

Geometries of Weakly Interacting Clusters Using Electrostatics and Ab initio Methods

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*A dissertation submitted for the partial fulfilment of
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Certificate of Examination

This is to certify that the dissertation titled “**Geometries of Weakly Interacting Clusters Using Electrostatics and Ab initio Methods**” submitted by **Mr. Geetananda Thingujam** (Reg. No. MS10022) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Date: 22 April 2016

DECLARATION

The work presented in this dissertation has been carried out by me under the guidance of Dr. P. Balanarayan at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. P. Balanarayan

(Supervisor)

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Notations

cc-pVNZ basis set: These basis sets are designed such that they can converge systematically to the complete basis set limit. Here, N=D,T,Q,5,6,... etc. “cc-p” stands for correlation-consistent polarised. “V” stands for valence.

cc-pVDZ -Double Zeta

cc-pVTZ -Triple Zeta

aug-cc-pVDZ: augmented version of cc-PVDZ with added diffuse functions

aug-cc-pVTZ: augmented version of cc-PVTZ with added diffuse functions

SCF: Self Consistent Field

MO: Molecular Orbital

HF: Hartree-Fock theory

DFT: Density Functional Theory

ABSTRACT

The water dimer consists of two water molecules loosely bound by a hydrogen bond. The hydrogen bond in water dimer has received the most theoretical attention. The water dimer is small in size and obtaining experimental results for this species is difficult. So, it is an ideal candidate to be a model system for studying hydrogen bonding in water. In first part of this project, the water dimer, $(\text{H}_2\text{O})_2$, has been used as a model for optimization of the structure of dimers using electrostatics. A hydrogen bond network is also found in ammonia clusters and it plays a key role in understanding the properties of species which are embedded in ammonia. The structures of neutral ammonia clusters dictate this network. In the second part, we concentrated on hydrogen bonded neutral clusters of ammonia, $(\text{NH}_3)_n$ ($n = 2-6$) and these clusters have been theoretically investigated employing the basis set aug-cc-pvdz at the Hartree-Fock (HF) level as well as with M06L level of theory.

Chapter 1

Introduction

1.1. General

Water is a universal solvent. It is essential to life on Earth. Water has many anomalous properties, including unusually high boiling point, low coefficient of thermal expansion, non-monotonic compressibility with temperature and the fact that water contracts upon melting (density maximum is at 277 K) and thus, it has attracted a lot of interest although it is very familiar.

For the first part of this project, the water dimer has been used as a model for optimization of the structure of dimers. The two water molecules in water dimer are loosely bound by a hydrogen bond. A hydrogen bond actually consists of the interaction between the covalent A-H bond of one molecule and the lone electron pair of the B atom of another molecule, presuming both A and B are electronegative atoms like O, N, or F. It is an ostensibly simple interaction and one of the most important in all of chemistry, as well as one of the most intriguing. The hydrogen bond plays a critical role in a wide range of chemical and biological phenomena. Moreover, it is important for describing the behaviour of many synthetic materials.

The hydrogen bond found between two water molecules is the prototypical hydrogen bond and has received the most theoretical attention. The water dimer is very small in size and it is difficult to obtain experimental results for this species. Hence, it is an ideal candidate to be a model system for studying hydrogen bonding in water and it has been the target of so many theoretical and later experimental studies.

Moreover, hydrogen bonding can also be observed in ammonia clusters. A hydrogen bond network in ammonia is dictated by the structures of neutral clusters and it plays a key role in understanding the properties of species which are embedded in ammonia.

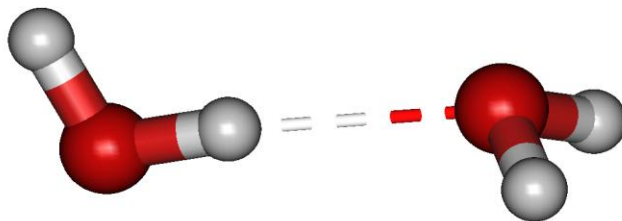


Fig. 1.1: Hydrogen bonding in Water dimer.

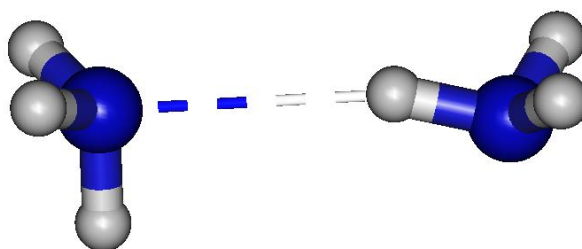


Fig. 1.2: Hydrogen bonding in ammonia dimer.

It is known that structures of small ammonia clusters have been investigated both theoretically and experimentally¹⁻¹⁷. In the second part of this project, we revised structures and interaction energies of hydrogen bonded neutral clusters of ammonia, $(\text{NH}_3)_n$ ($n = 2-6$), employing the basis set aug-cc-pvdz at the Hartree-Fock (HF) and M06L levels of theory to compare their performances in the description of the structures.

1.2. Classical Electrostatics

Consider an electric potential V_E at a point \mathbf{r} in a static electric field \mathbf{E} , given by the line integral

$$V_E = -\int_C \mathbf{E} \cdot d\mathbf{l} \quad (1.21)$$

where C is an arbitrary path from \mathbf{r} to the point with zero potential. When $\nabla \times \mathbf{E}$ is zero, the line integral depends only on its end points, not on the specific path C chosen and the electric field is conservative. It is determined by gradient of the potential:

$$\mathbf{E} = -\nabla V_E \quad (1.22)$$

Then, by Gauss's law, the potential satisfies Poisson's equation:

$$\nabla \cdot \mathbf{E} = \nabla \cdot (-\nabla V_E) = -\nabla^2 V_E = \rho/\epsilon_0 \quad (1.23)$$

,where $\nabla \cdot$ denotes the divergence and ρ is the total charge density which includes bound charge.

Potential energy and the concept of electric potential are closely linked. An electric potential energy U_E associated with a test charge q is given by

$$U_E = qV \quad (1.24)$$

The electric potential at a distance r (relative to the potential at infinity), generated by a point charge Q is

$$V_E = (1/(4\pi \epsilon_0)) \times Q/r \quad (1.25)$$

where ϵ_0 is the electric constant . This is known as the Coulomb potential.

In the case of a system of point charges, the sum of the point charges' individual electric potentials is equal to the electric potential due to the system of point charges. Owing to this fact, calculations have been simplified significantly as addition of the potential (scalar) fields is much easier than addition of the electric (vector) fields.

1.3. Molecular Electrostatic Potential

If the atoms in a dimer are considered as a set of point charges $\{q_a\}$ placed at $\{\mathbf{r}_a\}$, the interaction energy associated with this assembly of charges is given by

$$U = \frac{1}{2} \sum_{i \neq j} \left\{ \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\} \quad (1.31)$$

This can also be written as

$$U = \frac{1}{2} \sum_j q_j \sum_{i \neq j} \left\{ \frac{q_i}{4\pi\epsilon_0 r_{ij}} \right\} \quad (1.32)$$

In order to avoid double counting of the electrostatic interactions, the inclusion of the factor 1/2 is necessary in Eqs. 1.31 and 1.32. Moreover, the term in the curly brackets in Eq.1.32 is the electrostatic potential V_j generated at \mathbf{r}_j by point charges $\{q_i\}$ located at sites $\{r_i\}$. Thus, it can also be written as

$$U = \frac{1}{2} \sum_j q_j V_j \quad (1.33)$$

1.4. Description of the code

The code for optimizing dimers was written in c++ programming language. First, a grid was constructed and one of the molecules is placed fixed at the centre of the grid and the other at the grid points. Then, the latter is rotated at various angles using Euler Angles Rotation Matrix. The interaction energies for various angles are calculated and the energies are sorted. The geometry with the lowest energy is the most stable geometry.

1.4.1. Grid construction

A grid of length ' l ' units, breadth ' b ' units and height ' h ' units is constructed in such a way that the number of points along the length, the breadth and the height are m , n & o respectively and the origin is at the centre of the grid. The origin need not be a grid point.

1.4.2. Rotation of the molecule

One of the molecules is placed such that the centre of mass of the molecule is at the origin of the grid and the other so that its centre of mass is at the grid points. The latter is rotated using Euler angles rotation matrix.

1.4.2.1. Euler Angles

Euler angles are very useful means of representing the spatial orientation of any reference frame, which can either be a coordinate system or a basis, as a composition of three elemental rotations starting from a known standard orientation, represented by another frame, which is sometimes referred to as the *original* or *fixed* reference frame or standard basis. The reference orientation can be considered as an initial orientation from which the frame is virtually rotated to reach its actual orientation. In a coordinate system, the axes of the original frame are denoted as x,y,z and the axes of the rotated frame are denoted as X,Y,Z . The rotated coordinate system is considered to be rigidly attached to a rigid body and is called a "local" coordinate system. It represents both the position and the orientation of the body actually.

The geometrical definition is based on the axes of the original reference frame, the axes of rotated reference frames and an additional axis called the line of nodes. The line of nodes (N) can be defined as the intersection of the coordinate planes of xy and XY . We can also say that it is a line passing through the common origin of both frames, and perpendicular to the zZ plane, on which both z and Z lie. The three Euler angles φ , θ and ψ are defined as the angle between the x axis and the N axis, the angle between the z axis and the Z axis the angle between the N axis and the X axis respectively. This definition

implies that ϕ , θ and ψ represent rotations around the z axis, the N axis and the Z axis respectively.

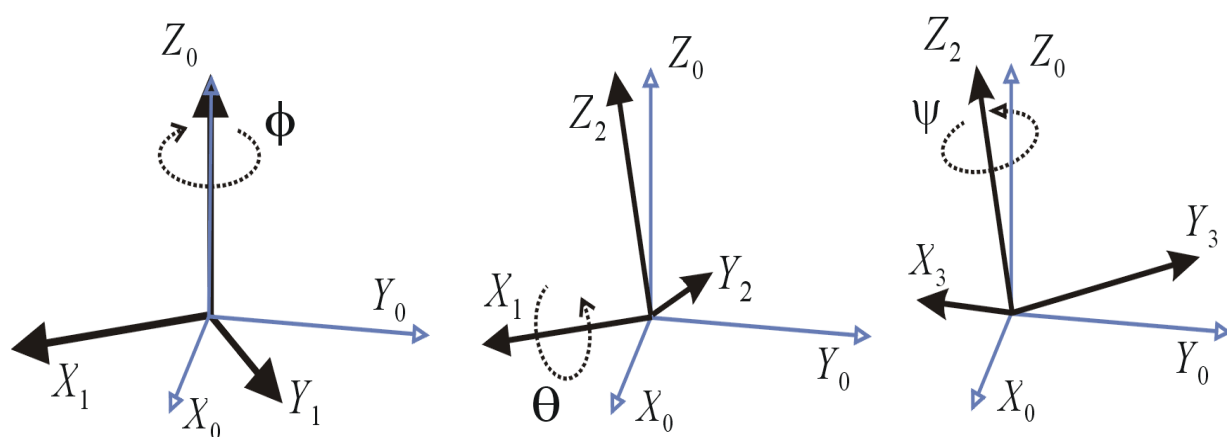


Fig. 1.3: Euler Angles

The Rotation matrix R is

$$R = \begin{pmatrix} \cos\psi \cos\phi - \cos\theta \sin\phi \sin\psi & \cos\psi \sin\phi + \cos\theta \cos\phi \sin\psi & \sin\psi \sin\theta \\ -\sin\psi \cos\phi - \cos\theta \sin\phi \cos\psi & -\sin\psi \sin\phi + \cos\theta \cos\phi \cos\psi & \cos\psi \sin\theta \\ \sin\theta \sin\phi & -\sin\theta \cos\phi & \cos\theta \end{pmatrix}$$

And the new co-ordinates of the rotated molecule is given by

$$\mathbf{A} = \mathbf{R} \times \mathbf{X} \text{ where } \mathbf{R} = \text{Rotation matrix}$$

$$\mathbf{X} = \text{Original co-ordinate matrix}$$

1.4.3. Interaction Energy

After the rotation of the second molecule, the interaction energy associated with the dimer is calculated.

The interaction energy between the molecules is given by

$$U = \frac{1}{2} \sum_{i \neq j} \left\{ \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\} \quad (1.41)$$

,where q_i and q_j are the charges of the i^{th} and the j^{th} atom and r_{ij} is the distance between the two atoms.

After calculating the energies at various angles of rotation, the energies are sorted either in ascending order or descending order. The geometry with minimum energy is the *most stable geometry* of all the geometries.

1.5. Computational Methods

For the ammonia clusters, computational methods have been implemented for revision of structures and interaction energies of hydrogen bonded neutral clusters of ammonia, $(\text{NH}_3)_n$ ($n = 2-6$), and the structures have been studied with the basis set aug-cc-pvdz at the Hartree-Fock (HF) level as well as with M06L level of theory employing the Gaussian 09²⁴ suite of programs.

1.5.1. Geometry Optimization

Geometry optimization (or energy minimization) is the process of minimizing molecular potential energy E . For finding the local minimum of a function which depends on several variables, there are a lot of algorithms. A local minimum of E in the neighbourhood of the initial geometry provided can be found using these algorithms. Geometry optimizations are needed to be performed carefully. All the possible conformations of a molecule must be optimized carefully if the molecule has more than one conformation. This helps in locating the structure with global minimum.

1.5.2. The Computational Part

For optimization of the geometry of a molecule, we usually start with a possible guess structure for the equilibrium geometry. In my work, this guess geometry is generated using Gabedit software. Once the guess geometry is provided, we look for the minimum nearest geometry in its neighbourhood. For solving the electronic Schrödinger equation to get E and its gradient at that guess geometry, a basis set is chosen and SCF MO or some other method is performed. Using the calculated E and its gradient ∇E , the geometry optimization program then creates a new set of values for the $3N-6$ coordinates. This new set of values is more likely to be closer to the minimum geometry structure and the E and its gradient ∇E at the new set of values are calculated by the program. Again, another improved set is generated and SCF calculation is repeated using the calculated values of E and its gradient. This process is repeated until a value of ∇E which differs negligibly from zero is obtained. A value of ∇E which differs negligibly from zero is an indication that a minimum geometry may have been found. The threshold potential is decided beforehand and it can be varied.

1.5.3. Hartree-Fock Theory

In Hartree-Fock theory, the wave function Ψ_0 is defined as a product of one electron wave functions which are referred to as molecular spin orbitals. The wave function Ψ_0 is antisymmetric with respect to electron coordinate interchange. This is called a Slater determinant form of the wave function. The molecular spin orbitals can be expanded in terms of linear combination of atom centred basis functions. In this method, due to all other electrons, each electron moves in the average field. The molecular orbitals that we obtain from this calculation are the eigen functions of the Fock operator and its expansion coefficients are determined in a self consistent way. However, due to motions of different electrons, taking care of the correlation is not possible in HF theory. The correlation due to motions of opposite spin electrons is completely neglected in HF theory in spite of the fact that the inherent antisymmetry property of this type of wave function takes care of the correlation of electron of the same spin partially and thus, HF theory doesn't account for a certain component of energy which is important to understand bonding and geometry even if it is able to account for the most of the total energy of a molecule. This

can be solved by the electron correlation techniques. The electron correlation energy has been defined as the difference between the HF energy and the exact nonrelativistic energy of a system. For the accurate understanding of molecular geometries and energies, electron correlation energy is necessary and should be taken into account.

1.5.4. M06L Theory

M06L level of theory is a DFT belongs to the M06 suite of functionals which are M06-L, M06, M06-2X and M06-HF, with a different amount of exact exchange on each one. M06-L is fully local without HF exchange while M06, M06-2X and M06-HF has 27%, 54% and 100% of HF exchange respectively. They are constructed with empirical fitting of their parameters, but constraining to the uniform electron gas. M06-L is fast and good for transition metals, inorganic and organometallics while M06 is mainly used for main group, organometallics, kinetics and non-covalent bonds. On the other hand M06-2X is used for main group and kinetics whereas M06-HF is for charge transfer TD-DFT and systems where self interaction is pathological.

1.6. Aim of our Study

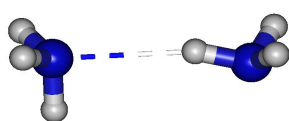
In first part this project, we are trying to optimize the structure of dimers using electrostatics. The water dimer, $(\text{H}_2\text{O})_2$, has been used as a model and we considered writing a program for optimisation of the structures of dimers. In the second part, we concentrated on hydrogen bonded neutral clusters of ammonia, $(\text{NH}_3)_n$ ($n = 2-6$) and have been theoretically investigated employing the basis set aug-cc-pvdz at the Hartree-Fock (HF) level as well as with M06L level of theory.

CHAPTER 2

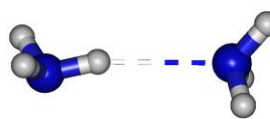
Results and Discussions

The clusters of ammonia, $(\text{NH}_3)_n$ ($n = 2-6$), (along with a search for their corresponding energetically close isomers) were optimized at the HF and M06L levels of theory with the aug-cc-pvdz basis set to compare their performances in the description of the structures.

Fig. 2.1-2.6 shows the optimized geometries of ammonia clusters:



(a) $\text{NH}_3\text{DIMER1}$



(b) $\text{NH}_3\text{DIMER2}$

Fig. 2.1: Two geometries for ammonia dimer, (a) “eclipsed” (b) “staggered”.

Among the two geometries of ammonia dimer, the staggered geometry is more stable than the eclipsed geometry.

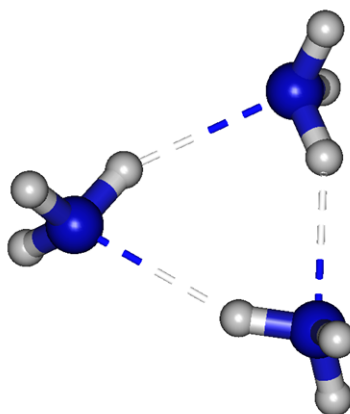
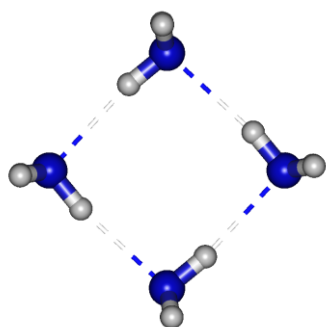
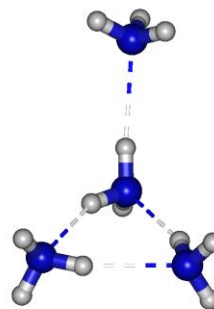


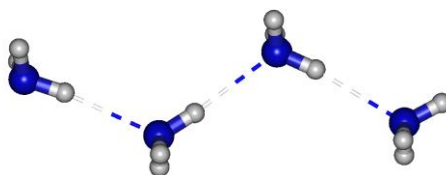
Fig. 2.2: Single geometry for ammonia trimer



(a) NH₃TETRAMER1



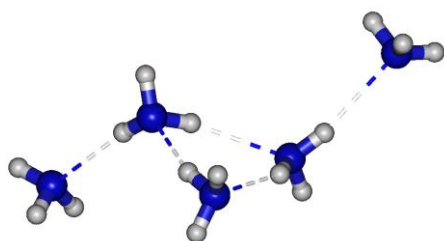
(b) NH₃TETRAMER2



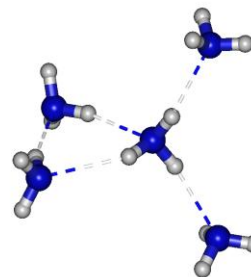
(c) NH₃TETRAMER3

Fig. 2.3: Three structures for ammonia tetramer.

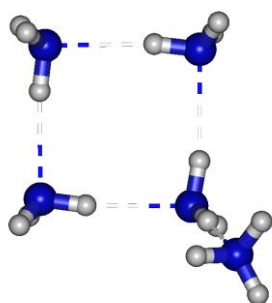
Among these three structures of ammonia tetramer, the first structure is the most stable since there is a full co-operative network of hydrogen bonds.



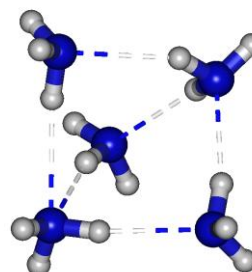
(a) NH₃PENTAMER1



(b) NH₃PENTAMER2



(c) NH₃PENTAMER3



(d) NH₃PENTAMER4

Fig. 2.4: Four structures of ammonia pentamer.

Among these four structures of ammonia pentamer, the fourth structure is found to be the most stable.

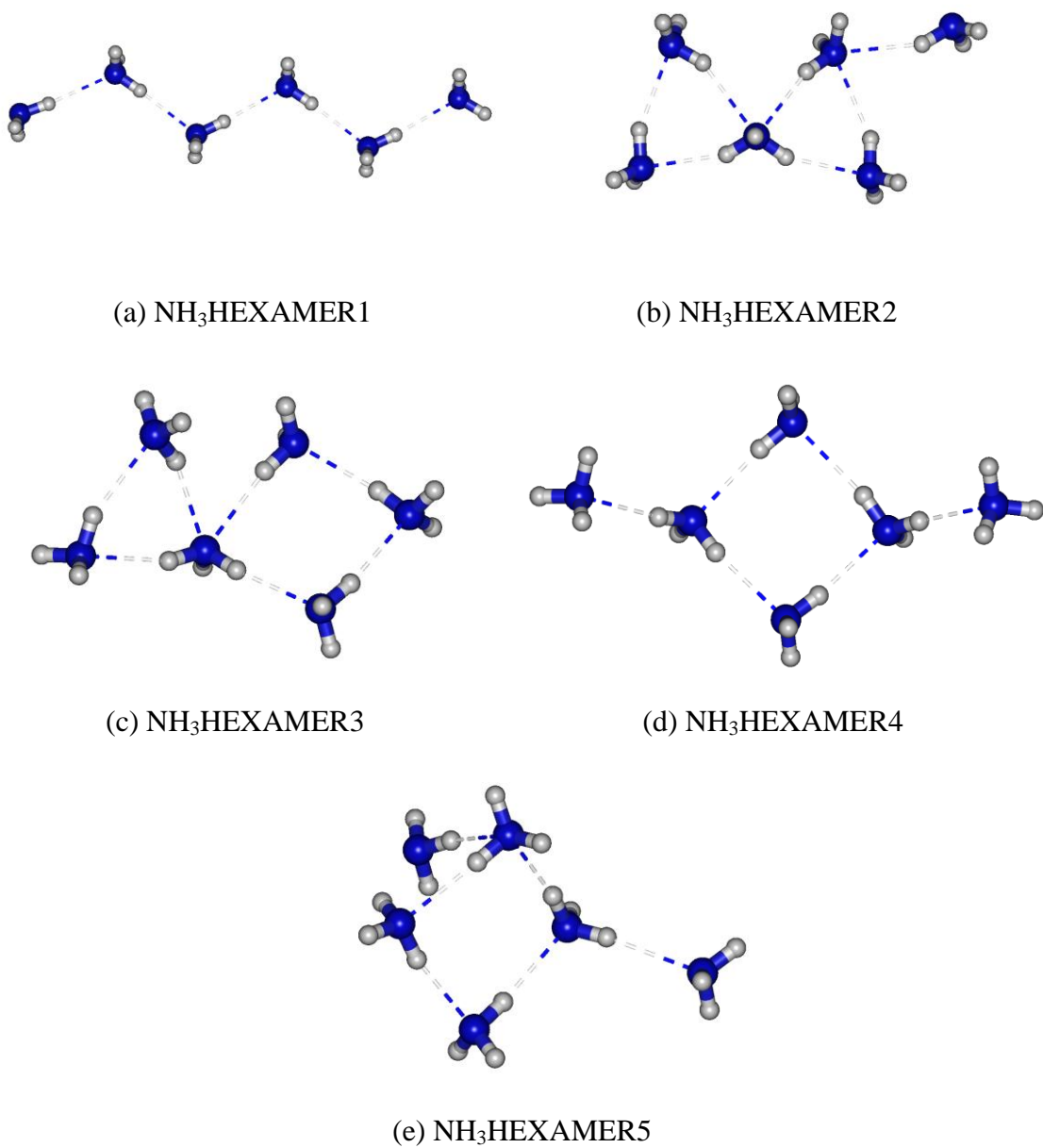


Fig. 2.5: Five structures of ammonia hexamer.

Among these five structures of ammonia pentamer, the third structure is found to be the most stable.

Table 2.1: Interaction Energies in kcal/mol of Ammonia clusters

Cluster	RHF	M06L
NH ₃ DIMER1	-2.12	-2.80
NH ₃ DIMER2	-2.08	-2.76
NH ₃ TRIMER1	-6.94	-10.18
NH ₃ TETRAMER1	-10.88	-15.57
NH ₃ TETRAMER2	-8.62	-12.48
NH ₃ TETRAMER3	-7.06	-9.60
NH ₃ PENTAMER1	-10.11	-14.44
NH ₃ PENTAMER2	-9.71	-13.97
NH ₃ PENTAMER3	-12.38	-17.58
NH ₃ PENTAMER4	-12.72	-20.48
NH ₃ HEXAMER1	-12.41	-17.09
NH ₃ HEXAMER2	-14.10	-21.74
NH ₃ HEXAMER3	-16.10	-24.21
NH ₃ HEXAMER4	-13.73	Not found
NH ₃ HEXAMER5	-14.50	Not found

The energy (in au) values of NH₃ at various levels are: RHF = -56.2056 , M06L = -56.5591

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