國 立 交 通 大 學

應用化學系分子科學碩士班

碩 士 論 文

由耦合簇理論計算建立用於

電荷自洽密度泛函緊束縛法參數化程序的位能函式庫

Constructing A Library of Potential Energy Functions from Coupled Cluster Calculations to Be Used in the SCC-DFTB Parameterization

研 究 生：楊博宇

指導教授：魏恆理　博士

中 華 民 國 一 百 年 八 月

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中文摘要

電荷自洽密度泛函緊束縛法(以下簡稱SCC-DFTB)是量子化學領域中一種強大的半經驗方法，可應用於大尺度化學分子系統的計算。但是SCC-DFTB仍然存在一些應用上的限制，第一個是以目前的SCC-DFTB參數組無法同時得到精確的能量、平衡結構和振動頻率，這是由於目前該方法在參數化程序中使用太少的參考位能面來擬合參數；第二個限制則是來自目前的SCC-DFTB參數組只能應用在少部分特定元素的計算。為了克服這些限制，在參數化的程序中必須使用多樣化的參考位能面來擬合各種元素間不同的鍵結狀態。在我們快速的參數化程序中，大多數高階的精確量子化學方法都因為太過於昂貴而不適用於產生這些參考位能面，因此，我們建構出一種類力場的位能函數，利用四階泰勒近似來展開這些位能函數。藉由精確的耦合簇理論計算，我們的位能函數不僅提供精確的位能面，並且節省了許多計算的時間。我們建構的位能函式庫總共包含了74種常見化學分子的位能函數，這些分子不但包含了週期表中前三週期的元素，並且存在這些元素之間最典型的鍵結狀態。在建構位能函式庫的過程中，我們設計了驗證程序來評估其精確性；在擬合函數的程序中，我們將每個位能函數的均方根誤差值控制在小於10^{-4} a.u.；另外我們也將這些位能函數實作到可被Gaussian09程式調用的外部程式當中，並進行結構優化和振動頻率計算。對於所有選定的化學分子，我們的位能函數可以得到和耦合簇理論計算(CCSD(T)/cc-pVTZ)幾乎相同的平衡結構和振動頻率，而且振動頻率的誤差皆小於$10cm^{-1}$。

Constructing A Library of Potential Energy Functions from Coupled Cluster Calculations to Be Used in the SCC-DFTB Parameterization

Student: Po-Yu Yang Advisor: Dr. Henryk Witek

M. S. Program,
Institute of Molecular Science
Department of Applied Chemistry

Abstract

The SCC-DFTB method is a powerful semi-empirical method of quantum chemistry, which is able to treat huge molecular systems. However, SCC-DFTB has certain limitations, which diminish its strength for particular chemical applications. The first limitation concerns the fact that accurate energies, equilibrium geometries, and vibrational frequencies cannot be obtained with the existing parameter sets simultaneously. In the current parameterization of SCC-DFTB, insufficient number of reference potential energy surfaces were used for determination of the parameters. The second limitation comes from the fact that the current SCC-DFTB parameter sets are available only for few selected elements. To overcome those limitations, numerous reference potential energy surfaces representing various bonding mechanisms between atoms are required in the parameterization process. For generating reference potential energy surfaces usable in a fast parameterization process, most of high-level accurate quantum chemical methods are too expensive to be employed. Therefore,

we construct a collection of force-field like potential energy functions on the 4-th order Taylor approximation to expand those functions. Generated by accurate Coupled cluster calculations, our potential energy function not only provide us with accurate potential energy surfaces but also allow for substantial savings in the computational time. The final library of potential energy functions were determined for 74 common molecules containing the elements of the first, second, and third row of the periodic table of elements. The list of these molecules attempts to represent the most typical bonding situations between these elements. We conclude the derivation of the library of potential energy functions by presenting a verification algorithm designed to validate the accuracy of our library. In the fitting process, we are able to control the RMS error to be less than 10^{-4} a.u. in all the studied cases. We have also implemented each of potential energy function as an external program, which can be invoked from the Gaussian09 program, for performing geometry optimization and calculating vibrational frequencies. In all of studied cases, our library of potential energy functions can reproduce the equilibrium geometry and vibrational frequencies giving results almost identical with those from the CCSD(T)/cc-pVTZ calculation. For all the calculated vibrational frequencies, the error to CCSD(T) is smaller than 10 cm^{-1}.

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Chapter 1

Introduction

In recent years, owing to dynamic development of computational science and quantum chemistry, molecular simulations became a powerful and useful tool used by many chemists in their research. There exist many quantum chemical methods, which can be applied successfully to various chemical problems. Most of these methods can be classified as post-Hartree-Fock techniques or various variants of density functional theory (DFT). However, if one wants to generate a potential energy surface, determine vibrational frequencies, or obtain other physicochemical information for large molecules, those accurate methods are probably too expensive to be used. Therefore, another class of somewhat less accurate methods commonly known as semi-empirical methods was developed for huge chemical systems.

Self-consistent charge density-functional tight-binding (SCC-DFTB) method[1] is one of such powerful semi-empirical methods. It was primarily developed as an approximation of DFT[2, 3], applicable to very large molecular systems appearing in either physical or chemical considerations. SCC-DFTB is based on tight-binding (TB) theory[4] and on the second-order Taylor expansion of energy with respect to the charge density fluctuations. SCC-DFTB is able

to treat huge molecular systems with more than 1000 atoms. Its development can be considered as an important contribution to computational chemistry and solid-state material science.

However, SCC-DFTB has certain limitations, which diminish its strength for particular chemical applications; removing some of these limitations is one of the most important directions of development of the SCC-DFTB method. The first limitation concerns the fact that the accurate energies, equilibrium geometries, and vibrational frequencies cannot be obtained with SCC-DFTB parameter sets simultaneously.[5] This is related to the fact that SCC-DFTB does not represent the potentials between two elements in a very accurate fashion. In the current parameterization of SCC-DFTB, insufficient reference potential energy surfaces to be used for constructing the parameters, which is the primary reason for the current situation. The second limitation comes from the fact that currently the SCC-DFTB parameter sets are available only for a set of few selected elements.

To overcome those limitations, we decided to generate numerous reference potential energy surfaces required in the parameterization process. In order to keep a high level of accuracy in the reference potential energy surfaces, high level quantum chemical calculations are needed. Most of the available techniques are too expensive to be employed in a fast parameterization process. To solve this problem, we construct potential energy functions by fitting accurate quantum chemical calculation. The resulting function can generate the

required potential energy surface with similar degree of accuracy but in much shorter time.

In order to represent most typical bonding situations between the elements of the first, second, and third row of the periodic table of elements, we construct a library of the potential energy functions for 73 common molecules containing those elements. For generating each potential energy function, we perform a series of accurate quantum chemical calculations using coupled-cluster theory. The accuracy of each potential energy function is verified via determination of equilibrium geometries and harmonic frequencies.

This chapter contains a general introduction to the topics studied in this Thesis. Details concerning our choice of potential energy function are shown in Chapter 2. A short outline of coupled-cluster theory is briefly discussed in Chapter 3. In Chapter 4, we describe the verification process and discuss the simulation techniques used in our work. In Chapter 5, we present the results and give a discussion of our work. In Chapter 6 we suggest how to apply our potential energy functions to the SCC-DFTB parameterization process.

Chapter 2

Definition of the Potential Energy Function

2.1 The Force-field-like Potential Energy Function

The force-field functions used routinely in molecular mechanics methods provide a relationship between energy and the molecular geometry close to the equilibrium.[6] Usually, the force-field functions are derived from experimental data or accurate quantum mechanical calculations. Following the previous description, we want to generate a potential energy function for each molecule in form of a force-field-like function. By fitting the parameters to accurate quantum mechanical calculations, the potential energy function can reproduce accurate energies for a wide range of molecular geometries.

2.2 Taylor Series

According to Taylor theorem[7], all sufficiently smooth function can locally be approximated by polynomials. Therefore, we use Taylor series to expand our potential energy functions. The Taylor expansion of a real function $f(x)$ that is infinitely many times differentiable in a neighborhood of x_e can be expressed in form of a power series

$$f(x) = f(x_e) + f'(x_e)(x - x_e) + \frac{f''(x_e)}{2!}(x - x_e)^2 + \frac{f^{(3)}(x_e)}{3!}(x - x_e)^3 + \cdots \quad (2.1)$$

In other words, this power series can describe the function f around a given point x_e. Replacing the formal derivatives terms $\frac{f^{(i)}(x_e)}{i!}$ by adjustable parameters k_i

$$\begin{aligned} f(x) &= k_0 + k_1(x-x_e) + k_2(x-x_e)^2 + k_3(x-x_e)^3 + \cdots \\ &= \sum_{i=0}^{\infty} k_i (x-x_e)^i \end{aligned} \tag{2.2}$$

yields a formally equivalent series that can be used to describe the behavior of f around x_e. We further truncate the infinite Taylor series to a finite form, which is usually referred to as the *n*-th order Taylor approximation

$$f(x) \approx \sum_{i=0}^{n} k_i (x-x_e)^i \tag{2.3}$$

Though higher-order approximations may provide a better description of reality, they can also increase the computational effort. Thus, in our work, the potential energy function is expressed in a form of the 4th-order Taylor function, which combines reasonable accuracy with affordable computational load.

To construct our potential energy functions, we expand the energy in a Taylor series around the equilibrium geometry. Thus, the point x_e in Eq. (2.3) can be regarded as the equilibrium geometry. The point x is an arbitrary geometry located around the equilibrium geometry. For representing the geometric variation of the arbitrary geometry x, the geometries are expressed by some internal coordinates. The point x_e and x are transformed into internal coordinates (a_e ,b_e ,c_e ...) and (a ,b ,c ...). For example, the 4-th order potential energy function with three internal coordinates (a ,b ,c ...) can be expanded

as

$$E(a,b,c) = k_{000} + k_{100}(a-a_e) + k_{010}(b-b_e) + k_{001}(c-c_e) +$$

$$k_{200}(a-a_e)^2 + k_{020}(b-b_e)^2 + k_{002}(c-c_e)^2 +$$

$$k_{110}(a-a_e)(b-b_e) + k_{101}(a-a_e)(c-c_e) + k_{011}(b-b_e)(c-c_e) + \cdots$$

$$E(a,b,c) = \sum_{\alpha,\beta,\gamma=0}^{\alpha+\beta+\gamma=4} k_{\alpha\beta\gamma}(a-a_e)^{\alpha}(b-b_e)^{\beta}(c-c_e)^{\gamma} \qquad (2.4)$$

In the fitting process, we determine the parameters $k_{\alpha\beta\gamma}$ using the following steps. First, we perform CCSD(T) geometry optimization to determine the equilibrium geometry and the corresponding energy. Second, we generate a large number of geometries around the equilibrium geometry, and compute the corresponding CCSD(T) single point energies. The CCSD(T) calculations, using the cc-pVTZ basis sets, are performed with the MOLPRO2k9 program.[8] Third, we transfer the equilibrium geometry and all the non-equilibrium geometries into their corresponding internal coordinates and substitute them into the potential energy function. For each of the non-equilibrium geometries, we can obtain one equation from the potential energy function. If the number of equations is larger than the number of unknown geometric parameters used for constructing the potential energy function, the resulting overdetermined system of linear equations may be solved by the QR decomposition technique. The details of the QR decomposition will be given in Section 4.1.

2.3 The Types of Internal Coordinates

Following the previous description, the internal coordinates in potential energy functions are used to represent the geometry variation. In order to represent the molecular potential energy surfaces more accurately by our functions, the representation of molecular motions are also important for internal coordinates.

For small molecules, we can use bond lengths and bond angles as internal coordinates. Below, we discuss H_2, H_2O and NH_3 as examples of internal coordinates.

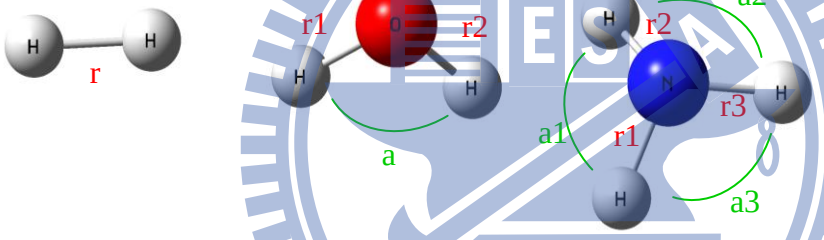


Figure 2.1
The internal coordinates in H_2, H_2O and NH_3

In the H_2 molecule, one internal coordinate is sufficient to represent the H-H stretching: the bond length between the two hydrogens. In the H_2O molecule, there are three internal coordinates. Two of them are the O-H bond lengths, which correspond to the O-H stretching. The third one is the angle formed between two O-H bonds, which represent the bending between the two O-H bonds. In the NH_3 molecule, there are six internal coordinates. Three of them are the N-H bond lengths, which correspond to the N-H stretching. Other three are the angles formed between three N-H bonds, which represent the bending and wagging of those N-H bonds.

When the size of a molecule becomes larger, the interrelation between bond lengths and bond angles may become complicated. Therefore, in the molecular systems which have more than five atoms, we set all the interatomic distances to be the internal coordinates. Below, we discuss methane and ethane as examples of internal coordinates.

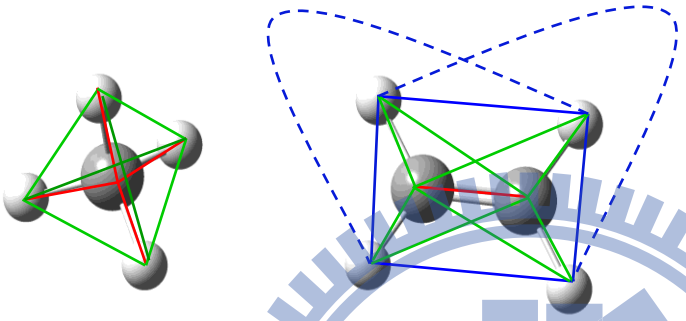


Figure 2.2
The internal coordinates in CH_4 and C_2H_4

For methane, there are ten internal coordinates in total, which are separated into two types. One type is the C-H bond lengths (red lines), which correspond to the C-H stretching. And another is the distances between two hydrogens (green lines) which represent the bending, rocking, wagging or twisting between the C-H bonds. For ethene, there are fifteen internal coordinates in total, which are separated into three types. The first type is the C-C bond length (red line), which represent the C-C stretching. The second type is the distances between any carbon and hydrogen (green lines). And the third type is the distances between any two hydrogens (blue lines). Using these three types of internal coordinates, we can represent all the motions of those C-H bonds successfully.

For some molecular systems (more than eight atoms), if we use all the distances between

any two atoms as the internal coordinates, the number of coordinates and the size of potential energy functions may become too large and hard to determine the parameters. In order to balance the accuracy and computational load, some of the distances are ignored. The number of internal coordinates for each molecule is shown in Appendix A.

2.4 Symmetry Adaptation

The examples given in last section, suggest that there are symmetry links between some of internal coordinates. The coefficients of those symmetry-related internal coordinates in the potential energy functions are identical. If we can figure out those symmetry-relations between the internal coordinates and organize them together in the potential energy function, then the number of parameters will be greatly reduced. This step will speed up the process of QR decomposition.

In this work, we use symmetry operation to determine the symmetry-adapted internal coordinates for each molecule. First, we check the point group of a molecule, and construct the symmetry operations for this molecule. The operation may permutate some of the internal coordinates, which allows for separating the internal coordinates into many different symmetry classes. The water molecule has the "C_{2v}" symmetry, with symmetry operations: E, C_2, σ_v' and σ_v". The operator E and σ_v' can be ignored because they do not interchange any atoms nor internal coordinates, while the operators C_2 and σ_v" exchange the hydrogen atoms.

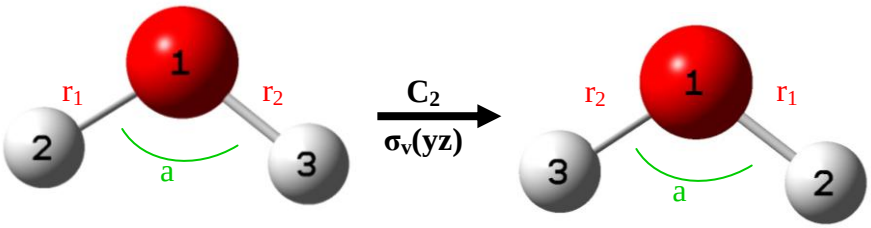


Figure 2.3
Do symmetry operations on water

From Figure 2.3, we observe the permutation between the internal coordinate r_1 and r_2. Therefore, we can determine r_1 and r_2 are the symmetry-equivalent internal coordinates. The original potential energy function of the water molecule is

$$\begin{aligned} E(r_1,r_2,a) = {} & k_{000} + k_{100}(r_1 - r_{1e}) + k_{010}(r_2 - r_{2e}) + k_{001}(a - a_e) + \\ & k_{200}(r_1 - r_{1e})^2 + k_{020}(r_1 - r_{1e})^2 + k_{002}(a - a_e)^2 + \\ & k_{110}(r_1 - r_{1e})(r_2 - r_{2e}) + k_{101}(r_1 - r_{1e})(a - a_e) + k_{011}(r_2 - r_{2e})(a - a_e) + \cdots \end{aligned} \tag{2.5}$$

After collecting the symmetry-equivalent internal coordinates together, the Eq. (2.5) can be rewritten as

$$\begin{aligned} E(r_1,r_2,a) = {} & k_1 + k_2\left[(r_1 - r_{1e}) + (r_2 - r_{2e})\right] + k_3(a - a_e) + \\ & k_4\left[(r_1 - r_{1e})^2 + (r_1 - r_{1e})^2\right] + k_5(a - a_e)^2 + \\ & k_6(r_1 - r_{1e})(r_2 - r_{2e}) + k_7\left[(r_1 - r_{1e})(a - a_e) + (r_2 - r_{2e})(a - a_e)\right] + \cdots \end{aligned} \tag{2.6}$$

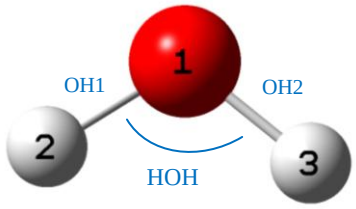
This process is called symmetry adaptation. It can not only reduce the computational load in the fitting process, but it can also increase the evaluation speed of the potential energy functions, especially for large and high-symmetry molecular system. For the water molecule, the number of parameters is reduced from 35 to 22; for cyclopropane, the number of

parameters is reduced from 91390 to 8986. The number of parameters before and after the symmetry adaptation is shown in Appendix A for each molecule.

2.5 Generation of the Data Points

In the fitting process, the quality and quantity of the data points in solving the overdetermined system of linear equations are both important. If the geometries are far from the equilibrium geometry, our potential energy functions may not generate an accurate potential energy surface. Therefore, we use z-matrix to generate the geometries of data points, since those geometries can be easily controlled.

The z-matrix is a way to represent a system built of atoms. It provides a description of each atom in a molecule in terms of its atomic number, a bond length, a bond angle and a dihedral angle. To describe a molecular system with less than four atoms, we can only use bond lengths and bond angles. For example for water molecule,




```
O
H   1   OH1
H   1   OH2   2   HOH
```

Figure 2.4
The z-matrix input for water molecule.

where the OH1 and OH2 are the O-H bond lengths and the HOH is the angle between two O-H bonds. In this case, the z-matrix is totally identical with the definition of our internal

coordinates.

In the molecular system with more than four atoms, the new term is introduced into the z-matrix, which is called dihedral angle. In Figure 2.5, we show the definition of dihedral angle δ, defined as the angle between two planes, plane 2-1-3 and plane 1-3-4.

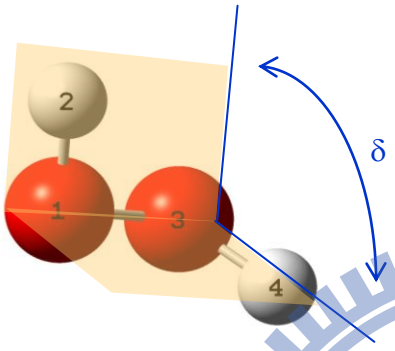
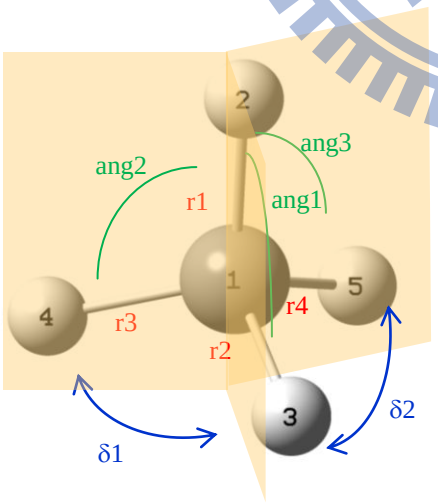


Figure 2.5
The dihedral angle in four atoms molecular system.

The z-matrix input for methane shown in Figure 2.6 should contain four bond lengths (R1, R2, R3, R4), three bond angles (A1, A2, A3) and 2 dihedral angles (δ1, δ2). The z-matrix input of methane can be shown as:




```
C
H   1   R1
H   1   R2   2   A1
H   1   R3   2   A2   3   δ1
H   1   R4   2   A3   3   δ2
```

Figure 2.6
The z-matrix input of methane molecule.

By using the z-matrix, we can use a random generator to produce easily the data points. In our work, the bond lengths are distributed in the range of $\pm 10\%$ from the equilibrium bond length, and angles are distributed in the range of $\pm 10^{o}$ of the equilibrium bond angles.

Chapter 3

Coupled-Cluster Theory

Coupled-cluster (CC) theory[9],[10] is a post-Hartree-Fock technique, which constructs a multi-electron wavefunction using the exponential cluster operator applied to the Hartree-Fock determinant $|\Psi_{HF}\rangle$. Over the past years, this method has developed as perhaps the most reliable computational method for prediction of molecular properties.

Coupled-cluster theory constructs an approximate solution to the time-independent Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{3.1}$$

where $\hat{H}$ is the Hamiltonian of the system and the CC wavefunction $|\Psi\rangle$ is written in an exponential form

$$|\Psi\rangle = e^{\hat{T}}|\Psi_{HF}\rangle \tag{3.2}$$

The exponential term in Eq. (3.2) can be expanded as

$$e^{\hat{T}} = \sum_{N=0}^{\infty} \frac{\hat{T}^N}{N!} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots \tag{3.3}$$

In Eq. (3.3), $\hat{T}$ is a cluster operator, which includes all possible excitation operators.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots \hat{T}_n \tag{3.4}$$

where $\hat{T}_1$ correspond to all single excitations, $\hat{T}_2$ correspond to all double excitations, and

so on. In the formalism of second quantization these excitation operators are conveniently expressed as

$$\hat{T}_1 = \sum_{ik} c_i^k a_k^+ a_i \tag{3.12}$$

$$\hat{T}_2 = \frac{1}{4} \sum_{i,j,k,l} c_{ij}^{kl} a_k^+ a_l^+ a_i a_j \tag{3.13}$$

In the above formula, a^+ and a are denoted as creation and annihilation operators respectively and i, j stand for occupied and k, l for unoccupied orbitals.

The exponential form of cluster operator usually recovers more correlation energy than configuration interaction (CI), and it also guarantee the size extensively of the solution, but makes the computations very expensive. Thus, we usually reduce the number of operators in $\hat{T}$. For example, if we only keep $\hat{T}_1$ and $\hat{T}_2$ in $\hat{T}$ then the reduced technique is called the CCSD method. If we only keep $\hat{T}_2$ then it is called the CCD method. One of high accurate reduced techniques is called CCSD(T), which is applied in our work. In the CCSD(T), the cluster operator not only contains $\hat{T}_1$ and $\hat{T}_2$, but also includes the contribution from $\hat{T}_3$ in perturbative fashion.

Chapter 4

Verification Process and Other Techniques

4.1 Verification process

For verifying the accuracy of our potential energy functions, we have implemented each of them as an external FORTRAN program, which can be invoked from the Gaussian09 program[11] that is used as a convenient external tool for performing the geometry optimization and calculating the vibrational frequencies. By comparing the equilibrium geometries and vibrational frequencies with the results obtained with CCSD(T)/cc-pVTZ, we get a direct evidence supporting the accuracy of our potential energy functions. The verification process employs numerical energy gradient for optimization and double numerical hessian for the vibrational analysis. The details are discussed in the following sections.

4.2 Solving the Overdetermined System of Linear Equations

Following the description in Section 2.1, we introduce the QR decomposition technique to solve the overdetermined system of linear equations. We use m data points as the input

for the potential energy function, which depends on n unknown fit parameters, and we get a system of m linear equations, which can be expressed in matrix formalism as

$$E_i = \sum_{j=1}^{n} X_{ij} k_j \quad (i = 1,2,...,m) \tag{4.1}$$

where X_{ij} is a matrix of powers of the displacements of the internal coordinates, E_i is a vector of the corresponding CCSD(T) energies, and k_j denotes a vector of the unknown fit parameters. Next, we transform those m linear equations into a matrix form,

$$E = XK \tag{4.2}$$

where

$$E = \begin{bmatrix} E_1 \\ E_2 \\ \vdots \\ E_m \end{bmatrix}, \quad X = \begin{bmatrix} X_{11} & X_{12} & \cdots & X_{1n} \\ X_{21} & X_{22} & \cdots & X_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ X_{m1} & X_{m2} & \cdots & X_{mn} \end{bmatrix}, \quad K = \begin{bmatrix} k_1 \\ k_2 \\ \vdots \\ k_m \end{bmatrix} \tag{4.3}$$

The least squares approach for solving this problem is based on the concept of minimization of the sum of squares of "errors" between the right- and left-hand sides of Eq. (4.2), that is to find the minimum of the function

$$\left\| E - XK \right\|^2 \tag{4.4}$$

For finding the best solution K, I have written a program in the FORTRAN language involving a routine called DGELS from Linear Algebra PACKage (LAPACK) library[12]. The DGELS routine uses QR decomposition of matrix X to solve an overdetermined system of linear equation. For each potential energy function, the minimized root-mean-square (RMS)

errors from the fitting process are shown in the Appendix A.

4.3 Numerical Energy Gradient

For determination of the energy gradient in the geometry optimization process, we apply numerical differentiation in our program. To ensure good numerical accuracy of calculations, the five-points stencil formulas are employed for each coordinate dimension. Assume that the spacing between points in the grid is h, the one-dimensional five-point stencil of a point x is $\{x-2h,\ x-h,\ x,\ x+h,\ x+2h\}$. The first derivative of a function f at the point x can be obtained by writing out the function f at the remaining four points of the stencil as a Taylor series:

$$f(x+h) = f(x) + h\frac{\partial f(x)}{\partial x} + \frac{h^2}{2!}\frac{\partial^2 f(x)}{\partial x^2} + \frac{h^3}{3!}\frac{\partial^3 f(x)}{\partial x^3}(x) + O_{1+}(h^4) \tag{4.6}$$

$$f(x-h) = f(x) - h\frac{\partial f(x)}{\partial x} + \frac{h^2}{2!}\frac{\partial^2 f(x)}{\partial x^2} - \frac{h^3}{3!}\frac{\partial^3 f(x)}{\partial x^3} + O_{1-}(h^4) \tag{4.7}$$

$$f(x+2h) = f(x) + 2h\frac{\partial f(x)}{\partial x} + \frac{4h^2}{2!}\frac{\partial^2 f(x)}{\partial x^2} + \frac{8h^3}{3!}\frac{\partial^3 f(x)}{\partial x^3} + O_{2+}(h^4) \tag{4.8}$$

$$f(x+2h) = f(x) - 2h\frac{\partial f(x)}{\partial x} + \frac{4h^2}{2!}\frac{\partial^2 f(x)}{\partial x^2} - \frac{8h^3}{3!}\frac{\partial^3 f(x)}{\partial x^3} + O_{2-}(h^4) \tag{4.9}$$

Evaluating Eq. (4.6) – Eq. (4.7) and Eq. (4.8) – Eq. (4.9) gives us

$$f(x+h) - f(x-h) = 2h\frac{\partial f(x)}{\partial x} + \frac{h}{3}\frac{\partial^3 f(x)}{\partial x^3} + O_1(h^4) \tag{4.10}$$

$$f(x+2h) - f(x-2h) = 4h\frac{\partial f(x)}{\partial x} + \frac{8h}{3}\frac{\partial^3 f(x)}{\partial x^3} + O_2(h^4) \tag{4.11}$$

We evaluate $8\times$Eq. (4.10) – Eq (4.11) to eliminate the $\frac{\partial^3 f(x)}{\partial x^3}$ term, which gives us

$$8f(x+h) - 8f(x-h) - f(x+2h) + f(x-2h) = 12h\frac{\partial f(x)}{\partial x} + O(h^4) \tag{4.12}$$

Then we get $\frac{\partial f(x)}{\partial x}$ as

$$\frac{\partial f(x)}{\partial x} = \frac{8f(x+h) - 8f(x-h) - f(x+2h) + f(x-2h)}{12h} + O(h^4)$$
$$\approx \frac{8f(x+h) - 8f(x-h) - f(x+2h) + f(x-2h)}{12h} \quad (4.13)$$

The magnitude of the error in this approximation is $O(h^4)$, which evaluates to 10^{-12} u with the choice of h of 0.001 a.u. in our program.

4.4 Vibrational Frequency Analysis

In quantum mechanics, the molecular motion in a normal vibration can be described as a kind of simple harmonic motion. According to Hook's Law and Newton's Law, the vibrational frequency v in harmonic oscillator can be expanded as

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad (4.14)$$

where k is the force constant and m is the mass. In molecular mechanics, the force constant can be calculated from the Hessian matrix, which is the second partial derivation of the total energy E with respect to the Cartesian displacements of the atoms. For a molecular system, containing N atoms, the force constants matrix F can be expand as a $3N \times 3N$ hessian matrix.

$$F_{ij} = \frac{\partial^2 E}{\partial \xi_i \partial \xi_j} = \begin{bmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial y_1} & \frac{\partial^2 E}{\partial x_1 \partial z_1} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial z_N} \\ \frac{\partial^2 E}{\partial y_1 \partial x_1} & \frac{\partial^2 E}{\partial y_1^2} & \frac{\partial^2 E}{\partial y_1 \partial z_1} & \cdots & \frac{\partial^2 E}{\partial y_1 \partial z_N} \\ \frac{\partial^2 E}{\partial z_1 \partial x_1} & \frac{\partial^2 E}{\partial z_1 \partial y_1} & \frac{\partial^2 E}{\partial z_1^2} & \cdots & \frac{\partial^2 E}{\partial z_1 \partial z_N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial z_N \partial x_1} & \frac{\partial^2 E}{\partial z_N \partial y_1} & \frac{\partial^2 E}{\partial z_N \partial z_1} & \cdots & \frac{\partial^2 E}{\partial z_N^2} \end{bmatrix} \tag{4.15}$$

Each element of the hessian matrix can be evaluated by numerical differentiation with a displacement h. There are two kinds of elements in the hessian matrix. The first type, $\frac{\partial f^2(x)}{\partial x^2}$, is located on the diagonal of the matrix. Those elements can be determined as follows:

Evaluating Eq. (4.6) + Eq. (4.7) gives us

$$f(x+h) + f(x-h) = 2f(x) + h^2 \frac{\partial^2 f(x)}{\partial x^2} + O_1(h^4) \tag{4.16}$$

The element $\frac{\partial^2 f(x)}{\partial x^2}$ can be determined as

$$\begin{aligned} \frac{\partial^2 f(x)}{\partial x^2} &= \frac{f(x+h) + f(x-h) - 2f(x)}{h^2} + O_1(h^4) \\ &\approx \frac{f(x+h) + f(x-h) - 2f(x)}{h^2} \end{aligned} \tag{4.17}$$

The second type has a two-dimensional form $\frac{\partial^2 f(x,y)}{\partial x \partial y}$. It can be obtained by writing out the function f at the six points of the two-dimensional stencil as a Taylor series:

$$f(x+h, y) = f(x,y) + h\frac{\partial f(x,y)}{\partial x} + \frac{1}{2!}h^2 \frac{\partial f^2(x,y)}{\partial x^2} + O_{1+}(h^3) \tag{4.18}$$

$$f(x-h, y) = f(x,y) - h\frac{\partial f(x,y)}{\partial x} + \frac{1}{2!}h^2 \frac{\partial f^2(x,y)}{\partial x^2} + O_{1-}(h^3) \tag{4.19}$$

$$f(x, y+h) = f(x,y) + h\frac{\partial f(x,y)}{\partial y} + \frac{1}{2!}h^2 \frac{\partial f^2(x,y)}{\partial y^2} + O_{2+}(h^3) \tag{4.20}$$

$$f(x,y-h)=f(x,y)-h\frac{\partial f(x,y)}{\partial y}+\frac{1}{2!}h^2\frac{\partial f^2(x,y)}{\partial y^2}+O_{2-}(h^3) \tag{4.21}$$

$$\begin{aligned} f(x+h,y+h)=&\ f(x,y)+h\frac{\partial f(x,y)}{\partial x}+h\frac{\partial f(x,y)}{\partial y} \\ &+\frac{1}{2!}h^2\frac{\partial f^2(x,y)}{\partial x^2}+\frac{1}{2!}h^2\frac{\partial f^2(x,y)}{\partial y^2}+h^2\frac{\partial f^2(x,y)}{\partial x\partial y}+O_{3+}(h^3) \end{aligned} \tag{4.22}$$

$$\begin{aligned} f(x-h,y-h)=&\ f(x,y)-h\frac{\partial f(x,y)}{\partial x}-h\frac{\partial f(x,y)}{\partial y} \\ &+\frac{1}{2!}h^2\frac{\partial f^2(x,y)}{\partial x^2}+\frac{1}{2!}h^2\frac{\partial f^2(x,y)}{\partial y^2}+h^2\frac{\partial f^2(x,y)}{\partial x\partial y}+O_{3-}(h^3) \end{aligned} \tag{4.23}$$

Evaluating Eq. (4.18) + Eq. (4.19) and ignore the error function O

$$h^2\frac{\partial f^2(x,y)}{\partial x^2}\approx f(x+h,y)+f(x-h,y)-2f(x,y) \tag{4.24}$$

Evaluating Eq. (4.20) + Eq. (4.21) and ignore the error function O

$$h^2\frac{\partial f^2(x,y)}{\partial y^2}\approx f(x,y+h)+f(x,y-h)-2f(x,y) \tag{4.25}$$

Evaluating Eq. (4.22) + Eq. (4.23) and also ignore the error function O

$$\begin{aligned} f(x+h,y+h)+f(x-h,y-h)\approx&\ 2f(x,y)+h^2\frac{\partial f^2(x,y)}{\partial x^2} \\ &+h^2\frac{\partial f^2(x,y)}{\partial y^2}+2h^2\frac{\partial f^2(x,y)}{\partial x\partial y} \end{aligned} \tag{4.26}$$

From Eq. (4.24) and Eq. (4.25), we can rewrite Eq. (4.26) as

$$\begin{aligned} f(x+h,y+h)+f(x-h,y-h)\approx&-2f(x,y)+f(x+h,y)+f(x-h,y) \\ &+f(x,y+h)+f(x,y-h)+2h^2\frac{\partial f^2(x,y)}{\partial x\partial y} \end{aligned} \tag{4.27}$$

Finally, the element $\frac{\partial^2 f(x,y)}{\partial x\partial y}$ can be determined as

$$\begin{aligned} \frac{\partial^2 f(x,y)}{\partial x\partial y}\approx\frac{1}{2h^2}\big[&f(x+h,y+h)+f(x-h,y-h)+2f(x,y) \\ &-f(x+h,y)-f(x-h,y)-f(x,y+h)-f(x,y-h)\big] \end{aligned} \tag{4.28}$$

To determine the vibrational frequencies in Eq. (4.14), the force constants matrix has been divided by the mass, giving us so called mass weighted force constant matrix.

$$F_{m.w.c.} = \frac{F_{cart,ij}}{\sqrt{m_i m_j}} \tag{4.29}$$

Diagonalization of the mass weighted force constant $F_{m.w.c.}$ yields a set of $3N$ eigenvectors and $3N$ eigenvalues. After separating the translation and rotation modes, the roots of the eigenvalues determine the harmonic frequencies of the molecule.

Chapter 5

Results and Discussions

For constructing available library in SCC-DFTB parameterization process, I have fitted the potential energy functions for 73 common molecules, representing the most common bonding situations between the elements of the first-, second- and third-rows of the periodic table. Our potential energy functions can reproduce the potential energy as accurate as CCSD(T)/cc-pVTZ. Our function can be easily invoked by the SCC-DFTB parameterization program. The input for the potential energy routine is the molecular geometry; the routine returns the corresponding energy.

For evaluating the accuracy of our potential energy functions, I first evaluate the RMS error of the fitting process. For the cases with large errors, I try to put more data points or remove some data points with large displacements from the equilibrium. If the error problem still cannot be solved, improving the definition of internal coordinates sometimes is effective. In order to represent the variation of the geometry or the motions of atoms in the molecule accurately, I change the types of internal coordinate or use a larger number of coordinates. Finally in all the studied cases we are able to control the RMS error to be less than 10^{-4} a.u. Details are shown in the Appendix A.

A potential energy function characterized by small RMS error does not necessarily generate an accurate potential energy surface. Therefore, following the previous description in Section 4.1, we also verify the accuracy of potential energy function by performing geometry optimization and vibrational frequency analysis. Most of the potential energy functions can reproduce the equilibrium geometry and vibrational frequency giving results almost identical with those from the CCSD(T)/cc-pVTZ calculation. In a few cases, some vibrational modes have larger errors. We have figured out an effective way to overcome this problem. Following the eigenvector of such a vibrational mode, we generate an additional set of geometries. After we put those extra data points into the potential energy linear fitting procedure, we can obtain acceptable vibrational frequencies for each molecule. For all vibrational frequencies, we request the error to be smaller than 10 cm^{-1}. The detailed information about the geometries and vibrational frequencies is shown in Appendix B.

Though our scheme could be successfully applied for generating potential energy functions for many different molecules, there are still 5 molecules, for which the potential energy function could not be determined in a satisfactory fashion. For benzene, furane and pyrrole, our potential energy functions produce good equilibrium geometries but the accurate vibrational frequencies have substantial errors. For acetone and cyclopropane, the geometry optimization process has failed.

So far, the work of building the references potential energy surfaces is almost done. In

last chapter, we briefly describe the future work about applying our references potential energy surfaces to the parameterization process of SCC-DFTB.

Chapter 6

The Parameterization of the SCC-DFTB Repulsive Potentials

In the SCC-DFTB method, the total energy function is separated into an electronic part and a repulsive part.[1] The electronic part is described by a Hamiltonian, which is derived from DFT. SCC-DFTB uses as the reference density the superposition of neutral atomic densities together with a minimal basis of valence atomic wave functions. By applying the variational principle, the electronic energy can be determined by solving a generalized eigenvalue problem set up by the Hamiltonian and the overlap SCC-DFTB matrices. It is important to mention that SCC-DFTB uses the frozen-core approximation to reduce the computational effort. As a result, SCC-DFTB considers only the valence atomic orbitals (AOs) in the calculation. The remaining part of energy: the core-core repulsion, nuclear-nuclear repulsion and other energy contributions not included in the electronic part are accounted for in the repulsive part.[(13)] The repulsive energy is approximated in SCC-DFTB as a sum of short-range pair potentials between all atomic pairs.

In the SCC-DFTB calculations, the two-center Hamiltonian and overlap integrals are pre-computed and stored in tables for each elements pair. In addition, the repulsive potentials

are expressed as a collection of spline functions for each elements pair.[14] Looking up the integrals in the pre-computed tables makes the SCC-DFTB method fast and enables one to apply it to huge chemical systems.

In SCC-DFTB, the repulsive potential is represented on a grid defined by a set of interatomic distances $\{r_i\}$; $I_0 = [0, r_1)$, $I_1 = [r_1, r_2)\ldots$, $I_n = [r_n, r_{n+1})$, and $I_{n+1} = [r_{n+1}, r_\infty)$.

For the first interval I_0, the repulsive potential has an exponential form

$$S_0(r) = \alpha \exp(\beta r + \gamma) \tag{6.1}$$

For other intervals, the repulsive potentials is represented by a cubic spline

$$S_i(r) = \sum_{k=0}^{3} a_{k,i}(r - r_i)^k \tag{6.2}$$

In the original parameterization procedure, the repulsive potentials are constructed using as a reference set of data the difference between the electronic SCC-DFTB energy and the DFT energy. The free parameters defining the spline functions are determined from a linear regression fit. For some chemical systems, accurate energies and vibrational frequencies cannot be obtained with the existing SCC-DFTB parameters. This problem may relate to the fact that the linear regression fitting is not a good way to solve those nonlinear equations. In addition, insufficient number of molecules were used in the parameterization process.

Therefore, we are planning to employ another method in the parameterization process, called particle swarm optimization (PSO).[15] This method can solve an optimization problem

by iterative improvement to a candidate solution. First, we guess many random candidate solutions and construct the new repulsive potentials for each such a candidate solution. Second, we use each of the new repulsive potentials to generate a new potential energy surface. By comparing with the reference potential energy surface, we can compute the error for each candidate solution. This allows us for assessing the quality of each candidate. If the new candidate solution is characterized by better fitness than any of the previously formed candidate solutions, it becomes a new PSO minimum used for giving the after PSO particles. After several cycles of optimization, we can obtain a solution with small error, which is usually a good approximation to the real global minimum. The accuracy of the reference potential energy surfaces is important here, especially in the PSO method, thus the high accurate quantum chemical calculations are required, e.g. CCSD(T).

The CCSD(T) calculations are very expensive and slow. In addition, we cannot predict how many CCSD(T) energies are required to obtain a good solution in the PSO optimization. The CCSD(T) calculations can be regarded as the bottleneck of the PSO procedure since they seriously reduce the speed of the parameterization process. Therefore, our potential energy functions can be a feasible way to replace the expensive CCSD(T) calculations.

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Appendix A

I. Details of the Fitting Procedure

This section shows various information concerning the fitting procedure, which include:

(1) the number of internal coordinates (IC) used for construction of the potential energy function

(2) the number of original parameters in the potential energy function

(3) the number of parameters* after the symmetry adaptation process

(4) the number of data points used in the fitting work

(5) the RMS error in the linear-least square fitting process

1. Hydrogen Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
H_2	1	5	5	11	3.599E-7

2. Lithium Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
Li_2	1	5	5	11	1.094E-7
HLi	1	5	5	11	3.784E-7
CLi_4	10	1000	83	10000	7.412E-6
Li_3N	6	210	47	10000	6.649E-6
Li_2O	3	35	22	1331	3.871E-6
FLi	1	5	5	11	2.712E-6
Li_2S	3	35	22	1331	3.148E-6

ClLi	1	5	5	11	2.489E-6

3. Beryllium Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
BeH_2	3	35	22	1331	1.082E-6
Be=O	1	5	5	11	4.249E-6
BeF_2	3	35	22	1331	6.720E-6
$BeCl_2$	3	35	22	1331	6.440E-6

4. Boron Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
BH_3	6	210	47	10890	1.780E-6
BF_3	6	210	47	10000	5.057E-5
BCl_3	6	210	47	10000	1.129E-5

5. Carbon Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
CH_4	10	1001	83	10000	6.089E-6
CH_3-CH_3	28	35960	3361	11000	1.717E-5
CH_2=CH_2	15	3876	1056	10000	3.601E-6
CH≡CH	6	210	120	10000	4.756E-6
CH_2=C=CH_2	21	12650	2379	10000	3.085E-5
C_3H_6 (Cyclopropane)	36	91390	8986	10000	5.747E-6
CH_3-NH_2	21	12650	6490	10000	2.282E-6

CH_2=NH	10	1001	1001	10000	4.584E-6
CH≡N	3	35	35	1331	7.348E-6
NH=C=NH	10	1001	525	10000	7.296E-6
C=O	1	5	5	11	8.229E-6
CO_2	3	35	22	1331	1.219E-5
CH_2=O	6	210	120	10000	5.946E-6
CH_3-OH	15	3876	2180	12000	3.591E-6
CH_3-O-CH_3	27	31459	8439	12000	1.136E-5
CH_3COOH	23	17549	10235	11000	8.699E-7
C_2H_4O (Epoxide)	21	12650	3330	10000	2.344E-6
CF_4	10	1001	83	10000	9.218E-5
CCl_4	10	1001	83	10000	5.104E-5

6. Nitrogen Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
N_2	1	5	5	11	8.949E-6
NH_3	6	210	47	10500	3.262E-6
N_2H_2 (Z form)	6	210	120	10000	6.038E-6
N_2H_2 (E form)	6	210	120	10000	6.891E-6
NH_2-NH_2	15	3876	1996	10000	5.668E-6
NH_2-OH	10	1001	561	10000	5.992E-6
NH=O	3	35	35	1331	8.276E-6

HNO_3	10	1001	1001	10000	1.824E-5
F_3N	6	210	47	10000	2.717E-5
Cl_3N	6	210	47	10000	2.226E-5

7. Oxygen Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
O_2	1	5	5	11	8.484E-6
O_3	3	35	22	1331	4.051E-6
H_2O	3	35	22	1331	2.648E-6
H_2O_2	6	210	120	10000	5.404E-6
F_2O	3	35	22	1331	1.368E-5
Cl_2O	3	35	22	1331	6.372E-6

8. Fluorine Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
F_2	1	5	5	11	4.520E-6
HF	1	5	5	11	2.103E-6
FNa	1	5	5	11	3.791E-6
F_2Mg	3	35	22	1331	9.144E-6
AlF_3	6	210	47	10000	1.096E-5
F_4Si	10	1001	83	10000	1.563E-5
F_3P	6	210	47	10000	2.305E-5
F_2S	3	35	22	1331	1.486E-5

9. Sodium Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
HNa	1	5	5	11	6.300E-7
Na_2S	3	35	22	1331	4.405E-6
NaCl	1	5	5	11	3.798E-6

10. Magnesium Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
H_2Mg	3	35	22	1331	1.088E-6
Cl_2Mg	3	35	22	1331	7.514E-6

11. Aluminum Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
AlH_3	10	210	47	10000	2.994E-6
$AlCl_3$	10	210	47	10000	9.676E-4

12. Silicon Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
H_4Si	10	1001	83	10000	4.701E-6
Cl_4Si	10	1001	83	10000	1.439E-5

13. Phosphorus Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
H_3P	6	210	47	10000	3.953E-6

Cl_3P	6	210	47	10000	1.929E-5

14. Sulfur Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
H_2S	3	35	22	1331	2.825E-6
Cl_2S	3	35	22	1331	1.411E-5

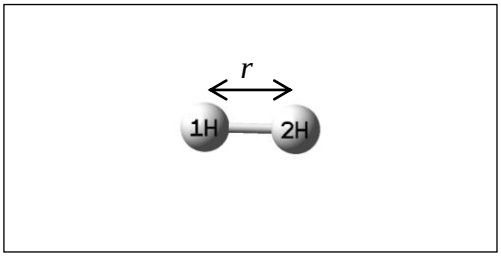
15. Chlorine Group

Formula	IC	Parameters	Parameters*	Data points	RMS error
Cl_2	1	5	5	11	7.902E-6

II. The Form of Potential Energy Function

This section, shows the complete form of the potential energy function and parameters used for the following molecules: H_2, H_2O, and CH_2O. The potential energy functions are expressed in a form of the 4th-order Taylor function, and the parameters are determined from the linear-least square technique. Detailed discussion of these three molecules helps understanding the form of our potential energy functions.

1. H_2



Cartesian coordinates (a.u.):

Atoms	X	Y	Z
1H	H_{1x}	H_{1y}	H_{1z}
2H	H_{2x}	H_{2y}	H_{2z}

Internal coordinates:

$$r = \sqrt{(H_{1x} - H_{2x})^2 + (H_{1y} - H_{2y})^2 + (H_{1z} - H_{2z})^2}$$

Constants:

$r_{eq} = 1.403412$ a.u.

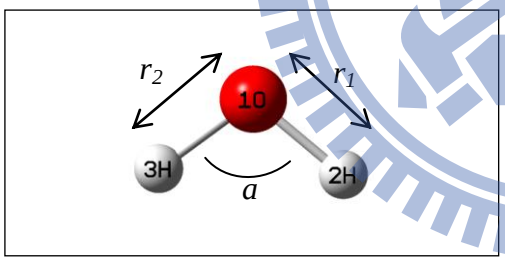
Potential energy function:

$$E(Hartrees) = P(1) + P(2) \times (r - r_{eq}) + P(3) \times (r - r_{eq})^2 + P(4) \times (r - r_{eq})^3 + P(5) \times (r - r_{eq})^4$$

Parameters:

$P(1) = -1.172337$	*Equilibriun energy*
$P(2) = 0.000038$	*1st-order stretch*
$P(3) = 0.185324$	*2nd-order stretch*
$P(4) = -0.216571$	*3rd-order stretch*
$P(5) = 0.181181$	*4th-order stretch*

2. H_2O



Cartesian coordinates (a.u.):

Atoms	X	Y	Z
1O	O_{1x}	O_{1y}	O_{1z}
2H	H_{2x}	H_{2y}	H_{2z}
3H	H_{3x}	H_{3y}	H_{3z}

Internal coordinates:

$$r_1 = \sqrt{(O_{1x} - H_{2x})^2 + (O_{1y} - H_{2y})^2 + (O_{1z} - H_{2z})^2}$$

$$r_2 = \sqrt{(O_{1x} - H_{3x})^2 + (O_{1y} - H_{3y})^2 + (O_{1z} - H_{3z})^2}$$

$$a = \cos^{-1}\left[\frac{(H_{2x} - O_{1x})(H_{3x} - O_{1x}) + (H_{2y} - O_{1y})(H_{3y} - O_{1y}) + (H_{2z} - O_{1z})(H_{3z} - O_{1z})}{r_1 \times r_2}\right]$$

Constants:

$r_{eq} = 1.403412$ a.u.

$a_{eq} = 1.807874$ a.u.

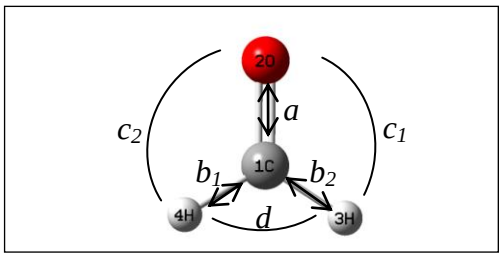
Potential energy function:

$$E(Hartree) = P(1) + P(2)\times\sum_{i=1}^{2}(r_i - r_{eq}) + P(3)\times(a - a_{eq}) +$$
$$P(4)\times\sum_{i=1}^{2}(r_i - r_{eq})^2 + P(5)\times(a - a_{eq})^2 + P(6)\times\left[(r_1 - r_{eq})(r_2 - r_{eq})\right] + P(7)\times\sum_{i=1}^{2}\left[(r_i - r_{eq})(a - a_{eq})\right] +$$
$$P(8)\times\sum_{i=1}^{2}(r_i - r_{eq})^3 + P(9)\times(a - a_{eq})^3 + P(10)\times\left[(r_1 - r_{eq})^2(r_2 - r_{eq}) + (r_1 - r_{eq})(r_2 - r_{eq})^2\right] +$$
$$P(11)\times\sum_{i=1}^{2}\left[(r_i - r_{eq})^2(a - a_{eq})\right] + P(12)\times\sum_{i=1}^{2}\left[(r_i - r_{eq})(a - a_{eq})^2\right] +$$
$$P(13)\times\left[(r_1 - r_{eq})(r_2 - r_{eq})(a - a_{eq})\right] + P(14)\times\sum_{i=1}^{2}(r_i - r_{eq})^4 + P(15)\times(a - a_{eq})^4 +$$
$$P(16)\times\left[(r_1 - r_{eq})^3(r_2 - r_{eq}) + (r_1 - r_{eq})(r_2 - r_{eq})^3\right] + P(17)\times\sum_{i=1}^{2}\left[(r_i - r_{eq})^3(a - a_{eq})\right] +$$
$$P(18)\times\sum_{i=1}^{2}\left[(r_i - r_{eq})(a - a_{eq})^3\right] + P(19)\times\sum_{i=1}^{2}\left[(r_i - r_{eq})^2(a - a_{eq})^2\right] +$$
$$P(20)\times\left[(r_1 - r_{eq})^2(r_2 - r_{eq})^2\right] + P(21)\times\left[(r_1 - r_{eq})^2(r_2 - r_{eq})(a - a_{eq}) + (r_1 - r_{eq})(r_2 - r_{eq})^2(a - a_{eq})\right] +$$
$$P(22)\times\left[(r_1 - r_{eq})(r_2 - r_{eq})(a - a_{eq})^2\right]$$

Parameters:

P(1)=-76.332216	*Equilibriun energy*	*P(12)=-0.018773*	*3rd-order stretch/bend coupling*
P(2)=0.000099	*1st-order stretch*	*P(13)=-0.033802*	*3rd-order stretch/bend coupling*
P(3)=0.000009	*1st-order bend*	*P(14)=0.280525*	*4th-order stretch*
P(4)=0.272209	*2nd-order stretch*	*P(15)=-0.005940*	*4th-order bend*
P(5)=0.083040	*2nd-order bend*	*P(16)=-0.002280*	*4th-order stretch/stretch coupling*
P(6)=-0.00619	*2nd-order stretch/stretch coupling*	*P(17)=-0.008572*	*4th-order stretch/bend coupling*
P(7)=0.033186	*2nd-order stretch/bend coupling*	*P(18)=0.014224*	*4th-order stretch/bend coupling*
P(8)=-0.340899	*3rd-order stretch*	*P(19)=-0.004180*	*4th-order stretch/bend coupling*
P(9)=-0.026569	*3rd-order bend*	*P(20)=0.000815*	*4th-order stretch/stretch coupling*
P(10)=-0.000822	*3rd-order stretch/stretch coupling*	*P(21)=0.004672*	*4th-order stretch/bend coupling*
P(11)=-0.003748	*3rd-order stretch/bend coupling*	*P(22)=0.018809*	*4th-order stretch/bend coupling*

3. CH_2O



Cartesian coordinates (a.u.):

Atoms	X	Y	Z
1C	C_{1x}	C_{1y}	C_{1z}
2O	O_{2x}	O_{2y}	O_{2z}
3H	H_{3x}	H_{3y}	H_{3z}
4H	H_{4x}	H_{4y}	H_{4z}

Internal coordinates:

$$a_1 = \sqrt{(C_{1x} - O_{2x})^2 + (C_{1y} - O_{2y})^2 + (C_{1z} - O_{2z})^2}$$

$$b_1 = \sqrt{(C_{1x} - H_{3x})^2 + (C_{1y} - H_{3y})^2 + (C_{1z} - H_{3z})^2}$$

$$b_2 = \sqrt{(C_{1x} - H_{4x})^2 + (C_{1y} - H_{4y})^2 + (C_{1z} - H_{4z})^2}$$

$$c_1 = \cos^{-1}\left[\frac{(O_{2x} - C_{1x})(H_{3x} - C_{1x}) + (O_{2y} - C_{1y})(H_{3y} - C_{1y}) + (O_{2z} - C_{1z})(H_{3z} - C_{1z})}{a \times b_1}\right]$$

$$c_2 = \cos^{-1}\left[\frac{(O_{2x} - C_{1x})(H_{4x} - C_{1x}) + (O_{2y} - C_{1y})(H_{4y} - C_{1y}) + (O_{2z} - C_{1z})(H_{4z} - C_{1z})}{a \times b_2}\right]$$

$$d = \cos^{-1}\left[\frac{(H_{3x} - O_{1x})(H_{4x} - O_{1x}) + (H_{3y} - O_{1y})(H_{4y} - O_{1y}) + (H_{3z} - O_{1z})(H_{4z} - O_{1z})}{b_1 \times b_2}\right]$$

Constants:

$a_{eq} = 1.403412$ a.u.

$b_{eq} = 1.403412$ a.u.

$c_{eq} = 2.127631$ a.u.

$d_{eq} = 2.027924$ a.u.

Potential energy function:

$$E(Hartree) = P(1) + P(2)\times\sum_{i=1}^{2}(b_i - b_{eq}) + P(3)\times\sum_{i=1}^{2}(c_i - c_{eq}) + P(4)\times(a - a_{eq}) + P(5)\times(d - d_{eq}) +$$

$$P(6)\times(a - a_{eq})^2 + P(7)\times(d - d_{eq})^2 + P(8)\times\sum_{i=1}^{2}(c_i - c_{eq})^2 + P(9)\times\sum_{i=1}^{2}(b_i - b_{eq})^2 +$$

$$P(10)\times\left[(b_2 - b_{eq})(c_2 - c_{eq}) + (b_1 - b_{eq})(c_1 - c_{eq})\right] + P(11)\times\sum_{i=1}^{2}(b_i - b_{eq})(d - d_{eq}) +$$

$$P(12)\times\sum_{i=1}^{2}(a - a_{eq})(b_i - b_{eq}) + P(13)\times\left[(c_1 - c_{eq})(c_2 - c_{eq})\right] + P(14)\times\sum_{i=1}^{2}(a - a_{eq})(c_i - c_{eq}) +$$

$$P(15)\times\left[(b_1 - b_{eq})(b_2 - b_{eq})\right] + P(16)\times\sum_{i=1}^{2}(d - d_{eq})(c_i - c_{eq}) +$$

$$P(17)\times\left[(b_1 - b_{eq})(c_2 - c_{eq}) + (b_2 - b_{eq})(c_1 - c_{eq})\right] + P(18)\times\left[(a - a_{eq})(d - d_{eq})\right] +$$

$$P(19)\times\sum_{i=1}^{2}(c_i - c_{eq})^3 + P(20)\times\sum_{i=1}^{2}(b_i - b_{eq})^3 + P(21)\times(d - d_{eq})^3 + P(22)\times(a - a_{eq})^3 +$$

$$P(23)\times\sum_{i=1}^{2}(c_i - c_{eq})(d - d_{eq})^2 + P(24)\times\sum_{i=1}^{2}(b_i - b_{eq})^2(d - d_{eq}) +$$

$$P(25)\times\left[(b_1 - b_{eq})(c_1 - c_{eq})^2 + (b_2 - b_{eq})(c_2 - c_{eq})^2\right] + P(26)\times\left[(b_1 - b_{eq})^2(b_2 - b_{eq}) + (b_1 - b_{eq})(b_2 - b_{eq})^2\right] +$$

$$P(27)\times\left[(a - a_{eq})(d - d_{eq})^2\right] + P(28)\times\left[(b_1 - b_{eq})^2(c_1 - c_{eq}) + (b_2 - b_{eq})^2(c_2 - c_{eq})\right] +$$

$$P(29)\times\sum_{i=1}^{2}(a - a_{eq})(c_i - c_{eq})^2 + P(30)\times\sum_{i=1}^{2}(a - a_{eq})^2(b_i - b_{eq}) + P(31)\times\sum_{i=1}^{2}(b_i - b_{eq})(d - d_{eq})^2 +$$

$$P(32)\times\left[(b_1-b_{eq})^2(c_2-c_{eq})+(b_2-b_{eq})^2(c_1-c_{eq})\right]+P(33)\times\left[(a-a_{eq})^2(d-d_{eq})\right]+$$

$$P(34)\times\left[(b_1-b_{eq})(c_2-c_{eq})^2+(b_2-b_{eq})(c_1-c_{eq})^2\right]+P(35)\times\sum_{i=1}^{2}(c_i-c_{eq})^2(d-d_{eq})+$$

$$P(36)\times\sum_{i=1}^{2}(a-a_{eq})(b_i-b_{eq})^2+P(37)\times\left[(c_1-c_{eq})(c_2-c_{eq})^2+(c_1-c_{eq})^2(c_2-c_{eq})\right]+$$

$$P(38)\times\left[(a-a_{eq})^2(c_1-c_{eq})+(a-a_{eq})^2(c_2-c_{eq})\right]+$$

$$P(39)\times\left[(b_2-b_{eq})(d-d_{eq})(c_1-c_{eq})+(b_1-b_{eq})(d-d_{eq})(c_2-c_{eq})\right]+$$

$$P(40)\times\left[(b_1-b_{eq})(b_2-b_{eq})(c_2-c_{eq})+(b_1-b_{eq})(b_2-b_{eq})(c_1-c_{eq})\right]+$$

$$P(41)\times\left[(a-a_{eq})(b_1-b_{eq})(b_2-b_{eq})\right]+P(42)\times\sum_{i=1}^{2}(b_i-b_{eq})(c_1-c_{eq})(c_2-c_{eq})+$$

$$P(43)\times\left[(a-a_{eq})(b_1-b_{eq})(c_1-c_{eq})+(a-a_{eq})(b_2-b_{eq})(c_2-c_{eq})\right]+$$

$$P(44)\times\left[(b_2-b_{eq})(d-d_{eq})(c_2-c_{eq})+(b_1-b_{eq})(d-d_{eq})(c_1-c_{eq})\right]+$$

$$P(45)\times\left[(a-a_{eq})(b_i-b_{eq})(d-d_{eq})\right]+P(46)\times\left[(d-d_{eq})(c_1-c_{eq})(c_2-c_{eq})\right]+$$

$$P(47)\times\sum_{i=1}^{2}(a-a_{eq})(d-d_{eq})(c_i-c_{eq})+$$

$$P(48)\times\left[(a-a_{eq})(b_1-b_{eq})(c_2-c_{eq})+(a-a_{eq})(b_2-b_{eq})(c_1-c_{eq})\right]+$$

$$P(49)\times\left[(b_1-b_{eq})(b_2-b_{eq})(d-d_{eq})\right]+P(50)\times\left[(a-a_{eq})(c_1-c_{eq})(c_2-c_{eq})\right]+$$

$$P(51)\times\sum_{i=1}^{2}(b_i-b_{eq})^4+P(52)\times\sum_{i=1}^{2}(c_i-b_{eq})^4+P(53)\times(a-a_{eq})^4+P(54)\times(d-d_{eq})^4+$$

$$P(55)\times\sum_{i=1}^{2}(c_i-c_{eq})(d-d_{eq})^3+P(56)\times\left[(b_2-b_{eq})(c_1-c_{eq})^3+(b_1-b_{eq})(c_2-c_{eq})^3\right]+$$

$$P(57)\times\left[(b_2-b_{eq})^3(c_2-c_{eq})+(b_1-b_{eq})^3(c_1-c_{eq})\right]+$$

$$P(58)\times\left[(b_1-b_{eq})^3(b_2-b_{eq})+(b_1-b_{eq})(b_2-b_{eq})^3\right]+$$

$$P(59)\times\sum_{i=1}^{2}(a-a_{eq})(b_i-b_{eq})^3+P(60)\times\left[(a-a_{eq})^3(d-d_{eq})\right]+$$

$$P(61)\times\sum_{i=1}^{2}(c_i-c_{eq})^3(d-d_{eq})+P(62)\times\left[(a-a_{eq})(d-d_{eq})^3\right]+$$

$$P(63)\times\left[(c_1-c_{eq})^3(c_2-c_{eq})+(c_1-c_{eq})(c_2-c_{eq})^3\right]+$$

$$P(64)\times\left[(b_1-b_{eq})^3*(c_2-c_{eq})+(b_2-b_{eq})^3*(c_1-c_{eq})\right]+$$

$$P(65)\times\sum_{i=1}^{2}(a-a_{eq})(c_i-c_{eq})^3+P(66)\times\sum_{i=1}^{2}(a-a_{eq})(b_i-b_{eq})^3+$$

$$P(67)\times\sum_{i=1}^{2}(a-a_{eq})^3(c_i-c_{eq})+P(68)\times\sum_{i=1}^{2}(b_i-b_{eq})^3(d-d_{eq})+P(69)\times\sum_{i=1}^{2}(b_i-b_{eq})(d-d_{eq})^3$$

$$P(70)\times\left[(b_2-b_{eq})(c_2-c_{eq})^3+(b_1-b_{eq})(c_1-c_{eq})^3\right]+$$

$$P(71)\times\left[(b_2-b_{eq})^2(c_1-c_{eq})^2+(b_1-b_{eq})^2(c_2-c_{eq})^2\right]+$$

$$P(72)\times\sum_{i=1}^{2}(b_i-b_{eq})^2(d-d_{eq})^2+P(73)\times\sum_{i=1}^{2}(a-a_{eq})^2(b_i-b_{eq})^2+$$

$$P(74)\times\sum_{i=1}^{2}(a-a_{eq})^2(c_i-c_{eq})^2+P(75)\times((b_2-b_{eq})^2*(c_2-c_{eq})^2+(b_1-b_{eq})^2*(c_1-c_{eq})^2)+$$

$$P(76)\times\sum_{i=1}^{2}(c_i-c_{eq})^2(d-d_{eq})^2+P(77)\times\left[(c_1-c_{eq})^2(c_2-c_{eq})^2\right]+$$

$$P(78)\times\left[(b_1-b_{eq})^2(b_2-b_{eq})^2\right]+P(79)\times\left[(a-a_{eq})^2(d-d_{eq})^2\right]+$$

$$P(80)\times\left[(b_2-b_{eq})(d-d_{eq})(c_2-c_{eq})^2+(b_1-b_{eq})(d-d_{eq})(c_1-c_{eq})^2\right]+$$

$$P(81)\times\left[(b_1-b_{eq})(d-d_{eq})^2(c_2-c_{eq})+(b_2-b_{eq})(d-d_{eq})^2(c_1-c_{eq})\right]+$$

$$P(82)\times\sum_{i=1}^{2}(a-a_{eq})(b_i-b_{eq})(d-d_{eq})^2+P(83)\times\sum_{i=1}^{2}(a-a_{eq})^2(d-d_{eq})(c_i-c_{eq})+$$

$$P(84)\times\left[(b_2-b_{eq})(c_1-c_{eq})(c_2-c_{eq})^2+(b_1-b_{eq})(c_1-c_{eq})^2(c_2-c_{eq})\right]+$$

$$P(85)\times\left[(b_2-b_{eq})(d-d_{eq})(c_1-c_{eq})^2+(b_1-b_{eq})(d-d_{eq})(c_2-c_{eq})^2\right]+$$

$$P(86)\times\sum_{i=1}^{2}(b_i-b_{eq})^2(c_1-c_{eq})(c_2-c_{eq})+$$

$$P(87)\times\left[(a-a_{eq})(b_2-b_{eq})^2(c_1-c_{eq})+(a-a_{eq})(b_1-b_{eq})^2(c_2-c_{eq})\right]+$$

$$P(88)\times\left[(a-a_{eq})(b_1-b_{eq})(c_2-c_{eq})^2+(a-a_{eq})(b_2-b_{eq})(c_1-c_{eq})^2\right]+$$

$$P(89)\times\left[(a-a_{eq})(b_1-b_{eq})^2(b_2-b_{eq})+(a-a_{eq})(b_1-b_{eq})(b_2-b_{eq})^2\right]+$$

$$P(90)\times\left[(a-a_{eq})^2(b_2-b_{eq})(c_1-c_{eq})+(a-a_{eq})^2(b_1-b_{eq})(c_2-c_{eq})\right]+$$

$$P(91)\times\left[(b_2-b_{eq})(c_1-c_{eq})^2(c_2-c_{eq})+(b_1-b_{eq})(c_1-c_{eq})(c_2-c_{eq})^2\right]+$$

$$P(92)\times\left[(b_1-b_{eq})(b_2-b_{eq})^2(c_1-c_{eq})+(b_1-b_{eq})^2(b_2-b_{eq})(c_2-c_{eq})\right]+$$

$$P(93)\times\left[(b_1-b_{eq})^2(b_2-b_{eq})(d-d_{eq})+(b_1-b_{eq})(b_2-b_{eq})^2(d-d_{eq})\right]+$$

$$P(94)\times\left[(a-a_{eq})(b_1-b_{eq})^2(c_1-c_{eq})+(a-a_{eq})(b_2-b_{eq})^2(c_2-c_{eq})\right]+$$

$$P(95)\times\left[(b_1-b_{eq})^2(d-d_{eq})(c_1-c_{eq})+(b_2-b_{eq})^2(d-d_{eq})(c_2-c_{eq})\right]+$$

$$P(96)\times\sum_{i=1}^{2}(a-a_{eq})(c_i-c_{eq})^2(d-d_{eq})+P(97)\times\sum_{i=1}^{2}(a-a_{eq})^2(b_i-b_{eq})(c_i-c_{eq})+$$

$$P(98)\times\sum_{i=1}^{2}(a-a_{eq})^2(b_i-b_{eq})(d-d_{eq})$$

$$P(99)\times\left[(d-d_{eq})(c_1-c_{eq})^2(c_2-c_{eq})+(d-d_{eq})(c_1-c_{eq})(c_2-c_{eq})^2\right]+$$

$$P(100)\times\left[(b_2-b_{eq})(d-d_{eq})^2(c_2-c_{eq})+(b_1-b_{eq})(d-d_{eq})^2(c_1-c_{eq})\right]+$$

$$P(101)\times\left[(b_1-b_{eq})(b_2-b_{eq})^2(c_2-c_{eq})+(b_1-b_{eq})^2(b_2-b_{eq})(c_1-c_{eq})\right]+$$

$$P(102)\times\left[(a-a_{eq})(c_1-c_{eq})(c_2-c_{eq})^2+(a-a_{eq})(c_1-c_{eq})^2(c_2-c_{eq})\right]+$$

$$P(103)\times\left[(a-a_{eq})^2(c_1-c_{eq})(c_2-c_{eq})\right]+P(104)\times\sum_{i=1}^{2}(b_1-b_{eq})(b_2-b_{eq})(c_i-c_{eq})^2+$$

$$P(105)\times\left[(b_1-b_{eq})^2(d-d_{eq})(c_2-c_{eq})+(b_2-b_{eq})^2(d-d_{eq})(c_1-c_{eq})\right]+$$

$$P(106)\times\left[(d-d_{eq})^2(c_1-c_{eq})(c_2-c_{eq})\right]+P(107)\times\sum_{i=1}^{2}(a-a_{eq})(d-d_{eq})^2(c_i-c_{eq})+$$

$$P(108)\times\left[(a-a_{eq})(b_2-b_{eq})(c_2-c_{eq})^2+(a-a_{eq})(b_1-b_{eq})(c_1-c_{eq})^2\right]+$$

$$P(109)\times\left[(a-a_{eq})^2(b_1-b_{eq})(b_2-b_{eq})\right]+P(110)\times\left[(b_1-b_{eq})(b_2-b_{eq})(d-d_{eq})^2\right]+$$

$$P(111)\times\sum_{i=1}^{2}(a-a_{eq})(b_i-b_{eq})^2(d-d_{eq})+P(112)\times\sum_{i=1}^{2}(a-a_{eq})(b_i-b_{eq})(c_1-c_{eq})(c_2-c_{eq})+$$

$$P(113)\times\left[(a-a_{eq})(b_2-b_{eq})(d-d_{eq})(c_2-c_{eq})+(a-a_{eq})(b_1-b_{eq})(d-d_{eq})(c_1-c_{eq})\right]+$$

$$P(114)\times\sum_{i=1}^{2}(b_1-b_{eq})(b_2-b_{eq})(d-d_{eq})(c_i-c_{eq})+P(115)\times\left[(a-a_{eq})(d-d_{eq})(c_1-c_{eq})(c_2-c_{eq})\right]+$$

$$P(116)\times\left[(a-a_{eq})(b_1-b_{eq})(b_2-b_{eq})(d-d_{eq})\right]+P(117)\times\sum_{i=1}^{2}(b_i-b_{eq})(d-d_{eq})(c_1-c_{eq})(c_2-c_{eq})+$$

$$P(118)\times\left[(a-a_{eq})(b_1-b_{eq})(d-d_{eq})(c_2-c_{eq})+(a-a_{eq})(b_2-b_{eq})(d-d_{eq})(c_1-c_{eq})\right]+$$

$$P(119)\times\left[(b_1-b_{eq})(b_2-b_{eq})(c_1-c_{eq})(c_2-c_{eq})\right]+P(120)\times\sum_{i=1}^{2}(a-a_{eq})(b_1-b_{eq})(b_2-b_{eq})(c_i-c_{eq})$$

Parameters:

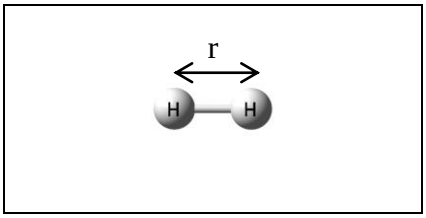
P(1)=-114.333872	*Equilibriun energy*	*P(21)=-0.023873*	*3rd-order bend*
P(2)=0.000051	*1st-order stretch*	*P(22)=-0.510095*	*3rd-order stretch*
P(3)=-0.075606	*1st-order bend*	*P(23)=-0.003830*	*3rd-order bend/bend coupling*
P(4)=0.000196	*1st-order stretch*	*P(24)=0.007774*	*3rd-order stretch/bend coupling*
P(5)=-0.075585	*1st-order bend*	*P(25)=-0.013125*	*3rd-order stretch/bend coupling*
P(6)=0.418373	*2nd-order stretch*	*P(26)=-0.000130*	*3rd-order stretch/stretch coupling*
P(7)=0.057733	*2nd-order bend*	*P(27)=-0.013319*	*3rd-order stretch/bend coupling*
P(8)=0.069779	*2nd-order bend*	*P(28)=0.007148*	*3rd-order stretch/bend coupling*
P(9)=0.155652	*2nd-order stretch*	*P(29)=-0.068192*	*3rd-order stretch/bend coupling*
P(10)=0.012903	*2nd-order stretch/bend coupling*	*P(30)=-0.036734*	*3rd-order stretch/stretch coupling*
P(11)=0.020411	*2nd-order stretch/bend coupling*	*P(31)=-0.010336*	*3rd-order stretch/bend coupling*
P(12)=0.034303	*2nd-order stretch/stretch coupling*	*P(32)=0.003165*	*3rd-order stretch/bend coupling*
P(13)=-0.050762	*2nd-order bend/bend coupling*	*P(33)=0.013109*	*3rd-order stretch/bend coupling*
P(14)=0.078777	*2nd-order stretch/bend coupling*	*P(34)=-0.001882*	*3rd-order stretch/bend coupling*
P(15)=0.005378	*2nd-order stretch/stretch coupling*	*P(35)=-0.009028*	*3rd-order bend/bend coupling*
P(16)=-0.017036	*2nd-order bend/bend coupling*	*P(36)=0.010576*	*3rd-order stretch/bend coupling*
P(17)=0.000660	*2nd-order stretch/bend coupling*	*P(37)=0.015480*	*3rd-order bend/bend coupling*
P(18)=0.022882	*2nd-order stretch/bend coupling*	*P(38)=-0.018463*	*3rd-order stretch/bend coupling*
P(19)=-0.037196	*3rd-order bend*	*P(39)=0.009152*	*3rd-order stretch/bend coupling*
P(20)=-0.167513	*3rd-order stretch*	*P(40)=0.003493*	*3rd-order stretch/bend coupling*

P(41)=-0.013310	*3rd-order stretch/stretch coupling*
P(42)=0.005923	*3rd-order stretch/bend coupling*
P(43)=-0.034033	*3rd-order stretch/bend coupling*
P(44)=-0.002146	*3rd-order stretch/bend coupling*
P(45)=-0.005513	*3rd-order stretch/bend coupling*
P(46)=0.012826	*3rd-order bend/bend coupling*
P(47)=-0.001213	*3rd-order stretch/bend coupling*
P(48)=0.003990	*3rd-order stretch/bend coupling*
P(49)=-0.021451	*3rd-order bend/bend coupling*
P(50)=0.020490	*3rd-order stretch/bend coupling*
P(51)=0.115902	*4-th order stretch*
P(52)=0.010706	*4-th order bend*
P(53)=0.376792	*4-th order stretch*
P(54)=0.018295	*4-th order bend*
P(55)=0.044970	*4-th order bend/bend coupling*
P(56)=0.011182	*4-th order stretch/bend coupling*
P(57)=-0.000296	*4-th order stretch/bend coupling*
P(58)=-0.003722	*4-th order stretch/stretch coupling*
P(59)=-0.006682	*4-th order stretch/stretch coupling*
P(60)=-0.008268	*4-th order stretch/bend coupling*
P(61)=0.039042	*4-th order bend/bend coupling*
P(62)=-0.016431	*4-th order stretch/bend coupling*
P(63)=0.021347	*4-th order bend/bend coupling*
P(64)=0.003198	*4-th order stretch/bend coupling*
P(65)=0.005702	*4-th order stretch/bend coupling*
P(66)=0.020173	*4-th order stretch/stretch coupling*
P(67)=-0.003164	*4-th order stretch/bend coupling*
P(68)=-0.002329	*4-th order stretch/bend coupling*
P(69)=0.012268	*4-th order stretch/bend coupling*
P(70)=0.010922	*4-th order stretch/bend coupling*
P(71)=-0.004520	*4-th order stretch/bend coupling*
P(72)=-0.009661	*4-th order stretch/bend coupling*
P(73)=-0.003653	*4-th order stretch/stretch coupling*
P(74)=0.025455	*4-th order stretch/bend coupling*
P(75)=-0.003802	*4-th order stretch/bend coupling*
P(76)=0.061059	*4-th order bend/bend coupling*
P(77)=0.052883	*4-th order bend/bend coupling*
P(78)=0.000351	*4-th order stretch/stretch coupling*
P(79)=0.002912	*4-th order stretch/bend coupling*
P(80)=0.023812	*4-th order stretch/bend coupling*
P(81)=0.021872	*4-th order stretch/bend coupling*
P(82)=0.008463	*4-th order stretch/bend coupling*
P(83)=0.000710	*4-th order stretch/bend coupling*
P(84)=0.006141	*4-th order stretch/bend coupling*
P(85)=0.024574	*4-th order stretch/bend coupling*
P(86)=0.004370	*4-th order stretch/bend coupling*
P(87)=-0.010734	*4-th order stretch/bend coupling*
P(88)=0.009631	*4-th order stretch/bend coupling*
P(89)=0.001292	*4-th order stretch/bend coupling*
P(90)=-0.000851	*4-th order stretch/bend coupling*
P(91)=0.016076	*4-th order stretch/bend coupling*
P(92)=-0.000046	*4-th order stretch/bend coupling*
P(93)=0.002300	*4-th order stretch/bend coupling*
P(94)=-0.011977	*4-th order stretch/bend coupling*
P(95)=0.004285	*4-th order stretch/bend coupling*
P(96)=-0.075013	*4-th order stretch/bend coupling*
P(97)=0.037460	*4-th order stretch/bend coupling*
P(98)=0.003895	*4-th order stretch/bend coupling*
P(99)=0.088141	*4-th order bend/bend coupling*
P(100)=0.032807	*4-th order stretch/bend coupling*
P(101)=-0.001005	*4-th order stretch/bend coupling*
P(102)=-0.091263	*4-th order stretch/bend coupling*
P(103)=0.007829	*4-th order stretch/bend coupling*
P(104)=0.001945	*4-th order stretch/bend coupling*
P(105)=-0.002864	*4-th order stretch/bend coupling*
P(106)=0.104939	*4-th order bend/bend coupling*
P(107)=-0.072217	*4-th order stretch/bend coupling*
P(108)=0.032381	*4-th order stretch/bend coupling*
P(109)=0.012860	*4-th order stretch/stretch coupling*
P(110)=0.021776	*4-th order stretch/bend coupling*
P(111)=-0.008427	*4-th order stretch/bend coupling*
P(112)=-0.003465	*4-th order stretch/bend coupling*
P(113)=0.022826	*4-th order stretch/bend coupling*
P(114)=0.002354	*4-th order stretch/bend coupling*
P(115)=-0.164093	*4-th order stretch/bend coupling*
P(116)=0.003766	*4-th order stretch/bend coupling*
P(117)=0.041534	*4-th order stretch/bend coupling*
P(118)=0.000706	*4-th order stretch/bend coupling*
P(119)=0.001903	*4-th order stretch/bend coupling*
P(120)=-0.008387	*4-th order stretch/bend coupling*

Appendix B
Critical Evaluation of Equilibrium Geometry and Harmonic Vibrational Frequencies

Below we present a comparison between equilibrium geometries and harmonic vibrational frequencies derived from our potential energy function (PEF) and those obtained using CCSD(T). The potential energy functions are implemented into an external program, which can be invoked from Gaussian 09 program. The CCSD(T) calculations are using the cc-pVTZ basis sets and are performed with the MOLPRO2k9 program. For Both of PEF and CCSD(T) calculations, the numerical energy gradient is employed in the geometry optimization process. The vibrational frequencies are obtained by diagonalizing the numerical hessian, with the rotations and translations projected out. The source code of the external programs and the Gaussian input/output files are stored in the CD-ROM.

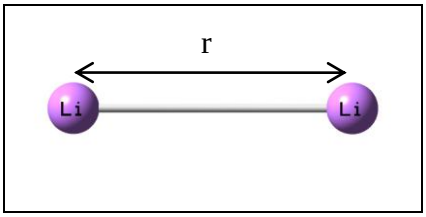
1. H_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	0.7426 Å	0.7426 Å	0.0000 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	4408.9 cm^{-1}	4409.5 cm^{-1}	0.6 cm^{-1}

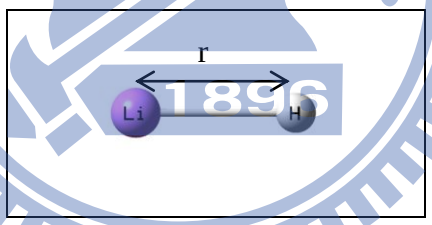
2. Li_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.7006 Å	2.7005 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	346.6 cm^{-1}	344.7 cm^{-1}	-1.9 cm^{-1}

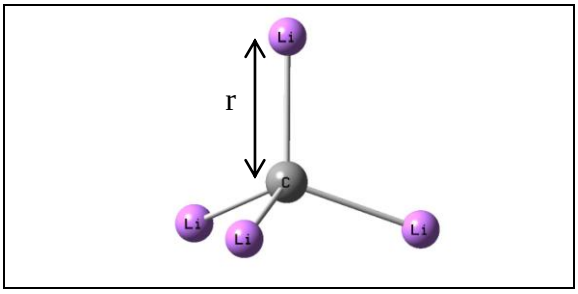
3. HLi



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.6081 Å	1.6080 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	1395.8 cm^{-1}	1395.1 cm^{-1}	-0.7 cm^{-1}

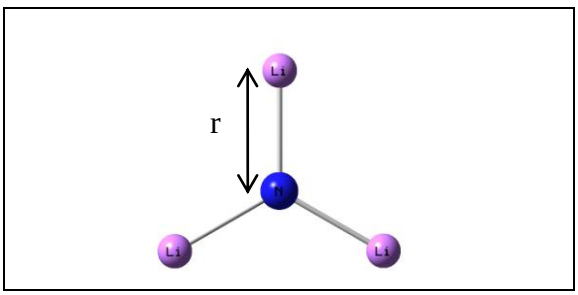
4. CLi_4



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.9019 Å	1.9016 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	121.8 cm^{-1}	120.9 cm^{-1}	-0.9 cm^{-1}
2	122.0 cm^{-1}	121.0 cm^{-1}	-1.0 cm^{-1}
3	122.4 cm^{-1}	121.0 cm^{-1}	-1.4 cm^{-1}
4	174.7 cm^{-1}	173.6 cm^{-1}	-1.1 cm^{-1}
5	174.7 cm^{-1}	173.6 cm^{-1}	-1.1 cm^{-1}
6	534.5 cm^{-1}	531.9 cm^{-1}	-2.6 cm^{-1}
7	693.8 cm^{-1}	692.1 cm^{-1}	-1.7 cm^{-1}
8	693.8 cm^{-1}	692.1 cm^{-1}	-1.7 cm^{-1}
9	693.9 cm^{-1}	692.1 cm^{-1}	-1.8 cm^{-1}

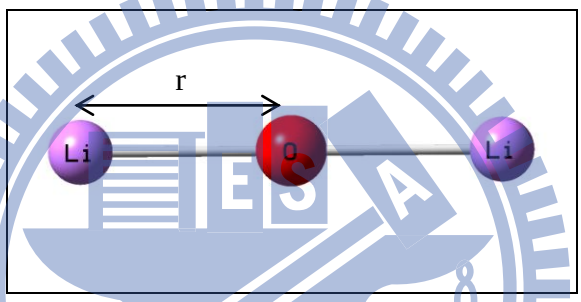
5. Li_3N



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7486 Å	1.7484 Å	-0.0002 Å

Vibrational mode	CCSD(T)/	PEF	Deviation
1	62.9 cm^{-1}	59.9 cm^{-1}	-3.0 cm^{-1}
2	193.3 cm^{-1}	191.7 cm^{-1}	-1.6 cm^{-1}
3	193.4 cm^{-1}	191.7 cm^{-1}	-1.7 cm^{-1}
4	653.1 cm^{-1}	649.6 cm^{-1}	-3.5 cm^{-1}
5	851.7 cm^{-1}	849.1 cm^{-1}	-2.6 cm^{-1}
6	851.7 cm^{-1}	849.1 cm^{-1}	-2.6 cm^{-1}

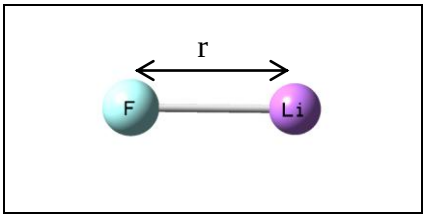
6. Li_2O



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.6330 Å	1.6328 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	103.8 cm^{-1}	102.6 cm^{-1}	-1.2 cm^{-1}
2	103.8 cm^{-1}	102.6 cm^{-1}	-1.2 cm^{-1}
3	779.6 cm^{-1}	775.4 cm^{-1}	-4.2 cm^{-1}
4	1023.3 cm^{-1}	1020.5 cm^{-1}	-2.8 cm^{-1}

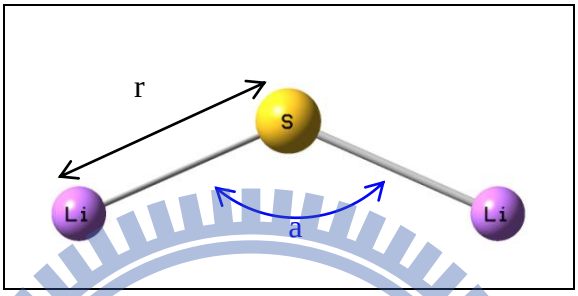
7. FLi



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.5836 Å	1.5834 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	912.4 cm^{-1}	909.0 cm^{-1}	-3.4 cm^{-1}

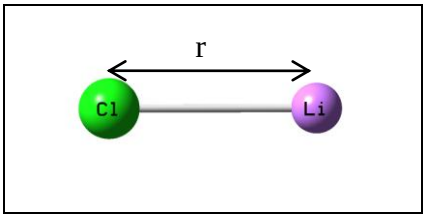
8. Li_2S



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0990 Å	2.0987 Å	-0.0003 Å
a	132.228°	132.324°	0.096°

Vibrational mode	CCSD(T)	PEF	Deviation
1	49.3 cm^{-1}	49.3 cm^{-1}	0.0 cm^{-1}
2	590.6 cm^{-1}	587.9 cm^{-1}	-2.7 cm^{-1}
3	661.8 cm^{-1}	659.7 cm^{-1}	-2.1 cm^{-1}

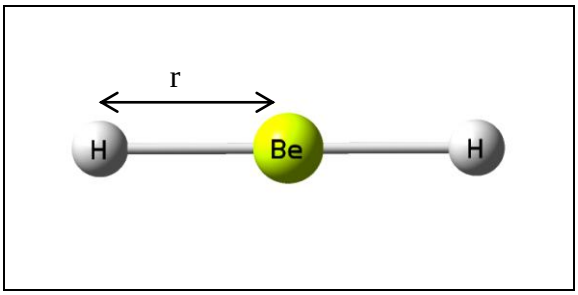
9. ClLi



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0418 Å	2.0415 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	639.9 cm^{-1}	637.9 cm^{-1}	-2.0 cm^{-1}

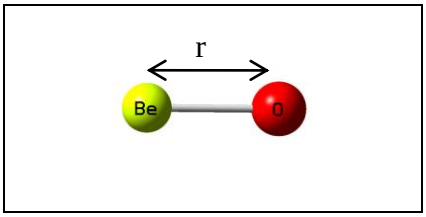
10. BeH_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3339 Å	1.3338 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	709.0 cm^{-1}	709.0 cm^{-1}	0.0 cm^{-1}
2	709.0 cm^{-1}	709.0 cm^{-1}	0.0 cm^{-1}
3	2029.1 cm^{-1}	2029.4 cm^{-1}	0.3 cm^{-1}
4	2237.7 cm^{-1}	2238.1 cm^{-1}	0.4 cm^{-1}

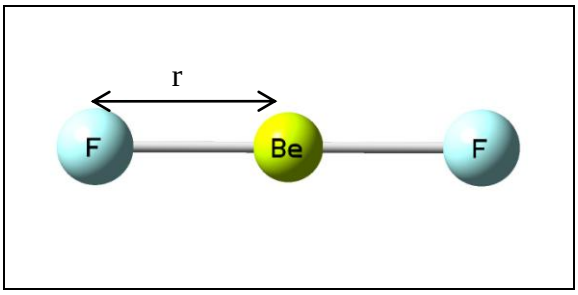
11. BeO



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3443 Å	1.3442 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	1458.7 cm^{-1}	1459.0 cm^{-1}	0.3 cm^{-1}

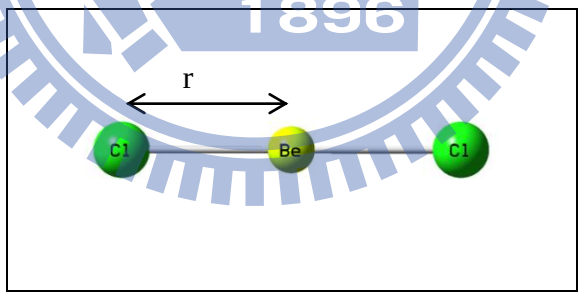
12. BeF_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3821 Å	1.3819 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	333.4 cm^{-1}	333.5 cm^{-1}	0.1 cm^{-1}
2	333.4 cm^{-1}	333.5 cm^{-1}	0.1 cm^{-1}
3	726.8 cm^{-1}	727.0 cm^{-1}	0.2 cm^{-1}
4	1584.0 cm^{-1}	1584.4 cm^{-1}	0.4 cm^{-1}

13. $BeCl_2$

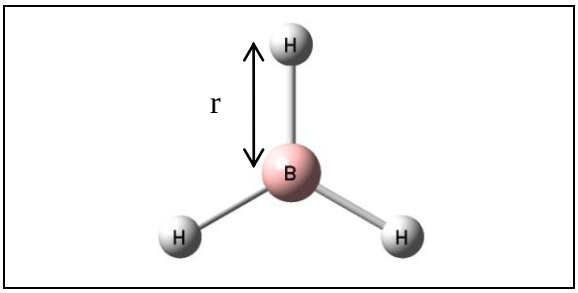


Geometric parameter	CCSD(T)	PEF	Deviation
r	1.8061 Å	1.8059 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	235.2 cm^{-1}	235.1 cm^{-1}	-0.1 cm^{-1}
2	235.2 cm^{-1}	235.1 cm^{-1}	-0.1 cm^{-1}
3	399.2 cm^{-1}	402.0 cm^{-1}	2.8 cm^{-1}

4	1143.4 cm^{-1}	1144.7 cm^{-1}	1.3 cm^{-1}

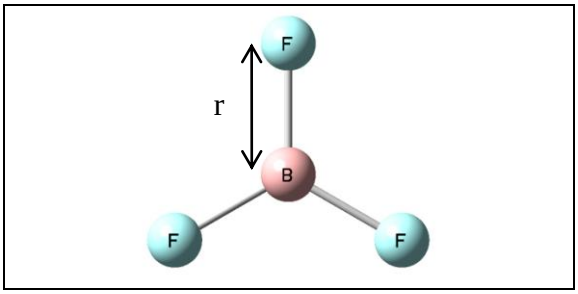
14. BH_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.9105 Å	1.1908 Å	0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	1162.4 cm^{-1}	1160.0 cm^{-1}	-2.4 cm^{-1}
2	1223.8 cm^{-1}	1223.0 cm^{-1}	-0.8 cm^{-1}
3	1223.8 cm^{-1}	1223.0 cm^{-1}	-0.8 cm^{-1}
4	2564.4 cm^{-1}	2564.6 cm^{-1}	0.2 cm^{-1}
5	2700.1 cm^{-1}	2697.3 cm^{-1}	-2.8 cm^{-1}
6	2700.2 cm^{-1}	2697.3 cm^{-1}	-2.9 cm^{-1}

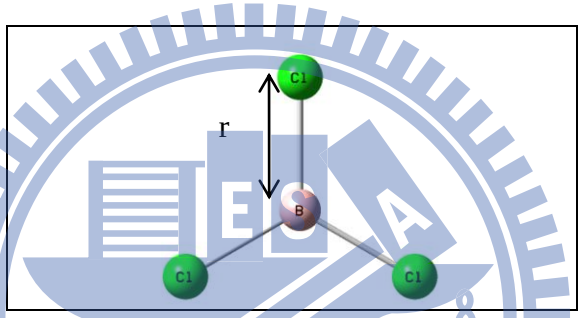
15. BF_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3128 Å	1.3126 Å	0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	484.0 cm^{-1}	482.3 cm^{-1}	-1.7 cm^{-1}
2	484.0 cm^{-1}	482.3 cm^{-1}	-1.7 cm^{-1}
3	705.6 cm^{-1}	698.8 cm^{-1}	-6.8 cm^{-1}
4	899.2 cm^{-1}	900.2 cm^{-1}	1.0 cm^{-1}
5	1503.4 cm^{-1}	1496.6 cm^{-1}	6.8 cm^{-1}
6	1503.4 cm^{-1}	1496.6 cm^{-1}	6.8 cm^{-1}

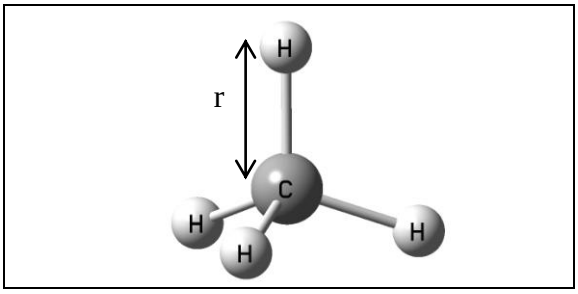
16. BCl_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7466 Å	1.7464Å	-0.0002Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	255.6 cm^{-1}	257.2 cm^{-1}	1.6 cm^{-1}
2	255.6 cm^{-1}	257.2 cm^{-1}	1.6 cm^{-1}
3	465.3 cm^{-1}	461.6 cm^{-1}	-3.7 cm^{-1}
4	473.1 cm^{-1}	476.9 cm^{-1}	3.8 cm^{-1}
5	979.1 cm^{-1}	974.1 cm^{-1}	-5.0 cm^{-1}
6	979.1 cm^{-1}	974.1 cm^{-1}	-5.0 cm^{-1}

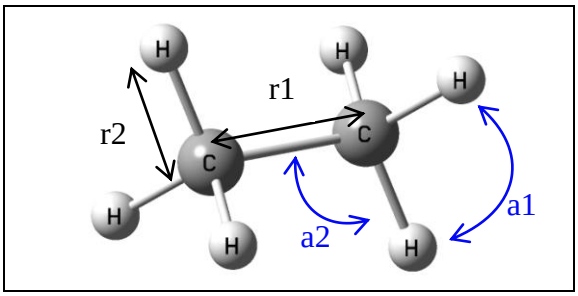
17. CH_4



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.0890 Å	1.0889Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	1343.7 cm^{-1}	1344.8 cm^{-1}	1.1 cm^{-1}
2	1343.8 cm^{-1}	1344.8 cm^{-1}	1.0 cm^{-1}
3	1343.9 cm^{-1}	1344.8 cm^{-1}	0.9 cm^{-1}
4	1570.6 cm^{-1}	1571.8 cm^{-1}	1.2 cm^{-1}
5	1570.7 cm^{-1}	1571.9 cm^{-1}	1.2 cm^{-1}
6	3034.4 cm^{-1}	3035.6 cm^{-1}	1.2 cm^{-1}
7	3153.3 cm^{-1}	3154.2 cm^{-1}	0.9 cm^{-1}
8	3153.3 cm^{-1}	3154.2 cm^{-1}	0.9 cm^{-1}
9	3153.3 cm^{-1}	3154.2 cm^{-1}	0.9 cm^{-1}

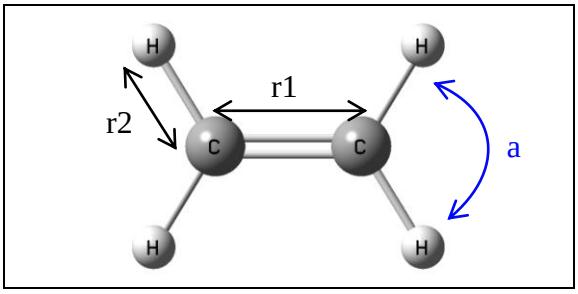
18. CH_3-CH_3



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.5290 Å	1.5286 Å	-0.0004 Å
r2	1.0918 Å	1.0917 Å	-0.0001 Å
a1	107.692˚	107.697˚	0.005˚
a2	111.196˚	111.192˚	-0.004˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	309.1 cm^{-1}	310.0 cm^{-1}	0.9 cm^{-1}
2	820.8 cm^{-1}	821.1 cm^{-1}	0.3 cm^{-1}
3	820.9 cm^{-1}	821.1 cm^{-1}	0.2 cm^{-1}
4	1013.4 cm^{-1}	1014.8 cm^{-1}	1.4 cm^{-1}
5	1224.4 cm^{-1}	1225.8 cm^{-1}	1.4 cm^{-1}
6	1224.4 cm^{-1}	1225.8 cm^{-1}	1.4 cm^{-1}
7	1406.3 cm^{-1}	1408.1 cm^{-1}	1.8 cm^{-1}
8	1427.1 cm^{-1}	1429.0 cm^{-1}	1.9 cm^{-1}
9	1510.6 cm^{-1}	1509.7 cm^{-1}	-0.9 cm^{-1}
10	1510.6 cm^{-1}	1509.7 cm^{-1}	-0.9 cm^{-1}
11	1512.2 cm^{-1}	1514.6 cm^{-1}	2.4 cm^{-1}
12	1512.4 cm^{-1}	1514.6 cm^{-1}	2.4 cm^{-1}
13	3037.6 cm^{-1}	3039.2 cm^{-1}	1.6 cm^{-1}
14	3039.0 cm^{-1}	3039.3 cm^{-1}	0.3 cm^{-1}
15	3096.3 cm^{-1}	3098.2 cm^{-1}	1.9 cm^{-1}
16	3096.4 cm^{-1}	3098.2 cm^{-1}	1.8 cm^{-1}
17	3119.6 cm^{-1}	3120.8 cm^{-1}	1.2 cm^{-1}
18	3119.6 cm^{-1}	3120.8 cm^{-1}	1.2 cm^{-1}

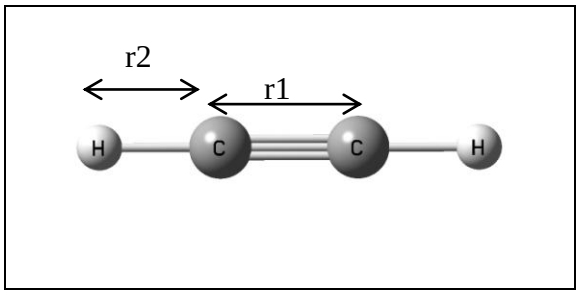
19. $CH_2=CH_2$



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.3370 Å	1.3370 Å	0.0000 Å
r2	1.0381 Å	1.0831 Å	0.0000 Å
a	117.1°	117.1°	0.000°

Vibrational mode	CCSD(T)	PEF	Deviation
1	822.9 cm^{-1}	823.0 cm^{-1}	0.1 cm^{-1}
2	941.6 cm^{-1}	940.9 cm^{-1}	-0.7 cm^{-1}
3	966.7 cm^{-1}	967.1 cm^{-1}	0.4 cm^{-1}
4	1046.8 cm^{-1}	1047.2 cm^{-1}	0.4 cm^{-1}
5	1241.7 cm^{-1}	1242.0 cm^{-1}	0.3 cm^{-1}
6	1368.7 cm^{-1}	1368.8 cm^{-1}	0.1 cm^{-1}
7	1478.8 cm^{-1}	1479.2 cm^{-1}	0.4 cm^{-1}
8	1671.0cm^{-1}	1671.9 cm^{-1}	0.9 cm^{-1}
9	3138.6 cm^{-1}	3139.3 cm^{-1}	0.7 cm^{-1}
10	3156.6 cm^{-1}	3157.3 cm^{-1}	0.7 cm^{-1}
11	3218.7 cm^{-1}	3219.6 cm^{-1}	0.9 cm^{-1}
12	3245.6 cm^{-1}	3246.5 cm^{-1}	0.9 cm^{-1}

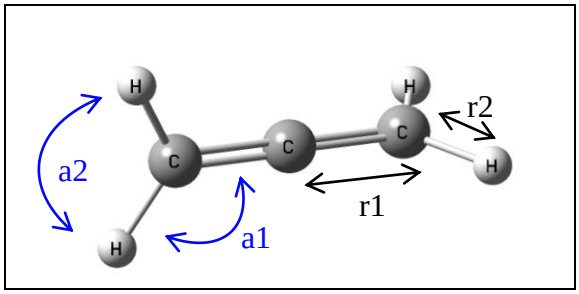
20. CH≡CH



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2097 Å	1.2096 Å	-0.0001 Å
r2	1.0637 Å	1.0637 Å	0.0000 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	577.6 cm^{-1}	577.9 cm^{-1}	0.3 cm^{-1}
2	577.6 cm^{-1}	577.9 cm^{-1}	0.3 cm^{-1}
3	746.4 cm^{-1}	746.0 cm^{-1}	-0.4 cm^{-1}
4	746.4 cm^{-1}	746.0 cm^{-1}	-0.4 cm^{-1}
5	2000.0 cm^{-1}	2000.9 cm^{-1}	0.9 cm^{-1}
6	3409.5 cm^{-1}	3410.4 cm^{-1}	0.9 cm^{-1}
7	3510.3 cm^{-1}	3511.1 cm^{-1}	0.8 cm^{-1}

21. CH_2CCH_2

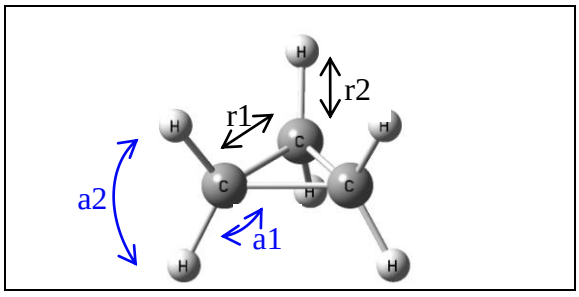


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.3133 Å	1.3133 Å	0.0000 Å
r2	1.0832 Å	1.0833 Å	0.0001 Å

a1	120.9˚	120.9 ˚	0.0˚
a2	118.2˚	118.2˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	347.6 cm^{-1}	349.1 cm^{-1}	1.5 cm^{-1}
2	347.9 cm^{-1}	349.2 cm^{-1}	1.3 cm^{-1}
3	856.6 cm^{-1}	858.0 cm^{-1}	1.4 cm^{-1}
4	856.6 cm^{-1}	858.0 cm^{-1}	1.4 cm^{-1}
5	871.0 cm^{-1}	861.2 cm^{-1}	-9.8 cm^{-1}
6	1017.4 cm^{-1}	1015.9 cm^{-1}	-1.5 cm^{-1}
7	1017.5 cm^{-1}	1016.0 cm^{-1}	-1.5 cm^{-1}
8	1080.3 cm^{-1}	1080.8 cm^{-1}	0.5 cm^{-1}
9	1438.0 cm^{-1}	1438.3 cm^{-1}	0.3 cm^{-1}
10	1488.2 cm^{-1}	1484.4 cm^{-1}	-3.8 cm^{-1}
11	2011.1 cm^{-1}	2012.2 cm^{-1}	1.1 cm^{-1}
12	3142.2 cm^{-1}	3141.5 cm^{-1}	-0.7 cm^{-1}
13	3144.0 cm^{-1}	3151.1 cm^{-1}	7.1 cm^{-1}
14	3225.9 cm^{-1}	3224.4 cm^{-1}	-1.5 cm^{-1}
15	3226.0 cm^{-1}	3224.7 cm^{-1}	-1.3 cm^{-1}

22. C_3H_6

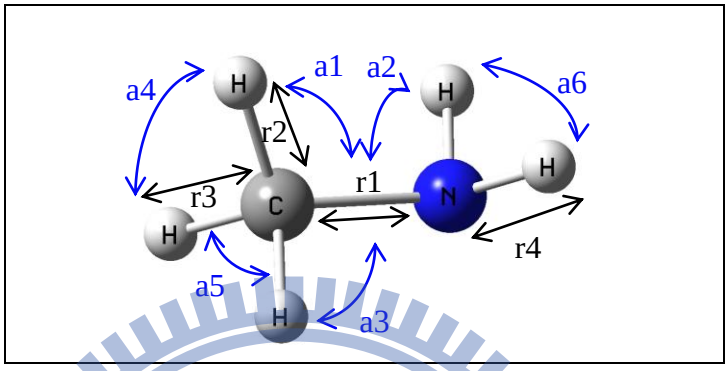


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.5100 Å	1.5099 Å	-0.0001 Å
r2	1.0814 Å	1.0813 Å	-0.0001 Å
a1	117.8˚	117.8˚	0.0˚
a2	114.9˚	114.9˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	739.9 cm^{-1}	737.3 cm^{-1}	-2.6 cm^{-1}
2	740.1 cm^{-1}	747.3 cm^{-1}	7.2 cm^{-1}
3	857.2 cm^{-1}	851.3 cm^{-1}	-5.9 cm^{-1}
4	891.3 cm^{-1}	895.0 cm^{-1}	3.7 cm^{-1}
5	891.4 cm^{-1}	894.5 cm^{-1}	3.1 cm^{-1}
6	1060.0 cm^{-1}	1062.2 cm^{-1}	2.2 cm^{-1}
7	1060.2 cm^{-1}	1063.3 cm^{-1}	3.1 cm^{-1}
8	1088.4 cm^{-1}	1085.5 cm^{-1}	-2.9 cm^{-1}
9	1160.4 cm^{-1}	1160.4 cm^{-1}	0.0 cm^{-1}
10	1213.8 cm^{-1}	1209.5 cm^{-1}	-4.3 cm^{-1}
11	1216.8 cm^{-1}	1216.1 cm^{-1}	-0.7 cm^{-1}
12	1216.8 cm^{-1}	1216.8 cm^{-1}	0.0 cm^{-1}
13	1478.1 cm^{-1}	1478.1 cm^{-1}	0.0 cm^{-1}
14	1478.2 cm^{-1}	1479.8 cm^{-1}	1.6 cm^{-1}
15	1527.9 cm^{-1}	1528.9 cm^{-1}	1.0 cm^{-1}
16	3145.6 cm^{-1}	3146.3 cm^{-1}	0.7 cm^{-1}
17	3145.8 cm^{-1}	3146.6 cm^{-1}	0.8 cm^{-1}
18	3156.4 cm^{-1}	3157.8 cm^{-1}	1.4 cm^{-1}

19	3228.0 cm^{-1}	3227.1 cm^{-1}	-0.9 cm^{-1}
20	3228.2 cm^{-1}	3231.1 cm^{-1}	2.9 cm^{-1}
21	3248.1 cm^{-1}	3248.6 cm^{-1}	0.5 cm^{-1}

23. CH_3NH_2

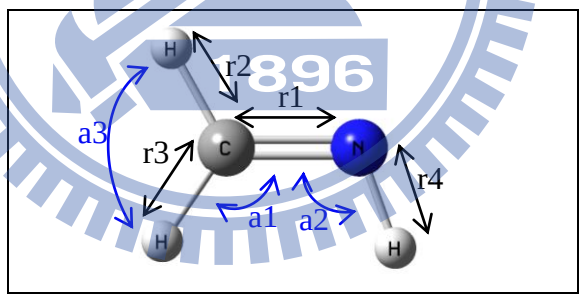


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4691 Å	1.4686 Å	-0.0005 Å
r2	1.0986 Å	1.0970 Å	-0.0016 Å
r3	1.0903 Å	1.0909 Å	0.0006 Å
r4	1.0136 Å	1.0136 Å	0.0000Å
a1	114.4˚	115.1˚	0.7˚
a2	109.1˚	109.2˚	0.1˚
a3	109.5˚	109.1˚	-0.4˚
a4	107.0˚	108.0˚	1.0˚
a5	109.5˚	107.2˚	2.3˚
a6	105.4˚	105.4˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	306.5 cm^{-1}	307.4 cm^{-1}	0.9 cm^{-1}
2	878.4 cm^{-1}	877.9 cm^{-1}	-0.5 cm^{-1}
3	976.3 cm^{-1}	975.9 cm^{-1}	-0.4 cm^{-1}

4	1065.2 cm^{-1}	1065.6 cm^{-1}	0.4 cm^{-1}
5	1187.8 cm^{-1}	1187.6 cm^{-1}	-0.2 cm^{-1}
6	1359.2 cm^{-1}	1361.4 cm^{-1}	2.2 cm^{-1}
7	1457.8 cm^{-1}	1457.8 cm^{-1}	0.0 cm^{-1}
8	1508.0 cm^{-1}	1508.0 cm^{-1}	0.0 cm^{-1}
9	1527.6 cm^{-1}	1530.6 cm^{-1}	3.0 cm^{-1}
10	1667.2 cm^{-1}	1666.9 cm^{-1}	-0.3 cm^{-1}
11	2996.5 cm^{-1}	2997.3 cm^{-1}	0.8 cm^{-1}
12	3079.5 cm^{-1}	3079.8 cm^{-1}	0.3 cm^{-1}
13	3114.9 cm^{-1}	3115.6 cm^{-1}	0.7 cm^{-1}
14	3497.7 cm^{-1}	3498.3 cm^{-1}	0.6 cm^{-1}
15	3578.6 cm^{-1}	3579.2 cm^{-1}	0.6 cm^{-1}

24. CH_2NH

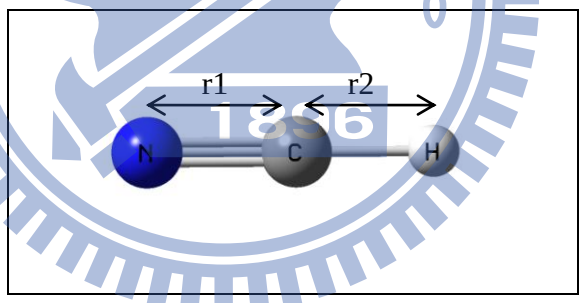


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2275 Å	1.2774 Å	-0.0001 Å
r2	1.0882 Å	1.0881 Å	-0.0001 Å
r3	1.0924 Å	1.0923 Å	-0.0001 Å
r4	1.0217 Å	1.0216 Å	-0.0001 Å
a1	124.6˚	124.6˚	0.0˚
a2	109.5˚	109.5˚	0.0˚

a3	118.6˚	118.6˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1072.7 cm^{-1}	1073.4 cm^{-1}	0.7 cm^{-1}
2	1080.7 cm^{-1}	1082.2 cm^{-1}	1.5 cm^{-1}
3	1162.1 cm^{-1}	1163.4 cm^{-1}	1.3 cm^{-1}
4	1386.5 cm^{-1}	1387.4 cm^{-1}	0.9 cm^{-1}
5	1482.9 cm^{-1}	1483.7 cm^{-1}	0.8 cm^{-1}
6	1674.7 cm^{-1}	1675.9 cm^{-1}	1.2 cm^{-1}
7	3051.6 cm^{-1}	3052.0 cm^{-1}	0.4 cm^{-1}
8	3151.7 cm^{-1}	3152.0 cm^{-1}	0.3 cm^{-1}
9	3440.2 cm^{-1}	3440.7 cm^{-1}	0.5 cm^{-1}

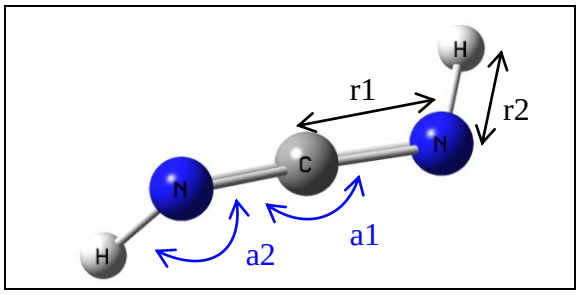
25. CHN



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.1601 Å	1.1600 Å	-0.0001 Å
r2	1.0669 Å	1.0668 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	716.0 cm^{-1}	716.6 cm^{-1}	0.6 cm^{-1}
2	716.0 cm^{-1}	716.6 cm^{-1}	0.6 cm^{-1}
3	2110.7 cm^{-1}	2111.7 cm^{-1}	1.0 cm^{-1}
4	3442.8 cm^{-1}	3443.7 cm^{-1}	0.9 cm^{-1}

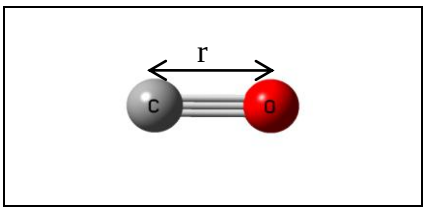
26. NHCNH



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2300 Å	1.2299 Å	-0.0001Å
r2	1.0120 Å	1.0119 Å	-0.0001Å
a1	170.6°	170.6°	0.0°
a2	116.7°	116.7°	0.0°

Vibrational mode	CCSD(T)	PEF	Deviation
1	525.8 cm^{-1}	526.0 cm^{-1}	0.2 cm^{-1}
2	527.0 cm^{-1}	527.2 cm^{-1}	0.2 cm^{-1}
3	761.9 cm^{-1}	763.9 cm^{-1}	2.0 cm^{-1}
4	944.8 cm^{-1}	945.2 cm^{-1}	0.4 cm^{-1}
5	954.5 cm^{-1}	954.4 cm^{-1}	-0.1 cm^{-1}
6	1247.4 cm^{-1}	1247.8 cm^{-1}	0.4 cm^{-1}
7	2187.3 cm^{-1}	2188.5 cm^{-1}	1.2 cm^{-1}
8	3594.0 cm^{-1}	3594.9 cm^{-1}	0.9 cm^{-1}
9	3594.4 cm^{-1}	3595.0 cm^{-1}	0.6 cm^{-1}

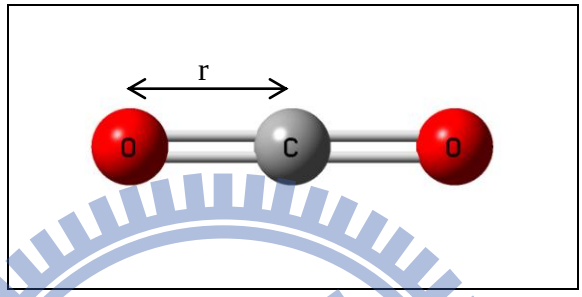
27. CO



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.1357 Å	1.1356 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	2152.9 cm^{-1}	2154.1 cm^{-1}	1.2 cm^{-1}

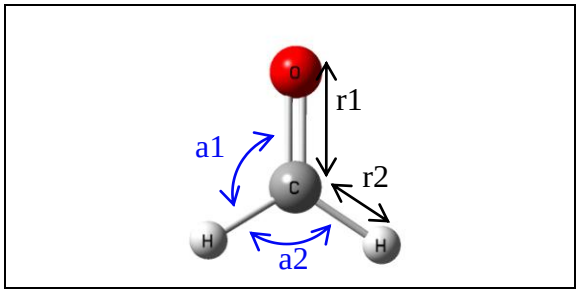
28. CO_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.1663 Å	1.1662 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	660.2 cm^{-1}	660.6 cm^{-1}	0.4 cm^{-1}
2	660.2 cm^{-1}	660.6 cm^{-1}	0.4 cm^{-1}
3	1345.9 cm^{-1}	1346.4 cm^{-1}	0.5 cm^{-1}
4	2395.2 cm^{-1}	2396.9 cm^{-1}	1.7 cm^{-1}

29. CH_2O

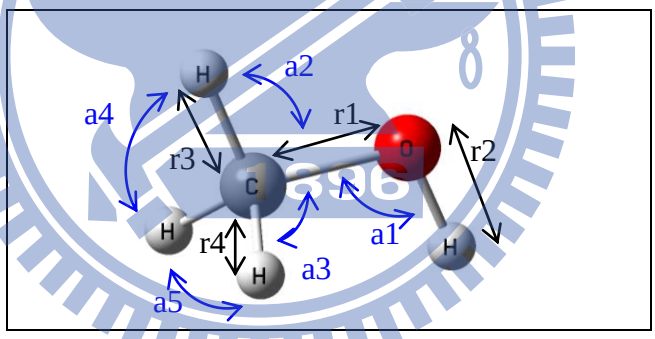


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2096 Å	1.2095 Å	-0.0001 Å

r2	1.1033 Å	1.1032 Å	-0.0001 Å
a1	121.9˚	121.9˚	0.0˚
a2	116.2˚	116.2˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1192.0 cm^{-1}	1192.3 cm^{-1}	0.3 cm^{-1}
2	1274.6 cm^{-1}	1274.8 cm^{-1}	0.2 cm^{-1}
3	1542.8 cm^{-1}	1543.2 cm^{-1}	0.4 cm^{-1}
4	1780.1 cm^{-1}	1781.0 cm^{-1}	0.9 cm^{-1}
5	2929.0 cm^{-1}	2929.6 cm^{-1}	0.6 cm^{-1}
6	2995.5 cm^{-1}	2996.0 cm^{-1}	0.5 cm^{-1}

30. CH_3OH

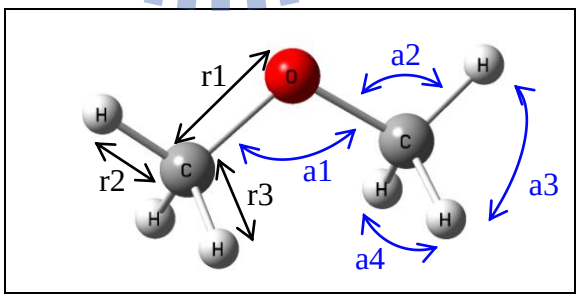


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4211 Å	1.4207 Å	-0.0004 Å
r2	0.9593 Å	0.9594 Å	0.0001 Å
r3	1.0876 Å	1.0888 Å	0.0012 Å
r4	1.0955 Å	1.0947 Å	-0.0008 Å
a1	107.3˚	107.4˚	0.1˚
a2	107.5˚	106.9˚	-0.6˚
a3	112.0˚	112.3˚	0.3˚

a4	109.3˚	108.2˚	-1.1˚
a5	106.9˚	108.8˚	1.9˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	304.6 cm^{-1}	305.3 cm^{-1}	0.7 cm^{-1}
2	1064.8 cm^{-1}	1066.0 cm^{-1}	1.2 cm^{-1}
3	1095.3 cm^{-1}	1096.2 cm^{-1}	0.9 cm^{-1}
4	1179.4 cm^{-1}	1179.1 cm^{-1}	-0.3 cm^{-1}
5	1393.6 cm^{-1}	1394.9 cm^{-1}	1.3 cm^{-1}
6	1487.5 cm^{-1}	1487.4 cm^{-1}	-0.1 cm^{-1}
7	1507.7 cm^{-1}	1507.6 cm^{-1}	-0.1 cm^{-1}
8	1523.0 cm^{-1}	1523.6 cm^{-1}	0.6 cm^{-1}
9	3009.0 cm^{-1}	3009.7 cm^{-1}	0.7 cm^{-1}
10	3064.1 cm^{-1}	3064.6 cm^{-1}	0.5 cm^{-1}
11	3127.7 cm^{-1}	3128.1 cm^{-1}	0.4 cm^{-1}
12	3864.5 cm^{-1}	3865.4 cm^{-1}	0.9 cm^{-1}

31. CH_3OCH_3



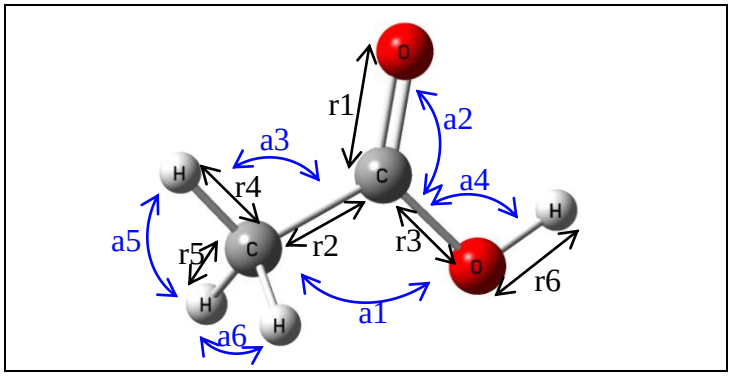
Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4109 Å	1.4108 Å	-0.0001 Å
r2	1.0889 Å	1.0888 Å	-0.0001 Å
r3	1.0979 Å	1.0978 Å	-0.0001 Å

a1	110.8˚	110.7˚	-0.1˚
a2	107.6˚	107.6˚	0.0˚
a3	109.0˚	109.0˚	0.0˚
a4	108.4˚	108.4˚	0.0˚

Vibrational mode	**CCSD(T)**	**PEF**	**Deviation**
1	206.4 cm^{-1}	200.1 cm^{-1}	-6.3 cm^{-1}
2	259.1 cm^{-1}	256.7 cm^{-1}	-2.4 cm^{-1}
3	418.1 cm^{-1}	418.7 cm^{-1}	0.6 cm^{-1}
4	963.7 cm^{-1}	964.3 cm^{-1}	0.6 cm^{-1}
5	1129.1 cm^{-1}	1128.6 cm^{-1}	0.5 cm^{-1}
6	1169.5 cm^{-1}	1169.8 cm^{-1}	0.3 cm^{-1}
7	1202.6 cm^{-1}	1202.2 cm^{-1}	-0.4 cm^{-1}
8	1212.2 cm^{-1}	1211.6 cm^{-1}	-0.6 cm^{-1}
9	1277.0 cm^{-1}	1275.7 cm^{-1}	-1.3 cm^{-1}
10	1460.4 cm^{-1}	1462.2 cm^{-1}	1.8 cm^{-1}
11	1490.8 cm^{-1}	1491.0 cm^{-1}	0.2 cm^{-1}
12	1495.3 cm^{-1}	1496.4 cm^{-1}	1.1 cm^{-1}
13	1499.8 cm^{-1}	1500.8 cm^{-1}	1.0 cm^{-1}
14	1508.4 cm^{-1}	1510.7 cm^{-1}	2.3 cm^{-1}
15	1527.4 cm^{-1}	1526.5 cm^{-1}	-0.9 cm^{-1}
16	2978.2 cm^{-1}	2978.8 cm^{-1}	0.6 cm^{-1}
17	2987.0 cm^{-1}	2987.7 cm^{-1}	0.7 cm^{-1}
18	3030.5 cm^{-1}	3028.7 cm^{-1}	-1.8 cm^{-1}
19	3036.2 cm^{-1}	3036.5 cm^{-1}	0.3 cm^{-1}
20	3128.8 cm^{-1}	3130.7 cm^{-1}	1.9 cm^{-1}

21	3130.7 cm^{-1}	3130.7 cm^{-1}	0.0 cm^{-1}

32. CH_3COOH

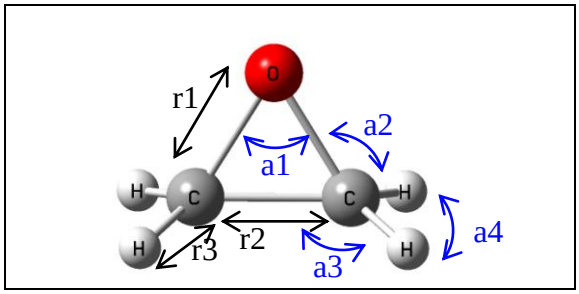


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2071 Å	1.2070 Å	-0.0001 Å
r2	1.5041 Å	1.5042Å	0.0001 Å
r3	1.3571 Å	1.3571 Å	0.0000 Å
r4	1.0904 Å	1.0904 Å	0.0000 Å
r5	1.0861 Å	1.0860 Å	-0.0001 Å
r6	0.9676 Å	0.9675 Å	-0.0001 Å
a1	111.3˚	111.3˚	0.0˚
a2	122.5˚	122.5˚	0.0˚
a3	109.4˚	109.6˚	0.2˚
a4	105.5˚	105.5˚	0.0˚
a5	110.3˚	110.3˚	0.0˚
a6	107.7˚	110.3˚	2.6˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	75.0 cm^{-1}	83.2 cm^{-1}	8.2 cm^{-1}
2	418.5 cm^{-1}	416.9 cm^{-1}	-1.6 cm^{-1}

3	545.7 cm^{-1}	547.9 cm^{-1}	2.2 cm^{-1}
4	583.9 cm^{-1}	583.4 cm^{-1}	-0.5 cm^{-1}
5	664.7 cm^{-1}	662.0 cm^{-1}	-2.7 cm^{-1}
6	869.3 cm^{-1}	869.8 cm^{-1}	0.5 cm^{-1}
7	1004.7 cm^{-1}	1003.7 cm^{-1}	-1.0 cm^{-1}
8	1071.0 cm^{-1}	1070.0 cm^{-1}	-1.0 cm^{-1}
9	1220.0 cm^{-1}	1219.6 cm^{-1}	-0.4 cm^{-1}
10	1354.9 cm^{-1}	1355.8 cm^{-1}	0.9 cm^{-1}
11	1421.8 cm^{-1}	1421.5 cm^{-1}	-0.3 cm^{-1}
12	1480.9 cm^{-1}	1485.3 cm^{-1}	4.4 cm^{-1}
13	1487.6 cm^{-1}	1488.8 cm^{-1}	1.2 cm^{-1}
14	1836.4 cm^{-1}	1836.8 cm^{-1}	0.4 cm^{-1}
15	3064.6 cm^{-1}	3066.1 cm^{-1}	1.5 cm^{-1}
16	3136.8 cm^{-1}	3136.1 cm^{-1}	-0.7 cm^{-1}
17	3180.1 cm^{-1}	3181.3 cm^{-1}	1.2 cm^{-1}
18	3775.8 cm^{-1}	3777.6 cm^{-1}	1.8 cm^{-1}

33. C_2H_4O

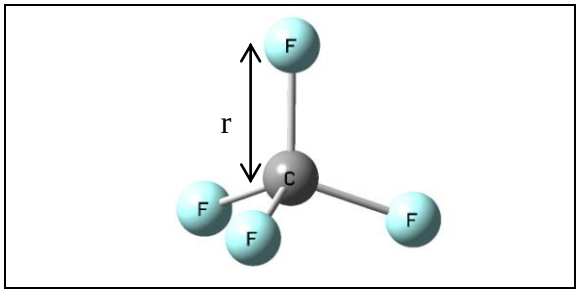


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4319 Å	1.4318 Å	-0.0001 Å
r2	1.4683 Å	1.4681 Å	-0.0002 Å

r3	1.0845 Å	1.0844 Å	-0.0001 Å
a1	61.7˚	61.7˚	0.0˚
a2	115.1˚	115.1˚	0.0˚
a3	119.3˚	119.3˚	0.0˚
a4	116.0˚	116.0˚	0.0˚

Vibrational mode	**CCSD(T)**	**PEF**	**Deviation**
1	816.1 cm^{-1}	816.3 cm^{-1}	0.2 cm^{-1}
2	849.7 cm^{-1}	850.3 cm^{-1}	0.6 cm^{-1}
3	899.3 cm^{-1}	899.8 cm^{-1}	0.5 cm^{-1}
4	1052.1 cm^{-1}	1052.4 cm^{-1}	0.3 cm^{-1}
5	1156.5 cm^{-1}	1157.2 cm^{-1}	0.7 cm^{-1}
6	1157.7 cm^{-1}	1158.2 cm^{-1}	0.5 cm^{-1}
7	1174.9 cm^{-1}	1175.4 cm^{-1}	0.5 cm^{-1}
8	1176.3 cm^{-1}	1176.8 cm^{-1}	0.5 cm^{-1}
9	1299.6 cm^{-1}	1300.4 cm^{-1}	0.8 cm^{-1}
10	1513.1 cm^{-1}	1513.3 cm^{-1}	0.2 cm^{-1}
11	1549.4 cm^{-1}	1550.4 cm^{-1}	1.0 cm^{-1}
12	3108.8 cm^{-1}	3109.3 cm^{-1}	0.5 cm^{-1}
13	3117.0 cm^{-1}	3117.5 cm^{-1}	0.5 cm^{-1}
14	3195.7 cm^{-1}	3196.4 cm^{-1}	0.7 cm^{-1}
15	3210.4 cm^{-1}	3210.9 cm^{-1}	0.5 cm^{-1}

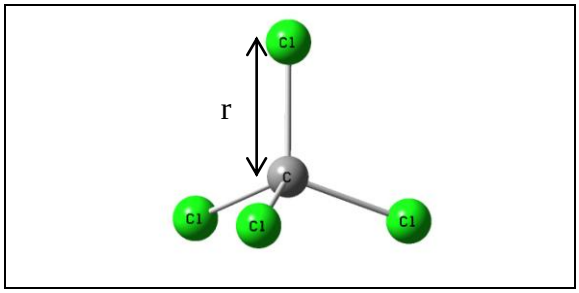
34. CF_4



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3192 Å	1.3189 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	440.0 cm^{-1}	438.4 cm^{-1}	-1.6 cm^{-1}
2	440.0 cm^{-1}	438.8 cm^{-1}	-1.2 cm^{-1}
3	638.9 cm^{-1}	636.9 cm^{-1}	-2.0 cm^{-1}
4	638.9 cm^{-1}	637.1 cm^{-1}	-1.8 cm^{-1}
5	638.9 cm^{-1}	637.4 cm^{-1}	-1.5 cm^{-1}
6	923.1 cm^{-1}	922.7 cm^{-1}	-0.4 cm^{-1}
7	1322.4 cm^{-1}	1325.0 cm^{-1}	2.6 cm^{-1}
8	1322.4 cm^{-1}	1325.0 cm^{-1}	2.6 cm^{-1}
9	1322.4 cm^{-1}	1325.0 cm^{-1}	2.6 cm^{-1}

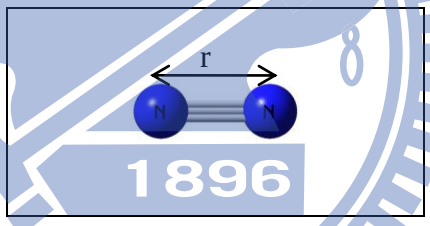
35. CCl_4



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7769 Å	1.7766 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	216.4 cm^{-1}	217.3 cm^{-1}	0.9 cm^{-1}
2	216.4 cm^{-1}	217.5 cm^{-1}	1.1 cm^{-1}
3	313.8 cm^{-1}	315.2 cm^{-1}	1.4 cm^{-1}
4	313.8 cm^{-1}	315.4 cm^{-1}	1.6 cm^{-1}
5	313.8 cm^{-1}	315.6 cm^{-1}	1.8 cm^{-1}
6	458.6 cm^{-1}	461.9 cm^{-1}	3.3 cm^{-1}
7	800.6 cm^{-1}	802.2 cm^{-1}	1.6 cm^{-1}
8	800.6 cm^{-1}	802.2 cm^{-1}	1.6 cm^{-1}
9	800.6 cm^{-1}	802.2 cm^{-1}	1.6 cm^{-1}

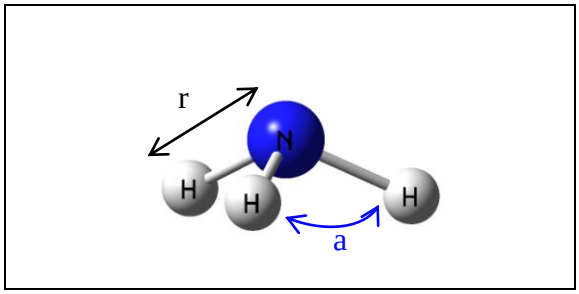
36. N_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.1038 Å	1.1037 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	2345.5 cm^{-1}	2346.4 cm^{-1}	0.9 cm^{-1}

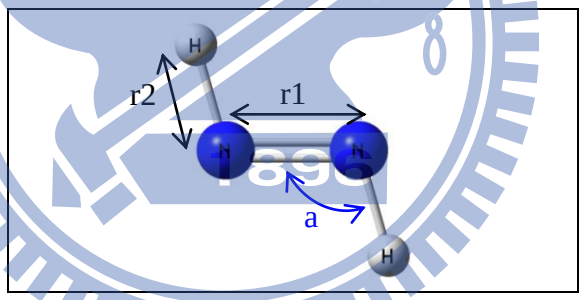
37. NH_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.0141Å	1.0140Å	-0.0001 Å
a	105.7˚	105.6˚	-0.1˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1108.3 cm^{-1}	1108.8 cm^{-1}	0.5 cm^{-1}
2	1687.7 cm^{-1}	1688.0 cm^{-1}	0.3 cm^{-1}
3	1687.8 cm^{-1}	1688.0 cm^{-1}	0.2 cm^{-1}
4	3471.6 cm^{-1}	3472.0 cm^{-1}	0.4 cm^{-1}
5	3597.3 cm^{-1}	3597.9 cm^{-1}	0.6 cm^{-1}
6	3597.4 cm^{-1}	3597.9 cm^{-1}	0.5 cm^{-1}

38. N_2H_2 (Z form)

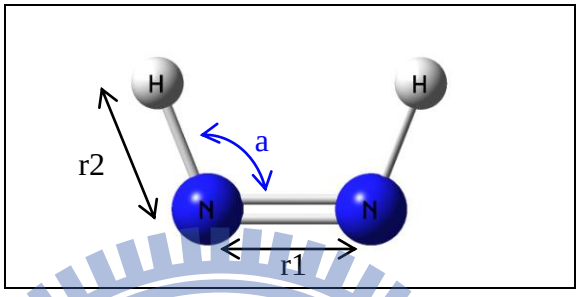


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2536 Å	1.2535 Å	-0.0001 Å
r2	1.0310 Å	1.0308 Å	-0.0002 Å
a	105.7˚	105.7˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1328.4 cm^{-1}	1328.2 cm^{-1}	-0.2 cm^{-1}
2	1350.1 cm^{-1}	1349.7 cm^{-1}	-0.4 cm^{-1}
3	1558.0 cm^{-1}	1558.4 cm^{-1}	0.4 cm^{-1}

4	1621.6 cm^{-1}	1621.7 cm^{-1}	0.1 cm^{-1}
5	3269.2 cm^{-1}	3270.2 cm^{-1}	1.0 cm^{-1}
6	3301.0 cm^{-1}	3301.8 cm^{-1}	0.8 cm^{-1}

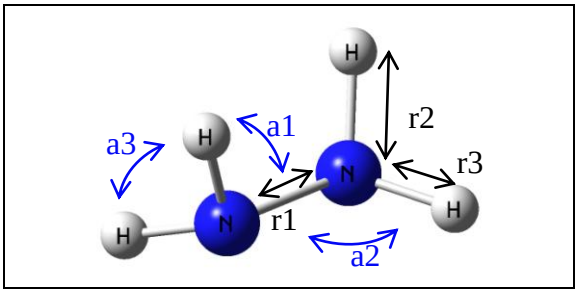
39. N_2H_2 (E form)



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2512 Å	1.2511 Å	-0.0001 Å
r2	1.0360 Å	1.0359 Å	-0.0001 Å
a	111.6°	111.6°	0.0°

Vibrational mode	CCSD(T)	PEF	Deviation
1	1258.6 cm^{-1}	1259.3 cm^{-1}	0.7 cm^{-1}
2	1371.2 cm^{-1}	1372.0 cm^{-1}	0.8 cm^{-1}
3	1565.0 cm^{-1}	1565.8 cm^{-1}	0.8 cm^{-1}
4	1575.2 cm^{-1}	1575.8 cm^{-1}	0.6 cm^{-1}
5	3145.8 cm^{-1}	3146.5 cm^{-1}	0.7 cm^{-1}
6	3235.2 cm^{-1}	3236.6 cm^{-1}	1.4 cm^{-1}

40. NH_2NH_2

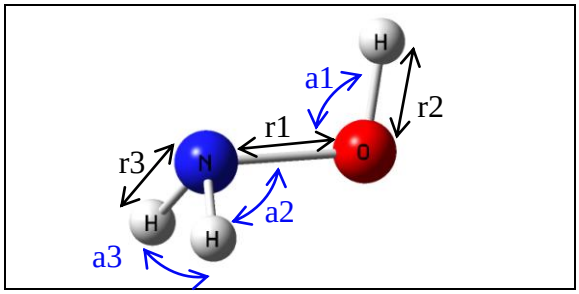


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4448 Å	1.4446 Å	-0.0002 Å
r2	1.0154 Å	1.0153 Å	-0.0001 Å
r3	1.0120 Å	1.0119 Å	-0.0001 Å
a1	110.8˚	110.8˚	0.0˚
a2	106.2˚	106.2˚	0.0˚
a3	106.6˚	106.6˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	400.5cm^{-1}	402.8 cm^{-1}	2.3 cm^{-1}
2	857.8 cm^{-1}	858.6 cm^{-1}	0.8 cm^{-1}
3	1047.1 cm^{-1}	1047.0 cm^{-1}	-0.1 cm^{-1}
4	1126.3 cm^{-1}	1126.5 cm^{-1}	0.2 cm^{-1}
5	1314.1 cm^{-1}	1314.8 cm^{-1}	0.7 cm^{-1}
6	1347.4 cm^{-1}	1348.3 cm^{-1}	0.9 cm^{-1}
7	1676.4 cm^{-1}	1676.8 cm^{-1}	0.4 cm^{-1}
8	1690.2 cm^{-1}	1690.8 cm^{-1}	0.6 cm^{-1}
9	3464.2 cm^{-1}	3465.3 cm^{-1}	1.1 cm^{-1}
10	3476.1 cm^{-1}	3477.6 cm^{-1}	1.5 cm^{-1}
11	3571.5 cm^{-1}	3572.7 cm^{-1}	1.2 cm^{-1}

12	3576.8 cm^{-1}	3577.6 cm^{-1}	0.8 cm^{-1}

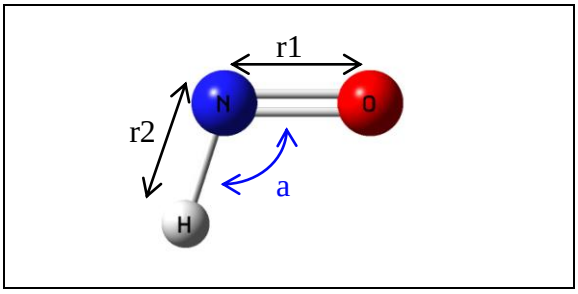
41. NH_2OH



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4486 Å	1.4483 Å	-0.0003 Å
r2	0.9598 Å	0.9597Å	-0.0001 Å
r3	1.0167 Å	1.0166 Å	-0.0001 Å
a1	101.4˚	101.5˚	0.1˚
a2	103.2˚	103.2˚	0.0˚
a3	104.9˚	104.9˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	407.1 cm^{-1}	407.3 cm^{-1}	0.2 cm^{-1}
2	930.9 cm^{-1}	931.5 cm^{-1}	0.6 cm^{-1}
3	1169.6 cm^{-1}	1169.5 cm^{-1}	-0.1 cm^{-1}
4	1330.7 cm^{-1}	1331.5 cm^{-1}	0.8 cm^{-1}
5	1419.0 cm^{-1}	1419.7 cm^{-1}	0.7 cm^{-1}
6	1670.6 cm^{-1}	1671.0 cm^{-1}	0.4 cm^{-1}
7	3452.1 cm^{-1}	3453.4 cm^{-1}	1.3 cm^{-1}
8	3536.3 cm^{-1}	3537.6 cm^{-1}	1.3 cm^{-1}
9	3855.6 cm^{-1}	3856.8 cm^{-1}	1.2 cm^{-1}

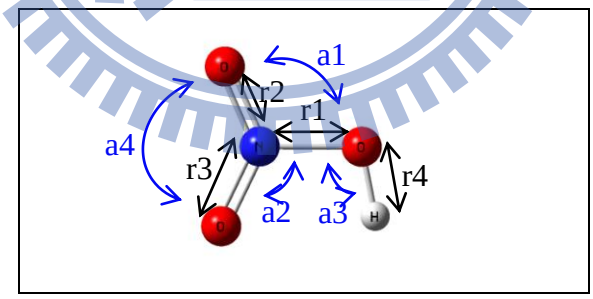
42. NHO



Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.2144 Å	1.2142 Å	-0.0002 Å
r2	1.0554 Å	1.0553 Å	-0.0001 Å
a	107.8˚	107.9˚	0.1˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1540.2 cm^{-1}	1541.1 cm^{-1}	0.9 cm^{-1}
2	1596.5 cm^{-1}	1597.4 cm^{-1}	0.9 cm^{-1}
3	2937.6 cm^{-1}	2938.2 cm^{-1}	0.6 cm^{-1}

43. HNO_3

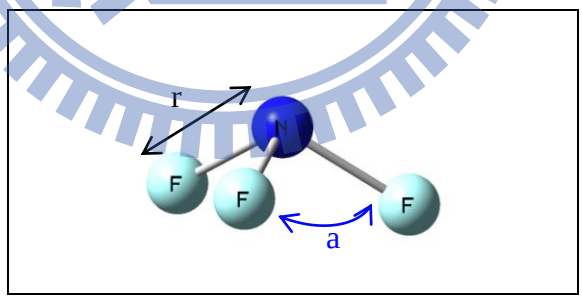


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4053 Å	1.4050 Å	-0.0003 Å
r2	1.1972 Å	1.1970 Å	-0.0002 Å
r3	1.2127 Å	1.2125 Å	-0.0002 Å
r4	0.9701 Å	0.9700 Å	-0.0001 Å
a1	114.0˚	114.1˚	0.1˚

a2	115.4˚	115.4˚	0.0˚
a3	101.5˚	101.5˚	0.0˚
a4	130.5˚	130.5˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	486.7 cm^{-1}	485.6 cm^{-1}	-2.1 cm^{-1}
2	588.2 cm^{-1}	588.6 cm^{-1}	0.4 cm^{-1}
3	663.7 cm^{-1}	664.1 cm^{-1}	0.4 cm^{-1}
4	779.6 cm^{-1}	780.0 cm^{-1}	0.4 cm^{-1}
5	914.0 cm^{-1}	914.5 cm^{-1}	0.5 cm^{-1}
6	1337.7 cm^{-1}	1339.1 cm^{-1}	1.4 cm^{-1}
7	1357.7 cm^{-1}	1359.4 cm^{-1}	1.7 cm^{-1}
8	1772.1 cm^{-1}	1773.3 cm^{-1}	1.2 cm^{-1}
9	3752.6 cm^{-1}	3752.7 cm^{-1}	0.1 cm^{-1}

44. F_3N

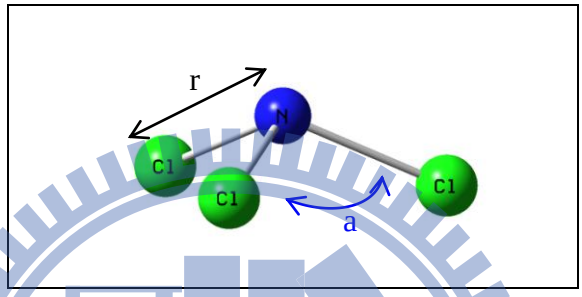


Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3717 Å	1.3715 Å	-0.0002 Å
a	101.9˚	101.9˚	-0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	502.2 cm^{-1}	506.9 cm^{-1}	4.7 cm^{-1}

2	502.3 cm^{-1}	506.9 cm^{-1}	4.6 cm^{-1}
3	659.7 cm^{-1}	663.3 cm^{-1}	3.6 cm^{-1}
4	949.2 cm^{-1}	956.7 cm^{-1}	7.5 cm^{-1}
5	949.2 cm^{-1}	956.7 cm^{-1}	7.5 cm^{-1}
6	1058.2 cm^{-1}	1064.5 cm^{-1}	6.3 cm^{-1}

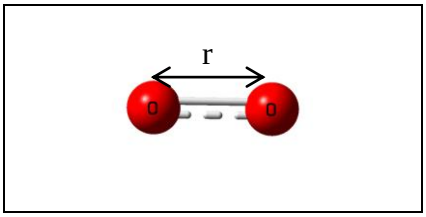
45. Cl_3N



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7765 Å	1.7763 Å	-0.0002 Å
a	107.2˚	107.2˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	257.1 cm^{-1}	260.0 cm^{-1}	-1.1 cm^{-1}
2	257.1 cm^{-1}	256.0 cm^{-1}	-1.1 cm^{-1}
3	348.9 cm^{-1}	352.7 cm^{-1}	3.8 cm^{-1}
4	548.4 cm^{-1}	551.7 cm^{-1}	3.3 cm^{-1}
5	663.1 cm^{-1}	662.8 cm^{-1}	-0.3 cm^{-1}
6	663.1 cm^{-1}	662.8 cm^{-1}	-0.3 cm^{-1}

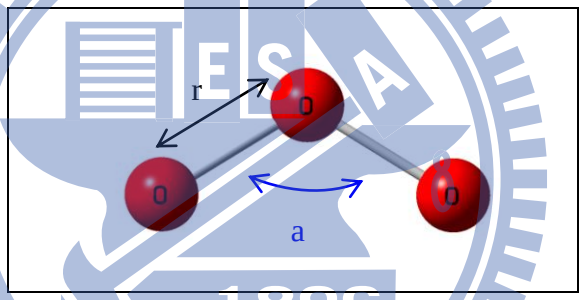
46. O_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.2120 Å	1.2117 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	1585.8 cm^{-1}	1586.7 cm^{-1}	0.9 cm^{-1}

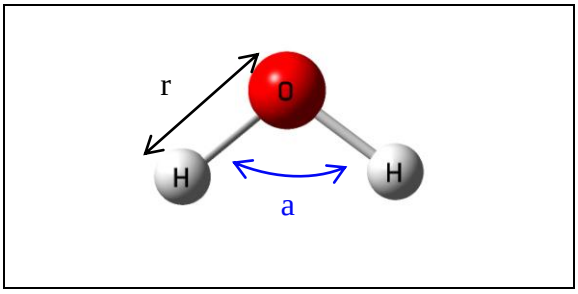
47. O_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.2755 Å	1.2754 Å	-0.0001 Å
a	117.0°	117.0°	0.0°

Vibrational mode	CCSD(T)	PEF	Deviation
1	715.6 cm^{-1}	715.7 cm^{-1}	0.1 cm^{-1}
2	1054.0 cm^{-1}	1055.8 cm^{-1}	1.8 cm^{-1}
3	1152.9 cm^{-1}	1151.8 cm^{-1}	-1.1 cm^{-1}

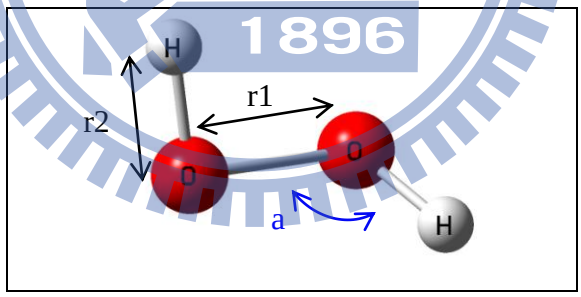
48. H_2O



Geometric parameter	CCSD(T)	PEF	Deviation
r	0.9595 Å	0.9594 Å	-0.0001 Å
a	103.6˚	103.6˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1668.0 cm^{-1}	1668.9 cm^{-1}	0.9 cm^{-1}
2	3840.6 cm^{-1}	3841.3 cm^{-1}	0.7 cm^{-1}
3	3945.1 cm^{-1}	3946.0 cm^{-1}	0.9 cm^{-1}

49. H_2O_2

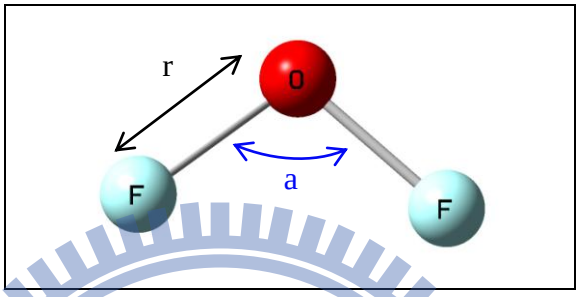


Geometric parameter	CCSD(T)	PEF	Deviation
r1	1.4579 Å	1.4576 Å	-0.0003 Å
r2	0.9640 Å	0.9639 Å	-0.0001 Å
a	99.5˚	99.6˚	0.1˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	372.3 cm^{-1}	372.5 cm^{-1}	0.2 cm^{-1}
2	911.6 cm^{-1}	912.5 cm^{-1}	0.9 cm^{-1}

3	1323.6 cm^{-1}	1324.2 cm^{-1}	0.6 cm^{-1}
4	1435.9 cm^{-1}	1436.7 cm^{-1}	0.8 cm^{-1}
5	3807.2 cm^{-1}	3808.6 cm^{-1}	1.4 cm^{-1}
6	3808.6 cm^{-1}	3810.0 cm^{-1}	1.4 cm^{-1}

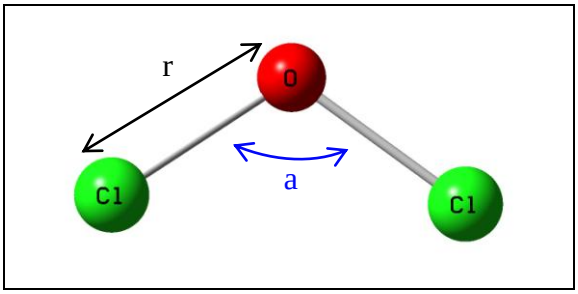
50. F_2O



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.4097 Å	1.4094 Å	-0.0003 Å
a	103.2 °	103.1°	-0.1°

Vibrational mode	CCSD(T)	PEF	Deviation
1	469.2 cm^{-1}	469.5 cm^{-1}	0.3 cm^{-1}
2	867.3 cm^{-1}	867.7 cm^{-1}	0.4 cm^{-1}
3	950.0 cm^{-1}	950.6 cm^{-1}	0.6 cm^{-1}

51. Cl_2O

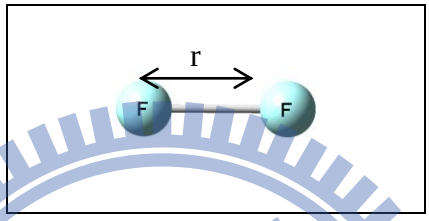


Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7151 Å	1.7148 Å	-0.0003 Å

a	110.9˚	110.8˚	-0.1˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	291.9 cm^{-1}	294.0 cm^{-1}	2.1 cm^{-1}
2	642.2 cm^{-1}	644.0 cm^{-1}	1.8 cm^{-1}
3	698.6 cm^{-1}	700.2 cm^{-1}	1.6 cm^{-1}

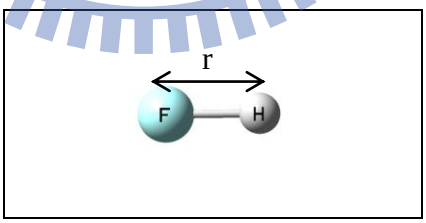
52. F_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.4158 Å	1.4156 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	919.9 cm^{-1}	920.3 cm^{-1}	0.4 cm^{-1}

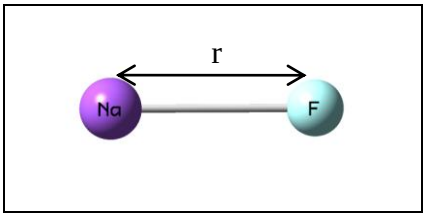
53. HF



Geometric parameter	CCSD(T)	PEF	Deviation
r	0.9173 Å	0.9172 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	4176.8 cm^{-1}	4177.7 cm^{-1}	0.9 cm^{-1}

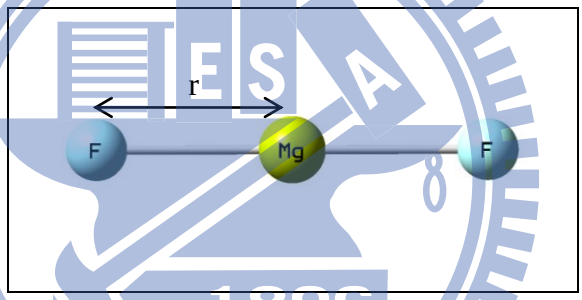
54. FNa



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.9793 Å	1.9790 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	548.6 cm^{-1}	549.5 cm^{-1}	0.9 cm^{-1}

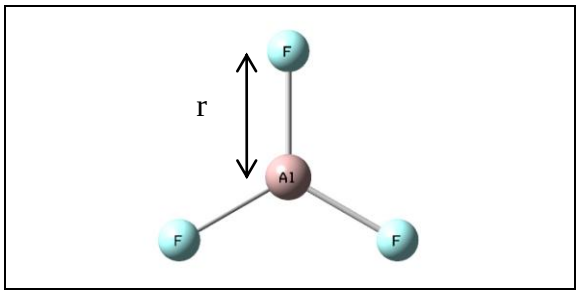
55. F_2Mg



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7564 Å	1.7561 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	156.6 cm^{-1}	157.1 cm^{-1}	0.5 cm^{-1}
2	156.6 cm^{-1}	157.1 cm^{-1}	0.5 cm^{-1}
3	571.6 cm^{-1}	571.8 cm^{-1}	0.2 cm^{-1}
4	892.4 cm^{-1}	896.4 cm^{-1}	4.0 cm^{-1}

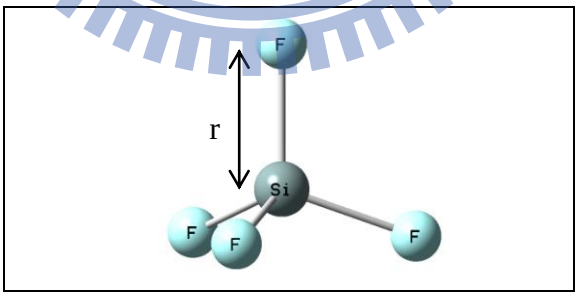
56. AlF_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.6424 Å	1.6422 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	240.8 cm^{-1}	241.0 cm^{-1}	0.2 cm^{-1}
2	240.9 cm^{-1}	241.0 cm^{-1}	0.1 cm^{-1}
3	302.2 cm^{-1}	303.1 cm^{-1}	0.9 cm^{-1}
4	691.9 cm^{-1}	692.2 cm^{-1}	0.3 cm^{-1}
5	960.0 cm^{-1}	960.4 cm^{-1}	0.4 cm^{-1}
6	960.0 cm^{-1}	960.4 cm^{-1}	0.4 cm^{-1}

57. F_4Si

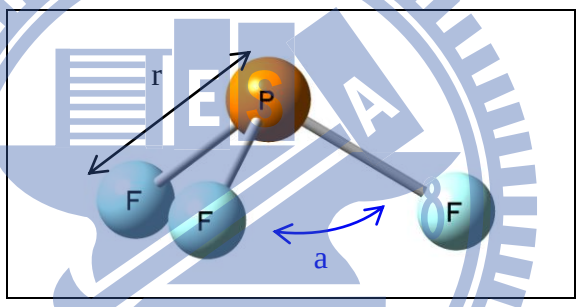


Geometric parameter	CCSD(T)	PEF	Deviation
r	1.5695 Å	1.5693 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	259.6 cm^{-1}	259.7 cm^{-1}	0.1 cm^{-1}

2	259.6 cm^{-1}	259.7 cm^{-1}	0.1 cm^{-1}
3	384.0 cm^{-1}	384.3 cm^{-1}	0.3 cm^{-1}
4	384.0 cm^{-1}	384.3 cm^{-1}	0.3 cm^{-1}
5	384.1 cm^{-1}	384.3 cm^{-1}	0.2 cm^{-1}
6	794.8 cm^{-1}	795.1 cm^{-1}	0.3 cm^{-1}
7	1035.3 cm^{-1}	1036.7 cm^{-1}	1.4 cm^{-1}
8	1035.3 cm^{-1}	1036.7 cm^{-1}	1.4 cm^{-1}
9	1035.4 cm^{-1}	1036.7 cm^{-1}	1.3 cm^{-1}

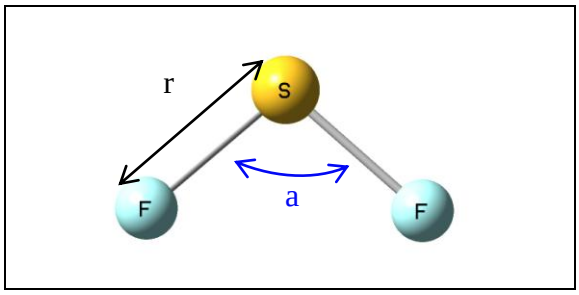
58. F_3P



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.5762 Å	1.5760 Å	-0.0002 Å
a	97.5°	97.5°	0.0°

Vibrational mode	CCSD(T)	PEF	Deviation
1	345.3 cm^{-1}	348.9 cm^{-1}	3.6 cm^{-1}
2	345.3 cm^{-1}	348.9 cm^{-1}	3.6 cm^{-1}
3	485.9 cm^{-1}	487.8 cm^{-1}	1.9 cm^{-1}
4	877.8 cm^{-1}	880.2 cm^{-1}	2.4 cm^{-1}
5	877.8 cm^{-1}	880.2 cm^{-1}	2.4 cm^{-1}
6	905.6 cm^{-1}	907.9 cm^{-1}	2.3 cm^{-1}

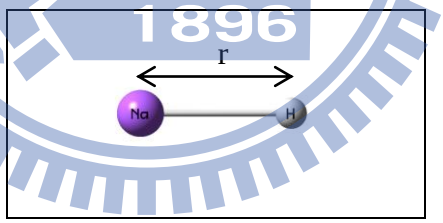
59. F_2S



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.6032 Å	1.6029 Å	-0.0003 Å
a	98.3˚	98.2˚	-0.1˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	349.8 cm^{-1}	350.3 cm^{-1}	0.5 cm^{-1}
2	825.3 cm^{-1}	826.2 cm^{-1}	0.9 cm^{-1}
3	846.6 cm^{-1}	847.5 cm^{-1}	0.9 cm^{-1}

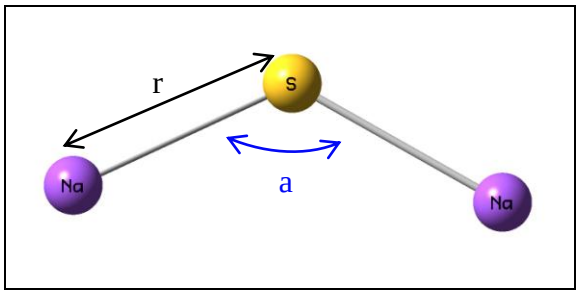
60. HNa



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.9232 Å	1.9231 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	1131.5 cm^{-1}	1131.7 cm^{-1}	0.2 cm^{-1}

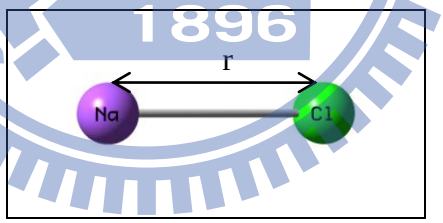
61. Na_2S



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.4614 Å	2.4610 Å	-0.0004 Å
a	125.6˚	125.6˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	46.4 cm^{-1}	46.3 cm^{-1}	-0.1 cm^{-1}
2	300.1 cm^{-1}	300.3 cm^{-1}	0.2 cm^{-1}
3	389.3 cm^{-1}	389.7 cm^{-1}	0.4 cm^{-1}

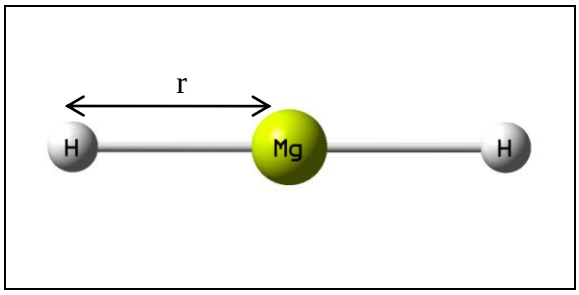
62. NaCl



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.4049 Å	2.4044 Å	-0.0005 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	352.2 cm^{-1}	353.3 cm^{-1}	1.1 cm^{-1}

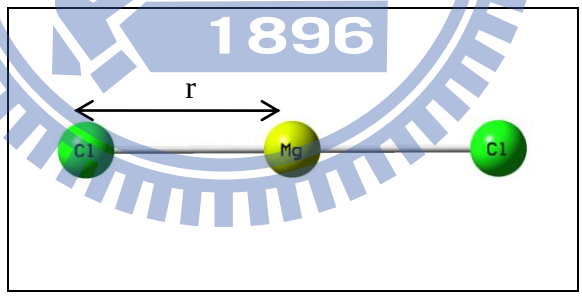
63. H_2Mg



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.7121 Å	1.7120 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	439.1 cm^{-1}	439.3 cm^{-1}	0.2 cm^{-1}
2	439.1 cm^{-1}	439.3 cm^{-1}	0.2 cm^{-1}
3	1605.8 cm^{-1}	1606.0 cm^{-1}	0.2 cm^{-1}
4	1632.8 cm^{-1}	1633.8 cm^{-1}	1.0 cm^{-1}

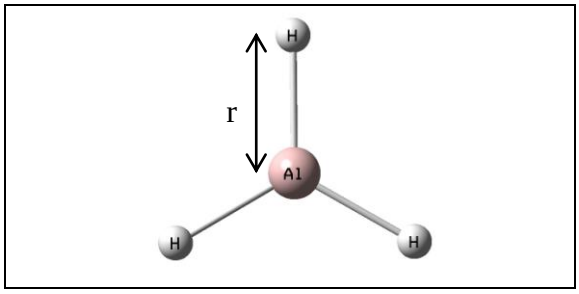
64. Cl_2Mg



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.1838 Å	2.1834 Å	-0.0004 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	107.6 cm^{-1}	108.3 cm^{-1}	0.7 cm^{-1}
2	107.6 cm^{-1}	108.3 cm^{-1}	0.7 cm^{-1}
3	323.7 cm^{-1}	326.0 cm^{-1}	2.3 cm^{-1}
4	623.0 cm^{-1}	627.5 cm^{-1}	4.5 cm^{-1}

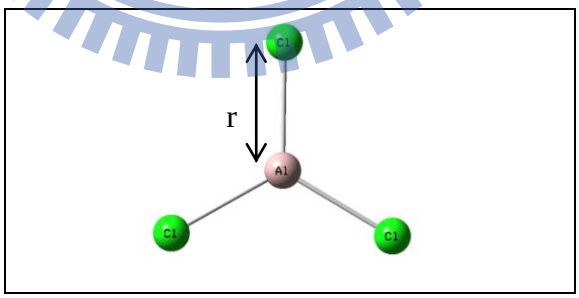
65. AlH_3



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.5851 Å	1.5850 Å	-0.0001 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	717.4 cm^{-1}	717.3 cm^{-1}	-0.1 cm^{-1}
2	791.4 cm^{-1}	791.8 cm^{-1}	0.4 cm^{-1}
3	791.4 cm^{-1}	791.8 cm^{-1}	0.4 cm^{-1}
4	1940.6 cm^{-1}	1941.0 cm^{-1}	0.4 cm^{-1}
5	1947.2 cm^{-1}	1947.7 cm^{-1}	0.5 cm^{-1}
6	1947.2 cm^{-1}	1947.7 cm^{-1}	0.5 cm^{-1}

66. $AlCl_3$

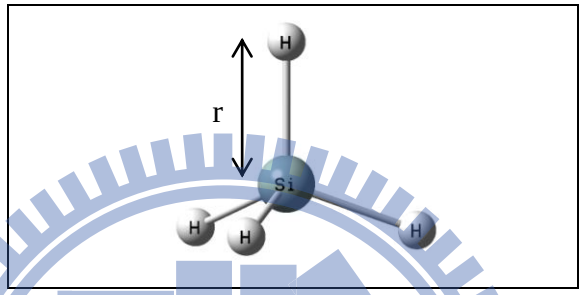


Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0834 Å	2.0831 Å	-0.0003 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	145.4 cm^{-1}	146.3 cm^{-1}	0.9 cm^{-1}

2	145.4 cm^{-1}	146.3 cm^{-1}	0.9 cm^{-1}
3	207.0 cm^{-1}	207.3 cm^{-1}	0.3 cm^{-1}
4	385.5 cm^{-1}	388.4 cm^{-1}	2.9 cm^{-1}
5	626.7 cm^{-1}	628.5 cm^{-1}	1.8 cm^{-1}
6	626.7 cm^{-1}	628.5 cm^{-1}	1.8 cm^{-1}

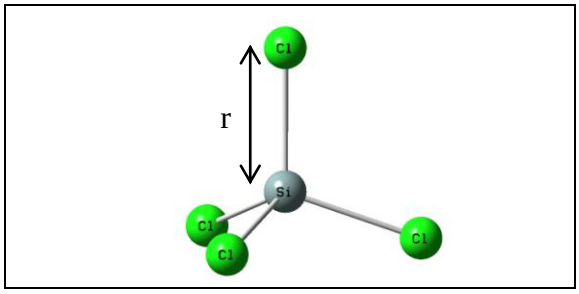
67. H_4Si



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.4826 Å	1.4824 Å	-0.0002 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	930.5 cm^{-1}	931.4 cm^{-1}	0.9 cm^{-1}
2	930.7 cm^{-1}	931.4 cm^{-1}	0.7 cm^{-1}
3	930.7 cm^{-1}	931.4 cm^{-1}	0.7 cm^{-1}
4	983.7 cm^{-1}	984.7 cm^{-1}	1.0 cm^{-1}
5	983.8 cm^{-1}	984.7 cm^{-1}	0.9 cm^{-1}
6	2250.3 cm^{-1}	2251.2 cm^{-1}	0.9 cm^{-1}
7	2258.0 cm^{-1}	2258.9 cm^{-1}	0.9 cm^{-1}
8	2258.1 cm^{-1}	2259.0 cm^{-1}	0.9 cm^{-1}
9	2258.1 cm^{-1}	2259.0 cm^{-1}	0.9 cm^{-1}

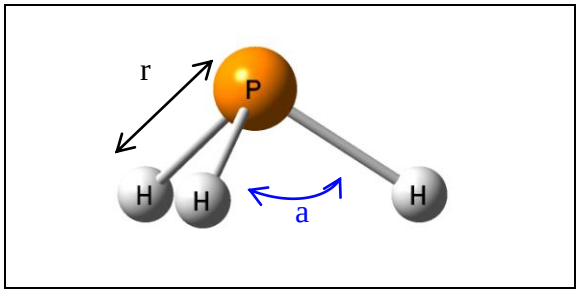
68. Cl_4Si



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0357 Å	2.0353 Å	-0.0004 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	144.3 cm^{-1}	145.4 cm^{-1}	1.1 cm^{-1}
2	144.3 cm^{-1}	145.4 cm^{-1}	1.1 cm^{-1}
3	218.5 cm^{-1}	220.0 cm^{-1}	1.5 cm^{-1}
4	218.6 cm^{-1}	220.1 cm^{-1}	1.5 cm^{-1}
5	218.6 cm^{-1}	220.1 cm^{-1}	1.5 cm^{-1}
6	419.8 cm^{-1}	422.9 cm^{-1}	3.1 cm^{-1}
7	623.2 cm^{-1}	625.8 cm^{-1}	2.6 cm^{-1}
8	623.2 cm^{-1}	625.8 cm^{-1}	2.6 cm^{-1}
9	623.2 cm^{-1}	625.8 cm^{-1}	2.6 cm^{-1}

69. H_3P

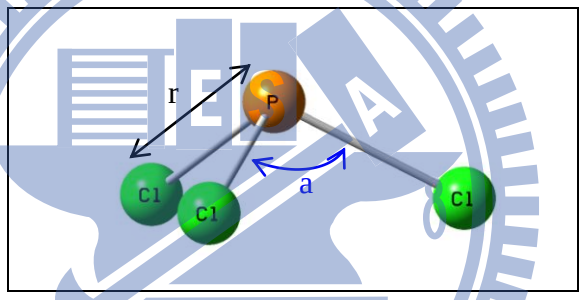


Geometric parameter	CCSD(T)	PEF	Deviation
r	1.4185 Å	1.4184 Å	-0.0001 Å

a	93.5˚	93.5˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1018.1 cm^{-1}	1020.2 cm^{-1}	2.1 cm^{-1}
2	1142.1 cm^{-1}	1143.9 cm^{-1}	1.8 cm^{-1}
3	1142.1 cm^{-1}	1143.9 cm^{-1}	1.8 cm^{-1}
4	2412.5 cm^{-1}	2411.9 cm^{-1}	-0.6 cm ^{1}
5	2421.3 cm^{-1}	2420.8 cm^{-1}	-0.5 cm^{-1}
6	2421.3 cm^{-1}	2420.8 cm^{-1}	-0.5 cm^{-1}

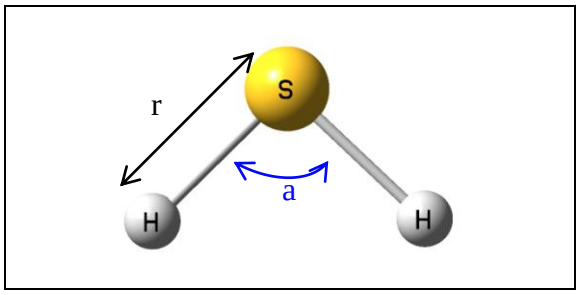
70. Cl_3P



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0648Å	2.0644 Å	-0.0004 Å
a	100.3˚	100.3˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	184.6 cm^{-1}	187.5 cm^{-1}	2.9 cm^{-1}
2	184.6 cm^{-1}	187.5 cm^{-1}	2.9 cm^{-1}
3	256.5 cm^{-1}	259.1 cm^{-1}	2.6 cm^{-1}
4	507.7 cm^{-1}	510.7 cm^{-1}	3.0 cm^{-1}
5	507.7 cm^{-1}	510.7 cm^{-1}	3.0 cm^{-1}
6	507.7 cm^{-1}	518.9 cm^{-1}	1.2 cm^{-1}

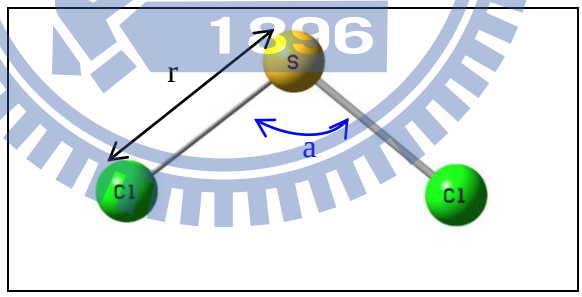
71. H_2S



Geometric parameter	CCSD(T)	PEF	Deviation
r	1.3407 Å	1.3406 Å	-0.0001 Å
a	92.3˚	92.3˚	0.0˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	1203.8 cm^{-1}	1204.5 cm^{-1}	0.7 cm^{-1}
2	2716.8 cm^{-1}	2717.5 cm^{-1}	0.7 cm^{-1}
3	2732.6 cm^{-1}	2733.2 cm^{-1}	0.6 cm^{-1}

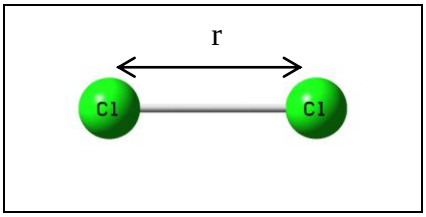
72. Cl_2S



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0411 Å	2.0406 Å	-0.0005 Å
a	102.7˚	102.6˚	-0.1˚

Vibrational mode	CCSD(T)	PEF	Deviation
1	201.5 cm^{-1}	202.7 cm^{-1}	1.2 cm^{-1}
2	519.4 cm^{-1}	521.6 cm^{-1}	2.2 cm^{-1}
3	520.4 cm^{-1}	522.8 cm^{-1}	2.4 cm^{-1}

73. Cl_2



Geometric parameter	CCSD(T)	PEF	Deviation
r	2.0178 Å	2.0174 Å	-0.0004 Å

Vibrational mode	CCSD(T)	PEF	Deviation
1	542.0 cm^{-1}	546.0 cm^{-1}	4.0 cm^{-1}