Solving for Eigenvalues and Eigenvectors of a MOF-5 Lennard-Jones Potential

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May 16, 2017

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Chapter 1

Introduction

1.1 Executive Summary

Metal-Organic Frameworks, or MOFs, are porous crystals produced in a lab. This porous structure gives MOFs properties that can be used for applications such as gas filters or gas storage. These gases interact with the MOF in such a way that they do not bond with them, but instead stick due to van der Waal and electrostatic forces. The focus is on a particular crystal called MOF 5. Gases like hydrogen (H_2) can interact with MOF 5 enough to stick at low temperatures and still escape at higher temperatures. H_2 has an isotope deuterium (D_2) which is nearly chemically identical making a mixture of the isotopes very hard to separate. In MOF 5 D_2 escapes at a slightly higher energy or temperature than H_2 making a simple way of separating the two gases. Using this difference we can explore the phenomenon further while testing current techniques of modeling the situation.

The aim of this thesis is to create a simple model that gives the potential energy around the primary site of MOF 5 where these gases are believed to interact the strongest. This location is known based on previous experimentation[1, 2]. The potential is created for a small scale cubic space around this primary site by creating a 3D grid with each point having a potential energy value for that position.

This created potential energy grid is then inputted into a recently created program called NuSol created by Graen et. al.[3]. The program uses the potential to output energies and solutions to the quantum mechanical system. We may then gain a better understanding of the location of the H_2 or D_2 molecule in MOF 5's primary site. In addition, by comparing to experimental values the model can be tested for how well it represents the reality of MOF 5 in the primary site. This also may reveal whether or not these techniques are of use in this context.

1.2 Motivation

Metal organic frameworks are metal ion clusters connected by organic ligands. The multitude of combinations of possible structures allows for a wide range of possible characteristics. MOFs' pores allow gases to diffuse through them at higher temperatures. At lower temperatures quantum tunneling effects emerge. These characteristics show potential for many applications such as gas separation and possibly hydrogen storage[4].

Isotopes of a gas such as Hydrogen (H_2) and Deuterium (D_2) are difficult to separate due to their being almost chemically identical. Their only difference is that D_2 has 2 neutrons more than H_2. MOFs have been shown to easily separate the two gases despite their near chemically identical properties because of their difference in desorption temperatures[5].

With the increasing impact of greenhouse gas emissions, the need for alternative fuel sources for transportation only grows. Cars powered by hydrogen would emit water through the combustion reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1.1}$$

This alternative fuel source would greatly reduce the impact of our transportation by replacing gas engines of cars. Studies have concluded that hydrogen as a source of fuel would reduce much of the pollutants from combustion engines and the petroleum product refining process[6]. A major barrier to this is hydrogen storage. Storing enough hydrogen in its gaseous state in a fuel tank would either require an excessively large fuel tank or infeasible storage pressures. Hydrogen is a gas above ~ 20 K. Liquefying hydrogen requires too much energy to be feasible for fueling cars. A possible answer is using MOFs to adsorb hydrogen gas to counter act intermolecular forces between hydrogen molecules allowing for tight packing. Finding a suitable MOF that can adsorb hydrogen at high enough temperatures, but not bind too strongly for removal is of major interest[7]. The estimated ideal binding energy at room temperature is $\sim$40 kJ/mol[8].

MOF structures are highly versatile and thus have the potential to be engineered for specific purposes. Due to their complexity there is no way to accurately predict the possible applications of a metal organic framework before it is constructed. Experimentation requires checking the numerous potential characteristics of each MOF one at a time for each MOF engineered. Due the large number of MOFs in existence or potentially created, it is not practical to produce and test them all. If methods of predicting their characteristics were accurate enough, these materials could be engineered for specific purposes expediting the process. However, theory cannot analytically solve the three-body problem, let alone a MOF structure. A potential solution lies in numerically solving various interactions of MOFs and gases.

Using various simulations to quickly answer basic questions is a starting point. Modeling H2 interactions in MOFs is complex due to the number of particles involved. Calculations involving electrons makes van der Waal interactions very computationally intensive because of the thousands of electrons involved in MOFs. Discussed is the creation of a model produced to simplify calculation. Also explored is the use of this model to solve the Schrodinger equation to find eigenstates of H_2 and its isotopes within the primary sites of MOF 5.

1.3   The Hydrogen Molecule

Hydrogen exists in nature as a diatomic molecule, H_2. This molecule, often visualized as a dumbbell, has 6 classical degrees of freedom. In addition to the 3 dimensions of translational freedom, there are also 2 rotational and 1 vibrational degrees of freedom.

In this simulation the rotational and vibrational motion is neglected, modeling H_2 as a sphere rather than a dumbbell. Neglecting the vibrational energy between the two H atoms is an acceptable approximation because it is not comparable to the translational energy of the molecule. Neglecting the rotational energy is not a good approximation because it is comparable to the translational energy. However, H_2 and D_2 are mostly in the spherically symmetric J=0 state at the temperatures

they adsorb to MOFs so this makes neglecting rotation more acceptable. This leaves the positional energy wavefunctions to be solved for.

H_2 is generally unpolarized unless there is some induced polarization. H_2 interacts through van der Wal forces with charged portions of MOFs to adsorb. This lack of polarization unless adsorbed is convenient for IR spectroscopy because H_2 does not absorb in the infrared until polarized.

The J=0 state provides spherical symmetry for electrostatics as well. Through the random motion of the electrons H_2 can also have a quadrupole moment. This is where the electrons are more concentrated in between the two hydrogen nuclei making the ends of the dumbbell relatively positively charged while the middle is more negatively charged. The quadrupole moment can be ignored because the positive and negative charges are centered about the same point. Gauss's law shows that a spherical shell around the molecule will have no net charge. Therefore no electric field will be produced by the quadrupole moment.

The approximation of H_2 being a sphere assumes that the vibrational state is $v = 0$ and the rotational state is $J = 0$ so the parameters for the polarization constant and quadrupole moment are 5.4 a_o^3 and 0.48 ea_o^2 respectively[9].

1.4   MOF 5

MOF 5 was chosen because it is well understood. It is a popular crystal for research because it showed potential for H_2 storage due to its high surface area per unit mass. The current target for H_2 storage is 9 wt % at ambient temperature including the mass of the whole carrying system[10]. MOF 5 has been found to have a gravimetric capacity of $\sim$5 wt % at 77 K[11]. Although not an obvious candidate for gas separation, the high surface area would allow for more gas to be separated per mass of crystal as well. In addition, there are available potential parameters that can easily be used for producing a potential. These parameters are given in section 2.3, "Producing the MOF 5 Potential".

MOF 5 is a nanoporous crystal that has cubic unit cells, with $Zn_4O(CO_2)_6$ at the corners. The edges connect these clusters with C_6H_4 ligands. The crystal structure and binding sites are known due to x-ray [12] and neutron diffraction studies[1, 2]. Shown in Figure 1.1 below are multiple stacked unit cells of MOF 5.

Due to the angle of the ligands the scaffold like structure has alternating pore sizes of 12 and 15 Å[12] accounting for $\sim$80% of the volume[13]. Multiple binding sites have been observed with the lowest potential or primary sites in the corners of the cubes near the metal ion clusters as shown in Figure 1.2. In general adsorbed molecules will fill the primary sites first then fill the rest sequentially by lowest energy first. This only does not occur if the system is cooled quickly in which case it will adsorb to the nearest local minimum of the potential within the MOF. The binding energy of this primary site is $\sim$4 kJ/mol. This is a stronger binding energy than the 3 and 2 kJ/mol of the two observed secondary sites so the molecules in secondary sites desorb at lower temperature than those in primary[13].

The primary site is the focus of this thesis. A potential is produced for a cubic space surrounding primary site depicted in Figure 1.2. Then the energies of H_2 and its isotopes are solved for in the context of this potential.
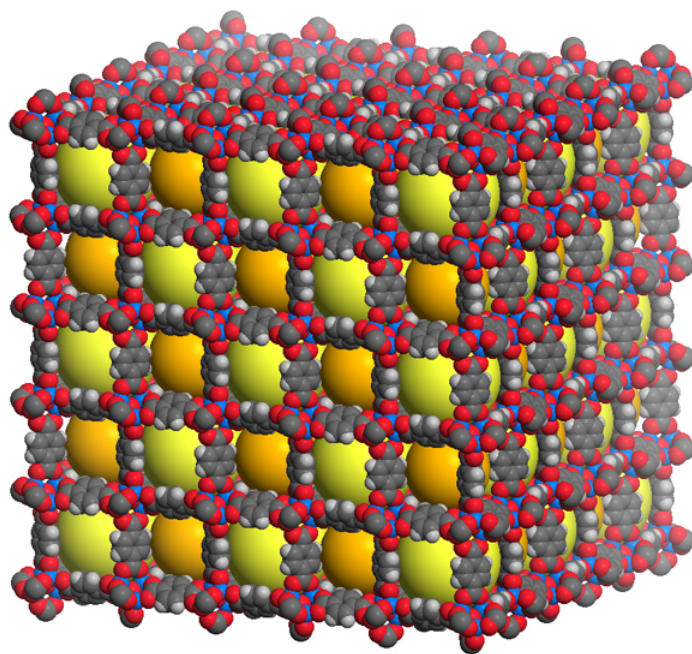
Figure 1.1: Depicted are stacked MOF 5 unit cells. Atoms are colored based on type: blue for Zn, red for O, dark grey for C and light grey for H. The orange and yellow spheres show the alternating in size nanopores in the scaffold like structure. Image courtesy of Professor Jesse Rowsell (Oberlin College).
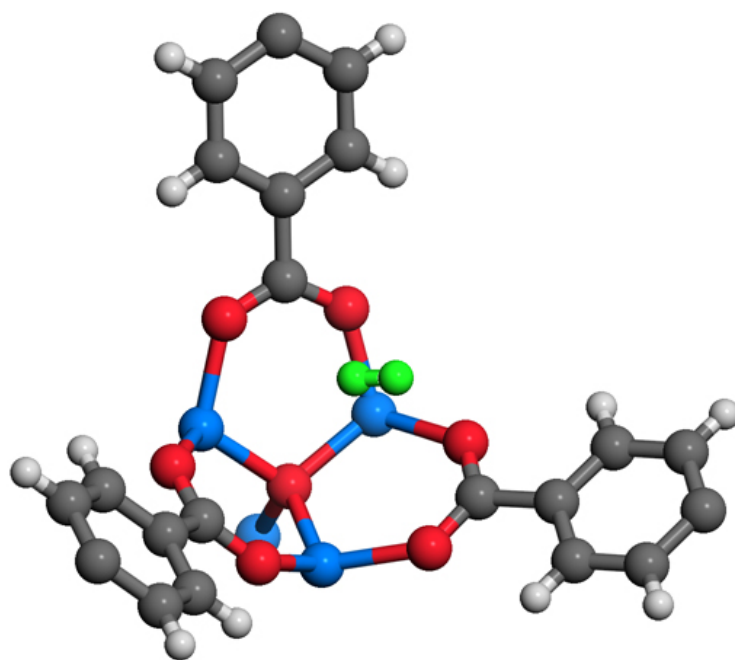
Figure 1.2: Depicted is an adsorbed diatomic molecule shown in green in the primary site of MOF 5. Other atoms are colored based on type: blue for Zn, red for O, dark grey for C and light grey for H. Image courtesy of Professor Jesse Rowsell (Oberlin College).

Chapter 2

Theory

2.1 Zero Point Energy

The zero point energy is the lowest possible energy any system can reach. This lowest possible energy cannot be a complete lack of energy even at absolute zero due to quantum mechanics. Absolute zero is only a temperature at which the system is at its ground state. Total energy is the sum of kinetic T and potential V energy, $E_{tot} = T + V$. To have minimum energy where $E_{tot} = V_{min}$ the kinetic energy must be zero so the momentum p must be zero since $T = \frac{p^2}{2m}$ where m is the mass. The uncertainty principle states that a momentum and position cannot both be well defined. To have momentum be well defined as $p = 0$ means that the position distribution would be infinite making the wavefunction non-normalizable.

The uncertainty principle is given by Equation 2.1 below where σ_x and σ_p are the standard deviations of position and momentum respectively and $\hbar$ is the reduced Planck's constant.

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \tag{2.1}$$

The product of the standard deviations of the position x and momentum p is constrained by the value $\frac{\hbar}{2}$. The standard deviation of a given property a is given by Equation 2.2 below.

$$\sigma_a = \sqrt{\langle a^2 \rangle - \langle a \rangle^2} \tag{2.2}$$

where,

$$\langle a \rangle = \langle \psi | \widehat{a} | \psi \rangle = \int \psi^* \widehat{a} \psi dV \tag{2.3}$$

The expectation value of some property a denoted $\langle a \rangle$ is defined by Equation 2.3 where ψ is the wavefunction of the particle and $\widehat{a}$ is the operator represented by the property a. The product of the complex conjugate of the wavefunction and the operator operating on the wavefunction is integrated over all space.

This required distribution of both position and momentum puts the ground state energy above V_{min} unless V_{min} is constant for some length like with the infinite square well. Since no potential is a perfect square well the minimum E_{tot} is always above V_{min}. Therefore even at absolute zero there is some amount of energy still in the system.

In the case of hydrogen molecules (H_2) and deuterium molecules (D_2), the difference in energy levels is not so apparent until they are near their zero point energies. The total energy of an adsorbed molecule is the sum of its rotational, translational and vibrational energies as shown in Equation 2.4.

$$E_{tot} = E_{rot} + E_{vib} + E_{trans} \tag{2.4}$$

As a part of the approximation of the diatomic molecules H_2 and D_2 being spheres the focus is on E_{trans}, the translational energy.

Despite their near identical chemical properties the difference in mass of H_2 and D_2 causes variation in energies that is noticeable near their ground state. This can be illustrated by discussing both H_2 and its isotope D_2 in the context of a quadratic potential of a simple harmonic oscillator. The well established energies of a simple harmonic oscillator, $n\hbar\omega$ (where n is the energy and ω is the frequency of oscillation) reveals the apparent difference in energies. Approximating as a classical simple harmonic oscillator ω can be rewritten as $\omega = \sqrt{\frac{k}{m}}$ where m is the mass of the particle and k is the spring constant defined by the second derivative of potential curve evaluated at V_{min}. The D_2 is about double the mass of H2 so it would have ω values that are $\frac{1}{\sqrt{2}}$ smaller and therefore energies that are that factor lower.

Separating similar gases such as D_2 and H_2 has proven to be difficult due to their near identical chemical properties. The difference in ground state energies makes separating deuterium gas from hydrogen gas a simpler process. MOFs are a convenient potential to introduce a mixture of gases to. Then all that is required is to be below the desorption temperature of D_2 and above the desorption temperature of H_2. This would result in only H_2 desorbing thus separating the 2 gases entirely. Current work is being done on using MOFs to separate gases[14].

2.2 Crystallography

Due to their patterned structure crystals can be produced using a small group of atoms rotated and translated in space to produce their entire structure. The space group is the symmetry operations that rotate, reflect and translate the set of atoms to produce the entire structure.

The structure of MOF 5 is understood using neutron diffraction data which determined a face center cubic structure[1, 2]. The set of atoms used to produce the entire MOF 5 face center cube structure was chosen to match that of Space et. al. from the University of South Florida. These atoms are Zn, O1, O2, C1, C2, C3, H in the positions shown in Figure 2.1 [15]. The coordinate axes were chosen such that the z-axis will come out of the page from the center oxygen atom. The x-y plane would be the parallel to the page. Since the aim was to solve the two body problem many times we needed altered parameters for producing the potential of the MOF. The parameters used for producing the potential were provided by B. Space who had a similar approach. The relative positions were given by a crystal maker file. Those positions were given as vectors in space which were scaled to be in units of Angstroms (10^{-10} m).

2.3 Producing the MOF 5 Potential

Due to the complexity of the calculation there currently is not a way to explicitly or numerically solve the Schrodinger equation without approximations. Because the potential of each individual
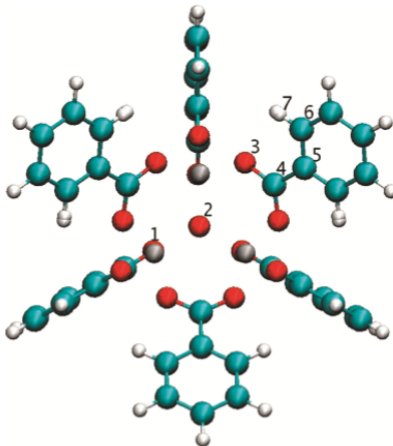
Figure 2.1: Shown are the atoms used to produce the potential. The numbered atoms, from reference [15], illustrate the atoms that underwent the symmetry operations to produce the entire structure. Grey is Zinc, Red is Oxygen, Blue is Carbon and White is Hydrogen.

contribution from each atom is dependent on the others this would make solving for the potential numerically an $O(n^n)$ calculation where the n is the number of individual contributors to the potential. To represent the potential to high accuracy would require considering each electron as a contributor to this potential. In addition there are characteristics which are dependent on the experienced potential at a given position or the orientation of the molecule such as polarization and quadrupole electrostatic interactions respectively. Even when considering the relatively small scale structure considered in this thesis the production of a truly accurate potential carries immense computational space and runtime. Modern computing technology cannot yet handle the computational complexity of these calculations. It should be expected that the simplified model used will not produce energies that are consistent with experiment numerically.

Another major assumption is that the atoms do not change position so phonons in the lattice are not considered. In reality the structure is better modeled as a bunch of atoms attached with springs rather than rigid bonds allowing lattice vibrations; however these vibrations are not thought to be a major factor in the adsorption of H2[16, 17]. Eliminating the MOF5 crystal structure's vibrations, greatly simplifies the problem by eliminating the need for time dependence.

The whole potential is the sum of individual contributing atom's potentials. The potential for each atom was some combination of Lennard-Jones 6-12 and electrostatic potentials. The potential is a 3D array storing values which are the magnitude of the summed potentials from all contributing atoms. The 3D array's indexes are steps in space, creating a Cartesian coordinate system. The parameters for the Lennard-Jones are from reference [17]. The following table shows the parameters used for each atom:

The potential calculation at some distance R from the source is given in Equation 2.5 where σ and ϵ are parameters provided in Table 2.1 and n is the number of atoms contributing to the potential.

$$U_{LJ}(R) = 4 \sum_{i=1}^{n} \epsilon_i \left(\left(\frac{\sigma_i}{R} \right)^{12} - \left(\frac{\sigma_i}{R} \right)^{6} \right) \tag{2.5}$$

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Atom	Label	$\sigma(\text{Å})$	$\epsilon(\text{K})$	$q(e^-)$
Zn	1	2.4616	62.3993	1.8529
O	2	3.118	30.19	-2.2568
O	3	3.118	30.19	-1.0069
C	4	3.431	52.84	1.0982
C	5	3.431	52.84	-0.1378
C	6	3.431	52.84	-0.0518
H	7	2.571	22.14	0.1489

Table 2.1: Parameters used for the Lennard-Jones and altered charges for electrostatic potentials[17].

The $(\frac{\sigma_i}{R})^{12}$ term models the repulsion due to these van der Waal interactions. The London dispersion attraction interaction is modeled by the $(\frac{\sigma_i}{R})^6$ term. Another common possible potential to have been considered would have been the Buckingham potential which replaces the repulsive term with an exponential term Ae^{-BR} where A and B are different parameters. Due to the fewer required and readily available parameters the Lennard-Jones was chosen as the model for the MOF 5 potential. Traditionally the Lennard-Jones has been chosen also to simplify calculation since the $(\frac{\sigma_i}{R})^6$ term only needs to be squared to yield the $(\frac{\sigma_i}{R})^{12}$.

The electrostatic interaction given in Equations 2.6 and 2.7 are the quadrupole and polarization components of the potential. The H_2 parameters α and Q are 5.4 $a_o^3 \approx 0.675$ Å^3 and 0.48 $a_o^2 \approx 0.12$ Å^2 provided by Silvera et. al. assuming the vibration state is $v = 0$ and rotational is $J = 0$[9]. The constant k is the electric force constant which in SI units is $k_e = \frac{1}{4\pi\epsilon_o}$ where ϵ_o is the vacuum permittivity.

$$U_{quad}(R) = k \sum_{i=1}^{N} \frac{Qq_i}{R^3} \tag{2.6}$$

$$U_{pol}(R) = -k\frac{\alpha}{2}[\sum_{i=1}^{N} \frac{q_i}{R^2}\hat{r}]^2 \tag{2.7}$$

For both potentials the distance R was the distance of the atom from the point in space in the Cartesian grid. The quadrupole is dependent on the orientation of the molecule with respect to the binding site. However, as a part of modeling H_2 as a sphere, the molecule is taken in the $J = 0$ rotational state so the quadrupole orientation dependence is averaged out.

Chapter 3

Set Up

3.1 Potential Used for Solving

The potential inputed in the NuSol program was a sum of 13 atomic Lennard-Jones contributions. The atoms are from the metal ion cluster in the corner of the cubic structure of MOF 5. In total 7 oxygen, 3 zinc and 3 carbon atoms were used as depicted in Figure 3.1. The 7 atom point group locations and the symmetry operations were given by a Crystal Maker text file. Using the point group the entire MOF 5 cubic structure was produced in a visualization using Paraview's python shell. The 13 atoms chosen for use were identified using this visualization based on proximity to the primary binding site known from neutron diffraction data[1, 2]. By allowing selection visually this method simplified choosing which atoms to incorporate to produce the potential.

Although the coordinates of the atoms were extracted from Crystal Maker, the structure was not conveniently arranged for calculating the ion cluster's potential. The coordinate vectors needed to be rotated such that the the z axis is directly out of the page from the center oxygen in Figure 3.1. The x-y plane was the perpendicular plane to this z-axis. The potential was evaluated for a 6 Å × 6 Å × 6 Å cube centered around the z-axis with the top and bottom face parallel to the x-y plane. The cube was placed so that the bottom face is 1.5 Å above the center oxygen to fully surround the minimum found which appeared to be ∼ 4.2 Å away from the center oxygen. The potential was a $10 \times 10 \times 10$ Cartesian grid. The number of divisions are odd to ensure that points were calculated along the centers of each dimension revealing the minimum along the z-axis.
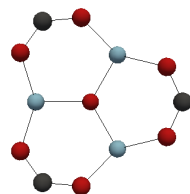

Figure 3.1: This grouping of atoms was used to make the potential. Other more distant atoms were not considered. Light Blue is Zinc, Red is Oxygen, Black is Carbon. Image produced using Paraview visualization of the MOF 5 crystal.

In order to make sure the potential was correct the potential was checked for certain defining

characteristics. First the minimum is expected to be somewhere along the z-axis. The zincs, carbons and outer oxygens are symmetric about the z-axis and raising in a bowl shape. This means the potential minima of each atom should combine symmetrically along the z-axis. Although the Lennard-Jones potential is not a complete quantum mechanical potential, the minimum is still expected to be of comparable magnitude to literature and experimental values. The minimum found is -350 K which is of the same order of magnitude as the the more completely calculated value by Matanovic et. al. of -772 K[18].

Second a planar slice parallel to the x-y plane must reveal 3 fold symmetry because the 13 atoms in the ion cluster have 3-fold symmetry. Shown below is the 3 fold symmetry at ~ 2.2 Å away from the center oxygen along the z-axis as seen in Figure 3.2.
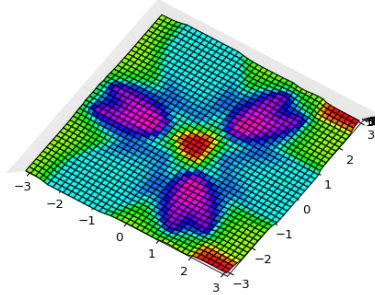

Figure 3.2: Apparent 3 fold symmetry in a planar slice at $z = \sim 2.2$ Å. The slice is 6×6 Å for both the x and y directions, centered with z-axis. The vertical axis is in Kelvin.

3.2 Expected Result

The result of the program should somewhat resemble the energies of a 3D simple harmonic oscillator. Inside the well of the potential produced by the MOF 5 primary site, it can be approximated that the potential is a harmonic oscillator. Below is the taylor expansion approximated to second order in the x direction.

$$V(x) = V(x_o) + V'(x_o)(x - x_o) + \frac{1}{2}V''(x_o)(x - x_o)^2 + ... \tag{3.1}$$

The approximation that the potential is a simple harmonic oscillator eliminates the first two terms with the axis centered about x_o which will be defined as $x_o = 0$. What is left is,

$$V(x) \approx \frac{1}{2}V''(0)x^2 = \frac{1}{2}kx^2, \tag{3.2}$$

where k is defined as the second derivative of the potential evaluated at $x_o = 0$. This can be approximated for all 3 directions for MOF 5; however, the x and y direction will be a significantly better approximation than the z which will deviate from the similarity shown by the x and y.

The energy levels of the 3D harmonic oscillator are discrete values given by Equation 3.3.

$$E_n = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega \tag{3.3}$$

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ω is the frequency of oscillation and is defined as $\omega = \sqrt{\frac{k}{m}}$ where m is the mass of the particle. If the energies of particles in MOF 5 resemble the 3D simple harmonic oscillator then it can be expected that there will be energies with degeneracy of 1 with an energy of $\frac{3}{2}\hbar\omega$ at the ground state then degeneracy of 3 with an energy of $\frac{5}{2}\hbar\omega$ in the first excited state. This continues with differences in energy levels of $\Delta E = \hbar\omega$. Knowing that this approximation is more rough in the z direction, it is expected that in the first excited state to see 2 energies that are near identical with a third deviating from the other 2. The immediate conclusion is that the 2 similar energies are the degeneracies in the x and y direction as $n_x = 1$ or $n_y = 1$. When $n_z = 1$ we expect the ω is very different due to a different k value. This is either because a 3D simple harmonic oscillator is a bad approximation of the potential in the z direction or because the potential is not symmetrical in this direction with the x and y directions or some combination of the two.

The next expectation is that if the energies follow that of the simple harmonic oscillator then the difference of H_2 and D_2 energy levels should be a factor of $1\sqrt{2}$. This immediately follows from $\omega_{H_2} = \sqrt{\frac{k}{m_{H_2}}}$ and since D_2 is twice as massive as H_2 the the new energy will be scaled by $\omega_{D_2} = \sqrt{\frac{k}{2m_{H_2}}} = \frac{1}{\sqrt{2}}\omega_{H_2}$. Therefore $E_{n,D_2} = \frac{1}{\sqrt{2}}E_{n,H_2}$.

3.3 How NuSol works

The solver program, NuSol.py, initially is called in the shell with the configuration file in the command. The configuration, here written as example_config.cfg, is parsed by the NuSol.py python program. In the shell the command is,

>> python NuSol.py example_config.cfg

The configuration file provides all of the information and parameters required to solve. NuSol.py solves with a cartesian system defined in the configuration file. The potential is either an explicit equation in the configuration file or a file path leading to a .npy file holding an array that is the potential. If you want to use an array potential the "USE_USER_FUNCTION:" prompt must be given a value of "False" and the field "USER_FUNCTION:" should be empty. NuSol solves with units in Hartree.

NuSol.py uses the library file (NuSol¿lib) in the NuSol file to assist with the process. NuSol_cfg.py reads the configuration file and creates a configuration object that holds all of the parameters and information inputted by the user. NuSol.py then calls for various information from the configuration object during the process. The NuSol_matrices.py builds the matrices required for solving. The type of matrix depends on the method of solving chosen by the user. NuSol.py then uses an external package to solve the matrix for its output of eigenenergies and eigenvectors. The sequence of solving is illustrated by Figure 3.3 below.
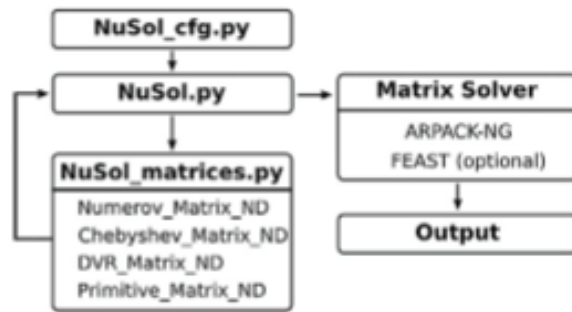
Figure 3.3: Flow chart of programs NuSol solving process. Image from the Graen et. al. paper, reference [3].

Chapter 4

Results and Analysis

4.1 Yielded Energies from NuSol

The potential revealed a minimum of ~ -350 K at 4.2 Å along the z-axis. Below are images of planar slices at various heights along the z-axis of a nearly identical potential inputted into NuSol. The images were improved with higher resolution and better centering for easy viewing. The planar slices also only plot up to certain maximums to maintain visible features.
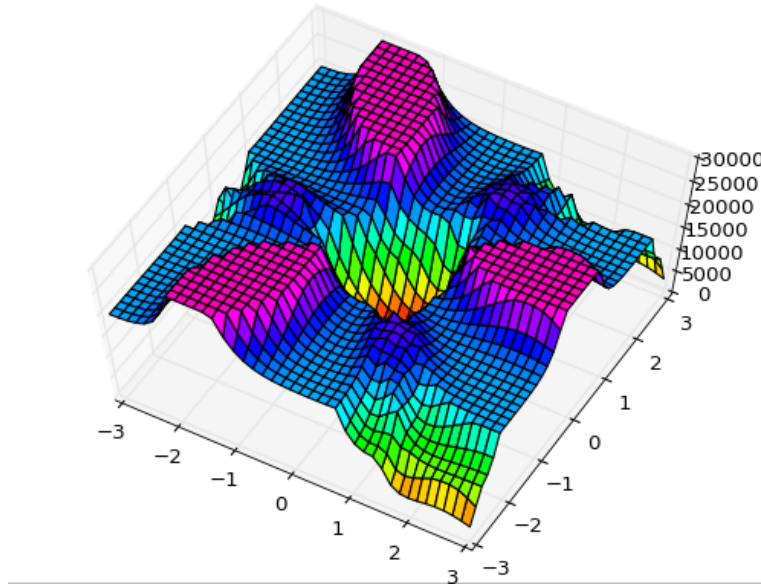

Figure 4.1: Potential slice at $z = 2.96$ Å which is closer to the corner oxygen than the minimum located at 4.28 Å for a $41 \times 41 \times 41$ grid in a 6 Å $\times$ 6 Å $\times$ 6 Å. Image is more centered and higher resolution than the solved potential. The vertical axis is in Kelvin and the x and y axis are in Å.

The planar slice at $z = 2.96$ Å closer to the ion cluster, reveals the dominating repulsive terms at this distance. The 3 branching out zinc, oxygen and carbon loops create a high potential zone that cups the minimum along the z-axis. Since the repulsive terms $(\frac{\sigma}{r})^{12}$ of the Lennard-Jones are dominating at this distance the minimum of this potential slice is still largely positive and the
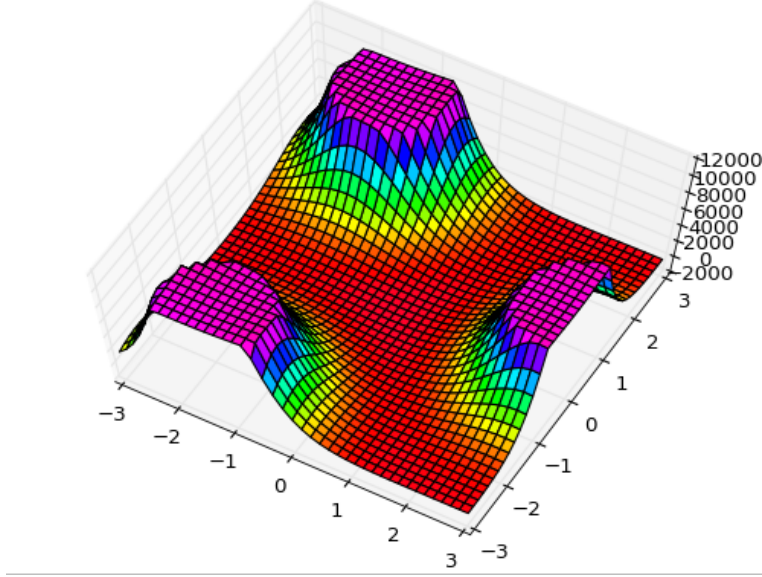
Figure 4.2: Potential slice at $z = 4.28$ Åwhich contains the minimum for a $41 \times 41 \times 41$ grid in a 6 Å $\times$ 6 Å $\times$ 6 Å. Image is more centered and higher resolution than the solved potential. The vertical axis is in Kelvin and the x and y axis are in Å.

Figure 4.3: Potential slice at $z = 5.89$ Åwhich is above the minimum for a $41 \times 41 \times 41$ grid in a 6 Å $\times$ 6 Å $\times$ 6 Å. Image is more centered and higher resolution than the solved potential. The vertical axis is in Kelvin and the x and y axis are in Å.
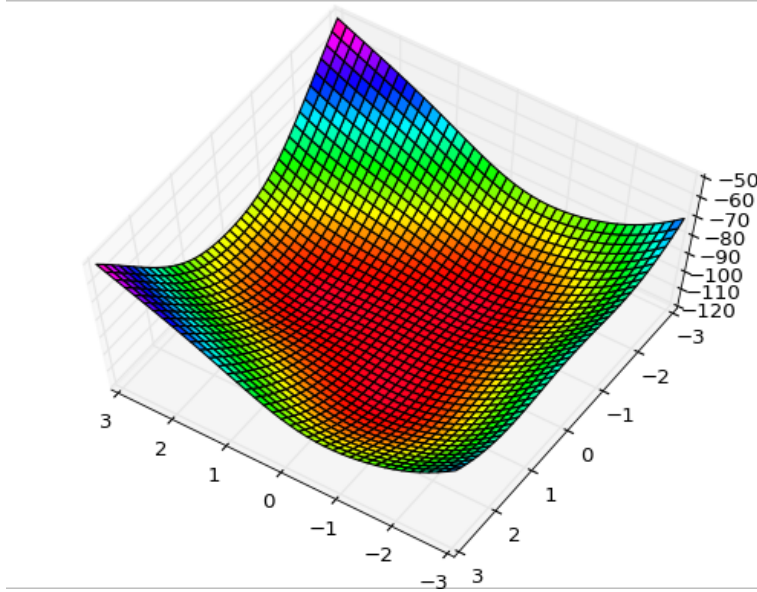
surrounding maximums even more so.

The planar slice that reveals the minimum of the entire potential at $z = 4.28$ Å depicts three

high spires that box in the potential with saddles in between them. This cups the minimum in the center at $x, y = 0$ Åwhere the attractive term $-(\frac{\sigma}{r})^6$ of the ion cluster's potential is dominating.

At $z = 5.89$ Å a planar slice reveals an entirely negative, attractive potential. The attractive terms of each the 13 atoms still combine along the z-axis to create a centered local minimum.

This trend is supported by finding the potential along the z-axis only. The potential values along the z-axis are also expected to reveal a potential curve similar to the Lennard-Jones potential. Figure 4.4 below depicts the potential along the z-axis showing the dominance of the repulsive term at low z and the switch to a more attractive potential further away.
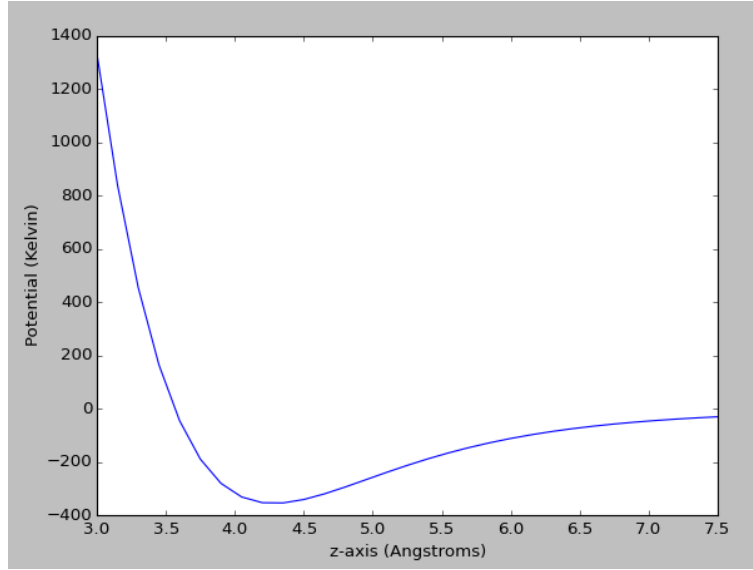

Figure 4.4: Depicted is the potential along the z-axis in Kelvin. This plot also made from a higher resolution and more centered version of the same potential.

The recently published NuSol program was used to numerically extract eigenvectors and eigenvalues of the particle in the produced potential[3]. 10 converged eigenstates and their eigenenergies outputted by the program are given in Table 4.1 below for H_2, D_2 and tritium (T_2). The NuSol program makes changing the mass of the particle in the potential trivial. However, the speed of convergence is affected by this mass and if the values do not converge fast enough, the code will fail after a certain number of iterations. As expected the more massive isotopes sit lower in the potential due to differences in zero point energies.

The energies are expected to follow the degeneracy of the 3D simple harmonic oscillator. This would mean a single ground state, triple degeneracy in the first excited state and six degeneracies at the second excited state. Although three significant figures are provided this only represents roughly the accuracy of the code's output and not confidence in these energies being representative of reality in terms of magnitude. Due to the neglect of many variables to simplify the model we are not confident in this potential producing energies close to experimental values.

As expected whether or not eigenvectors converged was dependent on the potential. The main dependency was the potential values within the grid which was directly dependent on the number of grid points and the dimensions of the space. Another dependency was the number of the lowest energies to be solved. Fewer energies requested does not necessarily constitute faster convergence.

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Expected State	H_2 Eigenvalues (K)	D_2 Eigenvalues (K)	T_2 Eigenvalues (K)
E_0	40.0	-101	-160
E_1	243	51.2	-26.3
E_1	251	65.6	-4.60
E_1	364	119	29.5
E_2	408	144	51.3
E_2	454	201	107
E_2	475	235	146
E_2	566	275	158
E_2	591	317	222
E_2	643	388	296

Table 4.1: Energies extracted from NuSol.py using H_2, D_2 and T_2 in the context of the produced potential. This is roughly the accuracy of the program; however, this is not the level of confidence we have in the model.
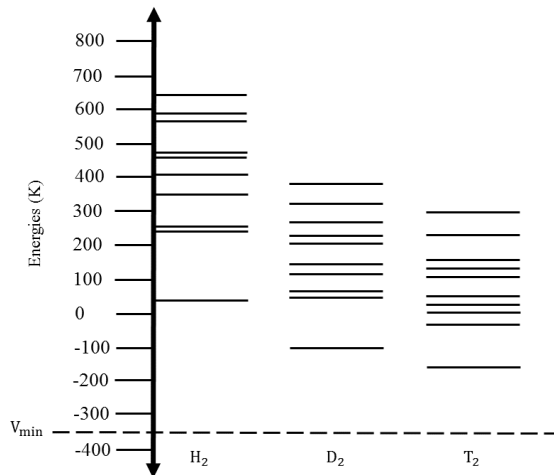

Figure 4.5: Depicted are the 10 energies stated in Table 4.1 for each of H_2, D_2 and T_2 in K.

Before deeming a potential not able to be solved with NuSol.py various numbers of requested energies should be attempted. If one of the four methods from NuSol.py did not have converging eigenvectors then the others usually would not as well.

4.2 Analysis

The potential minimum does not agree with literature values, but its location is consistent with other computational results. Matanovic et. al. gives theoretical distances of 3.95 Å, 3.72 Å and 3.6 Åaway from the center oxygen[19]. The potential used for NuSol had its minimum at 4.2 Å which is consistent with those from Matanovic et.al. although slightly above the reported values. My calculated minimum is not consistent with other experimental values found through neutron

diffraction [1, 2]. The agreement with experiment is entirely dependent on the accuracy of the potential model and the used parameters. Due to approximations and lack of computational power that is required to accurately represent reality, it is expected that the numerically extracted data does not compare well with experiment.

The minimum of the potential is used for NuSol is ~ -350 K. This is a less than half in magnitude as the Matanovic et. al. reported value of ~ -773 K[19]. Due to ambiguity in the wording of the paper which provided the parameters it is not clear if the parameters for the MOF 5 potential are for a single hydrogen atom instead of the diatomic molecule[17]. Further discussion with the author may reveal that this is the case. This would mean that it would be necessary to double the potential to account for two hydrogen atoms in the potential. Another factor is that Lennard-Jones potential is not a complete potential. Multiple properties are either approximated as negligible or not considered. Matanovic et. al. created a more complete potential which included a 5D coupled rotational and translational calculation of the potential for H_2. I neglect the rotational energy due to the assumption that the H2 is in the $J = 0$ state among other neglected characteristics.

As shown in Table 4.1 the ground state of H_2 is 40.0K, D_2 is -101 and T_2 is -160K. The zero point energies with defining $V_{min} = 0K$ are 390 K (H_2), 249 K (D_2) and 191 K (T_2). If the system was a true 3D simple harmonic oscillator with H_2 having a zero point energy of 390 K it is expected that D_2 will scale with a factor of $\frac{1}{\sqrt{2}}$ yielding and T_2 with a factor of $\frac{1}{3}$. This would yield the zero point energy for D_2 to be 276 K and T_2 to be 225 K. In both cases the energies calculated are around roughly 30 K below the 3D harmonic oscillator predictions, but this is to be expected since the MOF 5 potential is nowhere a perfect harmonic oscillator. The data is consistent with the prediction that the zero point energies sink deeper into the potential with more mass and do so by some factor that is not too far off from $\frac{1}{2}$ and $\frac{1}{3}$ for D_2 and T_2 respectively.

Chapter 5

Conclusion

5.1 Concluding Statements

A potential was created which was consistent in minimum location (4.2 Å), but not depth (~ -350 K)[19]. The potential was not consistent with neutron data[1, 2]. However, this was expected due to approximations chosen to simplify the calculation. Many of these approximations were required by the limitations of computational power available. Current models cannot yet accurately represent potential energies of complex structures.

A recently published wavefunction solving program NuSol was used with the above mentioned potential to better understand the difference in energies of the isotopes H_2 and D_2[3]. T_2 was also tested to emphasize the trend. This program has not yet been applied to prospective quantum sieves. The calculated ground states are 40K for H_2, -101 K for D_2 and -160 K for T_2 with zero point energies of 390 K, 249 K and 191 K above the potential minimum respectively. Although these calculated values exhibit the trend of sinking further into the potential and the program outputs with roughly 3 significant figure accuracy, my confidence in these numbers does not reach 3 significant figures due to inaccuracies of the model. I have more confidence in the energy levels relative to those of their isotopes.

Although still requiring much refining, computational methods have shown to be a way of solidifying understanding of the interactions within MOFs. The limitations of computability were not reached in this work and could be explored further to try to produce more accurate potential energies for MOF 5 and more.

5.2 Future Work

Figure 4.2 shows the minimum of the potential and 3 high spires and saddles between them. When using other variations to this potential, dimensions of more than 6 Å in the x, y and z direction had difficulty converging eigenvectors. This may be because the eigenvectors would have trouble converging on states that spread towards the edges and/or beyond the potential which could happen in the saddles such as those in Figure 4.2. More eigenstates may be found by further exploring the dependencies of the number of requested minimum energies and other parameters to the calculation.

Altering the potential further to get a more accurate output of energies that are closer to exper-

imental value will be crucial to improving the potential model. A major improvement would be to make the model more complete by not approximating the diatomic isotopes H_2 and D_2 as spheres. Their rotational and vibrational energies could provide more agreement in potential shape with neutron diffraction, x-ray diffraction and other computational data. Doing so would also introduce dependence on orientation of the "dumbbell" shaped diatomic molecules due to electrostatic interactions. In addition expanding the model to include more atoms. ¡odeling secondary and tertiary sites would provide a more complete picture.

Other MOFs should also be explored to better find the trends of the computational techniques' abilities to provide believable eigenstates. An example of possible further exploration is stated in Pierce's Oberlin College honors thesis. Pierce discusses that it appears that the MOF's potential's confinement of H_2 and D_2 determines whether or not the MOF is a good quantum sieve as opposed to the nanopore size[20]. Computational comparison of various MOFs with differing pore sizes and potential energy geometries may be able to add supportive evidence to this conclusion.

In addition, experiment is being conducted on combining MOFs with other materials such as graphite[21]. The combination of structures adds new possibilities for adsorbent surface area and more complex potential energies to model. Difficulties may arise due to asymmetries; however, this could shed light on the accuracy of current modeling techniques as well as possibly predict better materials for specified applications such as gas separation.

In the future more MOFs can be tested to improve understanding of MOFs' quantum mechanical interactions with fluids and the models that predict these interactions. This further study would also help the development of computational techniques for complex quantum mechanical systems. Improving the models and their ability to predict other materials in addition to MOF characteristics will hasten the search for finding and engineering materials for chosen applications.

Chapter 6

Appendix

6.1   Potential Code Problems

Difficulties and possible bugs in the NuSol program were identified. However, these could be due to user error. All notation is given in the syntax of the NuSol file's code.

1) When using certain methods of calculation, the program returned back an error saying that numpy (np) cannot np.reshape() an object of different dimensions. The conflict is in lines where, for a 3D example, the potential of dimensions, NGRIDX×NGRIDY×NGRIDZ is attempted to be reshaped to an array of length (NGRIDX-1)×(NGRIDY-1)×(NGRIDZ-1). This cannot happen or else loss of data will occur due to truncation hence the thrown error. However, the dimensions in the configuration must be equal to that of the potential. So I did not see a way to get around this problem. It is possible that this method is taking into consideration that the number grid lines will always be one more than the number of cubes the space is divided into despite that being seemingly unnecessary for this function. But I do not see a way to account for this in the configuration file.

2) The visualization program which outputs wavefunction plots using the eigenvectors generally worked. However, the 3D DVR solved wavefunction plot was missing a plt.show() command to show the plots.

6.2   Potential Generating Code

The latest iteration for producing the Lennard-Jones potential for the 13 ion cluster atoms used.

```python
#This program creates the potential energy of a space above the 13 atoms used
in the bowl of a corner of MOF-5 using Lennard-Jones
import os
import numpy as np
import math
import time
from mpl_toolkits.mplot3d import Axes3D
from matplotlib import cbook
from matplotlib import cm
from matplotlib.colors import LightSource
import matplotlib.pyplot as plt



def magnitude(r,rspace):
    #3D distance formula
    return np.sqrt((r[0]-rspace[0])**2+(r[1]-rspace[1])**2+(r[2]-
rspace[2])**2)
#The standard Leonard-Jones 6-12
def LJ6_12(sigma,e,r,rspace,q):
    #charge of e-
    #Q=0.48 #quatrupole moment ***CHECK UNITS***
    k=320000. #e^2/a0=1Hartree=320000K
    #get magnitude of r
    R=magnitude(r,rspace)
    #these are both in the same units so its okay even if use in Angstroms
    R=2*R #1 a0=0.5 A
    sigma=2*sigma
    #Potential calculation
    if (R==0.):
        #if going to inf. make 10000 instead
        return(10000.)
    else:
        LJ = 4*e*((sigma/R)**12-(sigma/R)**6)
        #Uquad=k*((Q*q)/(R**3)) Not using quadrupole moment
        U = LJ
        if (U>=10000.):
            #max out at 10000
            return(10000.)
        else:
            return(U)

def potential(Lz,L,Nz,N,r,e,sigma,q):
    Div=L/(N-1)
    Divz=Lz/(Nz-1)
    U=np.empty([Nz,N,N])
    for z in range (0,Nz):
        #Z coordinate in 3D space
        Uz=z*(Divz)+1.5#-.5*L #(z+1)(L/N)-0.5*L #From 0 to 4
        for y in range(0,N):
```

```
            #Y coordinate in 3D space
            Uy=y*(Div)-.5*L #From -2 to 2
            for x in range(0,N):
                #X coordinate in 3D space
                Ux=x*(Div)-.5*L #From -2 to 2
                #create vector to point in 3D space
                rspace=[Ux,Uy,Uz]
                #calculate potential for point
                U[z][y][x]=LJ6_12(sigma,e,r,rspace,q)
    print "Minimum of run: ", np.min(U)
    return U


def main():
    #Zn:0-2, O1:3, O2:4-9, C1:10-12
    r=[[-1.855325180842072, 0.0, -10.563315995147232], [0.9276625904210358, -
1.6067587388901914, -10.563315995147232],
        [0.9276625904210358, 1.6067587388901914, -10.563315995147232],[0.0,
0.0, -11.219359106027404],
        [-2.2071535575638297, -1.575575329839865, -9.474260182374842],
[2.468065039999284, -1.1236633859835425, -9.474260182374842],
        [-0.26091148243545437, 2.6992387158234075, -9.474260182374842],
[2.468065039999284, 1.1236633859835425, -9.474260182374842],
        [-0.2609114824354546, -2.6992387158234075, -9.474260182374842], [-
2.2071535575638292, 1.575575329839865, -9.474260182374842],
        [-1.46152887986063, -2.53144227664784, -9.152445142328544],
[2.92305775972126, 0.0, -9.152445142328544],
        [-1.4615288798606296, 2.53144227664784, -9.152445142328544]]
    sigma=[2.4616,3.118,3.118,3.431,3.431,3.431,2.571]
    #Zn,O1,O2,C1,C2,C3,H
    #epsilon
    e=[62.3993,30.19,30.19,52.84,52.84,52.84,22.14]
    #not using adjusted charges
    #q=[1.8529,-2.2568,-1.0069,1.0982,-0.1378,-0.0518,0.1489]
    #divisions of x and y
    N=41
    #length of x and y dimensions in Angstroms
    L=6.
    #divisions of z
    Nz=41
    #length of x and y dimensions in Angstroms
    Lz=6.
    #Make an empty array to as blank potential
    U=np.empty([Nz,N,N])
    #Loop through the atoms
    for i in range(len(r)):
        r[i][2]=r[i][2]+11.219359106027404 #Translate so center O is at
(0,0,0)
        if i<=2:
            U+=potential(Lz,L,Nz,N,r[i],e[0],sigma[0],q[0])
```

```python
        elif i==3:
            U+=potential(Lz,L,Nz,N,r[i],e[1],sigma[1],q[1])
        elif i>3 and i<=9:
            U+=potential(Lz,L,Nz,N,r[i],e[2],sigma[2],q[2])
        elif i>9 and i<=12:
            U+=potential(Lz,L,Nz,N,r[i],e[3],sigma[3],q[3])
    print np.min(U), np.where(U==np.min(U))

    #Convert to Hartree
    U=U*(1./320000.) #1Hartree=320000K
    print np.min(U), np.where(U==np.min(U))

    #plot a slice of the potential
    fig = plt.figure()
    #set axes
    x=np.linspace(-3,3,N)#N)
    y=np.linspace(-3,3,N)#N)
    #make X,Y 2D arrays that correspond to eachother
    X,Y=np.meshgrid(x,y)
    #Plot
    ax = fig.gca(projection='3d')
    ax.plot_surface(X,Y,U[19],rstride=1, cstride=1, cmap=cm.gist_rainbow) #Go
to 3.5A currently going to 3.6A


    #For printing along z axis if wanted (must comment out previous 2 lines
for this to work)
    #Z=[]
    #for i in range(N):
    #    Z.append(U[i][(N/2)-1][(N/2)-1])
    #print np.min(Z), np.where(Z==np.min(Z))
    ##print Z
    #z=np.linspace(0,6,N)
    #plt.plot(z[:],Z[:])

    #Show
    plt.show()

    #Save as .npy file for NuSol.py
    print type(U)
    print np.shape(U)
    name = raw_input('Name the file without an extension:') #naming the file
from user input
    data=U
    print ("New File being created: "+name+".npy")
    np.save(name+".npy",data)


main()
```

6.3   MOF 5 Structure Visualization Code

The code used as the python script to produce the MOF 5 visualization in Paraview.

```
#Creating The MOF-5 Structure
from paraview.simple import *
import math
#6 atoms by 48 symmetries (adding 24 atoms to finish)
M=144+24#H
N=192+48#H
#5 bonds by 24 symmetries plus 48 bonds to finish benzene rings and 48 bonds
for final oxygens and 24 H bonds
K=120+24#Hbonds
L=216+48#Hbonds
def Rotation(preRotation):
    postRotation=[0,0,0]
    #Rotation Matrix
    RotMatrix=[[-1/(math.sqrt(6)),2/(math.sqrt(6)),-
1/(math.sqrt(6))],[1/(math.sqrt(2)),0,-
1/(math.sqrt(2))],[1/(math.sqrt(3)),1/(math.sqrt(3)),1/(math.sqrt(3))]]
    #Identity Matrix
    #RotMatrix=[[1,0,0],[0,1,0],[0,0,1]]
    for i in range(3):
        for j in range(3):
            postRotation[i]+=RotMatrix[i][j]*preRotation[j]
    return postRotation


#Symmetry function
def sym(x,y,z,which):
    RETURNS=[]
    RETURNS=[[x,y,z],[-x,-y,z],[-x,y,-z],[x,-y,-z],[z,x,y], #1-5
    [z,-x,-y],[-z,-x,y],[-z,x,-y],[y,z,x],[-y,z,-x],         #6-10
    [y,-z,-x],[-y,-z,x],[y,x,-z],[-y,-x,-z],[y,-x,z],        #11-15
#Base Symmetries that produce most of the unit cell without overlap
    [-y,x,z],[x,z,-y],[-x,z,y],[-x,-z,-y],[x,-z,y],          #16-20
    [z,y,-x],[z,-y,x],[-z,y,x],[-z,-y,-x],                   #21-24
#The symmetries in addition to crystal maker's explicit symmetries
    [z,y,x],[-z,x,y],[y,x,z],[x,z,y],[x,-y,z],               #1-5
    [y,-x,-z],[x,-z,-y],[y,z,-x],[-z,y,-x],[z,x,-y],         #6-10
    [y,-z,x],[-z,-y,x],[-x,z,-y],[-y,-z,-x],[-y,-x,z],       #11-15
#Symmetries that finish the unit cell
    [-x,-y,-z],[-x,-z,y],[-y,z,x],[z,-x,y],[x,y,-z],         #16-20
    [-y,x,-z],[-x,y,z],[z,-y,-x],[-z,-x,-y]]                 #21-24

    preRotation=RETURNS[which]
    postRotation=Rotation(preRotation)
    return postRotation[0],postRotation[1],postRotation[2]



#create empty list of bonds
Bonds=[]
for i in range (L):
    Bonds.append(Line())
#Define Display Properties
```

```python
BondsDP=[]
for i in range(L):
    BondsDP.append(GetDisplayProperties(Bonds[i]))

#create empty list of atoms
unit = []
#make spheres radius LARGER TODO .015 .02
for i in range(N):
    unit.append(Sphere())


#Define Display Properties
unitDP=[]
for i in range(N):
    unitDP.append(GetDisplayProperties(unit[i]))

#Array of Coordinates (6 atoms by 3 coordinates O1-Zn-O2-C1-C2-C3-H)
unitCoord = [[6.4775, 6.4775, 6.4775], [7.6136, 5.3413, 5.3413], [7.2721,
5.6830, 3.4548], [6.4775, 6.4775, 2.8975], [6.4775, 6.4775, 1.3820], [7.3224,
5.6325, 0.6905], [7.9981, 4.9568, 1.2522]]
#U=number of atoms in basic group
U=7


#Application of Translation vector
#Tx, Ty and Tz denote a translation given as the components of a vector
Tx=0.
Ty=0.
Tz=0.

#Radius of all atoms-visulatization of atomic radius is not to scale
RADIUS=.3
#Alter parameters for each atom
for j in range (24): #Do the main picture with the first 24 symmetries
    for i in range(U):
        x=unitCoord[i][0]
        y=unitCoord[i][1]
        z=unitCoord[i][2]
        # Call one symmetry method
        x,y,z=sym(x,y,z,j)
        unit[i+U*j].Radius = RADIUS
        unit[i+U*j].PhiResolution = 15
        unit[i+U*j].ThetaResolution = 15
        unit[i+U*j].Center = (x+Tx,y+Ty,z+Tz)
    #make Zn light blue
        if (i==1):
            unitDP[i+U*j].DiffuseColor=[.6,.8,.9]
    #make O1,O2 Red
        elif (i==0 or i==2):
            unitDP[i+U*j].DiffuseColor=[.8,.1,.1]
    #make C1,C2,C3 Black
```

```python
        elif (i>2 and i<6):
            unitDP[i+U*j].DiffuseColor=[0.3,0.3,0.3]
    #don't alter H color
    for k in range(U-1):
        #make start point for bond
        x1=unitCoord[k][0]
        y1=unitCoord[k][1]
        z1=unitCoord[k][2]
        #make endpoint for bond
        x2=unitCoord[k+1][0]
        y2=unitCoord[k+1][1]
        z2=unitCoord[k+1][2]
        #Call same symmetry for both points
        x1,y1,z1=sym(x1,y1,z1,j)
        x2,y2,z2=sym(x2,y2,z2,j)
        Bonds[k+(U-1)*j].Point1=(x1+Tx,y1+Ty,z1+Tz)
        Bonds[k+(U-1)*j].Point2=(x2+Tx,y2+Ty,z2+Tz)
        BondsDP[k+(U-1)*j].DiffuseColor=[0.,0.,0.] #MAKE IT BLACK!

#Finish Benzene Rings and Final Oxygens
for a in range(24):
    #Oxygens (Spheres 192)
    xOxygen=unitCoord[2][0]
    yOxygen=unitCoord[2][1]
    zOxygen=unitCoord[2][2]
    # Call one symmetry method
    xOxygen,yOxygen,zOxygen=sym(xOxygen,yOxygen,zOxygen,a+24)
    unit[M+a].Radius = RADIUS
    unit[M+a].PhiResolution = 15
    unit[M+a].ThetaResolution = 15
    unit[M+a].Center = (xOxygen+Tx,yOxygen+Ty,zOxygen+Tz)
    unitDP[M+a].DiffuseColor=[.8,.1,.1]

    #OXYGEN BONDS
    #Bond to Oxygen 2-3
    x1=unitCoord[1][0]
    y1=unitCoord[1][1]
    z1=unitCoord[1][2]
    #make endpoint for bond
    x2=unitCoord[2][0]
    y2=unitCoord[2][1]
    z2=unitCoord[2][2]
    #Call same symmetry for both points
    x1,y1,z1=sym(x1,y1,z1,a+24)
    x2,y2,z2=sym(x2,y2,z2,a+24)
    Bonds[K+a].Point1=(x1+Tx,y1+Ty,z1+Tz)
    Bonds[K+a].Point2=(x2+Tx,y2+Ty,z2+Tz)
    BondsDP[K+a].DiffuseColor=[0.,0.,0.] #MAKE IT BLACK!
    #Bond from Oxygen 3-4
    x1=unitCoord[2][0]
```

```python
y1=unitCoord[2][1]
z1=unitCoord[2][2]
#make endpoint for bond
x2=unitCoord[3][0]
y2=unitCoord[3][1]
z2=unitCoord[3][2]
#Call same symmetry for both points
x1,y1,z1=sym(x1,y1,z1,a+24)
x2,y2,z2=sym(x2,y2,z2,a+24)
#First
Bonds[K+a+24].Point1=(x1+Tx,y1+Ty,z1+Tz)
Bonds[K+a+24].Point2=(x2+Tx,y2+Ty,z2+Tz)
BondsDP[K+a+24].DiffuseColor=[0.,0.,0.] #MAKE IT BLACK!

#Carbons
xCarbon=unitCoord[5][0]
yCarbon=unitCoord[5][1]
zCarbon=unitCoord[5][2]
# Call one symmetry method
xCarbon,yCarbon,zCarbon=sym(xCarbon,yCarbon,zCarbon,a+24)
unit[M+a+24].Radius = RADIUS
unit[M+a+24].PhiResolution = 15
unit[M+a+24].ThetaResolution = 15
unit[M+a+24].Center = (xCarbon+Tx,yCarbon+Ty,zCarbon+Tz)
unitDP[M+a+24].DiffuseColor=[0.3,0.3,0.3]

#Bond to Carbon Oxygen 5-6
x1=unitCoord[4][0]
y1=unitCoord[4][1]
z1=unitCoord[4][2]
#make endpoint for bond
x2=unitCoord[5][0]
y2=unitCoord[5][1]
z2=unitCoord[5][2]
#Call same symmetry for both points
x1,y1,z1=sym(x1,y1,z1,a+24)
x2,y2,z2=sym(x2,y2,z2,a+24)
Bonds[K+a+48].Point1=(x1+Tx,y1+Ty,z1+Tz)
Bonds[K+a+48].Point2=(x2+Tx,y2+Ty,z2+Tz)
BondsDP[K+a+48].DiffuseColor=[0.,0.,0.] #MAKE IT BLACK!

#Final H
Hx=unitCoord[6][0]
Hy=unitCoord[6][1]
Hz=unitCoord[6][2]
#Call one symmetry method
Hx,Hy,Hz=sym(Hx,Hy,Hz,a+24)
#print(M+a+48)
unit[M+a+48].Radius = RADIUS
unit[M+a+48].PhiResolution = 15
```

```python
        unit[M+a+48].ThetaResolution = 15
        unit[M+a+48].Center = (Hx+Tx,Hy+Ty,Hz+Tz)

        #Bond to Carbon Hydrogen 6-7
        x1=unitCoord[5][0]
        y1=unitCoord[5][1]
        z1=unitCoord[5][2]
        #make endpoint for bond
        x2=unitCoord[6][0]
        y2=unitCoord[6][1]
        z2=unitCoord[6][2]
        #Call same symmetry for both points
        x1,y1,z1=sym(x1,y1,z1,a+24)
        x2,y2,z2=sym(x2,y2,z2,a+24)
        Bonds[K+a+72].Point1=(x1+Tx,y1+Ty,z1+Tz)#3*24=72
        Bonds[K+a+72].Point2=(x2+Tx,y2+Ty,z2+Tz)
        BondsDP[K+a+72].DiffuseColor=[0.,0.,0.] #MAKE IT BLACK!


    #Final Benzene Ring Bonds
    for j in range (24):
        x1=unitCoord[5][0]
        y1=unitCoord[5][1]
        z1=unitCoord[5][2]
        #make endpoint for bond
        x2=unitCoord[5][0]
        y2=unitCoord[5][1]
        z2=-unitCoord[5][2]
        #Call same symmetry for both points
        x1,y1,z1=sym(x1,y1,z1,j)
        x2,y2,z2=sym(x2,y2,z2,j)
        Bonds[L-j-1].Point1=(x1+Tx,y1+Ty,z1+Tz)
        Bonds[L-j-1].Point2=(x2+Tx,y2+Ty,z2+Tz)
        BondsDP[L-j-1].DiffuseColor=[0.,0.,0.] #MAKE IT BLACK!

#Checks if coordinate is within range we are considering
#center = middle of circle, accept = radius of circle, coord = considered
coordinate
def inRangeSphere(center,accept,coord):
    if center=="None":
        return True
    else:
        #if distance is witin acceptable range then return True
        distance=magnitude(coord,center)
        if distance<=accept:
            return True
        else:
            return False

def magnitude(r,rspace):
```

```python
    #3D distance formula
    return math.sqrt((r[0]-rspace[0])**2+(r[1]-rspace[1])**2+(r[2]-
rspace[2])**2)

#Decide a portion of the structure to show
#If you want to show the whole thing put center="None"
center=[0,0,-11.2193591060274] #Currently set to have center at the lowest
atom on the z-axis which is a center oxygen in and ion cluster
#Acceptance radius
accept=3.61
#Show Spheres
for i in range(N):
    s=unit[i]
    if inRangeSphere(center,accept,s.Center):
        Show(s)
    else:
        Hide(s)
#Show Bonds
for i in range (L):
    Line=Bonds[i]
    if inRangeSphere(center,accept,Line.Point1) and
inRangeSphere(center,accept,Line.Point2):
        Show(Line)
    else:
        Hide(Line)


Render()
```

6.4   Acknowledgments

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