40	1.0917-1.4917 Å	0.01Å
rHN	45	0.8706-1.3206 Å	0.01Å
Bond Angle	19	85.14°-132.64°	2.5°

Figure 5: Tables Representing the Energy of the Equilibrium Geometry when Changing the X-Field and Y-Field Values

X-Field Strength (A.U.)	-0.003	-0.002	-0.001	0	0.001	0.002	0.003
E(MP2) Value (Energy)	-130.285346	-130.2849627	-130.284597	-130.2842488	-130.2839182	-130.2836051	-130.2833096

Y-Field Strength (A.U.)	-0.003	-0.002	-0.001	0	0.001	0.002	0.003
E(MP2) Value (Energy)	-130.2825851	-130.283125	-130.2836796	-130.2842488	-130.2848325	-130.2854307	-130.2860434

Once all of these calculations were completed, the dipole moments that each bond contributed to the entire dipole of the molecule were found. The x or y dipole moment of the entire molecule can be assumed to be the sum of the x or y dipole moments along the HN and NO bonds. For example, the x-dipole of rHN (dxHN) plus the x-dipole of rNO (dxNO) equals the x-dipole for the entire molecule (dxHNO). Also, the ratio $x_H/y_H = dxHN/dyHN$ was used. Lastly, dyNO was assumed to be 0 because the NO bond lies entirely on the x-axis. For the equilibrium geometry, the results are as follows: dxHN = -0.183286706 atomic units, dyHN = 0.576396429 atomic units, dxNO = -0.156124009 atomic units, and dyNO = 0. These dipole moments can be found in Figure 6. All four of these dipole moments were found for all 105 different geometries.

Figure 6: Dipole Moments for the Equilibrium Geometry

x-dipole (dx HNO)	y-dipole (dy HNO)	dy HN	dx HN	dx NO
-0.339410714	0.576396429	0.576396429	-0.183286706	-0.156124009

The atomic partial charges for each atom were then calculated using dipole moments and were labeled q_H , q_N , and q_O . In order to find the values of these three unknowns, three equations are needed. Because HNO is a neutral molecule and not an ion, one can assume that the sum of the partial charges equals 0. The x-dipole (dx_{HNO}) for the entire molecule equals $q_H \cdot x_H + q_N \cdot x_N + q_O \cdot x_O$. The y-dipole (dy_{HNO}) for the entire molecule is the product of q_H and y_H . This is because y_N and y_O both equal 0. Now that there are three equations, the three partial atomic charges can be found. For the equilibrium geometry, $q_H = 0.575705526$, $q_N = -0.447913098$ and $q_O = -0.127792428$. Figure 7 presents the atomic partial charges for the equilibrium geometry. All three partial charges were found for each of the 105 different geometries.

Figure 7: Atomic Partial Charges for the Equilibrium Geometry of Nitroxyl

q_H	q_N	q_O
0.575705526	-0.447913098	-0.127792428

Once the atomic partial charges for all 105 geometries were calculated, 9 different graphs were made that plotted each of the three atomic partial charges (q_H , q_N , and q_O) against each of the three geometric coordinates (r_{HN} , r_{NO} , and HNO bond angle). From these graphs, several observations can be made. Some of these observations are easily explainable while others will require deeper research to explain. This section will attempt to point out several of these explainable observations, while also mentioning ones that currently cannot be explained. These 9 graphs can be seen in Figures 8-16.

The relationship between r_{NO} and q_H can be seen in Figure 8. As r_{NO} becomes longer, q_H becomes more positive. This is because as the oxygen atom moves farther away from the entire molecule of nitroxyl, the bond between the hydrogen atom and the nitrogen atom acts

more like a simple HN bond by itself, rather than one that is part of nitroxyl. This makes the charge on hydrogen more positive, and, in turn, makes the charge on the nitrogen atom more negative. This effect can be seen in Figure 9. Two observations that are currently unexplainable is how q_H begins to become less positive as r_{NO} gets very large (greater than $1.45\text{\AA}$) and how q_N begins to become more negative as r_{NO} becomes very small (less than $1.1\text{\AA}$).

Figure 8: q_H dependence on NO Bond Length

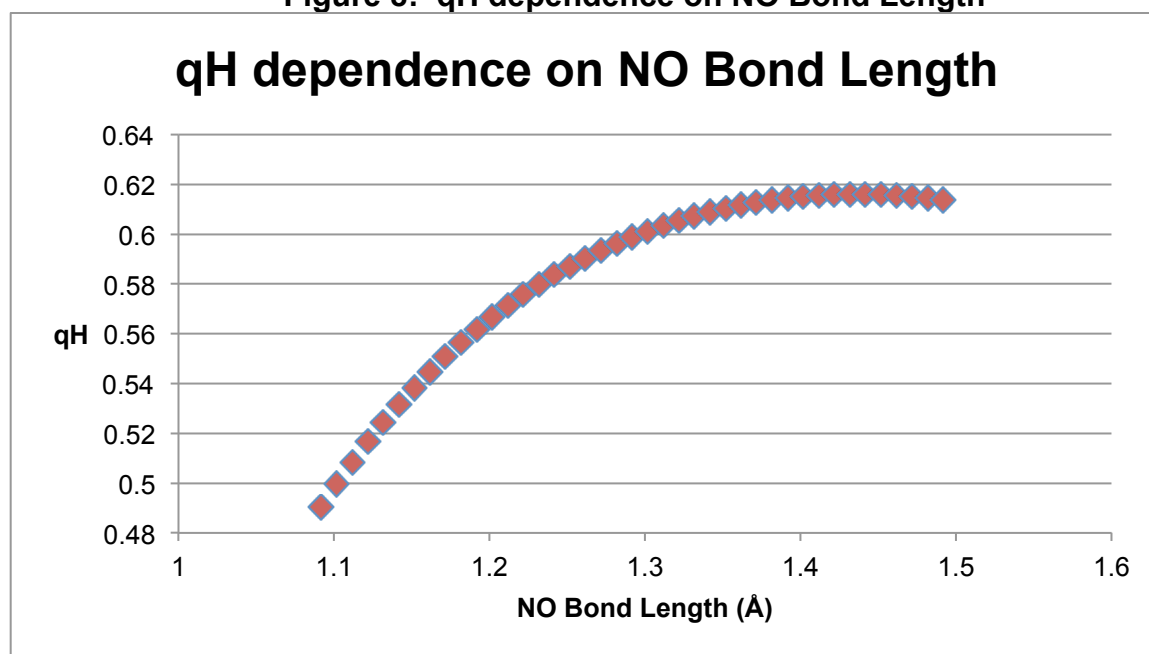
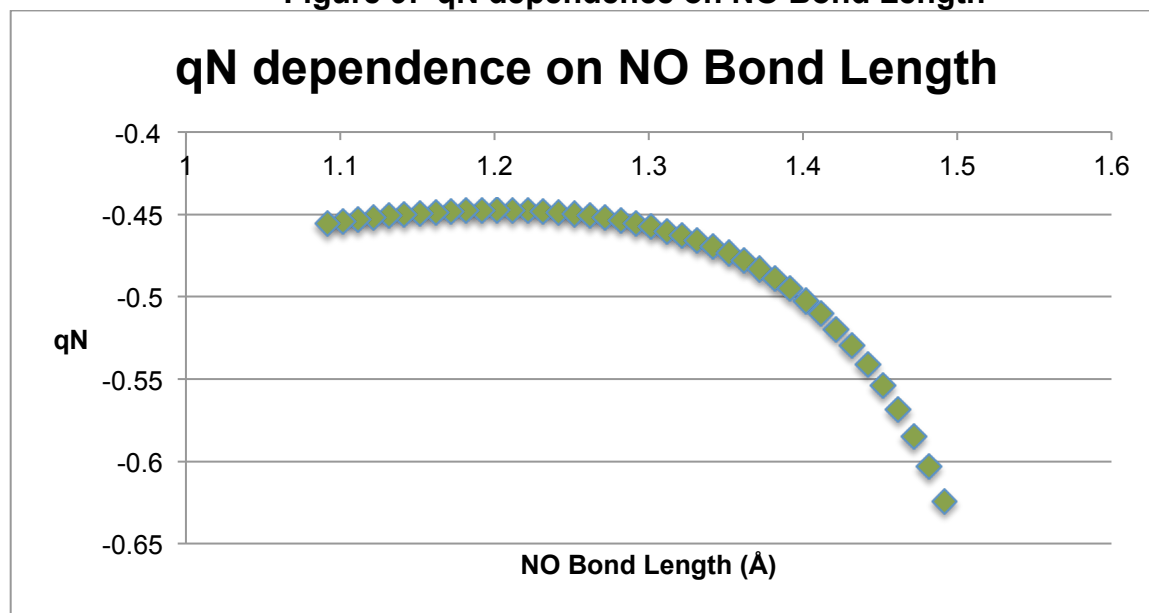


Figure 9: qN dependence on NO Bond Length



The relationship between NO bond length and qO can be seen in Figure 10. These points create an approximate parabola whose minimum value of qO can be found at an rNO value of about $1.3\text{\AA}$, which is longer than the equilibrium geometry. As rNO becomes very small or very large, qO becomes very small and will eventually go to zero as the NO bond length becomes bigger. This is because a long enough bond will be equivalent to the two atoms not sharing a bond whatsoever. This translates into a neutral oxygen atom by itself, giving it a charge of zero.

Figure 10: qO dependence on NO Bond Length

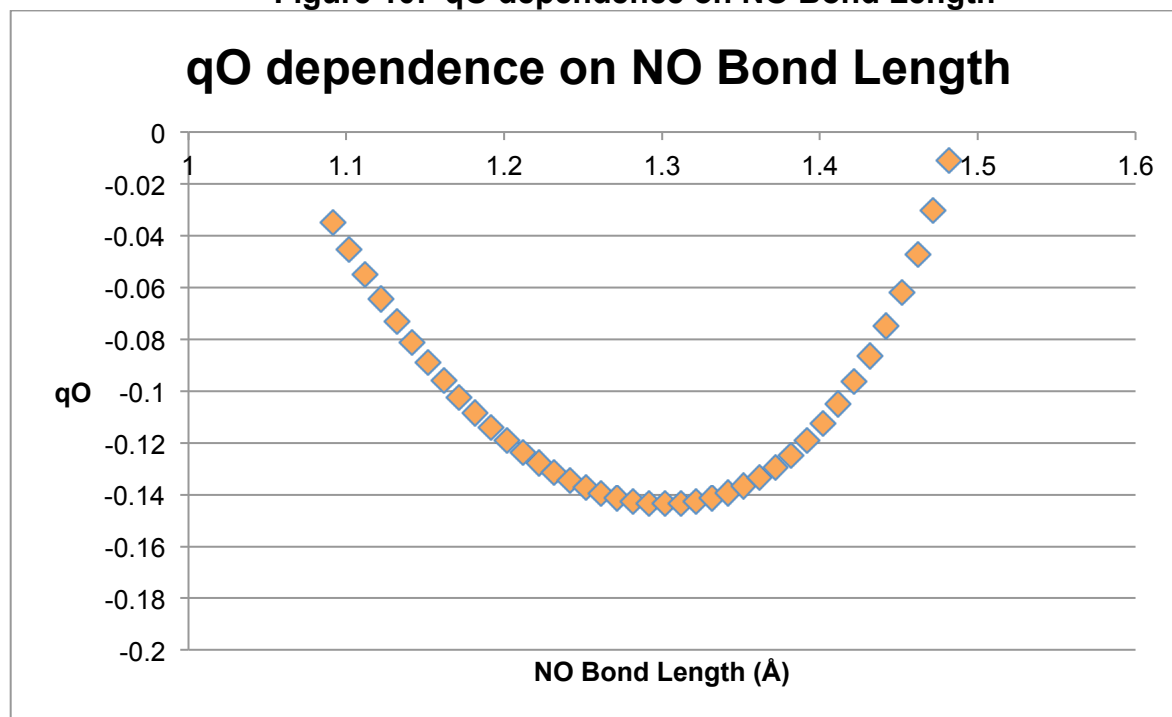
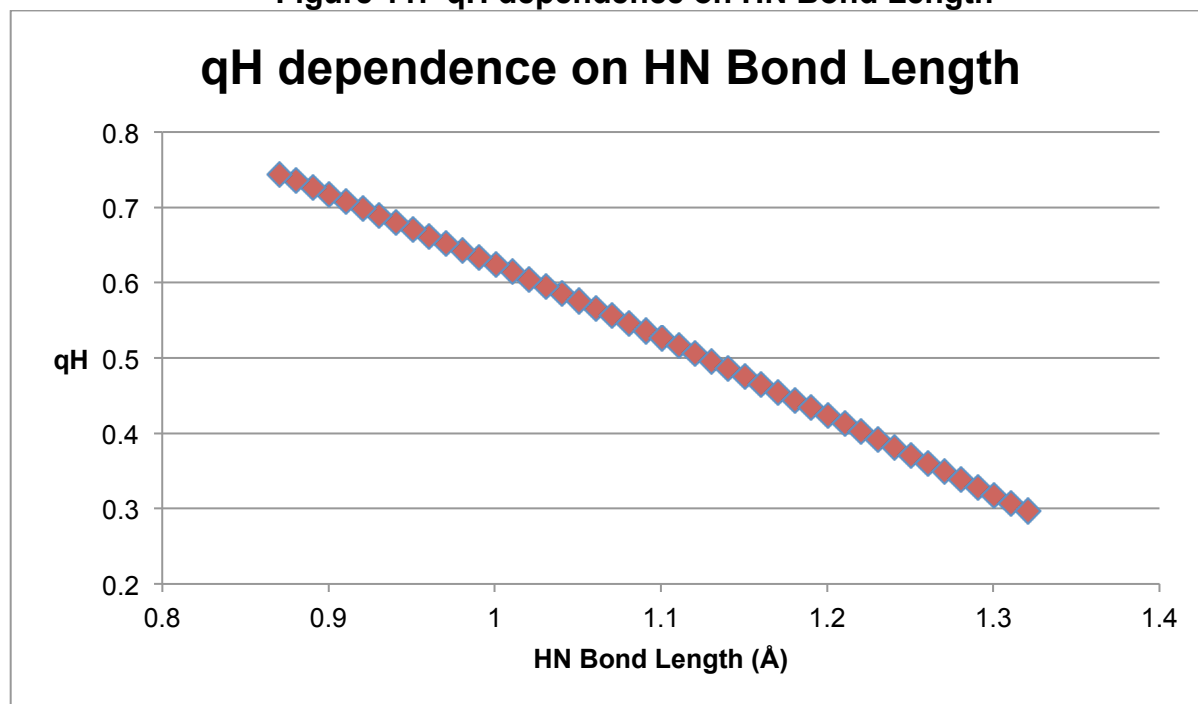


Figure 11 presents the relationship between the HN bond length and q_H . This relationship is similar to the previously discussed relationship between r_{NO} and q_O . As the bond length between the hydrogen and nitrogen atoms grows, the bond between the two becomes weaker and hydrogen begins to act more like a neutral atom, explaining why its atomic partial charge gets closer to zero as the bond length grows.

Figure 11: qH dependence on HN Bond Length



Figures 12 and 13 present the relationships between HN bond length, q_N , and q_O . As the distance between the hydrogen atom and nitrogen atom increases, the nitrogen atom begins to act more like a nitrogen only bonded to oxygen, rather than one bonded to hydrogen and oxygen. In a nitrogen-oxygen bond, oxygen is the more electronegative of the two atoms and therefore will have a more negative atomic partial charge. To compensate for this, the nitrogen atom will have a more positive partial charge on it. This means that as r_{HN} increases, q_N will become more positive. The relationship between r_{HN} and q_O is something that is currently unexplainable. The partial charge on oxygen also becomes more positive as the r_{HN} increases.

Figure 12: q_N dependence on HN Bond Length

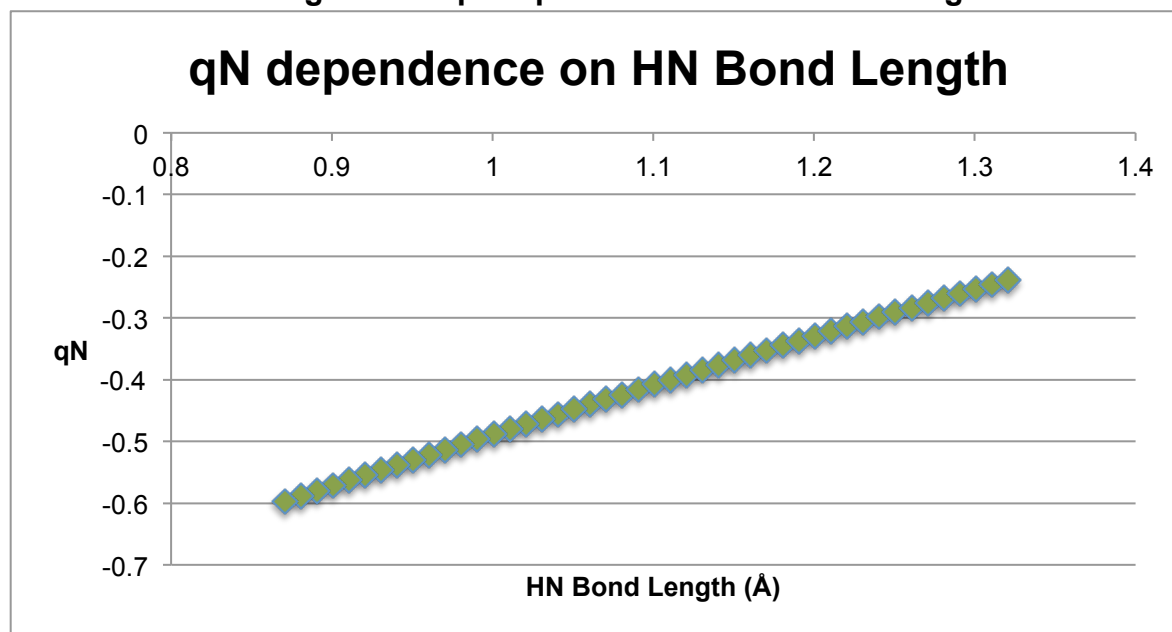
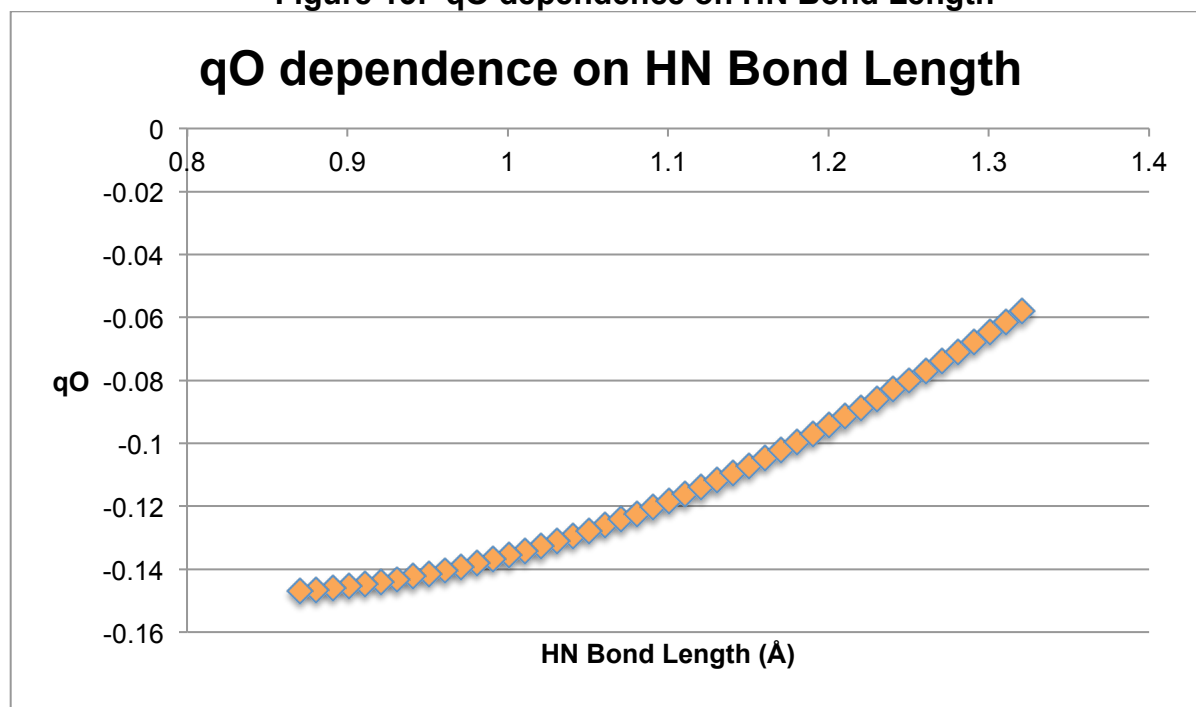


Figure 13: q_O dependence on HN Bond Length



Figures 14-16 present the relationship between the HNO bond angle and the three atomic partial charges. As the bond angle grows larger, q_H and q_O become more positive and q_N

become more negative. There is no easy explanation as to why all of these change in this manner, but it is still interesting to observe.

Figure 14: qH dependence on HNO Bond Angle

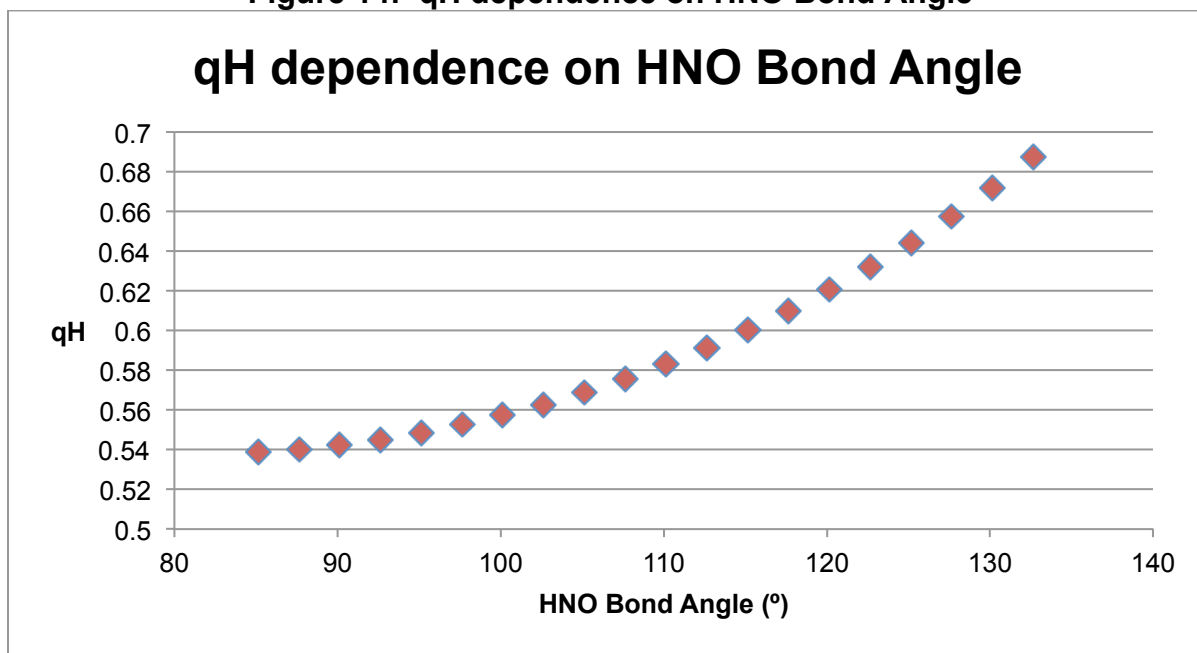


Figure 15: qN dependence on HNO Bond Angle

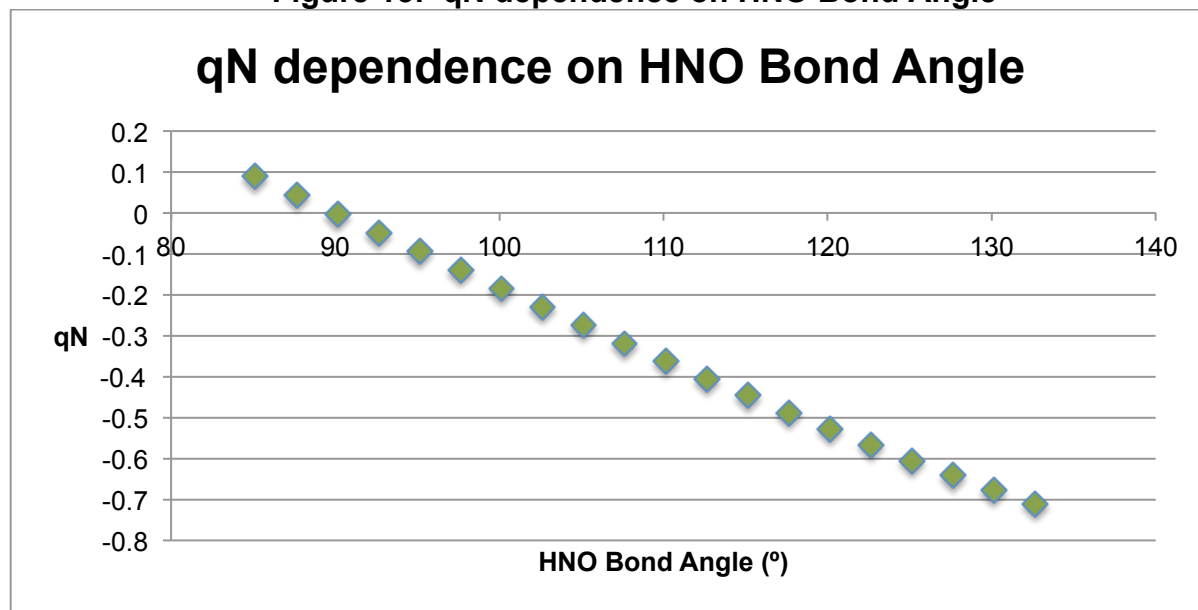
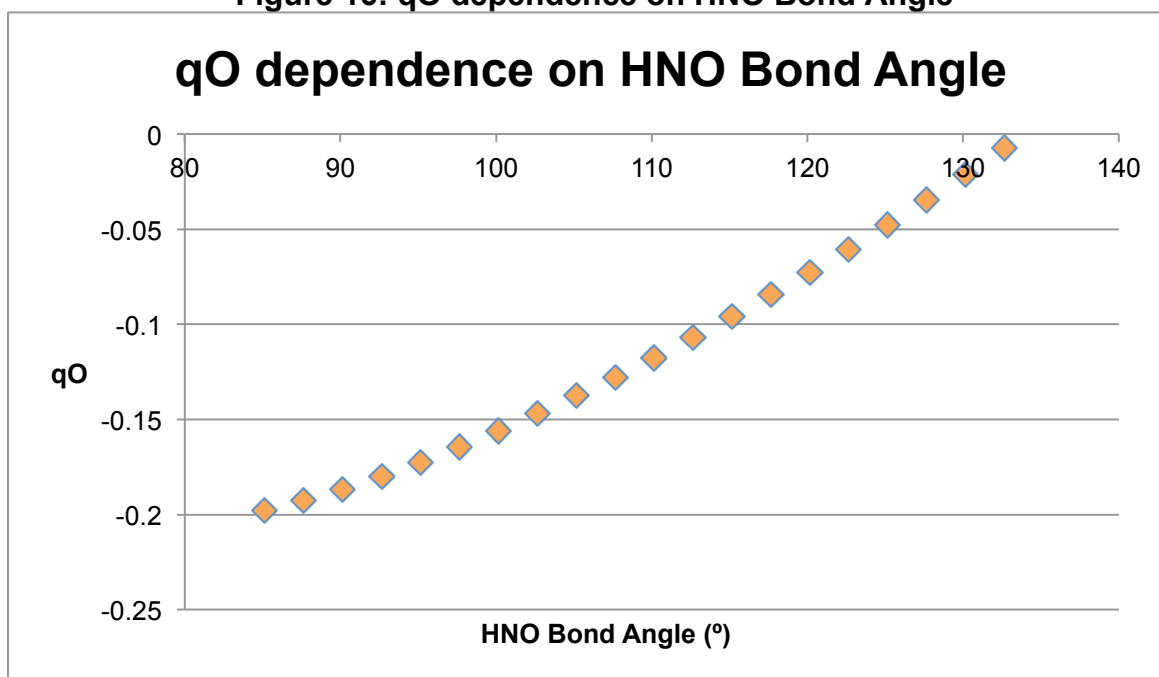


Figure 16: qO dependence on HNO Bond Angle



Before moving on to the next section of research, it is important to look at whether or not the ACCT^{6,7} basis set is reliable enough to produce results that are substantial. To do this, several tests using the ACCQ^{6,7} basis set were executed and compared to the ACCT results. As mentioned above, the ACCT basis set includes s, p, and d orbitals for the H atom, and s, p, d, and f orbitals for the N and O atoms. The ACCQ basis set looks at one extra orbital for each atom. It looks at the f orbital (in addition to the s, p, and d orbitals) for the hydrogen atom and looks at the g orbital (in addition to the s, p, d, and f orbitals) for the nitrogen and oxygen atoms. Doing this enables GAMESS to better represent the actual shape of the molecular orbitals, giving a more in depth look at the hybridization in the molecule. This means that it is safe to assume that using ACCQ will give better results than using ACCT. However, using ACCQ severely slows down the GAMESS program. One GAMESS test with ACCQ takes about 20-30 minutes to complete, while one with ACCT takes roughly one minute. If the ACCT results are only slightly different than the ACCQ results, then using ACCT for future tests would be acceptable it allows

research to be done more efficiently. The results from these tests can be seen in Appendices 11 and 12 and reveal that the ACCT and ACCQ outputs are very similar. For this reason, the rest of this report will continue to use GAMESS tests with the ACCT basis set.

Potential Energy Function and Vibrational Coupling:

Another way to describe the geometry of the HNO molecule is in terms of collective displacements of all three atoms from the equilibrium geometry. These collective displacements are called dimensionless normal modes³, and will be labeled q_1 , q_2 , and q_3 . When one of these three normal mode variables are changed, the three geometric parameters of HNO (the bond lengths r_{HN} and r_{NO} and the HNO bond angle) change in a coordinated way. When two normal modes have similar frequencies, then it is possible that the two modes can couple together⁹. Previous research on the HNO molecule suggests that the NO stretch frequency (represented by q_3) and the HNO bending frequency (represented by q_2) are similar¹⁰. Perhaps this is because the two corresponding normal modes are coupled together in the molecule's potential energy function. If the HNO molecule has no coupling between the NO bond and the bond angle, then the potential energy function when q_2 and q_3 change (keeping $q_1=0$) will simply be the sum of a function of q_2 and a function of q_3 . If there is coupling, then the potential energy function will be a sum of a function of q_2 and a function of q_3 plus a third function that is a function of q_2 and q_3 . This section of the report intends to investigate this.

To clarify, q_1 refers to the distortion along the HN stretch, q_2 refers to the HNO bond angle's distortion, and q_3 refers to the distortion along the NO stretch. Potential energy was calculated as a function of each mode, running each q -coordinate from -3 to 3 in increments of 0.5 and using values provided by Harkiran Dhah⁸ (found in Figure 17) that converted changes in q_1 , q_2 , and q_3 into changes in the atomic coordinates (found in figures 18 and 19). The final coordinates for each geometry were found by multiplying the q values with each respective q -coordinate for each atom and then calculating the sum of these for each of the three atoms in nitroxyl. The final coordinates for the equilibrium geometry (meaning $q_1=q_2=q_3=0$) can be

found in Figure 18 under the assumption that the center of mass is at the origin. The final coordinates for the geometry where $q_1=2$, $q_2=3$, and $q_3=1$ under the assumption that the center of mass is at the origin can be found in Figure 19.

Note: The coordinates in Figures 17-19 have units in Angstroms.

Figure 17: Values Used to Determine the Final Coordinates of Nitroxyl (E(MP2))

	X	Y	Z
base N	-0.59094776	-0.06258153	0
base O	0.63072383	-0.06255809	0
base H	-0.90932607	0.93861462	0
q1 N	0.00103899	-0.007230843	0
q1 O	0.000824951	0.000180421	0
q1 H	-0.02751817	0.097606288	0
q2 N	-0.008161171	0.009310035	0
q2 O	0.01469002	-0.006589491	0
q2 H	-0.119762159	-0.024751708	0
q3 N	0.028628201	0.004617818	0
q3 O	-0.021392871	-0.003222942	0
q3 H	-0.058273799	-0.012945978	0

Figure 18: Final Coordinates of Nitroxyl for the Equilibrium Geometry (assuming center of mass is at the origin) (E(MP2))

	X	Y	Z
final N	-0.59094776	-0.06258153	0
final O	0.63072383	-0.06255809	0
final H	-0.90932607	0.93861462	0

Figure 19: Final Coordinates of Nitroxyl with $q_1=2$, $q_2=3$, and $q_3=1$ (assuming center of mass is at the origin) (E(MP2))

	X	Y	Z
final N	-0.584725093	-0.044495294	0
final O	0.655050921	-0.085188661	0
final H	-1.381922687	1.046626093	0

These new coordinates were plugged into the GAMESS program (while keeping the electric field value at 0 for all tests) and the ACCT MP2 values for each geometry were recorded. The first tests studied each individual mode and assumed the other two normal mode coordinates equaled zero. For example, when q1 energy values were determined, q2 and q3 were assumed to be zero. The values for each mode were fit to several polynomial curves. This was done by using a Maple document (see Appendix 4). In all 3 cases, as the degree of the polynomial increased, the better the curve fits were. This meant that there were smaller errors in the 6th degree fits than there were in the 2nd, 3rd, 4th, and 5th degree fits. An example of this improved error can be seen in Figures 21 and 22 that compare the 4th order q2 energy error values to the 6th order q2 energy error values. The error values in Figure 22 are much smaller than the ones in Figure 21.

Figure 20: 6th Order Curve Fits for Individual Modes (E(MP2))

$$y = 0.000004909024325 \cdot x^6 - 0.00004217957113 \cdot x^5 + 0.0002760845891 \cdot x^4 - 0.001753502735 \cdot x^3 + 0.006913373772 \cdot x^2 - 130.2842488 \rightarrow 6^{\text{th}} \text{ order } q1$$

$$y = -3.974157524 \cdot 10^{(-7)} \cdot x^6 + 0.2270608149 \cdot 10^{-5} \cdot x^5 + 0.9314860116 \cdot 10^{-5} \cdot x^4 - 0.2208716979 \cdot 10^{-3} \cdot x^3 + 0.3595624833 \cdot 10^{-2} \cdot x^2 - 130.2842488 \rightarrow 6^{\text{th}} \text{ order } q2$$

$$y = 4.735331333 \cdot 10^{(-8)} \cdot x^6 + 4.001697689 \cdot 10^{(-7)} \cdot x^5 + 0.2567134858 \cdot 10^{-4} \cdot x^4 + 0.3881694535 \cdot 10^{-3} \cdot x^3 + 0.3361248824 \cdot 10^{-2} \cdot x^2 - 130.2842488 \rightarrow 6^{\text{th}} \text{ order } q3$$

Note: Energy vales are in units of Hartrees (Ha).

Figure 21: 4th Order q2 Error Values (E(MP2))

q2	4 th order q2 energy (Ha)	actual q2 energy (Ha)	error (Ha)
-3	-130.2459429	-130.2460115	6.85121E-05
-2.5	-130.2583547	-130.2582804	-7.42632E-05
-2	-130.2681206	-130.2680478	-7.27257E-05
-1.5	-130.2754216	-130.2753877	-3.39259E-05
-1	-130.2804323	-130.2804262	-6.16239E-06
-0.5	-130.2833208	-130.2833222	1.41411E-06
0	-130.2842488	-130.2842488	-5.09999E-09
0.5	-130.2833715	-130.2833766	5.11117E-06
1	-130.2808379	-130.2808628	2.49761E-05
1.5	-130.2767903	-130.2768444	5.40973E-05
2	-130.2713648	-130.271437	7.21887E-05
2.5	-130.2646911	-130.2647386	4.75107E-05
3	-130.2568923	-130.2568352	-5.70113E-05

Figure 22: 6th Order q2 Error Values (E(MP2))

q2	6th order q2 energy (Ha)	actual energy (Ha)	error (Ha)
-3	-130.2460116	-130.2460115	-1.55154E-07
-2.5	-130.2582799	-130.2582804	4.70402E-07
-2	-130.2680484	-130.2680478	-5.35992E-07
-1.5	-130.2753878	-130.2753877	-1.1751E-07
-1	-130.2804257	-130.2804262	5.19967E-07
-0.5	-130.2833218	-130.2833222	4.66583E-07
0	-130.2842488	-130.2842488	-5.09999E-09
0.5	-130.2833769	-130.2833766	-2.21128E-07
1	-130.2808629	-130.2808628	-1.38124E-08
1.5	-130.2768442	-130.2768444	1.6999E-07
2	-130.271437	-130.271437	-1.06367E-08
2.5	-130.2647387	-130.2647386	-1.13403E-07
3	-130.2568352	-130.2568352	7.25198E-08

Also, for each of these geometries, rHN, rNO, and the HNO bond angle were calculated and analyzed. These values can be found Figures 23-25. In the q1 tests, the rHN changed

significantly with every test, while rNO and the bond angle slightly changed. This suggests that q1 is predominately affected by the HN bond length and the effect that the other two parameters have on it are negligible. In the q2 and q3 tests, the rHN change was small, but both rNO and the bond angle changed to significant degrees. This further implies that there is likely coupling between q2 and q3. It is important to note that rNO changes slightly more in the q3 test and the HNO bond angle changes slightly more in the q2 test. This suggests that q3 might be affected the most by rNO and q2 might be affected the most by the bond angle, but this is only speculation. This is why this report identifies q2 with HNO bending and q3 with NO stretching.

Figure 23: Geometric Values for q1 Energy (E(MP2))

q1	Actual q1 Energy (Ha)	Relative Energy (Ha)	HN Length (Å)	NO Length (Å)	HO Distance (Å)	HNO Angle (°)
-3	-130.1386596	0.145589216	0.72504374	1.222515478	1.618523105	109.7617165
-2.5	-130.1974158	0.086832972	0.779278843	1.222346763	1.653026124	109.3454455
-2	-130.2360443	0.048204465	0.833526108	1.222189269	1.688348678	108.9607147
-1.5	-130.2603475	0.023901266	0.887783305	1.222043001	1.724440407	108.6017423
-1	-130.2744734	0.009775394	0.94204872	1.221907963	1.761254026	108.264077
-0.5	-130.2814103	0.002838511	0.996321008	1.221784158	1.798745211	107.9442364
0	-130.2842488	0	1.050599105	1.22167159	1.836872475	107.6394573
0.5	-130.2817821	0.002466744	1.104882154	1.221570263	1.875597028	107.3475196
1	-130.2779353	0.00631351	1.159169461	1.221480178	1.914882634	107.066619
1.5	-130.2726162	0.011632567	1.213460453	1.221401338	1.954695464	106.7952746
2	-130.2664294	0.017819351	1.267754657	1.221333747	1.995003954	106.5322591
2.5	-130.2598077	0.024441063	1.322051677	1.221277404	2.035778662	106.2765475
3	-130.2530543	0.031194513	1.37635118	1.221232313	2.076992131	106.0272767

Figure 24: Geometric Values for q2 Energy (E(MP2))

q2	Actual q2 Energy (Ha)	Relative Energy (Ha)	HN Length (Å)	NO Length (Å)	HO Distance (Å)	HNO Angle (°)
-3	-130.2460115	0.038237339	1.10350362	1.154105087	1.551286077	86.7773278
-2.5	-130.2582804	0.025968397	1.087063882	1.165222578	1.595226658	90.11979037
-2	-130.2680478	0.016200948	1.073546934	1.176399698	1.64079594	93.53620739
-1.5	-130.2753877	0.008861098	1.063064273	1.187634761	1.687862011	97.01299178
-1	-130.2804262	0.003822618	1.055706288	1.19892614	1.736303156	100.534368
-0.5	-130.2833222	0.000926549	1.051538576	1.210272258	1.78600749	104.0827823
0	-130.2842488	0	1.050599105	1.22167159	1.836872475	107.6394573
0.5	-130.2833766	0.00087216	1.052896515	1.23312266	1.888804344	111.1850521
1	-130.2808628	0.00338595	1.05840973	1.244624041	1.941717498	114.7003719
1.5	-130.2768444	0.007404411	1.067088906	1.256174349	1.995533878	118.1670648
2	-130.271437	0.012811794	1.078857637	1.267772249	2.050182358	121.5682431
2.5	-130.2647386	0.019510219	1.093616185	1.279416445	2.105598151	124.8889813
3	-130.2568352	0.027413555	1.111245432	1.291105685	2.161722246	128.1166589

Figure 25: Geometric Values for q3 Energy (E(MP2))

q3	Actual q3 Energy (Ha)	Relative Energy (Ha)	HN Length (Å)	NO Length (Å)	HO Distance (Å)	HNO Angle (°)
-3	-130.2624616	0.021787239	1.055464369	1.371936873	1.762046812	92.14891474
-2.5	-130.2683305	0.015918335	1.049986533	1.34686726	1.774224468	94.69178193
-2	-130.2735083	0.010740495	1.046359702	1.321807037	1.786522691	97.26112705
-1.5	-130.277869	0.00637979	1.044603157	1.296756747	1.79893901	99.84888217
-1	-130.2812507	0.002998097	1.044726332	1.271716978	1.811470996	102.4467402
-0.5	-130.2834555	0.000793294	1.046728562	1.246688364	1.824116264	105.0463401
0	-130.2842488	0	1.050599105	1.22167159	1.836872475	107.6394573
0.5	-130.2833583	0.000890486	1.056317423	1.196667399	1.849737334	110.2181882
1	-130.2804731	0.003775732	1.063853721	1.171676596	1.86270859	112.7751202
1.5	-130.275242	0.009006835	1.073169699	1.146700057	1.875784036	115.3034799
2	-130.2672716	0.01697718	1.084219484	1.121738734	1.888961507	117.7972515
2.5	-130.2561229	0.028125865	1.096950681	1.096793667	1.902238884	120.2512654
3	-130.2413057	0.042943048	1.111305506	1.07186599	1.915614089	122.6612532

Next, because there are strong reasons to believe that there is coupling, it is important to look at the energy when pairs of the variables change. Keeping $q_1=0$, q_2 and q_3 were changed first and calculations were run in the GAMESS file for all geometries with q_2 and q_3 values

between -3 and 3, stepping in increments on 0.5. After this, the pairings of q1,q2 and q1,q3 were done. Once completed, a Maple document was used for each of the three pairs to fit the data and create 6th order polynomials for each (see Appendix 5). These three different polynomials can be found in Figure 26.

Figure 26: 6th Order Curve Fits for Coupling between 2 Different q Values (E(MP2))

6th order polynomial for q1 and q2 coupling (q2=x, q1=y): $z = -3.243761995 \times 10^{-7} x^5 y + 0.1437720349 e-4 x^4 y^2 - 0.1773567466 e-5 x^3 y^3 - 0.2070836645 e-4 x^2 y^4 + 0.1450533790 e-5 x y^5 - 0.3925330444 e-4 x^4 y + 0.1178031211 e-5 x^3 y^2 + 0.1129347858 e-3 x^2 y^3 - 0.9451044851 e-5 x y^4 + 0.4407798222 e-4 x^3 y - 0.3776110678 e-3 x^2 y^2 + 0.4192004848 e-4 x y^3 + 0.3997099589 e-3 x^2 y - 0.4418714441 e-4 x y^2 - 0.3393826180 e-5 x y - 130.2842488$
6th order polynomial for q1 and q3 coupling (q1=x, q3=y): $z = 0.2817436608 e-5 x^5 y - 0.1270436541 e-4 x^4 y^2 - 0.5240092779 e-5 x^3 y^3 + 0.4890468606 e-5 x^2 y^4 + 0.1495807548 e-5 x y^5 - 0.1792457990 e-4 x^4 y + 0.7275504867 e-4 x^3 y^2 + 0.2285688779 e-4 x^2 y^3 - 0.1192949705 e-4 x y^4 + 0.1365308810 e-3 x^3 y - 0.2030014442 e-3 x^2 y^2 - 0.6023014104 e-4 x y^3 - 0.6735286339 e-3 x^2 y + 0.1195510382 e-3 x y^2 - 0.1184359991 e-4 x y - 130.2842488$
6th order polynomial for q2 and q3 coupling (q2=x, q3=y): $z = -6.849796067 \times 10^{-7} x^5 y - 0.1874997860 e-5 x^4 y^2 - 0.1758775727 e-5 x^3 y^3 - 5.948634815 \times 10^{-7} x^2 y^4 - 1.392963436 \times 10^{-7} x y^5 + 0.4240479774 e-5 x^4 y + 0.1163978215 e-5 x^3 y^2 + 6.605992224 \times 10^{-7} x^2 y^3 - 0.7082841498 e-5 x y^4 - 0.7344387140 e-5 x^3 y + 0.4527907301 e-4 x^2 y^2 - 0.5539727474 e-4 x y^3 + 0.1661485927 e-3 x^2 y - 0.4200219715 e-3 x y^2 + 0.2646158470 e-4 x y - 130.2842488$

So now it is important to determine the coupling component involving all three modes. Theoretically, the entire potential energy function should be the sum of the previously determined 6 formulas plus a formula that addresses coupling among all three q values. Seventy-two different tests that changed all three of the q values for each test were run in the GAMESS program and the MP2 energies of each test were recorded. The 72 different tests run can be found in the Appendix (see Appendix 7). Once all of these were determined, a Maple document

was used to find a polynomial of the three variables q1, q2, and q3 that would fit the data. The terms of this polynomial were limited by the requirement that the exponents of q1, q2, and q3 for each term must sum to six or less. The Maple document used can be found in the Appendix (see Appendix 6) and the curve fit can be found in Figure 27.

Figure 27: 6th Order Curve Fits for Coupling between All 3 q Values (q1=x, q2=y, q3=z) (E(MP2))

$$w = -0.1048937925e-2*x*y*z+0.5647822448e-3*x^2*y*z+0.8538976992e-4*x*y^2*z+0.8431901914e-4*x*y*z^2-0.8062502757e-5*x^2*y^2*z-0.3225654508e-4*x^2*y*z^2+0.9466487921e-4*x*y^2*z^2+0.1728486739e-4*x*y*z^3+0.7194319910e-4*x*y^3*z-0.1007534589e-3*x^3*y*z-0.3191279271e-4*x^2*y^2*z^2+0.2045147451e-4*x^4*y*z+0.3955198430e-5*x*y^4*z+0.4380099624e-5*x^3*y^2*z+0.8568487502e-5*x^3*y*z^2-0.2314838886e-4*x^2*y^3*z-0.4383846179e-5*x*y^3*z^2-0.1638288336e-4*x^2*y*z^3-0.1325827482e-4*x*y^2*z^3-130.2842488$$

With all seven necessary formulas representing each of the different potential energy functions, it is now possible to determine the potential energy function for the entire molecule. The way to do this is to add together all 7 of the potential energy functions. The sum of these formulas will give the potential energy function for nitroxyl. It is important to note that the constant (-130.2842488, which represents the MP2 energy when all q values equal zero) was not included in each formula when finding the sum of the formulas, and instead was placed at the end of the final potential energy function. This final potential energy formula can be found in Figure 28.

Figure 28: 6th Order Curve Fit for the Potential Energy Function of Nitroxyl, assuming center of mass is at the origin (q1=x, q2=y, q3=z) (E(MP2))

$$\begin{aligned}
 w = & -0.1048937925e-2*x*y*z+0.5647822448e-3*x^2*y*z+0.8538976992e- \\
 & 4*x*y^2*z+0.8431901914e-4*x*y*z^2-0.8062502757e-5*x^2*y^2*z-0.3225654508e- \\
 & 4*x^2*y*z^2+0.9466487921e-4*x*y^2*z^2+0.1728486739e-4*x*y*z^3+0.7194319910e- \\
 & 4*x*y^3*z-0.1007534589e-3*x^3*y*z-0.3191279271e-4*x^2*y^2*z^2+0.2045147451e- \\
 & 4*x^4*y*z+0.3955198430e-5*x*y^4*z+0.4380099624e-5*x^3*y^2*z+0.8568487502e- \\
 & 5*x^3*y*z^2-0.2314838886e-4*x^2*y^3*z-0.4383846179e-5*x*y^3*z^2-0.1638288336e- \\
 & 4*x^2*y*z^3-0.1325827482e-4*x*y^2*z^3+0.000004909024325*x^6- \\
 & 0.00004217957113*x^5+0.0002760845891*x^4- \\
 & 0.001753502735*x^3+0.006913373772*x^2-3.974157524*10^{(-7)}*y^6+0.2270608149e- \\
 & 5*y^5+0.9314860116e-5*y^4-0.2208716979e-3*y^3+0.3595624833e- \\
 & 2*y^2+4.735331333*10^{(-8)}*z^6+4.001697689*10^{(-7)}*z^5+0.2567134858e- \\
 & 4*z^4+0.3881694535e-3*z^3+0.3361248824e-2*z^2-3.243761995*10^{(-} \\
 & 7)*y^5*x+0.1437720349e-4*y^4*x^2-0.1773567466e-5*y^3*x^3-0.2070836645e- \\
 & 4*y^2*x^4+0.1450533790e-5*y*x^5-0.3925330444e-4*y^4*x+0.1178031211e- \\
 & 5*y^3*x^2+0.1129347858e-3*y^2*x^3-0.9451044851e-5*y*x^4+0.4407798222e- \\
 & 4*y^3*x-0.3776110678e-3*y^2*x^2+0.4192004848e-4*y*x^3+0.3997099589e-3*y^2*x- \\
 & 0.4418714441e-4*y*x^2-0.3393826180e-5*y*x+0.2817436608e-5*x^5*z- \\
 & 0.1270436541e-4*x^4*z^2-0.5240092779e-5*x^3*z^3+0.4890468606e- \\
 & 5*x^2*z^4+0.1495807548e-5*x*z^5-0.1792457990e-4*x^4*z+0.7275504867e- \\
 & 4*x^3*z^2+0.2285688779e-4*x^2*z^3-0.1192949705e-4*x*z^4+0.1365308810e- \\
 & 3*x^3*z-0.2030014442e-3*x^2*z^2-0.6023014104e-4*x*z^3-0.6735286339e- \\
 & 3*x^2*z+0.1195510382e-3*x*z^2-0.1184359991e-4*x*z-6.849796067*10^{(-7)}*y^5*z- \\
 & 0.1874997860e-5*y^4*z^2-0.1758775727e-5*y^3*z^3-5.948634815*10^{(-7)}*y^2*z^4- \\
 & 1.392963436*10^{(-7)}*y*z^5+0.4240479774e-5*y^4*z+0.1163978215e- \\
 & 5*y^3*z^2+6.605992224*10^{(-7)}*y^2*z^3-0.7082841498e-5*y*z^4-0.7344387140e- \\
 & 5*y^3*z+0.4527907301e-4*y^2*z^2-0.5539727474e-4*y*z^3+0.1661485927e-3*y^2*z- \\
 & 0.4200219715e-3*y*z^2+0.2646158470e-4*y*z-130.2842488
 \end{aligned}$$

With the potential energy formula completed, it is now crucial to determine how accurate this formula is. To do this, 100 random points with q1, q2, and q3 values ranging from -3 to 3 were created and the MP2 energy was found for each point using the GAMESS program. A table featuring all 100 of these tests and the calculated the MP2 energy values can be found in the Appendix (see Appendix 8). Along with running the 100 tests in the GAMESS program, they were also placed into the potential energy function of nitroxyl (Figure 28) and the predicted energy was recorded. These values were compared to the values found from the GAMESS program and the difference between the two values (along with the difference squared) for each

of the 100 tests was found. These results were then sorted in five different ways: decreasing formula value, decreasing distance from center (calculated as the square root of $q_1^2 + q_2^2 + q_3^2$), increasing q_1 value, increasing q_2 value, and increasing q_3 value. Each of these five organizations was then separated into intervals of ten. For each interval of ten, the lowest and highest differences found in the interval were recorded, along with the average difference squared. It can be assumed that the smaller the value of the average difference squared for an interval, the more accurate the formula output is to the actual GAMESS output. These results can be found in Figures 29-33. There were three significant observations from this part of the data

- The formula results were typically more accurate as the distance from the center decreased.
- The formula results were typically more accurate as the actual value grew closer to the actual value of the equilibrium geometry.
- Severely negative q_1 values gave MP2 values furthest from the formula results.

Figure 29: Summary of 100 Calculations Sorted by Decreasing Predicted Energy (E(MP2))

Average Formula Value (Ha)	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-130.1770832	-0.079541809	0.011648347	0.001402334
-130.2211513	-0.019553116	0.02280576	0.00011258
-130.2309001	-0.010217249	0.034207669	0.000249298
-130.239946	-0.010871746	0.000935799	2.98825E-05
-130.2461653	-0.002236583	0.00701783	5.90272E-06
-130.2514971	-0.001645678	-7.74343E-06	8.94699E-07
-130.2568296	-0.001288354	0.000156947	6.11008E-07
-130.2620131	-0.005029878	0.002222441	3.62408E-06
-130.2663447	-0.003940267	0.002465313	2.849E-06
-130.272881	-0.000656172	0.003003339	1.06668E-06

Figure 30: Summary of 100 Calculations Sorted by Decreasing Distance from Center (E(MP2))

Average Distance from Center (Å)	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
4.141141244	-0.079541809	-0.000837556	0.001216959
3.637893338	-0.032861086	0.034207669	0.00029043
3.40379011	-0.002422657	0.028622696	8.3518E-05
3.134776075	-0.027924273	0.016305681	0.000124934
2.889404919	-0.00265069	0.011648347	1.47742E-05
2.687510576	-0.019553116	0.004707115	5.37562E-05
2.514711694	-0.010770603	0.002222441	1.27325E-05
2.22637966	-0.002014303	0.00701783	5.77762E-06
2.046123026	-0.005029878	0.001408579	4.49175E-06
1.615222883	-0.000656172	0.003003339	1.66913E-06

Figure 31: Summary of 100 Calculations Sorted by Increasing q1 Value (E(MP2))

Average q1 Value	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-2.49428	-0.079541809	0.034207669	0.001346029
-1.9546	-0.019553116	0.028622696	0.00016419
-1.35921	-0.032861086	0.02280576	0.000254903
-0.35753	-0.003940267	0.003003339	3.27498E-06
0.23949	-0.002422657	0.000739485	9.99799E-07
0.85023	-0.002014303	0.002222441	1.48655E-06
1.48397	-0.009613586	0.000666042	1.76521E-05
1.82479	-0.008450775	0.000935799	7.7609E-06
2.33961	-0.003809098	-4.20488E-05	2.32411E-06
2.79891	-0.009167968	0.000439789	1.04219E-05

Figure 32: Summary of 100 Calculations Sorted by q2 Value (E(MP2))

Average q2 Value	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-2.75583	-0.079541809	5.66639E-05	0.000816371
-2.01682	-0.003809098	0.028622696	8.42416E-05
-1.53352	-0.003940267	0.02280576	8.14892E-05
-0.95355	-0.027924273	0.00701783	8.84376E-05
-0.19127	-0.000809612	0.003194756	1.4646E-06
0.32043	-0.000793441	0.011648347	1.43683E-05
0.73059	-0.000656172	0.034207669	0.000124428
1.32046	-0.038222427	0.00023478	0.000209862
2.00215	-0.010770603	0.000327861	1.76513E-05
2.69448	-0.059074143	-0.000772828	0.000370729

Figure 33: Summary of 100 Calculations Sorted by Increasing q3 Value (E(MP2))

Average q3 Value	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-2.57792	-0.032861086	0.034207669	0.000307038
-1.52807	-0.079541809	0.011648347	0.000651198
-1.14125	-0.027924273	0.001408579	7.88378E-05
-0.82092	-0.001806386	0.007997887	7.4632E-06
-0.39021	-0.00265069	0.000699992	8.60993E-07
0.09072	-0.001288354	0.000857649	6.2834E-07
0.6388	-0.059074143	0.00701783	0.00040958
1.20159	-0.008450775	0.016305681	3.43689E-05
2.03429	-0.010871746	0.028622696	0.000102962
2.67225	-0.038222427	0.02280576	0.000216105

One thing also considered is whether or not it was necessary to include the coupling involving all three modes. The potential energy function from Figure 28 was modified to represent this by taking out all of the parts that included all three modes. This modified function can be seen in Figure 34. The average difference squared values from this function were compared to the values from the function with q1,q2,q3 coupling for decreasing formula value and decreasing distance from center. These comparisons can be seen in Figures 35 and 36. From the data in these tables, it seems that the formula that did not include q1,q2,q3 coupling

gave better results than the formula that did include q1,q2,q3 coupling. While it is unclear what this means for future research on this molecule, it is still interesting to note.

Figure 34: 6th Order Curve Fit for the Potential Energy Function of Nitroxyl, without including coupling between all 3 modes (q1=x, q2=y, q3=z) (E(MP2))

$$w = 0.000004909024325x^6 - 0.00004217957113x^5 + 0.0002760845891x^4 - 0.001753502735x^3 + 0.006913373772x^2 - 3.974157524 \times 10^{-7}y^6 + 0.2270608149e-5y^5 + 0.9314860116e-5y^4 - 0.2208716979e-3y^3 + 0.3595624833e-2y^2 + 4.735331333 \times 10^{-8}z^6 + 4.001697689 \times 10^{-7}z^5 + 0.2567134858e-4z^4 + 0.3881694535e-3z^3 + 0.3361248824e-2z^2 - 3.243761995 \times 10^{-7}y^5x + 0.1437720349e-4y^4x^2 - 0.1773567466e-5y^3x^3 - 0.2070836645e-4y^2x^4 + 0.1450533790e-5yx^5 - 0.3925330444e-4y^4x + 0.1178031211e-5y^3x^2 + 0.1129347858e-3y^2x^3 - 0.9451044851e-5yx^4 + 0.4407798222e-4y^3x - 0.3776110678e-3y^2x^2 + 0.4192004848e-4yx^3 + 0.3997099589e-3y^2x - 0.4418714441e-4yx^2 - 0.3393826180e-5yx + 0.2817436608e-5x^5z - 0.1270436541e-4x^4z^2 - 0.5240092779e-5x^3z^3 + 0.4890468606e-5x^2z^4 + 0.1495807548e-5xz^5 - 0.1792457990e-4x^4z + 0.7275504867e-4x^3z^2 + 0.2285688779e-4x^2z^3 - 0.1192949705e-4xz^4 + 0.1365308810e-3x^3z - 0.2030014442e-3x^2z^2 - 0.6023014104e-4xz^3 - 0.6735286339e-3x^2z + 0.1195510382e-3xz^2 - 0.1184359991e-4xz - 6.849796067 \times 10^{-7}y^5z - 0.1874997860e-5y^4z^2 - 0.1758775727e-5y^3z^3 - 5.948634815 \times 10^{-7}y^2z^4 - 1.392963436 \times 10^{-7}yz^5 + 0.4240479774e-5y^4z + 0.1163978215e-5y^3z^2 + 6.605992224 \times 10^{-7}y^2z^3 - 0.7082841498e-5yz^4 - 0.7344387140e-5y^3z + 0.4527907301e-4y^2z^2 - 0.5539727474e-4yz^3 + 0.1661485927e-3y^2z - 0.4200219715e-3yz^2 + 0.2646158470e-4yz - 130.2842488$$

Figure 35: Table Investigating q1,q2,q3 Coupling for Decreasing Formula Value (E(MP2))

Average Formula Value	Average Difference Squared (Ha ²) (with q1,q2,q3 coupling)	Average Difference Squared (Ha ²) (without q1,q2,q3 coupling)
-130.1770832	0.001402334	0.00069146
-130.2211513	0.00011258	9.56481E-05
-130.2309001	0.000249298	2.85583E-05
-130.239946	2.98825E-05	1.52464E-05
-130.2461653	5.90272E-06	4.65413E-06
-130.2514971	8.94699E-07	5.2488E-07
-130.2568296	6.11008E-07	4.49555E-07
-130.2620131	3.62408E-06	1.63961E-06
-130.2663447	2.849E-06	5.25095E-07
-130.272881	1.06668E-06	2.08752E-07

Figure 36: Table Investigating q1,q2,q3 Coupling for Decreasing Distance (E(MP2))

Average Distance from Center (Å)	Average Difference Squared (Ha ²) (with q1,q2,q3 coupling)	Average Difference Squared (Ha ²) 3(without q1,q2,q3 coupling)
4.1411412440	0.001216959	0.000666483
3.637893338	0.00029043	7.99915E-05
3.40379011	8.3518E-05	1.19237E-05
3.134776075	0.000124934	3.61937E-05
2.889404919	1.47742E-05	8.12006E-06
2.687510576	5.37562E-05	2.43111E-05
2.514711694	1.27325E-05	9.15895E-06
2.22637966	5.77762E-06	6.11161E-07
2.046123026	4.49175E-06	1.80443E-06
1.615222883	1.66913E-06	1.52165E-07

Potential Energy Function and Vibration Coupling with SCS-MP2:

When calculating the HNO molecule's energy using the GAMESS program, there are always two outputs that are produced. The first is the MP2 energy that has been used for the entirety of this report up to this point. The second is a variation of the MP2 output called SCS-MP2. Research suggests that SCS-MP2 is a better way to understand the interactions between two different molecules. This is especially of interest to this report because of the matrix isolation technique that the Wyoming research group is using to study nitroxyl. The matrix isolation technique uses H_2 matrices so the SCS-MP2 calculations could be used to study a nitroxyl molecule surrounded by one or more H_2 molecule. This will mimic the environment that the Wyoming group has studied the HNO molecule under.

Before immediately using the SCS-MP2 calculations to study these interactions between HNO and H_2 , it is first important to decide whether or not the SCS-MP2 calculations accurately measure the HNO molecule by itself with no H_2 molecules surrounding it. To do this, it is necessary to carry out tests for a nitroxyl molecule with no H_2 molecules surrounding it for both MP2 and SCS-MP2. If both yield similar results for identical tests, then the SCS-MP2 output can be recognized as an alternative way to study HNO and can be useful for studying its interactions with several H_2 molecules.

To do this, the exact same tests that were carried out for the MP2 calculations were carried out for SCS-MP2 calculations. Different starting values were used to carry out these calculations and they were again provided by Harkiran Dhah⁸. Tables 17b-36b present the same data that was used for the MP2 calculations, with each SCS-MP2 table matching its respective MP2 table. For example, Table 17 and Table 17b are identical except the former gives values for the MP2 calculations and the latter gives values for the SCS-MP2 calculations. Overall, the

results suggest that the SCS-MP2 values are close enough to the MP2 values, so using SCS-MP2 in the future to study nitroxyl surrounded by H₂ molecules is appropriate.

Note: The coordinates in Figures 17b-19b have units in Angstroms.

Figure 17b: Values Used to Determine the Final Coordinates of Nitroxyl (SCS-MP2)

	X	Y	Z
base N	-0.586396973	-0.063613151	0
base O	0.632772924	-0.063398039	0
base H	-0.906375952	0.93701119	0
q1 N	0.001036304	-0.007214584	0
q1 O	0.000851835	0.000168732	0
q1 H	-0.027927025	0.097498538	0
q2 N	-0.008794036	0.009226362	0
q2 O	0.015121181	-0.006506388	0
q2 H	-0.117873577	-0.024896475	0
q3 N	0.028172364	0.004820927	0
q3 O	-0.020850252	-0.003364204	0
q3 H	-0.060595497	-0.013577142	0

Figure 18b: Final Coordinates of Nitroxyl for the Equilibrium Geometry (assuming center of mass is at the origin) (SCS-MP2)

	X	Y	Z
final N	-0.586396973	-0.063613151	0
final O	0.632772924	-0.063398039	0
final H	-0.906375952	0.93701119	0

Figure 19b: Final Coordinates of Nitroxyl with q1=2, q2=3, and q3=1 (assuming center of mass is at the origin) (SCS-MP2)

	X	Y	Z
final N	-0.582534109	-0.045542305	0
final O	0.658989885	-0.085943941	0
final H	-1.37644623	1.0437417	0

Figure 20b: 6th Order Curve Fits for Individual Modes (SCS-MP2)

$y = 0.4909133576e-5x^6 - 0.4218859117e-4x^5 + 0.2763705226e-3x^4 - 0.1756030541e-2x^3 + 0.6908818678e-2x^2 - 130.2776647 \rightarrow 6^{\text{th}} \text{ order } q1$
 $y = -3.543384841 \cdot 10^{(-7)}x^6 + 0.2203791911e-5x^5 + 0.8847229812e-5x^4 - 0.2267658660e-3x^3 + 0.3617116977e-2x^2 - 130.2776647 \rightarrow 6^{\text{th}} \text{ order } q2$
 $y = 2.536304451 \cdot 10^{(-8)}x^6 + 2.619070161 \cdot 10^{(-7)}x^5 + 0.2373132458e-4x^4 + 0.3712022545e-3x^3 + 0.3417873485e-2x^2 - 130.2776647 \rightarrow 6^{\text{th}} \text{ order } q3$

Figure 21b: 4th Order q2 Error Values (SCS-MP2)

q2	4th order q2 energy (Ha)	actual q2 (Ha)	error (Ha)
-3	-130.238999	-130.2390651	-6.60822E-05
-2.5	-130.2515421	-130.251471	7.10859E-05
-2	-130.2614038	-130.2613332	7.06275E-05
-1.5	-130.2687704	-130.2687368	3.36561E-05
-1	-130.2738217	-130.2738152	6.52822E-06
-0.5	-130.2767309	-130.2767322	-1.30672E-06
0	-130.2776647	-130.2776647	-3.82E-08
0.5	-130.2767832	-130.2767878	-4.56154E-06
1	-130.2742401	-130.2742634	-2.32857E-05
1.5	-130.2701825	-130.2702341	-5.1598E-05
2	-130.2647509	-130.264821	-7.01402E-05
2.5	-130.2580793	-130.2581266	-4.72451E-05
3	-130.2502954	-130.2502395	5.58402E-05

Figure 22b: 6th Order q2 Error Values (SCS-MP2)

q2	6th order q2 energy (Ha)	actual q2 (Ha)	error (Ha)
-3	-130.2390652	-130.2390651	1.071E-07
-2.5	-130.2514706	-130.251471	-3.78204E-07
-2	-130.2613337	-130.2613332	5.61691E-07
-1.5	-130.2687368	-130.2687368	4.81847E-08
-1	-130.2738145	-130.2738152	-6.80342E-07
-0.5	-130.2767316	-130.2767322	-6.35024E-07
0	-130.2776647	-130.2776647	-3.82E-08
0.5	-130.2767882	-130.2767878	3.65905E-07
1	-130.2742637	-130.2742634	2.46006E-07
1.5	-130.270234	-130.2702341	-5.20095E-08
2	-130.264821	-130.264821	-6.58352E-08
2.5	-130.2581266	-130.2581266	4.80006E-08
3	-130.2502395	-130.2502395	-2.12052E-08

Figure 23b: Geometric Values for q1 Energy (SCS-MP2)

q1	Actual q1 Energy (Ha)	Relative Energy (Ha)	HN Length (Å)	NO Length (Å)	HO Distance (Å)	HNO Angle (°)
-3	-130.1318458	0.145818957	0.724977309	1.219920519	1.616329852	109.784661
-2.5	-130.1909657	0.08669905	0.779216302	1.219767501	1.651017312	109.3819084
-2	-130.2298771	0.047787669	0.833466164	1.219625645	1.686518543	109.0089807
-1.5	-130.2543904	0.023274368	0.887724904	1.219494955	1.722783237	108.66041
-1	-130.2686643	0.009000394	0.941990987	1.219375435	1.759764196	108.3319869
-0.5	-130.275698	0.001966728	0.996263214	1.219267087	1.79741721	108.0204185
0	-130.2776647	0	1.050540632	1.219169915	1.835700925	107.7230924
0.5	-130.2761448	0.001519903	1.104822475	1.219083922	1.874576699	107.4379092
1	-130.27229	0.005374761	1.159108123	1.21900911	1.914008457	107.1631635
1.5	-130.2669397	0.01072506	1.213397065	1.21894548	1.953962538	106.897455
2	-130.2607034	0.016961299	1.267688877	1.218893035	1.994407553	106.6396237
2.5	-130.254019	0.02364574	1.321983206	1.218851776	2.035314234	106.3887007
3	-130.2471945	0.030470206	1.376279754	1.218821704	2.076655299	106.1438702

Figure 24b: Geometric Values for q2 Energy (SCS-MP2)

q2	Actual q2 Energy (Ha)	Relative Energy (Ha)	HN Length (Å)	NO Length (Å)	HO Distance (Å)	HNO Angle (°)
-3	-130.2390651	0.038599668	1.103016742	1.148403426	1.553777133	87.25669287
-2.5	-130.251471	0.02619373	1.086960205	1.160056141	1.597170481	90.53938876
-2	-130.2613332	0.016331551	1.073708713	1.171767809	1.642162176	93.89226909
-1.5	-130.2687368	0.008927952	1.063367137	1.183536682	1.688624464	97.30260631
-1	-130.2738152	0.00384953	1.056020973	1.195361068	1.736439302	100.7556515
-0.5	-130.2767322	0.000932507	1.051732988	1.207239338	1.78549803	104.2350012
0	-130.2776647	0	1.050540632	1.219169915	1.835700925	107.7230924
0.5	-130.2767878	0.000876954	1.052454425	1.23115128	1.886956665	111.2017931
1	-130.2742634	0.003401332	1.057457503	1.243181964	1.939181767	114.6530419
1.5	-130.2702341	0.007430653	1.065506351	1.255260549	1.992300001	118.0594799
2	-130.264821	0.012843713	1.076532653	1.267385665	2.046241815	121.4050236
2.5	-130.2581266	0.019538151	1.090446092	1.279555989	2.100943773	124.675332
3	-130.2502395	0.027425226	1.107137824	1.291770244	2.156348026	127.8581409

Figure 25b: Geometric Values for q3 Energy (SCS-MP2)

q3	Actual q3 Energy (Ha)	Relative Energy (Ha)	HN Length (Å)	NO Length (Å)	HO Distance (Å)	HNO Angle (°)
-3	-130.2550491	0.022615663	1.057182036	1.366462275	1.754768756	91.87159611
-2.5	-130.2611957	0.016469051	1.051203139	1.341885765	1.767919442	94.46956021
-2	-130.26659	0.011074736	1.047153921	1.317319539	1.781209395	97.09673677
-1.5	-130.2711084	0.006556326	1.045056811	1.292764184	1.794635524	99.74456215
-1	-130.2745937	0.003071067	1.044923564	1.268220333	1.808194793	102.4041769
-0.5	-130.2768545	0.000810273	1.046754929	1.243688664	1.821884231	105.0666303
0	-130.2776647	0	1.050540632	1.219169915	1.835700925	107.7230924
0.5	-130.2767631	0.0009016	1.056259659	1.194664881	1.849642023	110.3650603
1	-130.2738526	0.003812162	1.063880833	1.170174423	1.863704735	112.98455
1.5	-130.2685997	0.009065081	1.073363637	1.145699476	1.877886327	115.5742619
2	-130.2606336	0.017031163	1.084659246	1.121241055	1.892184127	118.1277151
2.5	-130.249544	0.028120771	1.097711699	1.096800267	1.90659552	120.6393456
3	-130.2348771	0.042787646	1.112459158	1.072378317	1.92111795	123.1045666

Figure 26b: 6th Order Curve Fits for Coupling between 2 Different q Values (SCS-MP2)

6th order polynomial for q1 and q2 coupling (q2=x, q1=y):

$$z = -5.363442830 \times 10^{-7} x^5 y + 0.1344679021 e^{-4} x^4 y^2 - 0.1166183709 e^{-5} x^3 y^3 - 0.2016091912 e^{-4} x^2 y^4 + 0.1314414528 e^{-5} x y^5 - 0.3678836790 e^{-4} x^4 y - 0.1042351306 e^{-5} x^3 y^2 + 0.1098862522 e^{-3} x^2 y^3 - 0.8411366909 e^{-5} x y^4 + 0.4995358211 e^{-4} x^3 y - 0.3617916020 e^{-3} x^2 y^2 + 0.3185369325 e^{-4} x y^3 + 0.3594695833 e^{-3} x^2 y - 0.4845583065 e^{-5} x y^2 - 0.8026093269 e^{-5} x y - 130.2776647382$$

6th order polynomial for q1 and q3 coupling (q1=x, q3=y):

$$z = 0.2716573997 e^{-5} x^5 y - 0.1324966971 e^{-4} x^4 y^2 - 0.5312504352 e^{-5} x^3 y^3 + 0.5335342449 e^{-5} x^2 y^4 + 0.1585379378 e^{-5} x y^5 - 0.1727755216 e^{-4} x^4 y + 0.7570671597 e^{-4} x^3 y^2 + 0.2309094556 e^{-4} x^2 y^3 - 0.1322191369 e^{-4} x y^4 + 0.1343687542 e^{-3} x^3 y - 0.2143763168 e^{-3} x^2 y^2 - 0.6233824585 e^{-4} x y^3 - 0.6688764716 e^{-3} x^2 y + 0.1332857987 e^{-3} x y^2 - 0.1089856523 e^{-4} x y - 130.2776647382$$

6th order polynomial for q2 and q3 coupling (q2=x, q3=y):

$$z = -0.1473049691 e^{-5} x^5 y - 0.1543143637 e^{-5} x^4 y^2 - 0.3836606898 e^{-5} x^3 y^3 - 1.903580105 \times 10^{-7} x^2 y^4 - 0.2143424798 e^{-5} x y^5 + 0.5609971762 e^{-5} x^4 y + 0.1805035093 e^{-5} x^3 y^2 + 0.1950809136 e^{-5} x^2 y^3 - 0.5318270008 e^{-5} x y^4 + 0.1677678763 e^{-4} x^3 y + 0.4234900325 e^{-4} x^2 y^2 - 0.1661811968 e^{-4} x y^3 + 0.1511880575 e^{-3} x^2 y - 0.4618519069 e^{-3} x y^2 - 0.1554721494 e^{-3} x y - 130.2776647382$$

Figure 27b: 6th Order Curve Fits for Coupling between All 3 q Values (q1=x, q2=y, q3=z) (SCS-MP2)

$$w = -0.1048937925e-2*x*y*z+0.5647822448e-3*x^2*y*z+0.8538976992e-4*x*y^2*z+0.8431901914e-4*x*y*z^2-0.8062502757e-5*x^2*y^2*z-0.3225654508e-4*x^2*y*z^2+0.9466487921e-4*x*y^2*z^2+0.1728486739e-4*x*y*z^3+0.7194319910e-4*x*y^3*z-0.1007534589e-3*x^3*y*z-0.3191279271e-4*x^2*y^2*z^2+0.2045147451e-4*x^4*y*z+0.3955198430e-5*x*y^4*z+0.4380099624e-5*x^3*y^2*z+0.8568487502e-5*x^3*y*z^2-0.2314838886e-4*x^2*y^3*z-0.4383846179e-5*x*y^3*z^2-0.1638288336e-4*x^2*y*z^3-0.1325827482e-4*x*y^2*z^3-130.2776647382$$

Note: The 72 points used to determine the coupling between all 3 q values can be found in Appendix 9.

Figure 28b: 6th Order Curve Fit for the Potential Energy Function of Nitroxyl, assuming center of mass is at the origin (q1=x, q2=y, q3=z) (SCS-MP2)

$$w = -0.1048937925e-2*x*y*z+0.5647822448e-3*x^2*y*z+0.8538976992e-4*x*y^2*z+0.8431901914e-4*x*y*z^2-0.8062502757e-5*x^2*y^2*z-0.3225654508e-4*x^2*y*z^2+0.9466487921e-4*x*y^2*z^2+0.1728486739e-4*x*y*z^3+0.7194319910e-4*x*y^3*z-0.1007534589e-3*x^3*y*z-0.3191279271e-4*x^2*y^2*z^2+0.2045147451e-4*x^4*y*z+0.3955198430e-5*x*y^4*z+0.4380099624e-5*x^3*y^2*z+0.8568487502e-5*x^3*y*z^2-0.2314838886e-4*x^2*y^3*z-0.4383846179e-5*x*y^3*z^2-0.1638288336e-4*x^2*y*z^3-0.1325827482e-4*x*y^2*z^3-5.363442830*10^(-7)*y^5*x+0.1344679021e-4*y^4*x^2-0.1166183709e-5*y^3*x^3-0.2016091912e-4*y^2*x^4+0.1314414528e-5*y*x^5-0.3678836790e-4*y^4*x-0.1042351306e-5*y^3*x^2+0.1098862522e-3*y^2*x^3-0.8411366909e-5*y*x^4+0.4995358211e-4*y^3*x-0.3617916020e-3*y^2*x^2+0.3185369325e-4*y*x^3+0.3594695833e-3*y^2*x-0.4845583065e-5*y*x^2-0.8026093269e-5*y*x+0.2716573997e-5*x^5*z-0.1324966971e-4*x^4*z^2-0.5312504352e-5*x^3*z^3+0.5335342449e-5*x^2*z^4+0.1585379378e-5*x*z^5-0.1727755216e-4*x^4*z+0.7570671597e-4*x^3*z^2+0.2309094556e-4*x^2*z^3-0.1322191369e-4*x*z^4+0.1343687542e-3*x^3*z-0.2143763168e-3*x^2*z^2-0.6233824585e-4*x*z^3-0.6688764716e-3*x^2*z+0.1332857987e-3*x*z^2-0.1089856523e-4*x*z-0.1473049691e-5*y^5*z-0.1543143637e-5*y^4*z^2-0.3836606898e-5*x^3*y^3-1.903580105*10^(-7)*x^2*y^4-0.2143424798e-5*y*z^5+0.5609971762e-5*y^4*z+0.1805035093e-5*y^3*z^2+0.1950809136e-5*y^2*z^3-0.5318270008e-5*y*z^4+0.1677678763e-4*y^3*z+0.4234900325e-4*y^2*z^2-0.1661811968e-4*y*z^3+0.1511880575e-3*y^2*z-0.4618519069e-3*y*z^2-0.1554721494e-3*y*z+0.4909133576e-5*x^6-0.4218859117e-4*x^5+0.2763705226e-3*x^4-0.1756030541e-2*x^3+0.6908818678e-2*x^2-3.543384841*10^(-7)*y^6+0.2203791911e-5*y^5+0.8847229812e-5*y^4-0.2267658660e-3*y^3+0.3617116977e-2*y^2-130.2776647+2.536304451*10^(-8)*z^6+2.619070161*10^(-7)*z^5+0.2373132458e-4*z^4+0.3712022545e-3*z^3+0.3417873485e-2*z^2-130.2776647$$

Figure 29b: Summary of 100 Calculations Sorted by Decreasing Predicted Energy (SCS-MP2)

Average Formula Value (Ha)	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-130.1702427	-0.079263668	0.008421833	0.001375278
-130.214083	-0.018640883	0.022462909	0.000111283
-130.2239171	-0.010281275	0.03445911	0.000246521
-130.2333785	-0.010294933	0.000868055	2.71329E-05
-130.2395446	-0.001714083	0.006687874	5.20112E-06
-130.244943	-0.008517999	0.000229868	7.86362E-06
-130.250078	-0.001487746	0.000245817	7.728E-07
-130.2552968	-0.004618557	0.001284206	3.13096E-06
-130.2596872	-0.003730471	0.002454202	2.70681E-06
-130.2662172	-0.000769221	0.002969885	1.08291E-06

Figure 30b: Summary of 100 Calculations Sorted by Decreasing Distance from Center (SCS-MP2)

Average Distance from Center (Å)	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
4.141141244	-0.079263668	-0.000706693	0.001197129
3.637893338	-0.032346979	0.03445911	0.000286697
3.40379011	-0.002230607	0.027934911	7.92796E-05
3.134776075	-0.028151985	0.015861463	0.000131964
2.889404919	-0.001831786	0.011850633	1.48372E-05
2.687510576	-0.018640883	0.004451194	4.87221E-05
2.514711694	-0.010139788	0.002145334	1.14586E-05
2.22637966	-0.002102773	0.006687874	5.31713E-06
2.046123026	-0.004618557	0.001389922	3.92855E-06
1.615222883	-0.000649261	0.002969885	1.64166E-06

Figure 31b: Summary of 100 Calculations Sorted by Increasing q1 Value (SCS-MP2)

Average q1 Value	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-2.49428	-0.079263668	0.03445911	0.001319945
-1.9546	-0.018640883	0.027934911	0.000153221
-1.35921	-0.032346979	0.022462909	0.000240941
-0.35753	-0.003730471	0.002969885	2.8711E-06
0.23949	-0.002230607	0.000785684	9.87818E-07
0.85023	-0.002102773	0.002145334	1.49604E-06
1.48397	-0.010281275	0.000534103	1.80635E-05
1.82479	-0.007971335	0.000868055	7.15173E-06
2.33961	-0.008517999	8.40799E-06	9.62851E-06
2.79891	-0.015426073	0.000229868	2.66691E-05

Figure 32b: Summary of 100 Calculations Sorted by q2 Value (SCS-MP2)

Average q2 Value	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-2.75583	-0.079263668	2.39654E-05	0.000801789
-2.01682	-0.003801569	0.027934911	8.08217E-05
-1.53352	-0.003730471	0.022462909	7.81499E-05
-0.95355	-0.028151985	0.006687874	8.90117E-05
-0.19127	-0.000748012	0.002993297	1.28549E-06
0.32043	-0.000781319	0.011850633	1.48297E-05
0.73059	-0.000985619	0.03445911	0.000126959
1.32046	-0.037568994	0.000515146	0.000199293
2.00215	-0.010139788	0.000290356	2.32513E-05
2.69448	-0.057312273	-0.000539267	0.000365583

Figure 33b: Summary of 100 Calculations Sorted by Increasing q3 Value (SCS-MP2)

Average q3 Value	Lowest Difference (Ha)	Highest Difference (Ha)	Average Difference Squared (Ha ²)
-2.57792	-0.032346979	0.03445911	0.000301117
-1.52807	-0.079263668	0.011850633	0.000646625
-1.14125	-0.028151985	0.001389922	8.03995E-05
-0.82092	-0.008517999	0.008421833	1.4998E-05
-0.39021	-0.001831786	0.00072858	5.26486E-07
0.09072	-0.001473093	0.000698446	7.45527E-07
0.6388	-0.057312273	0.006687874	0.000383042
1.20159	-0.007971335	0.015861463	3.20279E-05
2.03429	-0.010294933	0.027934911	0.000113136
2.67225	-0.037568994	0.022462909	0.000208356

Note: The random 100 points used for Figures 29b-33b can be seen in Appendix 10.

Figure 34b: 6th Order Curve Fit for the Potential Energy Function of Nitroxyl, without including coupling between all 3 modes (q1=x, q2=y, q3=z) (SCS-MP2)

$$\begin{aligned}
 w = & -5.363442830 \cdot 10^{(-7)} \cdot y^5 \cdot x + 0.1344679021e-4 \cdot y^4 \cdot x^2 - 0.1166183709e-5 \cdot y^3 \cdot x^3 - \\
 & 0.2016091912e-4 \cdot y^2 \cdot x^4 + 0.1314414528e-5 \cdot y \cdot x^5 - 0.3678836790e-4 \cdot y^4 \cdot x - \\
 & 0.1042351306e-5 \cdot y^3 \cdot x^2 + 0.1098862522e-3 \cdot y^2 \cdot x^3 - 0.8411366909e- \\
 & 5 \cdot y \cdot x^4 + 0.4995358211e-4 \cdot y^3 \cdot x - 0.3617916020e-3 \cdot y^2 \cdot x^2 + 0.3185369325e- \\
 & 4 \cdot y \cdot x^3 + 0.3594695833e-3 \cdot y^2 \cdot x - 0.4845583065e-5 \cdot y \cdot x^2 - 0.8026093269e- \\
 & 5 \cdot y \cdot x + 0.2716573997e-5 \cdot x^5 \cdot z - 0.1324966971e-4 \cdot x^4 \cdot z^2 - 0.5312504352e- \\
 & 5 \cdot x^3 \cdot z^3 + 0.5335342449e-5 \cdot x^2 \cdot z^4 + 0.1585379378e-5 \cdot x \cdot z^5 - 0.1727755216e- \\
 & 4 \cdot x^4 \cdot z + 0.7570671597e-4 \cdot x^3 \cdot z^2 + 0.2309094556e-4 \cdot x^2 \cdot z^3 - 0.1322191369e- \\
 & 4 \cdot x \cdot z^4 + 0.1343687542e-3 \cdot x^3 \cdot z - 0.2143763168e-3 \cdot x^2 \cdot z^2 - 0.6233824585e-4 \cdot x \cdot z^3 - \\
 & 0.6688764716e-3 \cdot x^2 \cdot z + 0.1332857987e-3 \cdot x \cdot z^2 - 0.1089856523e-4 \cdot x \cdot z - \\
 & 0.1473049691e-5 \cdot y^5 \cdot z - 0.1543143637e-5 \cdot y^4 \cdot z^2 - 0.3836606898e-5 \cdot x^3 \cdot y^3 - \\
 & 1.903580105 \cdot 10^{(-7)} \cdot x^2 \cdot y^4 - 0.2143424798e-5 \cdot y \cdot z^5 + 0.5609971762e- \\
 & 5 \cdot y^4 \cdot z + 0.1805035093e-5 \cdot y^3 \cdot z^2 + 0.1950809136e-5 \cdot y^2 \cdot z^3 - 0.5318270008e- \\
 & 5 \cdot y \cdot z^4 + 0.1677678763e-4 \cdot y^3 \cdot z + 0.4234900325e-4 \cdot y^2 \cdot z^2 - 0.1661811968e- \\
 & 4 \cdot y \cdot z^3 + 0.1511880575e-3 \cdot y^2 \cdot z - 0.4618519069e-3 \cdot y \cdot z^2 - 0.1554721494e- \\
 & 3 \cdot y \cdot z + 0.4909133576e-5 \cdot x^6 - 0.4218859117e-4 \cdot x^5 + 0.2763705226e-3 \cdot x^4 - \\
 & 0.1756030541e-2 \cdot x^3 + 0.6908818678e-2 \cdot x^2 - 3.543384841 \cdot 10^{(-7)} \cdot y^6 + 0.2203791911e-5 \cdot y^5 + 0.8847229812e-5 \cdot y^4 - 0.2267658660e- \\
 & 3 \cdot y^3 + 0.3617116977e-2 \cdot y^2 - 130.2776647 + 2.536304451 \cdot 10^{(-8)} \cdot z^6 + 2.619070161 \cdot 10^{(-7)} \cdot z^5 + 0.2373132458e-4 \cdot z^4 + 0.3712022545e- \\
 & 3 \cdot z^3 + 0.3417873485e-2 \cdot z^2 - 130.2776647
 \end{aligned}$$

Figure 35b: Table Investigating q1,q2,q3 Coupling for Decreasing Formula Value (SCS-MP2)

Average Formula Value (Ha)	Average Difference Squared (Ha ²) (with q1,q2,q3 coupling)	Average Difference Squared (Ha ²) (without q1,q2,q3 coupling)
-130.1702427	0.001375278	0.000660509
-130.214083	0.000111283	8.95216E-05
-130.2239171	0.000246521	2.60604E-05
-130.2333785	2.71329E-05	1.35958E-05
-130.2395446	5.20112E-06	1.17142E-05
-130.244943	7.86362E-06	4.44694E-07
-130.250078	7.728E-07	6.65508E-07
-130.2552968	3.13096E-06	1.41978E-06
-130.2596872	2.70681E-06	4.5093E-07
-130.2662172	1.08291E-06	2.32316E-07

Figure 36b: Table Investigating q1,q2,q3 Coupling for Decreasing Distance (SCS-MP2)

Average Distance from Center (Å)	Average Difference Squared (Ha ²) (with q1,q2,q3 coupling)	Average Difference Squared (Ha ²) (without q1,q2,q3 coupling)
4.141141244	0.001197129	0.00063103
3.637893338	0.000286697	7.8083E-05
3.40379011	7.92796E-05	1.21891E-05
3.134776075	0.000131964	4.36201E-05
2.889404919	1.48372E-05	7.17868E-06
2.687510576	4.87221E-05	2.1905E-05
2.514711694	1.14586E-05	8.22619E-06
2.22637966	5.31713E-06	5.55808E-07
2.046123026	3.92855E-06	1.56882E-06
1.615222883	1.64166E-06	2.57042E-07

Conclusion:

Over a two-year period, research was done on the HNO molecule, also known as nitroxyl. The end goal of this research was to find theoretical data that could be used to develop and infrared spectrum for nitroxyl. The first year was spent studying dipole moments and the atomic partial charges of the molecule, while the second year was spent studying vibrational coupling and the potential energy function. A large portion of this research used the GAMESS program, which calculates the energy of a molecule for a specific geometry and a specific basis set of functions used to approximate the molecule's molecular orbitals. Each year of research produced results that explained some things and also raised some interesting questions that future research might be able to explain.

The first year of research focused on studying dipole moments and the molecule's atomic partial charges. Over 1000 different tests using the GAMESS program were run to produce the MP2 energies for over 100 different nitroxyl geometries. These energies were plotted against electric field strength and the derivative of this plot was recorded. This is because the negative derivative of the energy with respect to field strength is equivalent to the dipole moment of the molecule along the direction of the field. Both the x-field and y-field dependence of the energy were studied so the x-dipole and y-dipole of the molecule could be found. These dipole moments were then used to find the atomic partial charges of each of the three atoms (H, N, and O) on nitroxyl. Graphs were made that plotted each of the three charges against each of the three geometric parameters (HN bond length, NO bond length, and HNO bond angle), giving a total of nine graphs. These nine graphs yielded some results that were easily explainable by using electronegativity concepts. Other trends were more difficult to explain, such as the instances

when the NO bond length grew longer than 1.3Å and all of the situations regarding change in the bond angle.

The second year of research focused on studying the vibrational coupling and the potential energy function of nitroxyl. As a nonlinear molecule, nitroxyl has three total dimensionless normal modes (q_1 , q_2 , and q_3) that represent the vibrations of the molecule. When the molecule vibrates, the values of q_1 , q_2 , and q_3 also change, along with the molecule's geometry. While not entirely accurate, for simplicity it is fine to assume that q_1 represents the HN stretch, q_2 represents the HNO angle bend, and q_3 represents the NO stretch. Previous research has also suggested that there is heavy coupling between the modes in nitroxyl, particularly the modes involving the angle bend and the NO stretch. For this reason, coupling for the entire molecule was investigated using the GAMESS program. Three equations were found that represented the molecule's potential energy as a function of each of the three q values when the other two q values were kept at zero. Three more functions were found that represented the molecule's potential energy as a function of pairs of the q values when the third value was kept at zero. These three equations represent coupling between pairs of q values. A final equation was found that represented the molecule's potential energy as a function of all three q values. This equation represents coupling between all three q values. The sum of these seven equations was assumed to be the potential energy function for nitroxyl.

Lastly, the accuracy of the potential energy function was investigated. 100 random points with q_1 , q_2 , and q_3 values ranging from -3 to 3 were created and the MP2 energy was found for each point using the GAMESS program. Along with running the 100 tests in the GAMESS program, they were also placed into the potential energy function of nitroxyl and the predicted energy was recorded. These values were compared to the values found from the

GAMESS program and the difference between the two values (along with the difference squared) for each of the 100 tests was found. These results were then sorted in five different ways: decreasing formula value, decreasing distance from center (calculated as the square root of $q_1^2 + q_2^2 + q_3^2$), increasing q_1 value, increasing q_2 value, and increasing q_3 value. Each of these five organizations was then separated into intervals of ten. For each interval of ten, the lowest and highest differences found in the interval were recorded, along with the average difference squared. It can be assumed that the smaller the value of the average difference squared for an interval, the more accurate the formula output is to the actual GAMESS output. Expectedly, the accuracy of the formula increased as the distance from the center decreased and as the actual energy value grew closer to the actual energy value of the equilibrium geometry. Surprisingly, severely negative q_1 values gave MP2 values furthest from the formula results. Also, the potential energy function was modified to omit the coupling between all three modes and these results were compared to the results that included this coupling. Unexpectedly, the formula that excluded the coupling between all three modes proved to be more accurate.

Appendix:

(1) HNO Input File for the Equilibrium Geometry with Nitrogen at the Origin

```
$CONTRL SCFTYP=RHF RUNTYP=ENERGY COORD=UNIQUE ISPHER=1 MPLEVL=2 NPRINT=-5
$END
$SYSTEM TIMLIM=60 PARALL=.FALSE. MWORDS=50 $END
$TRANS CUTTRF=1.0D-10 $END
$SCF CONV=2.5D-07 $END
-$EFIELD EVEC(1)=0.000,0.000,0.000 $END
$BASIS GBASIS=ACCT $END
$DATA
HNO molecule
Cs

N 7.0 0.0 0.0 0.0
O 8.0 1.2217 0.0 0.0
H 1.0 -0.318368849 1.001200098 0.0
$END
```

Note: When changing the coordinates of EFIELD, remove the minus sign before \$ if not using the components 0.000,0.000,0.000.

(2) HNO Output File for the Equilibrium Geometry with Nitrogen at the Origin

```
----- GAMESS execution script 'rungms' -----
This job is running on host James-Smiths-MacBook-Pro-2.local
under operating system Darwin at Wed Apr 15 18:40:47 EDT 2015
Available scratch disk space (Kbyte units) at beginning of the job is
Filesystem      1024-blocks      Used Available Capacity   iused   ifree
%iused  Mounted on
/dev/disk0s2     311731616  59856084  251619532      20% 15028019  62904883   19%
/
Copying input file HNO.inp to your run's scratch directory...
cp HNO.inp ../HNO.F05
unset echo
setenv AUXDATA ../auxdata
setenv EXTBAS /dev/null
setenv NUCBAS /dev/null
setenv POSBAS /dev/null
setenv ERICFMT ../auxdata/ericfmt.dat
setenv MCPPATH ../auxdata/MCP
setenv BASPATH ../auxdata/BASES
setenv QUANPOL ../auxdata/QUANPOL
setenv MAKEFP ../HNO.efp
setenv GAMMA ../HNO.gamma
setenv TRAJECT ../HNO.trj
setenv RESTART ../HNO.rst
setenv INPUT ../HNO.F05
setenv PUNCH ../HNO.dat
setenv AOINTS ../HNO.F08
setenv MOINTS ../HNO.F09
setenv DICTNRY ../HNO.F10
setenv DRTFILE ../HNO.F11
setenv CIVECTR ../HNO.F12
```

```
setenv CASINTS ../HNO.F13
setenv CIINTS ../HNO.F14
setenv WORK15 ../HNO.F15
setenv WORK16 ../HNO.F16
setenv CSFSAVE ../HNO.F17
setenv FOCKDER ../HNO.F18
setenv WORK19 ../HNO.F19
setenv DASORT ../HNO.F20
setenv DFTINTS ../HNO.F21
setenv DFTGRID ../HNO.F22
setenv JKFILE ../HNO.F23
setenv ORDINT ../HNO.F24
setenv EFPIND ../HNO.F25
setenv PCMDATA ../HNO.F26
setenv PCMINTS ../HNO.F27
setenv SVPWRK1 ../HNO.F26
setenv SVPWRK2 ../HNO.F27
setenv COSCAV ../HNO.F26
setenv COSDATA ~jamesmith/scr/HNO.cosmo
setenv COSPOT ~jamesmith/scr/HNO.pot
setenv MLTPL ../HNO.F28
setenv MLTPLT ../HNO.F29
setenv DAFL30 ../HNO.F30
setenv SOINTX ../HNO.F31
setenv SOINTY ../HNO.F32
setenv SOINTZ ../HNO.F33
setenv SORESC ../HNO.F34
setenv GCILIST ../HNO.F37
setenv HESSIAN ../HNO.F38
setenv QMMTEI ../HNO.F39
setenv SOCCDAT ../HNO.F40
setenv AABB41 ../HNO.F41
setenv BBAA42 ../HNO.F42
setenv BBBB43 ../HNO.F43
setenv MCQD50 ../HNO.F50
setenv MCQD51 ../HNO.F51
setenv MCQD52 ../HNO.F52
setenv MCQD53 ../HNO.F53
setenv MCQD54 ../HNO.F54
setenv MCQD55 ../HNO.F55
setenv MCQD56 ../HNO.F56
setenv MCQD57 ../HNO.F57
setenv MCQD58 ../HNO.F58
setenv MCQD59 ../HNO.F59
setenv MCQD60 ../HNO.F60
setenv MCQD61 ../HNO.F61
setenv MCQD62 ../HNO.F62
setenv MCQD63 ../HNO.F63
setenv MCQD64 ../HNO.F64
setenv NMRINT1 ../HNO.F61
setenv NMRINT2 ../HNO.F62
setenv NMRINT3 ../HNO.F63
setenv NMRINT4 ../HNO.F64
setenv NMRINT5 ../HNO.F65
setenv NMRINT6 ../HNO.F66
```

```

setenv DCPHFH2 ../HNO.F67
setenv DCPHF21 ../HNO.F68
setenv ELNUINT ../HNO.F67
setenv NUNUINT ../HNO.F68
setenv GVVPT ../HNO.F69
setenv NUMOIN ../HNO.F69
setenv NUMOCAS ../HNO.F70
setenv NUELMO ../HNO.F71
setenv NUELCAS ../HNO.F72
setenv RIVMAT ../HNO.F51
setenv RIT2A ../HNO.F52
setenv RIT3A ../HNO.F53
setenv RIT2B ../HNO.F54
setenv RIT3B ../HNO.F55
setenv GMCREF ../HNO.F70
setenv GMCO2R ../HNO.F71
setenv GMCROC ../HNO.F72
setenv GMCOOC ../HNO.F73
setenv GMCCC0 ../HNO.F74
setenv GMCHMA ../HNO.F75
setenv GMCEI1 ../HNO.F76
setenv GMCEI2 ../HNO.F77
setenv GMCEOB ../HNO.F78
setenv GMCEDT ../HNO.F79
setenv GMCERF ../HNO.F80
setenv GMCHCR ../HNO.F81
setenv GMCGJK ../HNO.F82
setenv GMCGAI ../HNO.F83
setenv GMCGEO ../HNO.F84
setenv GMCTE1 ../HNO.F85
setenv GMCTE2 ../HNO.F86
setenv GMCHEF ../HNO.F87
setenv GMCMOL ../HNO.F88
setenv GMCMOS ../HNO.F89
setenv GMCWGT ../HNO.F90
setenv GMCRM2 ../HNO.F91
setenv GMCRM1 ../HNO.F92
setenv GMCR00 ../HNO.F93
setenv GMCRP1 ../HNO.F94
setenv GMCRP2 ../HNO.F95
setenv GMCVEF ../HNO.F96
setenv GMCDIN ../HNO.F97
setenv GMC2SZ ../HNO.F98
setenv GMCCCS ../HNO.F99
unset echo
../ddikick.x ../gamess.Aug112011R1.x HNO -ddi 1 1 localhost -scr ./

```

Distributed Data Interface kickoff program.

Initiating 1 compute processes on 1 nodes to run the following command:

```
../gamess.Aug112011R1.x HNO
```

```

*****
*           GAMESS VERSION = 11 AUG 2011 (R1)           *
*           FROM IOWA STATE UNIVERSITY                   *
* M.W.SCHMIDT, K.K.BALDRIDGE, J.A.BOATZ, S.T.ELBERT, *

```

```

*   M.S.GORDON, J.H.JENSEN, S.KOSEKI, N.MATSUNAGA,   *
*           K.A. NGUYEN, S.J.SU, T.L.WINDUS,         *
*   TOGETHER WITH M.DUPUIS, J.A.MONTGOMERY           *
*           J.COMPUT.CHEM. 14, 1347-1363(1993)        *
***** 64 BIT LINUX VERSION *****

```

SINCE 1993, STUDENTS AND POSTDOCS WORKING AT IOWA STATE UNIVERSITY AND ALSO IN THEIR VARIOUS JOBS AFTER LEAVING ISU HAVE MADE IMPORTANT CONTRIBUTIONS TO THE CODE:

IVANA ADAMOVIC, CHRISTINE AIKENS, YURI ALEXEEV, POOJA ARORA, ANDREY ASADCHEV, ROB BELL, PRADIPTA BANDYOPADHYAY, JONATHAN BENTZ, BRETT BODE, GALINA CHABAN, WEI CHEN, CHEOL HO CHOI, PAUL DAY, ALBERT DEFUSCO, TIM DUDLEY, DMITRI FEDOROV, GRAHAM FLETCHER, MARK FREITAG, KURT GLAESEMAN, DAN KEMP, GRANT MERRILL, NORIYUKI MINEZAWA, JONATHAN MULLIN, TAKESHI NAGATA, SEAN NEDD, HEATHER NETZLOFF, BOSILJKA NJEGIC, RYAN OLSON, MIKE PAK, JIM SHOEMAKER, LYUDMILA SLIPCHENKO, SAROM SOK, JIE SONG, TETSUYA TAKETSUGU, SIMON WEBB, SOOHAENG YOO, FEDERICO ZAHARIEV

ADDITIONAL CODE HAS BEEN PROVIDED BY COLLABORATORS IN OTHER GROUPS:

IOWA STATE UNIVERSITY:

JOE IVANIC, LAIMUTIS BYTAUTAS, KLAUS RUEDENBERG

UNIVERSITY OF TOKYO: KIMIHIKO HIRAO, TAKAHITO NAKAJIMA,

TAKAO TSUNEDA, MUNEAKI KAMIYA, SUSUMU YANAGISAWA,

KIYOSHI YAGI, MAHITO CHIBA, SEIKEN TOKURA, NAOAKI KAWAKAMI

UNIVERSITY OF AARHUS: FRANK JENSEN

UNIVERSITY OF IOWA: VISVALDAS KAIRYS, HUI LI

NATIONAL INST. OF STANDARDS AND TECHNOLOGY: WALT STEVENS, DAVID

GARMER

UNIVERSITY OF PISA: BENEDETTA MENNUCCI, JACOPO TOMASI

UNIVERSITY OF MEMPHIS: HENRY KURTZ, PRAKASHAN KORAMBATH

UNIVERSITY OF ALBERTA: TOBY ZENG, MARIUSZ KLOBUKOWSKI

UNIVERSITY OF NEW ENGLAND: MARK SPACKMAN

MIE UNIVERSITY: HIROAKI UMEDA

MICHIGAN STATE UNIVERSITY:

KAROL KOWALSKI, MARTA WLOCH, JEFFREY GOUR, JESSE LUTZ, PIOTR

PIECUCH

UNIVERSITY OF SILESIA: MONIKA MUSIAL, STANISLAW KUCHARSKI

FACULTES UNIVERSITAIRES NOTRE-DAME DE LA PAIX:

OLIVIER QUINET, BENOIT CHAMPAGNE

UNIVERSITY OF CALIFORNIA - SANTA BARBARA: BERNARD KIRTMAN

INSTITUTE FOR MOLECULAR SCIENCE:

KAZUYA ISHIMURA, MICHIO KATOUDA, AND SHIGERU NAGASE

UNIVERSITY OF NOTRE DAME: DAN CHIPMAN

KYUSHU UNIVERSITY:

HARUYUKI NAKANO,

FENG LONG GU, JACEK KORCHOWIEC, MARCIN MAKOWSKI, AND YURIKO

AOKI,

HIROTOSHI MORI AND EISAKU MIYOSHI

PENNSYLVANIA STATE UNIVERSITY:

TZVETELIN IORDANOV, CHET SWALINA, JONATHAN SKONE,

SHARON HAMMES-SCHIFFER

WASEDA UNIVERSITY:

MASATO KOBAYASHI, TOMOKO AKAMA, TSUGUKI TOUMA,

TAKESHI YOSHIKAWA, YASUHIRO IKABATA, HIROMI NAKAI

UNIVERSITY OF NEBRASKA:

PEIFENG SU, DEJUN SI, NANDUN THELLAMUREGE, YALI WANG, HUI LI

UNIVERSITY OF ZURICH:

ROBERTO PEVERATI, KIM BALDRIDGE

N. COPERNICUS UNIVERSITY AND JACKSON STATE UNIVERSITY:

MARIA BARYSZ

EXECUTION OF GAMESS BEGUN Wed Apr 15 18:40:47 2015

ECHO OF THE FIRST FEW INPUT CARDS -

```
INPUT CARD> $CONTRL SCFTYP=RHF RUNTYP=ENERGY COORD=UNIQUE ISPHER=1
MPLEVL=2 NPRINT=-5
INPUT CARD> $END
INPUT CARD> $SYSTEM TIMLIM=60 PARALL=.FALSE. MWORDS=50 $END
INPUT CARD> $TRANS CUTTRF=1.0D-10 $END
INPUT CARD> $SCF CONV=2.5D-07 $END
INPUT CARD>-$FIELD EVEC(1)=0.000,0.000,0.000 $END
INPUT CARD> $BASIS GBASIS=ACCT $END
INPUT CARD> $DATA
INPUT CARD>HNO molecule
INPUT CARD>Cs
INPUT CARD>
INPUT CARD>N 7.0 0.0 0.0 0.0
INPUT CARD>O 8.0 1.2217 0.0 0.0
INPUT CARD>H 1.0 -0.318368849 1.001200098 0.0
INPUT CARD> $END
```

50000000 WORDS OF MEMORY AVAILABLE

BASIS OPTIONS

GBASIS=ACCT		IGAUSS=	0	POLAR=NONE	
NDFUNC=	0	NFFUNC=	0	DIFFSP=	F
NPFUNC=	0	DIFFS=	F	BASNAM=	

RUN TITLE

HNO molecule

THE POINT GROUP OF THE MOLECULE IS CS

THE ORDER OF THE PRINCIPAL AXIS IS 0

ATOM	ATOMIC CHARGE	X	Y	Z
N	7.0	0.0000000000	0.0000000000	0.0000000000
O	8.0	2.3086782392	0.0000000000	0.0000000000
H	1.0	-0.6016298876	1.8919938441	0.0000000000

INTERNUCLEAR DISTANCES (ANGS.)

	1 N	2 O	3 H
1 N	0.0000000	1.2217000 *	1.0506000 *
2 O	1.2217000 *	0.0000000	1.8369033 *

3 H 1.0506000 * 1.8369033 * 0.0000000

* ... LESS THAN 3.000

ATOMIC BASIS SET

THE CONTRACTED PRIMITIVE FUNCTIONS HAVE BEEN UNNORMALIZED
THE CONTRACTED BASIS FUNCTIONS ARE NOW NORMALIZED TO UNITY

SHELL	TYPE	PRIMITIVE	EXPONENT	CONTRACTION
COEFFICIENT(S)				

N

1	S	1	11420.0000000	0.000534980914
1	S	2	1712.0000000	0.004137663095
1	S	3	389.3000000	0.021250914908
1	S	4	110.0000000	0.082576298811
1	S	5	35.5700000	0.238413272749
1	S	6	12.5400000	0.443431666123
1	S	7	4.6440000	0.355431908787
1	S	8	0.5118000	-0.008702901759
2	S	9	11420.0000000	-0.000198776985
2	S	10	1712.0000000	-0.001547003493
2	S	11	389.3000000	-0.007992563300
2	S	12	110.0000000	-0.032025565056
2	S	13	35.5700000	-0.099110204811
2	S	14	12.5400000	-0.228292774736
2	S	15	4.6440000	-0.298182762726
2	S	16	0.5118000	1.037000518236
3	S	17	1.2930000	1.000000000000
4	S	18	0.1787000	1.000000000000
5	P	19	26.6300000	0.039807212297
5	P	20	5.9480000	0.249002660480
5	P	21	1.7420000	0.810479726693
6	P	22	0.5550000	1.000000000000
7	P	23	0.1725000	1.000000000000
8	D	24	1.6540000	1.000000000000
9	D	25	0.4690000	1.000000000000
10	F	26	1.0930000	1.000000000000
11	S	27	0.0576000	1.000000000000
12	P	28	0.0491000	1.000000000000

13	D	29	0.1510000	1.0000000000000
14	F	30	0.3640000	1.0000000000000
O				
15	S	31	15330.0000000	0.000520198307
15	S	32	2299.0000000	0.004023344781
15	S	33	522.4000000	0.020729083329
15	S	34	147.3000000	0.081082327080
15	S	35	47.5500000	0.236226352118
15	S	36	16.7600000	0.443518209420
15	S	37	6.2070000	0.358670588689
15	S	38	0.6882000	-0.008349797237
16	S	39	15330.0000000	-0.000197236012
16	S	40	2299.0000000	-0.001535010700
16	S	41	522.4000000	-0.007951183914
16	S	42	147.3000000	-0.032113452892
16	S	43	47.5500000	-0.100269643049
16	S	44	16.7600000	-0.234047111838
16	S	45	6.2070000	-0.301410927756
16	S	46	0.6882000	1.034919649508
17	S	47	1.7520000	1.0000000000000
18	S	48	0.2384000	1.0000000000000
19	P	49	34.4600000	0.041163489568
19	P	50	7.7490000	0.257762835858
19	P	51	2.2800000	0.802419274427
20	P	52	0.7156000	1.0000000000000
21	P	53	0.2140000	1.0000000000000
22	D	54	2.3140000	1.0000000000000
23	D	55	0.6450000	1.0000000000000
24	F	56	1.4280000	1.0000000000000
25	S	57	0.0737600	1.0000000000000
26	P	58	0.0597400	1.0000000000000
27	D	59	0.2140000	1.0000000000000
28	F	60	0.5000000	1.0000000000000
H				
29	S	61	33.8700000	0.025494863235
29	S	62	5.0950000	0.190362765893
29	S	63	1.1590000	0.852162022245

30	S	64	0.3258000	1.000000000000
31	S	65	0.1027000	1.000000000000
32	P	66	1.4070000	1.000000000000
33	P	67	0.3880000	1.000000000000
34	D	68	1.0570000	1.000000000000
35	S	69	0.0252600	1.000000000000
36	P	70	0.1020000	1.000000000000
37	D	71	0.2470000	1.000000000000

TOTAL NUMBER OF BASIS SET SHELLS = 37
 NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS = 135
 NOTE: THIS RUN WILL RESTRICT THE MO VARIATION SPACE TO SPHERICAL
 HARMONICS.
 THE NUMBER OF ORBITALS KEPT IN THE VARIATIONAL SPACE WILL BE PRINTED
 LATER.
 NUMBER OF ELECTRONS = 16
 CHARGE OF MOLECULE = 0
 SPIN MULTIPLICITY = 1
 NUMBER OF OCCUPIED ORBITALS (ALPHA) = 8
 NUMBER OF OCCUPIED ORBITALS (BETA) = 8
 TOTAL NUMBER OF ATOMS = 3
 THE NUCLEAR REPULSION ENERGY IS 30.0867864040

\$CONTRL OPTIONS

```

SCFTYP=RHF          RUNTYP=ENERGY      EXETYP=RUN
MPLEVL=             2      CITYP =NONE      CCTYP =NONE      VBTYP =NONE
DFTTYP=NONE         TDDFT =NONE
MULT  =             1      ICHARG=          0      NZVAR  =          0      COORD =UNIQUE
PP    =NONE         RELWFN=NONE         LOCAL =NONE      NUMGRD=
F
ISPHER=             1      NOSYM  =          0      MAXIT  =          30      UNITS  =ANGS
PLTORB=             F      MOLPLT=          F      AIMPAC=          F      FRIEND=
NPRINT=            -5      IREST  =          0      GEOM   =INPUT
NORMF  =             0      NORMP  =          0      ITOL   =          20      ICUT   =
9
INTTYP=BEST         GRDTYP=BEST         QMTTOL= 1.0E-06
  
```

\$SYSTEM OPTIONS

```

-----
REPLICATED MEMORY=      50000000 WORDS (ON EVERY NODE).
DISTRIBUTED MEMDDI=      0 MILLION WORDS IN AGGREGATE,
MEMDDI DISTRIBUTED OVER  1 PROCESSORS IS      0 WORDS/PROCESSOR.
TOTAL MEMORY REQUESTED ON EACH PROCESSOR=      50000000 WORDS.
TIMLIM=      60.00 MINUTES, OR      0.0 DAYS.
PARALL= F  BALTYP= DLB      KDIAG=      0      COREFL= F
MXSEQ2=      300 MXSEQ3=      150
  
```

 PROPERTIES INPUT

MOMENTS		FIELD		POTENTIAL		DENSITY	
IEMOM =	1	IEFLD =	0	IEPOT =	0	IEDEN =	0
WHERE =	COMASS	WHERE =	NUCLEI	WHERE =	NUCLEI	WHERE =	NUCLEI
OUTPUT=	BOTH	OUTPUT=	BOTH	OUTPUT=	BOTH	OUTPUT=	BOTH
IEMINT=	0	IEFINT=	0			IEDINT=	0
						MORB =	0

EXTRAPOLATION IN EFFECT

SOSCF IN EFFECT

ORBITAL PRINTING OPTION: NPREO= 1 135 2 1

 INTEGRAL TRANSFORMATION OPTIONS

NWORD = 0
 CUTOFF = 1.0E-10 MPTRAN = 0
 DIRTRF = F AOINTS = DUP

 INTEGRAL INPUT OPTIONS

NOPK = 1 NORDER= 0 SCHWRZ= F

 MP2 CONTROL INFORMATION

NACORE = 2 NBCORE = 2
 LMOMP2 = F AOINTS = DUP
 METHOD = 2 NWORD = 0
 MP2PRP = F OSPT = NONE
 CUTOFF = 1.00E-09 CPHFBS = BASISAO
 CODE = IMS

NUMBER OF CORE -A- ORBITALS = 2
 NUMBER OF CORE -B- ORBITALS = 2
 NUMBER OF OCC. -A- ORBITALS = 8
 NUMBER OF OCC. -B- ORBITALS = 8
 NUMBER OF MOLECULAR ORBITALS = 135
 NUMBER OF BASIS FUNCTIONS = 135

 THE POINT GROUP IS CS , NAXIS= 0, ORDER= 2

-- VARIATIONAL SPACE WILL BE RESTRICTED TO PURE SPHERICAL HARMONICS ONLY

--

AFTER EXCLUDING CONTAMINANT COMBINATIONS FROM THE CARTESIAN GAUSSIAN BASIS

SET, THE NUMBER OF SPHERICAL HARMONICS KEPT IN THE VARIATION SPACE IS 115

DIMENSIONS OF THE SYMMETRY SUBSPACES ARE
A' = 76 A'' = 39

..... DONE SETTING UP THE RUN
STEP CPU TIME = 0.00 TOTAL CPU TIME = 0.0 (0.0 MIN)
TOTAL WALL CLOCK TIME= 0.0 SECONDS, CPU UTILIZATION IS 0.00%
..... END OF ONE-ELECTRON INTEGRALS
STEP CPU TIME = 0.00 TOTAL CPU TIME = 0.0 (0.0 MIN)
TOTAL WALL CLOCK TIME= 0.0 SECONDS, CPU UTILIZATION IS 0.00%

GUESS OPTIONS

0 GUESS =HUCKEL NORB = 0 NORDER=
F MIX = F PRTMO = F PUNMO =
TOLZ = 1.0E-08 TOLE = 1.0E-05
SYMDEN= F PURIFY= F

INITIAL GUESS ORBITALS GENERATED BY HUCKEL ROUTINE.
HUCKEL GUESS REQUIRES 133293 WORDS.

SYMMETRIES FOR INITIAL GUESS ORBITALS FOLLOW. BOTH SET(S).
8 ORBITALS ARE OCCUPIED (2 CORE ORBITALS).
3=A' 4=A' 5=A' 6=A' ' 7=A' 8=A'
9=A' '
10=A' 11=A' 12=A' 13=A' 14=A' 15=A'
16=A'
17=A' 18=A'

..... END OF INITIAL ORBITAL SELECTION
STEP CPU TIME = 0.21 TOTAL CPU TIME = 0.2 (0.0 MIN)
TOTAL WALL CLOCK TIME= 0.2 SECONDS, CPU UTILIZATION IS 95.45%

AO INTEGRAL TECHNOLOGY

S,P,L SHELL ROTATED AXIS INTEGRALS, REPROGRAMMED BY
KAZUYA ISHIMURA (IMS) AND JOSE SIERRA (SYNSTAR).
S,P,D,L SHELL ROTATED AXIS INTEGRALS PROGRAMMED BY
KAZUYA ISHIMURA (INSTITUTE FOR MOLECULAR SCIENCE).
S,P,D,F,G SHELL TO TOTAL QUARTET ANGULAR MOMENTUM SUM 5,
ERIC PROGRAM BY GRAHAM FLETCHER (ELORET AND NASA ADVANCED
SUPERCOMPUTING DIVISION, AMES RESEARCH CENTER).
S,P,D,F,G,L SHELL GENERAL RYS QUADRATURE PROGRAMMED BY
MICHEL DUPUIS (PACIFIC NORTHWEST NATIONAL LABORATORY).
TOTAL NUMBER OF NONZERO TWO-ELECTRON INTEGRALS = 16494968
1100 INTEGRAL RECORDS WERE STORED ON DISK FILE 8.
..... END OF TWO-ELECTRON INTEGRALS
STEP CPU TIME = 2.66 TOTAL CPU TIME = 2.9 (0.0 MIN)
TOTAL WALL CLOCK TIME= 3.5 SECONDS, CPU UTILIZATION IS 80.85%

RHF SCF CALCULATION

DENSITY MATRIX CONV= 2.50E-07

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB.
GRAD						
1	0	0	-129.3982400149	-129.3982400149	0.464189632	
0.000000000						
-----START SECOND ORDER SCF-----						
2	1	0	-129.8130653002	-0.4148252853	0.038309641	
0.027017085						
3	2	0	-129.8327596506	-0.0196943504	0.032902786	
0.016121509						
4	3	0	-129.8366740046	-0.0039143540	0.006067874	
0.008761660						
5	4	0	-129.8371647792	-0.0004907747	0.002455970	
0.001316982						
6	5	0	-129.8372197060	-0.0000549267	0.001153149	
0.000677220						
7	6	0	-129.8372325857	-0.0000128797	0.000660668	
0.000383147						
8	7	0	-129.8372351763	-0.0000025906	0.000154396	
0.000078502						
9	8	0	-129.8372353898	-0.0000002135	0.000079833	
0.000021685						
10	9	0	-129.8372354108	-0.0000000210	0.000012521	
0.000004563						
11	10	0	-129.8372354116	-0.0000000008	0.000002972	
0.000001158						
12	11	0	-129.8372354116	-0.0000000001	0.000000698	
0.000000262						
13	12	0	-129.8372354116	0.0000000000	0.000000185	
0.000000064						
14	13	0	-129.8372354116	0.0000000000	0.000000040	
0.000000020						

DENSITY CONVERGED

TIME TO FORM FOCK OPERATORS= 4.0 SECONDS (0.3 SEC/ITER)
TIME TO SOLVE SCF EQUATIONS= 0.0 SECONDS (0.0 SEC/ITER)

FINAL RHF ENERGY IS -129.8372354116 AFTER 14 ITERATIONS
..... END OF RHF CALCULATION
STEP CPU TIME = 4.02 TOTAL CPU TIME = 6.9 (0.1 MIN)
TOTAL WALL CLOCK TIME= 7.6 SECONDS, CPU UTILIZATION IS 91.14%

-----		-----	
RHF-MP2 ENERGY CALCULATION		PROGRAM WRITTEN BY K.ISHIMURA	
-----		-----	
NUMBER OF OCCUPIED ORBITALS	= 8		
NUMBER OF CORRELATED OCCUPIED ORBITALS	= 6		
NUMBER OF VIRTUAL ORBITALS	= 107		
NUMBER OF BASIS FUNCTIONS	= 135		
NUMBER OF BASIS SHELLS	= 37		
AO-TRANSFORMED INTEGRAL THRESHOLD	= 1.00E-09		

```

HALF-TRANSFORMED INTEGRAL THRESHOLD      = 5.64E-12
TOTAL DISK REQUIRED (ALL PROCESSORS)=      2 MBYTES
      DISK SPACE PER CORE=                2 MBYTES, USING P=
1
MEMORY REQUIRED FOR TRANSFORMATION OF 1ST THREE INDICES=      369951
MEMORY REQUIRED FOR      4TH INDEX TRANSF. AND MP2 ENERGY=    377942
BEGINNING MP2 INTEGRAL TRANSFORMATION...
BEGINNING      1ST SHELL LOOP...
BEGINNING      26TH SHELL LOOP...

RESULTS OF MOLLER-PLESSET 2ND ORDER CORRECTION ARE
      E(0)=      -129.8372354116
      E(1)=          0.0
      E(2)=      -0.4470133819
      E(MP2)=     -130.2842487935
SPIN-COMPONENT-SCALED MP2 RESULTS ARE
      E(2S)=      -0.3362506971
      E(2T)=      -0.1107626848
      E(2ST)=     -0.4404217314 = 6/5 * E(2S) + 1/3 * E(2T)
      SCS-MP2=     -130.2776571431
..... DONE WITH MP2 ENERGY .....
STEP CPU TIME =      11.82 TOTAL CPU TIME =      18.7 (      0.3 MIN)
TOTAL WALL CLOCK TIME=      19.5 SECONDS, CPU UTILIZATION IS  96.05%
      580000 WORDS OF DYNAMIC MEMORY USED
EXECUTION OF GAMESS TERMINATED NORMALLY Wed Apr 15 18:41:07 2015
DDI: 263624 bytes (0.3 MB / 0 MWords) used by master data server.

-----
CPU timing information for all processes
=====
0: 16.875 + 1.844 = 18.719
1: 0.01 + 0.02 = 0.03
-----
ddikick.x: exited gracefully.
unset echo
----- accounting info -----
Files used on the master node James-Smiths-MacBook-Pro-2.local were:
-rwxr-xr-x@ 1 jamessmith  staff      356 Apr 15 18:40 ../HNO.F05*
-rw-r--r-- 1 jamessmith  staff 198017600 Apr 15 18:40 ../HNO.F08
-rw-r--r-- 1 jamessmith  staff  1865040 Apr 15 18:41 ../HNO.F10
-rw-r--r-- 1 jamessmith  staff   252127 Apr 15 18:40 ../HNO.dat
-rwxrwxrwx@ 1 jamessmith  staff      356 Apr 15 18:40 ../HNO.inp*
-rw-r--r-- 1 jamessmith  staff   24264 Apr 15 18:41 ../HNO.log
Wed Apr 15 18:41:10 EDT 2015
16.936u 1.898s 0:22.60 83.2% 0+0k 4+20io 0pf+0w

```

(3) Maple Worksheet Used to Calculate Dipole Moments

A Maple worksheet for quadratic fits of energy vs applied electric field

Note that you can use the # character to insert comments

First restart Maple to clear the memory

restart

Then load the statistics commands

with(stats)
`[anova, describe, fit, importdata, random, statevalf, statplots, transform]` **(1)**

Also load the plotting commands

with(plots)
`[animate, animate3d, animatecurve, arrow, changecoords, complexplot, complexplot3d, conformal, conformal3d, contourplot, contourplot3d, coordplot, coordplot3d, densityplot, display, dualaxisplot, fieldplot, fieldplot3d, gradplot, gradplot3d, implicitplot, implicitplot3d, inequal, interactive, interactiveparams, intersectplot, listcontplot, listcontplot3d, listdensityplot, listplot, listplot3d, loglogplot, logplot, matrixplot, multiple, odeplot, pareto, plotcompare, pointplot, pointplot3d, polarplot, polygonplot, polygonplot3d, polyhedra_supported, polyhedraplot, rootlocus, semilogplot, setcolors, setoptions, setoptions3d, spacecurve, sparsematrixplot, surfdata, textplot, textplot3d, tubeplot]` **(2)**

Then define the seven applied field strengths. Square brackets indicate a list of values.

efield := [-0.003, -0.002, -0.001, 0, 0.001, 0.002, 0.003]
`[-0.003, -0.002, -0.001, 0, 0.001, 0.002, 0.003]` **(3)**

Now define the energies.

energies := [-130.285346, -130.2849627, -130.284597, -130.2842488, -130.2839182, -130.2836051, -130.2833096]
`[-130.285346, -130.2849627, -130.284597, -130.2842488, -130.2839182, -130.2836051, -130.2833096]` **(4)**

Now calculate the fit.

fit[leastsquare][x, y, y = a·x² + b·x + c]([efield, energies])
`y = -8.791666667 x2 + 0.3394107143 x - 130.2842487` **(5)**

Save the right hand side of the above equation. The % means "the result of the previous command".

```
fit_eqn := rhs(%)
-8.791666667 x2 + 0.3394107143 x - 130.2842487
```

(6)

Make a plot of the fitting equation and save it as p1.

```
p1 := plot(fit_eqn, x = -0.0035 .. 0.0035, color = green)
PLOT(...)
```

(7)

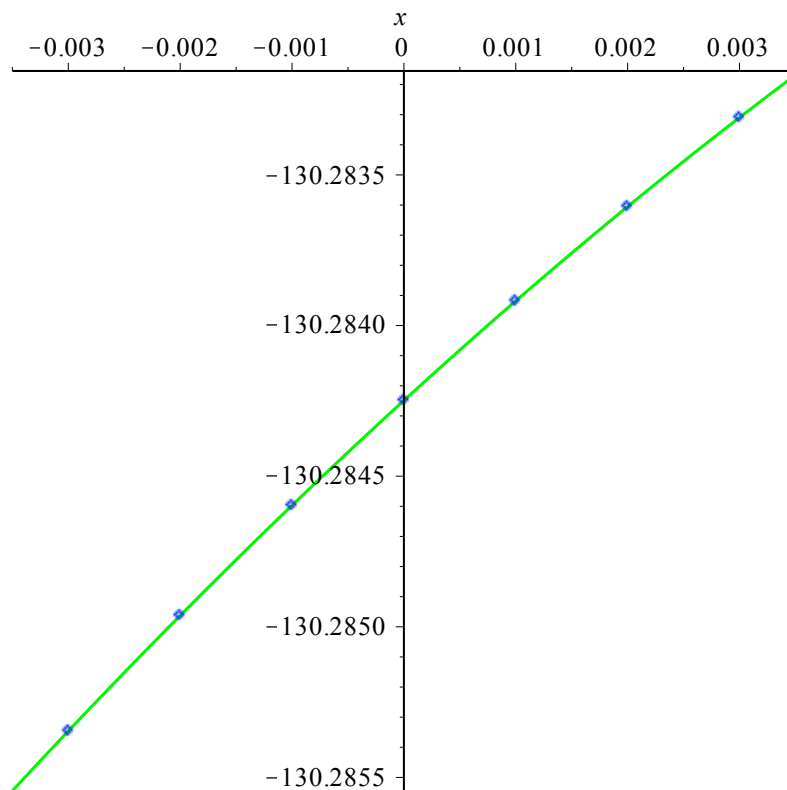
Make a plot of the raw data and save it as p2.

```
p2 := pointplot([seq([efield[i], energies[i]], i = 1 .. 7)], color = blue)
PLOT(...)
```

(8)

Show them both.

```
display(p1, p2)
```



Calculate the first derivative at field = 0.

$$\text{deriv} := \text{diff}(\text{fit_eqn}, x) \qquad -17.58333333 x + 0.3394107143 \qquad (9)$$

$$\text{subs}(x = 0, \text{deriv}) \qquad 0.3394107143 \qquad (10)$$

(4) Maple Worksheet Used to Evaluate q Values without Coupling

restart

paste the data from the CSV file here

```
data := [-130.2460115, -130.2582804, -130.2680478, -130.2753877, -130.2804262,
-130.2833222, -130.2842488, -130.2833766, -130.2808628, -130.2768444, -130.271437,
-130.2647386, -130.2568352]
```

```
[ -130.2460115, -130.2582804, -130.2680478, -130.2753877, -130.2804262, -130.2833222,
-130.2842488, -130.2833766, -130.2808628, -130.2768444, -130.271437,
-130.2647386, -130.2568352] (1)
```

these are the 13 distinct q values

```
qvalues := [-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3]
[-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3] (2)
```

just checking to make sure I typed in 13 values

```
nops(qvalues)
13 (3)
```

make the list of x and y values for fitting, chosen from the 13 q values

```
xvalues := [-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3]
[-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3] (4)
```

load the fitting package

```
with(stats)
[anova, describe, fit, importdata, random, statevalf, statplots, transform] (5)
```

define the fitting equation

```
fiteqn := a·x3 + b·x2 - 130.2842488
a x3 + b x2 - 130.2842488 (6)
```

do the fitting

```
fit[leastsquare]([x, y], y=fiteqn)([xvalues, data]);
y = -0.0002027649492 x3 + 0.003640988923 x2 - 130.2842488 (7)
```

(5) Maple Worksheet Used to Study Coupling between 2 q Values

restart

paste the data from the CSV file here

```
data := [-130.2219807, -130.2328523, -130.2422803, -130.2500444, -130.2560136, -130.2601425,  
-130.2624616, -130.263061, -130.2620701, -130.2596338, -130.2558883, -130.2509392,  
-130.244844, -130.2289658, -130.2400276, -130.2494285, -130.256999, -130.2626597,  
-130.2664133, -130.2683305, -130.2685311, -130.2671628, -130.2643777, -130.2603122,  
-130.2550688, -130.2487063, -130.2350954, -130.246338, -130.2557171, -130.2631166,  
-130.2685077, -130.2719368, -130.2735083, -130.2733643, -130.2716627, -130.2685568,  
-130.2641778, -130.2577135, -130.2519515, -130.2401539, -130.2515834, -130.2609645,  
-130.268234, -130.2734106, -130.2765786, -130.277869, -130.2774388, -130.2754503,  
-130.2720532, -130.2673722, -130.2615001, -130.2544964, -130.2438764, -130.2555208,  
-130.2649498, -130.2721512, -130.2771854, -130.2801683, -130.2812507, -130.2805982,  
-130.2783728, -130.2747192, -130.2697563, -130.2635742, -130.2562375, -130.2459498,  
-130.2578638, -130.2674124, -130.2746292, -130.2796111, -130.2824984, -130.2834555,  
-130.2826519, -130.2802474, -130.2763816, -130.2711701, -130.2647047, -130.2570586,  
-130.2460115, -130.2582804, -130.2680478, -130.2753877, -130.2804262, -130.2833222,  
-130.2842488, -130.2833766, -130.2808628, -130.2768444, -130.271437, -130.2647386,  
-130.2568352, -130.2436442, -130.256388, -130.2665038, -130.2740995, -130.2793247,  
-130.2823515, -130.2833583, -130.2825163, -130.2799813, -130.2758908, -130.2703652,  
-130.2635131, -130.2554367, -130.2383701, -130.2517468, -130.2623736, -130.2703863,  
-130.2759524, -130.2792539, -130.2804731, -130.2797822, -130.2773387, -130.2732845,  
-130.2677495, -130.2608564, -130.252727, -130.2296422, -130.2438517, -130.2551889,  
-130.2638121, -130.2699027, -130.2736506, -130.275242, -130.2748525, -130.2726449,  
-130.2687699, -130.2633707, -130.2565878, -130.2485642, -130.2168332, -130.2321229,  
-130.2444123, -130.2538775, -130.2607119, -130.2651126, -130.2672716, -130.2673711,  
-130.2655828, -130.2620705, -130.2569945, -130.2505156, -130.2427989, -130.1992233,  
-130.2158949, -130.2294272, -130.2400119, -130.2478532, -130.2531568, -130.2561229,  
-130.256944, -130.2558051, -130.2528866, -130.2483689, -130.2424348, -130.2352714,  
-130.1759849, -130.1944032, -130.2095278, -130.2215647, -130.2307298, -130.2372394,  
-130.2413057, -130.2431352, -130.2429298, -130.2408903, -130.2372188, -130.2321208,  
-130.225805]
```

```
[ -130.2219807, -130.2328523, -130.2422803, -130.2500444, -130.2560136, -130.2601425, (1)  
-130.2624616, -130.263061, -130.2620701, -130.2596338, -130.2558883,  
-130.2509392, -130.244844, -130.2289658, -130.2400276, -130.2494285,  
-130.256999, -130.2626597, -130.2664133, -130.2683305, -130.2685311,  
-130.2671628, -130.2643777, -130.2603122, -130.2550688, -130.2487063,  
-130.2350954, -130.246338, -130.2557171, -130.2631166, -130.2685077,  
-130.2719368, -130.2735083, -130.2733643, -130.2716627, -130.2685568,  
-130.2641778, -130.2577135, -130.2519515, -130.2401539, -130.2515834,  
-130.2609645, -130.268234, -130.2734106, -130.2765786, -130.277869,  
-130.2774388, -130.2754503, -130.2720532, -130.2673722, -130.2615001,  
-130.2544964, -130.2438764, -130.2555208, -130.2649498, -130.2721512,
```

-130.2771854, -130.2801683, -130.2812507, -130.2805982, -130.2783728,
-130.2747192, -130.2697563, -130.2635742, -130.2562375, -130.2459498,
-130.2578638, -130.2674124, -130.2746292, -130.2796111, -130.2824984,
-130.2834555, -130.2826519, -130.2802474, -130.2763816, -130.2711701,
-130.2647047, -130.2570586, -130.2460115, -130.2582804, -130.2680478,
-130.2753877, -130.2804262, -130.2833222, -130.2842488, -130.2833766,
-130.2808628, -130.2768444, -130.271437, -130.2647386, -130.2568352,
-130.2436442, -130.256388, -130.2665038, -130.2740995, -130.2793247,
-130.2823515, -130.2833583, -130.2825163, -130.2799813, -130.2758908,
-130.2703652, -130.2635131, -130.2554367, -130.2383701, -130.2517468,
-130.2623736, -130.2703863, -130.2759524, -130.2792539, -130.2804731,
-130.2797822, -130.2773387, -130.2732845, -130.2677495, -130.2608564,
-130.252727, -130.2296422, -130.2438517, -130.2551889, -130.2638121,
-130.2699027, -130.2736506, -130.275242, -130.2748525, -130.2726449,
-130.2687699, -130.2633707, -130.2565878, -130.2485642, -130.2168332,
-130.2321229, -130.2444123, -130.2538775, -130.2607119, -130.2651126,
-130.2672716, -130.2673711, -130.2655828, -130.2620705, -130.2569945,
-130.2505156, -130.2427989, -130.1992233, -130.2158949, -130.2294272,
-130.2400119, -130.2478532, -130.2531568, -130.2561229, -130.256944,
-130.2558051, -130.2528866, -130.2483689, -130.2424348, -130.2352714,
-130.1759849, -130.1944032, -130.2095278, -130.2215647, -130.2307298,
-130.2372394, -130.2413057, -130.2431352, -130.2429298, -130.2408903,
-130.2372188, -130.2321208, -130.225805]

these are the 13 distinct q values

qvalues := [-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3]
[-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3] (2)

just checking to make sure I typed in 13 values

nops(qvalues)
13 (3)

make the list of x and y values for fitting, chosen from the 13 q values

xvalues := [seq(seq(qvalues[i], i = 1..13), j = 1..13)]
[-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1,
1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1,
-0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5,
-2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2,
2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5,

```

0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2,
-1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, -3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3,
-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3]
yvalues := [seq(seq(qvalues[j], i = 1..13), j = 1..13)]
[-3, -3, -3, -3, -3, -3, -3, -3, -3, -3, -3, -3, -3, -2.5, -2.5, -2.5, -2.5, -2.5, -2.5, -2.5, (5)
-2.5, -2.5, -2.5, -2.5, -2.5, -2.5, -2, -2, -2, -2, -2, -2, -2, -2, -2, -2, -2, -2, -2,
-1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1.5, -1, -1, -1,
-1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -0.5, -0.5, -0.5, -0.5, -0.5, -0.5, -0.5, -0.5,
-0.5, -0.5, -0.5, -0.5, -0.5, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5,
0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1.5, 1.5, 1.5, 1.5, 1.5, 1.5, 1.5,
1.5, 1.5, 1.5, 1.5, 1.5, 1.5, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2.5, 2.5, 2.5, 2.5, 2.5, 2.5, 2.5,
2.5, 2.5, 2.5, 2.5, 2.5, 2.5, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3]
# load the fitting package

with(stats)
[anova, describe, fit, importdata, random, statevalf, statplots, transform] (6)
# define the fitting equation

fiteqn := a·x·y + b·x·y2 + c·x2·y - 130.2842488
a x y + b x y2 + c x2 y - 130.2842488 (7)
# do the fitting

fit[leastsquare][[x, y, z], z = fiteqn]([xvalues, yvalues, data]);
z = -0.0004724036469 x y - 0.0006691403763 x y2 + 0.0005927021436 x2 y - 130.2842488 (8)

```

(6) Maple Worksheet Used to Study Coupling between 3 q Values

restart

paste the data from the CSV file here

```
data := [-0.000241539, 0.000539034, 0.00045139, -0.000309523, 0.000937194, -0.001680582,
-0.001589264, 0.001434932, 0.000746628, 0.002159572, 0.00164123, -0.000799217,
0.005141574, -0.022406638, -0.019785749, 0.014142792, 0.004664055, 0.001459467,
0.000904743, -0.001204818, -0.009466697, -0.11982204, -0.100442347, 0.038723548,
0.000566852, 0.000448518, 6.65142E-05, 0.003044341, 0.002725817, 0.017567795, 0.001459487,
0.001417754, -8.26998E-05, 0.002191956, 0.001199953, -1.41643E-05, 0.008625262,
0.008527679, 0.030163989, -0.00137531, -0.001792707, -0.001137314, -0.014818464,
-0.00877426, -0.033727124, -0.00988768, -0.01020591, -0.030727514, 0.002059277,
0.001173256, 0.002334667, 0.008836103, 0.014526124, -0.00096319, 0.001028403,
-0.000478043, 0.002651101, -0.000120892, 0.000975524, 0.003173491, 0.034724569,
0.041746549, 0.010690478, -0.001134912, -0.000778735, -0.002755231, -0.046299882,
-0.071812962, -0.023768031, -0.053047484, -0.05024921, -0.01893269]
```

```
[ -0.000241539, 0.000539034, 0.00045139, -0.000309523, 0.000937194, -0.001680582,
-0.001589264, 0.001434932, 0.000746628, 0.002159572, 0.00164123, -0.000799217,
0.005141574, -0.022406638, -0.019785749, 0.014142792, 0.004664055, 0.001459467,
0.000904743, -0.001204818, -0.009466697, -0.11982204, -0.100442347, 0.038723548,
0.000566852, 0.000448518, 0.0000665142, 0.003044341, 0.002725817, 0.017567795,
0.001459487, 0.001417754, -0.0000826998, 0.002191956, 0.001199953, -0.0000141643,
0.008625262, 0.008527679, 0.030163989, -0.00137531, -0.001792707, -0.001137314,
-0.014818464, -0.00877426, -0.033727124, -0.00988768, -0.01020591, -0.030727514,
0.002059277, 0.001173256, 0.002334667, 0.008836103, 0.014526124, -0.00096319,
0.001028403, -0.000478043, 0.002651101, -0.000120892, 0.000975524, 0.003173491,
0.034724569, 0.041746549, 0.010690478, -0.001134912, -0.000778735, -0.002755231,
-0.046299882, -0.071812962, -0.023768031, -0.053047484, -0.05024921, -0.01893269]
```

(1)

these are the 13 distinct q values

```
qvalues := [-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3]
[-3, -2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3]
```

(2)

just checking to make sure I typed in 13 values

nops(qvalues)

13

(3)

make the list of x and y values for fitting, chosen from the 13 q values

```
xvalues := [1, 1, 1, 1, -1, -1, -1, -1, 2, 2, 2, 2, -2, -2, -2, -2, 3, 3, 3, 3, -3, -3, -3, -3, 1.5, 1.5, 3, -1.5,
-1.5, -3, 1.5, 1.5, 3, 1.5, 1.5, 3, -1.5, -1.5, -3, 1.5, 1.5, 3, -1.5, -1.5, -3, -1.5, -1.5, -3, 3, 3, 1.5, -3,
-3, -1.5, 3, 3, 1.5, 3, 3, 1.5, -3, -3, -1.5, 3, 3, 1.5, -3, -3, -1.5, -3, -3, -1.5]
```

```
[1, 1, 1, 1, -1, -1, -1, -1, 2, 2, 2, 2, -2, -2, -2, -2, 3, 3, 3, 3, -3, -3, -3, -3, 1.5, 1.5, 3,

```

(4)

```

-1.5, -1.5, -3, 1.5, 1.5, 3, 1.5, 1.5, 3, -1.5, -1.5, -3, 1.5, 1.5, 3, -1.5, -1.5, -3, -1.5,
-1.5, -3, 3, 3, 1.5, -3, -3, -1.5, 3, 3, 1.5, 3, 3, 1.5, -3, -3, -1.5, 3, 3, 1.5, -3, -3, -1.5,
-3, -3, -1.5]
yvalues := [1, 1, -1, -1, 1, 1, -1, -1, 2, 2, -2, -2, 2, 2, -2, -2, 3, 3, -3, -3, 3, 3, -3, -3, 1.5, 3, 1.5, 1.5, 3,
1.5, -1.5, -3, -1.5, 1.5, 3, 1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, 1.5, 3, 1.5, -1.5, -3, -1.5, 3, 1.5, 3, 3, 1.5,
3, -3, -1.5, -3, 3, 1.5, 3, -3, -1.5, -3, -3, -1.5, -3, 3, 1.5, 3, -3, -1.5, -3]
[1, 1, -1, -1, 1, 1, -1, -1, 2, 2, -2, -2, 2, 2, -2, -2, 3, 3, -3, -3, 3, 3, -3, -3, 1.5, 3, 1.5, 1.5,
3, 1.5, -1.5, -3, -1.5, 1.5, 3, 1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, 1.5, 3, 1.5, -1.5, -3,
-1.5, 3, 1.5, 3, 3, 1.5, 3, -3, -1.5, -3, 3, 1.5, 3, -3, -1.5, -3, -3, -1.5, -3, 3, 1.5, 3, -3,
-1.5, -3]
(5)

zvalues := [1, -1, 1, -1, 1, -1, 1, -1, 2, -2, 2, -2, 2, -2, 2, -2, 3, -3, 3, -3, 3, -3, 3, -3, 3, 1.5, 1.5, 3, 1.5,
1.5, 3, 1.5, 1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, 3, 1.5, 1.5, 1.5, 3, 3, 1.5, 3,
3, 1.5, 3, 3, -1.5, -3, -3, -1.5, -3, -3, -1.5, -3, -3, -1.5, -3, -3, 1.5, 3, 3]
[1, -1, 1, -1, 1, -1, 1, -1, 2, -2, 2, -2, 2, -2, 2, -2, 3, -3, 3, -3, 3, -3, 3, -3, 3, 1.5, 1.5, 3,
1.5, 1.5, 3, 1.5, 1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, -3, -1.5, -1.5, 3, 1.5,
1.5, 1.5, 3, 3, 1.5, 3, 3, 1.5, 3, 3, -1.5, -3, -3, -1.5, -3, -3, -1.5, -3, -3, -1.5, -3, -3,
1.5, 3, 3]
(6)

# load the fitting package

with(stats)
[anova, describe, fit, importdata, random, statevalf, statplots, transform]
(7)

# define the fitting equation

fiteqn := a·x·y·z + b·x2·y·z + c·x·y2·z + d·x·y·z2 - 130.2842488
a x y z + b x2 y z + c x y2 z + d x y z2 - 130.2842488
(8)

# do the fitting

fit[leastsquare[ [x, y, z, w], w = fiteqn ] ]( [xvalues, yvalues, zvalues, data ] );
(9)
w = -0.001153825035 x y z + 0.0004271220293 x2 y z + 0.00005944774235 x y2 z
+ 0.0001140988379 x y z2 - 130.2842488

```

(7) 72 Tests Used to Determine the Coupling with all Three Modes (E(MP2))

q1	q2	q3	E(MP2) energy
1	1	1	-130.2722146
1	1	-1	-130.2728266
1	-1	1	-130.2715997
1	-1	-1	-130.2708256
-1	1	1	-130.2714005
-1	1	-1	-130.26836
-1	-1	1	-130.2672384
-1	-1	-1	-130.2699953
2	2	2	-130.2459103
2	2	-2	-130.2461724
2	-2	2	-130.2355959
2	-2	-2	-130.2362579
-2	2	2	-130.2413365
-2	2	-2	-130.2081809
-2	-2	2	-130.1999163
-2	-2	-2	-130.2324908
3	3	3	-130.2189152
3	3	-3	-130.211589
3	-3	3	-130.1718405
3	-3	-3	-130.1925172
-3	3	3	-130.2067294
-3	3	-3	-130.07066
-3	-3	3	-130.046585
-3	-3	-3	-130.1869448
1.5	1.5	3	-130.2363688
1.5	3	1.5	-130.2406783
3	1.5	1.5	-130.2455951
-1.5	1.5	3	-130.2338195
-1.5	3	1.5	-130.2449172
-3	1.5	1.5	-130.1918014
1.5	-1.5	3	-130.2183798
1.5	-3	1.5	-130.2259298
3	-1.5	1.5	-130.2420483
1.5	1.5	-3	-130.2479339
1.5	3	-1.5	-130.2435345
3	1.5	-1.5	-130.238509
-1.5	-1.5	-3	-130.2423928
-1.5	-3	-1.5	-130.2325293

-3	-1.5	-1.5	-130.163391
1.5	-1.5	-3	-130.2351871
1.5	-3	-1.5	-130.2294336
3	-1.5	-1.5	-130.2351383
-1.5	1.5	-3	-130.2298101
-1.5	3	-1.5	-130.2341256
-3	1.5	-1.5	-130.1117014
-1.5	-1.5	3	-130.2003244
-1.5	-3	1.5	-130.2084777
-3	-1.5	1.5	-130.1301546
3	3	1.5	-130.2295475
3	1.5	3	-130.2282219
1.5	3	3	-130.223586
-3	3	1.5	-130.2124473
-3	1.5	3	-130.1961018
-1.5	3	3	-130.222613
3	-3	1.5	-130.2161642
3	-1.5	3	-130.208831
1.5	-3	3	-130.1772218
3	3	-1.5	-130.2229928
3	1.5	-3	-130.2236036
1.5	3	-3	-130.2346638
-3	-3	-1.5	-130.1785653
-3	-1.5	-3	-130.1793178
-1.5	-3	-3	-130.2208562
3	-3	-1.5	-130.2142359
3	-1.5	-3	-130.2138118
1.5	-3	-3	-130.2089623
-3	3	-1.5	-130.1311371
-3	1.5	-3	-130.0837498
-1.5	3	-3	-130.2139605
-3	-3	1.5	-130.1123579
-3	-1.5	3	-130.103633
-1.5	-3	3	-130.1501728

(8) 100 Random Tests Used to Determine the Accuracy of the Potential Energy Formula (E(MP2))

q1	q2	q3	E(MP2) energy
-2.1283	0.1113	-0.5779	-130.224674
2.0624	-0.3172	-2.9445	-130.2391428
-2.8227	0.4726	-0.9044	-130.1508119
1.9352	-1.7399	-0.2705	-130.2564632
-0.7053	2.6567	2.2377	-130.244872
1.6488	2.4748	2.9988	-130.2286861
-1.9461	-1.8251	2.1442	-130.2028835
0.4713	0.3752	1.6829	-130.2714681
2.9102	-0.8697	-1.65	-130.2396913
-1.8653	2.0112	-0.5657	-130.23673
-2.1723	0.238	0.115	-130.2259156
1.7236	-0.034	-0.9979	-130.2664943
2.5922	-0.3178	-0.6164	-130.256177
2.3863	-1.7612	2.732	-130.217391
-0.0106	-2.2783	1.6468	-130.2463008
0.9178	-1.5166	-1.7203	-130.259497
2.3498	0.8248	0.0705	-130.2604759
-2.223	-1.2568	0.5728	-130.2173951
1.0076	1.0876	-1.5485	-130.2689913
2.7023	0.201	-1.2005	-130.2505908
0.3625	-2.1509	-1.2765	-130.2587238
-1.8643	-0.3467	0.225	-130.2443324
-1.8541	0.1074	0.9823	-130.2462533
-2.1211	-1.728	1.2159	-130.2131679
0.3201	-1.8564	-0.788	-130.2674005
0.8615	-1.5161	-1.0233	-130.2666622
-0.8105	0.7916	-1.6069	-130.2690182
2.7372	0.3054	2.2411	-130.2451125
-1.6806	1.0276	1.7847	-130.2517791
2.7463	0.8563	1.148	-130.2540657
-1.0885	1.6203	0.6497	-130.2676707
1.591	-0.9231	-0.3046	-130.268555
1.121	1.4987	2.805	-130.2425725
1.1673	-1.6078	-0.2575	-130.2667072
-0.2152	2.3684	0.0389	-130.2667211
0.1251	-2.9888	-0.0832	-130.2463151
-2.1897	0.9743	-2.6768	-130.1955824
1.7136	1.9923	1.0515	-130.2558622

2.2915	1.1731	-1.0572	-130.2547012
-1.253	0.2094	-0.7456	-130.2663865
2.1863	2.0478	-0.9501	-130.2492951
2.1831	-0.3372	1.2235	-130.261565
-1.214	0.4006	-1.3692	-130.2631122
0.0149	0.3613	0.732	-130.2818914
-1.821	-1.1729	0.9284	-130.2394111
-2.9745	-0.7801	-1.1056	-130.1468849
-2.5388	-0.4023	0.485	-130.1951819
1.7061	2.804	-1.4376	-130.2441112
-2.5609	-2.9172	-1.4666	-130.2023212
2.4336	0.367	-0.6609	-130.2582895
1.7394	-1.9264	-0.0272	-130.2568373
-2.0188	1.5978	0.9433	-130.2432379
1.3481	2.4071	0.2298	-130.2566571
1.7938	-1.7645	0.0905	-130.2586607
-1.5241	-2.556	-2.5777	-130.2331722
1.7548	1.2641	0.3654	-130.2650427
2.7549	-1.4399	1.0695	-130.2490432
2.9133	0.5796	-0.7	-130.2504244
-2.186	-0.6571	0.2265	-130.2235297
2.4162	-1.3244	-0.05	-130.2558002
2.7041	-2.9578	-1.8289	-130.213979
1.8279	1.3131	-0.8083	-130.2616553
-2.5576	2.8775	0.8958	-130.2232905
0.2904	-2.4521	2.4842	-130.21855
1.9557	-2.4383	-1.4335	-130.2365959
0.2221	-1.5671	1.4058	-130.26427
-1.4595	1.3006	2.5126	-130.2458136
2.0631	-0.5012	-0.0118	-130.2655817
1.4015	-1.4544	-0.6144	-130.2645056
2.9463	2.9483	2.2281	-130.2270163
0.7679	1.8624	2.6035	-130.2455057
0.2715	0.754	-1.0151	-130.27914
1.6275	1.813	-2.7167	-130.2471221
-0.7127	-1.3464	-1.3287	-130.269363
-1.7436	-1.419	2.7849	-130.2019642
-0.161	2.0687	-0.1972	-130.2706803
0.2326	-1.9961	1.7045	-130.2514578
1.118	0.2782	-2.6791	-130.2584758
-0.348	-2.8163	-0.7959	-130.2496253

-0.2097	-2.8362	-2.7155	-130.2307331
0.9147	2.4579	-0.9861	-130.2593426
-0.8513	-1.1638	2.8535	-130.2273677
0.96	-0.1123	0.9487	-130.2763358
0.3466	2.9473	-1.3285	-130.2550816
1.7415	-2.958	1.3239	-130.2285373
1.5038	0.5229	-0.8699	-130.2697132
2.9823	-0.8864	0.5576	-130.25251
-1.0416	-0.2639	1.9895	-130.2587293
-0.054	0.7516	-2.825	-130.2646439
-2.5939	1.3217	2.5019	-130.2156379
1.1616	-2.2463	-0.4147	-130.2563445
-1.7359	-2.6376	-1.8383	-130.2333154
-2.2957	0.4682	-1.7194	-130.2004957
0.3072	2.9003	2.4461	-130.2371046
2.5068	-2.363	-1.2815	-130.233008
2.5794	0.7782	2.1129	-130.2478384
-0.3483	2.4157	2.2173	-130.2487733
0.2644	1.6642	-1.1264	-130.2722662
1.684	2.4623	-2.9767	-130.2384758
-1.7547	1.7864	0.258	-130.249542

(9) 72 Tests Used to Determine the Coupling with all Three Modes (SCS-MP2)

q1	q2	q3	SCS-MP2 energy
1	1	1	-130.2655944
1	1	-1	-130.2661746
1	-1	1	-130.264963
1	-1	-1	-130.2641873
-1	1	1	-130.2647279
-1	1	-1	-130.2616464
-1	-1	1	-130.2605915
-1	-1	-1	-130.2632735
2	2	2	-130.2393123
2	2	-2	-130.2393309
2	-2	2	-130.2287771
2	-2	-2	-130.2295708
-2	2	2	-130.234547
-2	2	-2	-130.2006
-2	-2	2	-130.1930766
-2	-2	-2	-130.224956
3	3	3	-130.2127633
3	3	-3	-130.2045384
3	-3	3	-130.1645013
3	-3	-3	-130.1859278
-3	3	3	-130.2003377
-3	3	-3	-130.0594887
-3	-3	3	-130.0392787
-3	-3	-3	-130.1773964
1.5	1.5	3	-130.2301738
1.5	3	1.5	-130.2339606
3	1.5	1.5	-130.2389714
-1.5	1.5	3	-130.2276085
-1.5	3	1.5	-130.2381219
-3	1.5	1.5	-130.1842649
1.5	-1.5	3	-130.2116211
1.5	-3	1.5	-130.2189468
3	-1.5	1.5	-130.2355489
1.5	1.5	-3	-130.2407402
1.5	3	-1.5	-130.2368932
3	1.5	-1.5	-130.2317052
-1.5	-1.5	-3	-130.2344805
-1.5	-3	-1.5	-130.2245644
-3	-1.5	-1.5	-130.1568447

1.5	-1.5	-3	-130.227731
1.5	-3	-1.5	-130.2227807
3	-1.5	-1.5	-130.228813
-1.5	1.5	-3	-130.2229292
-1.5	3	-1.5	-130.2265245
-3	1.5	-1.5	-130.1034105
-1.5	-1.5	3	-130.193732
-1.5	-3	1.5	-130.2009761
-3	-1.5	1.5	-130.1238455
3	3	1.5	-130.2389714
3	1.5	3	-130.2222387
1.5	3	3	-130.2172968
-3	3	1.5	-130.2044752
-3	1.5	3	-130.1898955
-1.5	3	3	-130.2164337
3	-3	1.5	-130.2094621
3	-1.5	3	-130.2023779
1.5	-3	3	-130.1696044
3	3	-1.5	-130.2161254
3	1.5	-3	-130.2163888
1.5	3	-3	-130.2278104
-3	-3	-1.5	-130.1699923
-3	-1.5	-3	-130.1722404
-1.5	-3	-3	-130.2116712
3	-3	-1.5	-130.2082664
3	-1.5	-3	-130.2068918
1.5	-3	-3	-130.2013804
-3	3	-1.5	-130.1196555
-3	1.5	-3	-130.0775434
-1.5	3	-3	-130.206304
-3	-3	1.5	-130.104255
-3	-1.5	3	-130.0983147
-1.5	-3	3	-130.1424748

(10) 100 Random Tests Used to Determine the Accuracy of the Potential Energy Formula (SCS-MP2)

q1	q2	q3	SCS-MP2
-2.1283	0.1113	-0.5779	-130.2180947
2.0624	-0.3172	-2.9445	-130.2318684
-2.8227	0.4726	-0.9044	-130.144039
1.9352	-1.7399	-0.2705	-130.2500648
-0.7053	2.6567	2.2377	-130.2383803
1.6488	2.4748	2.9988	-130.2224646
-1.9461	-1.8251	2.1442	-130.1961445
0.4713	0.3752	1.6829	-130.2648389
2.9102	-0.8697	-1.65	-130.2331762
-1.8653	2.0112	-0.5657	-130.2292562
-2.1723	0.238	0.115	-130.2192267
1.7236	-0.034	-0.9979	-130.2598727
2.5922	-0.3178	-0.6164	-130.2496826
2.3863	-1.7612	2.732	-130.2106466
-0.0106	-2.2783	1.6468	-130.2392865
0.9178	-1.5166	-1.7203	-130.2526212
2.3498	0.8248	0.0705	-130.2538622
-2.223	-1.2568	0.5728	-130.2108262
1.0076	1.0876	-1.5485	-130.2622501
2.7023	0.201	-1.2005	-130.2439681
0.3625	-2.1509	-1.2765	-130.2518317
-1.8643	-0.3467	0.225	-130.2377909
-1.8541	0.1074	0.9823	-130.2396419
-2.1211	-1.728	1.2159	-130.2064366
0.3201	-1.8564	-0.788	-130.2606736
0.8615	-1.5161	-1.0233	-130.2599976
-0.8105	0.7916	-1.6069	-130.2622889
2.7372	0.3054	2.2411	-130.2386825
-1.6806	1.0276	1.7847	-130.2451131
2.7463	0.8563	1.148	-130.2474594
-1.0885	1.6203	0.6497	-130.2609011
1.591	-0.9231	-0.3046	-130.2620462
1.121	1.4987	2.805	-130.2362443
1.1673	-1.6078	-0.2575	-130.2601784
-0.2152	2.3684	0.0389	-130.2600813
0.1251	-2.9888	-0.0832	-130.2394093
-2.1897	0.9743	-2.6768	-130.1891444
1.7136	1.9923	1.0515	-130.2491873

2.2915	1.1731	-1.0572	-130.2480042
-1.253	0.2094	-0.7456	-130.2597799
2.1863	2.0478	-0.9501	-130.2499637
2.1831	-0.3372	1.2235	-130.2549905
-1.214	0.4006	-1.3692	-130.2564551
0.0149	0.3613	0.732	-130.2752866
-1.821	-1.1729	0.9284	-130.2328155
-2.9745	-0.7801	-1.1056	-130.1408132
-2.5388	-0.4023	0.485	-130.1887
1.7061	2.804	-1.4376	-130.2374339
-2.5609	-2.9172	-1.4666	-130.1940566
2.4336	0.367	-0.6609	-130.2516976
1.7394	-1.9264	-0.0272	-130.2504043
-2.0188	1.5978	0.9433	-130.2361245
1.3481	2.4071	0.2298	-130.2500168
1.7938	-1.7645	0.0905	-130.2522186
-1.5241	-2.556	-2.5777	-130.2247714
1.7548	1.2641	0.3654	-130.25841
2.7549	-1.4399	1.0695	-130.2425767
2.9133	0.5796	-0.7	-130.2438177
-2.186	-0.6571	0.2265	-130.2170361
2.4162	-1.3244	-0.05	-130.2494248
2.7041	-2.9578	-1.8289	-130.2077855
1.8279	1.3131	-0.8083	-130.2549941
-2.5576	2.8775	0.8958	-130.2153424
0.2904	-2.4521	2.4842	-130.2112745
1.9557	-2.4383	-1.4335	-130.2301369
0.2221	-1.5671	1.4058	-130.2574815
-1.4595	1.3006	2.5126	-130.239363
2.0631	-0.5012	-0.0118	-130.2590785
1.4015	-1.4544	-0.6144	-130.2579882
2.9463	2.9483	2.2281	-130.2203879
0.7679	1.8624	2.6035	-130.2390899
0.2715	0.754	-1.0151	-130.2724911
1.6275	1.813	-2.7167	-130.2400825
-0.7127	-1.3464	-1.3287	-130.2624662
-1.7436	-1.419	2.7849	-130.1954501
-0.161	2.0687	-0.1972	-130.2640437
0.2326	-1.9961	1.7045	-130.2445242
1.118	0.2782	-2.6791	-130.2512803
-0.348	-2.8163	-0.7959	-130.242511

-0.2097	-2.8362	-2.7155	-130.2224867
0.9147	2.4579	-0.9861	-130.2527346
-0.8513	-1.1638	2.8535	-130.2206837
0.96	-0.1123	0.9487	-130.2697201
0.3466	2.9473	-1.3285	-130.2484796
1.7415	-2.958	1.3239	-130.2216888
1.5038	0.5229	-0.8699	-130.2630772
2.9823	-0.8864	0.5576	-130.2461046
-1.0416	-0.2639	1.9895	-130.2521332
-0.054	0.7516	-2.825	-130.2574948
-2.5939	1.3217	2.5019	-130.209103
1.1616	-2.2463	-0.4147	-130.2498096
-1.7359	-2.6376	-1.8383	-130.2253641
-2.2957	0.4682	-1.7194	-130.1940286
0.3072	2.9003	2.4461	-130.230628
2.5068	-2.363	-1.2815	-130.2267618
2.5794	0.7782	2.1129	-130.2413543
-0.3483	2.4157	2.2173	-130.2422755
0.2644	1.6642	-1.1264	-130.2656134
1.684	2.4623	-2.9767	-130.2314682
-1.7547	1.7864	0.258	-130.2423881

(11) ACCT vs ACCQ Comparison (x-dipole) (E(MP2))

NO Length	HN Length	HNO Bond Angle	ACCQ x-dipole	ACCT x-dipole	x-dipole difference
1.0917	1.0506	107.64	-0.198	-0.194092857	-0.003907143
1.1517	1.0506	107.64	-0.277321429	-0.273732143	-0.003589286
1.2217	1.0506	107.64	-0.342828571	-0.339410714	-0.003417857
1.3517	1.0506	107.64	-0.382692857	-0.379185714	-0.003507143
1.4917	1.0506	107.64	-0.183167857	-0.179903571	-0.003264286
1.2217	0.8706	107.64	-0.378203571	-0.375792857	-0.002410714
1.2217	0.9606	107.64	-0.366964286	-0.364028571	-0.002935714
1.2217	1.1806	107.64	-0.284778571	-0.280525	-0.004253571
1.2217	1.3206	107.64	-0.195292857	-0.18975	-0.005542857
1.2217	1.0506	85.14	-0.19555	-0.193542857	-0.002007143
1.2217	1.0506	97.64	-0.280939286	-0.278096429	-0.002842857
1.2217	1.0506	120.14	-0.420321429	-0.41615	-0.004171429
1.2217	1.0506	132.64	-0.502864286	-0.498039286	-0.004825

(12) ACCT vs. ACCQ Comparison (y-dipole) (E(MP2))

NO Length	HN Length	HNO Bond Angle	ACCQ y-dipole	ACCT y-dipole	y-dipole difference
1.0917	1.0506	107.64	0.493732143	0.490846429	0.002885714
1.1517	1.0506	107.64	0.541296429	0.538953571	0.002342857
1.2217	1.0506	107.64	0.578292857	0.576396429	0.001896429
1.3517	1.0506	107.64	0.612478571	0.611071429	0.001407143
1.4917	1.0506	107.64	0.615717857	0.614464286	0.001253571
1.2217	0.8706	107.64	0.617496429	0.617353571	0.000142857
1.2217	0.9606	107.64	0.606553571	0.605592857	0.000960714
1.2217	1.1806	107.64	0.5033	0.499667857	0.003632143
1.2217	1.3206	107.64	0.379371429	0.373339286	0.006032143
1.2217	1.0506	85.14	0.566403571	0.563925	0.002478571
1.2217	1.0506	97.64	0.577632143	0.575435714	0.002196429
1.2217	1.0506	120.14	0.5653	0.563810714	0.001489286
1.2217	1.0506	132.64	0.532325	0.531235714	0.001089286

References:

- ¹ B.L. Ulich, J.M. Hollis, and L.E. Snyder. *Astrophysical Journal Letters*, volume 217, p. L105 (1977)
- ² D.C. Gregg. *Principles of Chemistry*. (Allyn and Bacon, Inc., Boston, 1968).
- ³ P. Atkins and J. de Paula. *Physical Chemistry*. (W. H. Freeman and Company, New York 2014).
- ⁴ M.W. Schmidt, K.K. Baldridge, J.A. Boatz, et al., *J. Comput. Chem.* vol. 14, pp. 1347-1363 (1993).
- ⁵ U. Bozkaya, J.M. Turney, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* vol. 136, article 164303 (2012).
- ⁶ T.H. Dunning, Jr., *J. Chem. Phys.* vol. 90, p. 1007 (1989)
- ⁷ R.A. Kendall, T.H. Dunning, Jr., and R.J. Harrison, *J. Chem. Phys.* vol. 96, p. 6796 (1992)
- ⁸ Harkiran Dhah, personal communication, 2014.
- ⁹ M.D. Harmony. *Introduction to Molecular Energies and Spectra*. (Holt, Rinehart and Winston, Inc., New York, 1972).
- ¹⁰ T.J. Lee, *J. Chem. Phys.* vol. 99, p. 9783 (1993).
- ¹¹ L.E. Sutton, ed., *Tables of Interatomic Distances and Configuration in Molecules and Ions*, (London: The Chemical Society, 1958.)