

Estimating Energy with the Generalized Many-Body Expansion Method for an Atmospheric Nucleation System

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Abstract

Fragment-based estimation methods are very useful for determining the energy of chemical systems, because it gets increasingly less possible to calculate the actual energy of a system as it increases in size. The many-body expansion method circumvents this by combining sums of energies of smaller fragments of a system into terms which account for the energy of fragments, and the energies of the interactions between fragments. In this project, 2 variations of the many-body expansion method were performed on a $\text{NH}_3(\text{H}_2\text{O})_3$ system undergoing several proton transfer reactions. The 3-body method was able to estimate the energy of the $\text{NH}_3(\text{H}_2\text{O})_3$ system being studied with a mean absolute error of 1.21 kcal/mol. This estimate appeared to follow the same trends as the actual energy of the system. The 2-body method was able to estimate the energy of the system with a mean absolute error of 9.123 kcal/mol and did not appear to follow the same trends as the actual energy. Both the 2-body and 3-body estimates appear to perform worse when atoms are close to being between multiple fragments.

Introduction

One major goal of computational chemistry is to be able to calculate the potential energy of molecular systems. Knowing the energy of a system can allow predictions to be made about the system's reactivity and other chemical properties. Unfortunately for the exact energy of a system to be calculated, the time-dependent Schrodinger equation must be solved for the system. Since this quantum-mechanical equation must incorporate the interactions between each nucleus and each electron in the system, this quickly becomes impossible to solve as a system's size increases. This is the purpose of molecular fragmentation methods of estimation. The basic idea of fragment-based methods is that the total energy of a system can be determined by summing the energies of smaller fragments in the system. The Schrodinger equation for these fragments has fewer interactions to account for, and therefore it will be possible to solve for smaller fragments where it would be impossible to solve for an entire system.¹

Molecular fragmentation methods can be divided into three general categories.² The first category are the divide-and-conquer methods. These methods sum the electron density of subsystems to estimate the electron density of the overall system.³ The second category are the transferrable approaches. One example of this is the systematic molecular fragmentation method. This method has fragments which overlap, with some atoms being included in more than one fragment. This is the way that this method accounts for the interactions between fragments.⁴ The last category of fragmentation methods are the many-body methods. These methods utilize "many-body expansion," which include fragments made up of several smaller fragments.⁵ These fragments are incorporated in sums which account for the interactions between the smaller fragments. The methods used in this project are the 2-body and 3-body expansion methods. The 2-body method incorporates fragments made up of 2 smaller fragments while the 3-body method incorporates these as well as fragments made up of 3 smaller fragments.

The methods were tested on an $\text{NH}_3(\text{H}_2\text{O})_3$ system involved in atmospheric nucleation. A geometry optimization was performed on this system by Angie Hartman using GAMESS.⁶ In this optimization the positions of a nitrogen, a hydrogen, and an oxygen atom were all held constant. A minimum-energy geometry for the system was unable to be determined by GAMESS, but several proton transfer reactions occurred during the geometry optimization. Fifty steps of this optimization were performed by GAMESS to attempt to find an optimum geometry for this system.

The objective of this project was to determine how 2-body and 3-body estimates for the energy of this $\text{NH}_3(\text{H}_2\text{O})_3$ system at various points in the geometry optimization compared to the total energy of the system. This is a potentially challenging system to use a fragment-based method with due to the definition of each fragment changing as the proton transfers occurred. By looking for trends in how the many-body estimates differ from the actual energy, weaknesses of the methods can be determined, and new methods can be developed. If the energy of the $\text{NH}_3(\text{H}_2\text{O})_3$ system can be estimated accurately enough, larger atmospheric systems could possibly be studied by breaking them down into fragments which can be studied with the many-body expansion method.

Methods

The GAMESS output file from an attempted geometry optimization of a system including an NH_3 molecule and three H_2O molecules was used to obtain energy values, the coordinates of atoms, and the distances between each atom at various steps in several proton transfer reactions. Figure 1 shows four steps showing the overall proton transfer reactions.

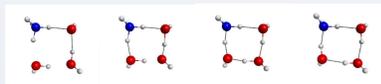


Figure 1. Visualizations of four steps in the proton transfer reactions. wxMacMolPlt⁷ was used to view the GAMESS output file as a visual model.

For each step that was tested, the value listed in the output file as FINAL R-B3LYP ENERGY was recorded as the GAMESS total energy for that step. The list of atom coordinates for each step were used in the GAMESS calculations of each of the fragments needed to estimate the total energy using the 2-body and 3-body methods. The nitrogen atom was set as the center of fragment A for each step, while the three oxygen atoms were set as the centers of fragments B, C, and D. These fragments also included whichever hydrogen atoms were closer to the center of that fragment than to the center of any other fragment at that step.

Fragments A, B, C, and D are the monomer fragments used in the many-body estimate calculations. The dimer fragments AB, AC, AD, BC, BD, and CD are each made up of all the atoms in the monomer fragments that make up that dimer (AB includes all the atoms in A and B). The trimer fragments ABC, ABD, ACD, and BCD are each made up of all the atoms in the monomer fragments that make up that trimer. GAMESS molecular energy calculations were performed on the atoms included in these fourteen fragments at nineteen steps in the reaction. The B3LYP^{8,9,10} method and the 6-311G^{11,12} basis set were used.

The energy of the 2-body estimate was calculated by summing the terms V_1 and V_2 . V_1 is equal to the sum of all the monomer fragment energies and V_2 is equal to the sum of six terms accounting for the energy of the interaction between monomers within the dimer fragments. E_i represents the energy of the fragment i .

$$V_1 = E_A + E_B + E_C + E_D$$

$$V_2 = (E_{AB} - E_A - E_B) + (E_{AC} - E_A - E_C) + (E_{AD} - E_A - E_D) + (E_{BC} - E_B - E_C) + (E_{BD} - E_B - E_D) + (E_{CD} - E_C - E_D)$$

The full calculation of the 2-body estimate is:

$$E_{2\text{-body}} = (E_A + E_B + E_C + E_D) + (E_{AB} - E_A - E_B) + (E_{AC} - E_A - E_C) + (E_{AD} - E_A - E_D) + (E_{BC} - E_B - E_C) + (E_{BD} - E_B - E_D) + (E_{CD} - E_C - E_D)$$

The energy of the 3-body estimate was calculated by summing the terms V_1 , V_2 , and V_3 . V_3 is equal to the sum of four terms accounting to the interaction between monomers within the trimer fragments.

$$V_3 = (E_{ABC} - (E_{AB} - E_A - E_B) - (E_{AC} - E_A - E_C) - (E_{BC} - E_B - E_C)) + (E_{ABD} - (E_{AB} - E_A - E_B) - (E_{AD} - E_A - E_D) - (E_{BD} - E_B - E_D)) + (E_{ACD} - (E_{AC} - E_A - E_C) - (E_{AD} - E_A - E_D) - (E_{CD} - E_C - E_D)) + (E_{BCD} - (E_{BC} - E_B - E_C) - (E_{BD} - E_B - E_D) - (E_{CD} - E_C - E_D))$$

The full calculation of the 3-body estimate is:

$$E_{3\text{-body}} = (E_A + E_B + E_C + E_D) + ((E_{AB} - E_A - E_B) + (E_{AC} - E_A - E_C) + (E_{AD} - E_A - E_D) + (E_{BC} - E_B - E_C) + (E_{BD} - E_B - E_D) + (E_{CD} - E_C - E_D)) + (E_{ABC} - (E_{AB} - E_A - E_B) - (E_{AC} - E_A - E_C) - (E_{BC} - E_B - E_C)) + (E_{ABD} - (E_{AB} - E_A - E_B) - (E_{AD} - E_A - E_D) - (E_{BD} - E_B - E_D)) + (E_{ACD} - (E_{AC} - E_A - E_C) - (E_{AD} - E_A - E_D) - (E_{CD} - E_C - E_D)) + (E_{BCD} - (E_{BC} - E_B - E_C) - (E_{BD} - E_B - E_D) - (E_{CD} - E_C - E_D))$$

Calculations of 2-body and 3 body estimates were performed using Microsoft Excel.

Results

The GAMESS total energy value at step 0 was subtracted from each energy value. The relative energy data calculated by GAMESS and estimated with the 2-body and 3-body methods were plotted on a graph (Figure 3).

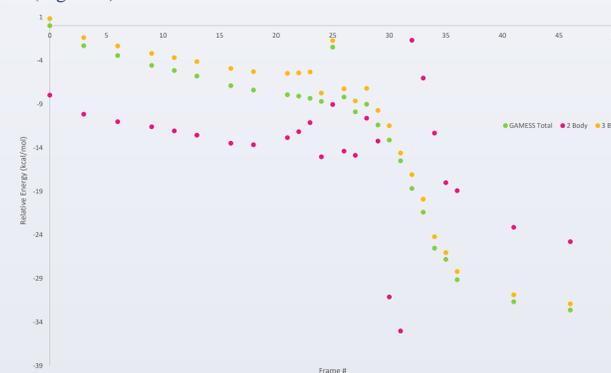


Figure 2. Relative energy values at nineteen points in the proton transfer. Total energy determined by GAMESS is shown as well as energy values estimated using the 2-body and 3-body methods.

For each of the steps tested, the GAMESS total energy was subtracted from the total energy estimated by the 3-body method. The difference between the values was graphed (Figure 4).

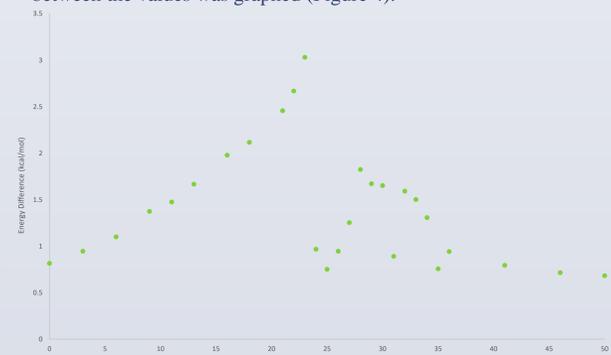


Figure 3. Differences between the GAMESS total energy and the energy estimated by the 3-body method at nineteen points in the proton transfer reactions.

For each of the steps tested, the GAMESS total energy was subtracted from the total energy estimated by the 2-body method. The difference between the values was graphed (Figure 4).



Figure 4. Differences between the GAMESS total energy and the energy estimated by the 2-body method at nineteen points in the proton transfer reactions.

The difference data in Figure 3 was used to determine the minimum, maximum, and mean absolute error for the 3-body method (Table 1).

Table 1. Minimum, maximum, and mean differences between the 3-body estimate and the GAMESS total energy.

	Energy Difference (kcal/mol)	Step
Minimum	0.682	50
Maximum	3.031	23
Mean	1.402	-

The difference data in Figure 4 was used to determine the minimum, maximum, and mean absolute error for the 2-body method (Table 2).

Table 2. Minimum, maximum, and mean differences between the 2-body estimate and the GAMESS total energy.

	Energy Difference (kcal/mol)	Step
Minimum	-1.605	28
Maximum	-19.523	31
Mean	9.126	-

Conclusions

Due to its low mean absolute error of 1.21 kcal/mol and clear matching of the trend of the actual energy, the 3-body method appears to be an accurate method of estimating the energy of the system being studied. Of the nineteen steps in the proton transfer reactions that were tested, the greatest variance of this estimate from the actual energy was 2.46 kcal/mol. When only using the 2-body method, the estimates are not nearly as good, with a mean absolute error of 9.13 kcal/mol. The 2-body estimates did not appear to follow the same trend as the actual energy values. The 2-body method appeared to perform the worst when it was ambiguous which fragment an atom belonged to. It appears that the worst performance of the 3-body method occurred in similar circumstances.

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