Theoretical Foundation

The topic of this project is Energy Minimization of a Molecule which is in the field of Quantum/Computational Chemistry. The process of minimizing the energy of a molecule is to be able to find an arrangement in space of a collection of atoms where the net inter-atomic forces are as close to zero as possible through the use of computational modeling of chemical bonding and where the potential energy surface is a stationary point. The molecule will also be affected by a force field, meaning it will be affected by parameters in which will be used to calculate the potential energy of a system of atoms in molecular mechanics. The focus at hand will be the minimization of energy of Butane using the CHARMM force field, meaning that I will be focusing on the Potential Energy of Butane while using Numerical methods to find where Butane has the optimal contortion and then use that to calculate the potential energy. To calculate the potential energy I will use the chemical/physical properties of butane which will affect the molecule. The potential energy equation is made of summations of bond lengths, bond angles, torsion, and nonbounded equations (Van Der Waal and Electrostatic forces). This is where I will have to know chemical properties as you will need to know how much symmetry there will be and how many interactions there will be. The following is the generalized Potential Energy equation for molecules.

$$PE = \sum_{i}^{\alpha}\sum_{j \neq i}^{\alpha} \frac{B_{i,j}}{r_{i,j}^{12}} - \frac{A_{i,j}}{r_{i,j}^{6}} + \sum_{i}^{\alpha}\sum_{j \neq i}^{\alpha} K\frac{q_i q_j}{r_{i,j}} + \sum_{i=1}^{\alpha} k_i(r_i - r_0)^2 + \sum_{i=1}^{\alpha} k_i(\theta_i - \theta_0)^2$$

$$+ \sum_{i=1}^{\alpha} k_i(1 + \cos(n_i\varphi_i + \delta_i))$$

$$B_{i,j} = \epsilon_{i,j}\sigma_{i,j}^{12}$$
$$A_{i,j} = 2\varepsilon_{i,j}\sigma_{i,j}^{6}$$
$$\epsilon_{i,j} = \sqrt{\epsilon_i \epsilon_j}$$
$$k_i = Constants\ for\ Bond\ Lengths\ \&\ Angles$$
$$K = Coulombs\ Constant$$

Bond lengths can stretch or compress like springs when finding a length for when they are in an optimized form. There will be two different equilibrium lengths (values I want to approximate to), one for Carbon and Hydrogen bonding and the other for Carbon and Carbon bonding. For Bond angles, there will be two equilibrium angles, one for C-C-C and another for H-C-C. Torsion is included for minimization of energy but since I was approximating it to its Anti conformation which is the optimized torsion for it, optimal energy would've been exactly zero thus I decided not to approximate this for Butane. Van der Wall interactions here will only be acting from one end of the molecule to the other end of the molecule as it is considered a faraway interaction and acts here only within three bond lengths. The Electrostatic forces here will be composed of H-H and C-H interactions. Thus, through all of these interactions, contortions, and stretching/compressing I will be finding the minimized energy for this molecule.
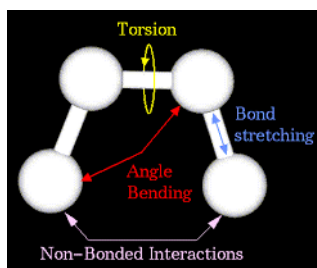
<div align="center">Methods</div>

To Minimize Energy of a Molecule, there are multiple ways to do this such as actually using a geometry simulator in which you insert the number and molecule and it does it for you. There are other ways to do this such as empirical/semi-empirical ways such as the methods that I applied to this project. Some possible methods are Newtons-Raphson, Quasi-Newton, Conjugate Gradient, and Steepest Descent Method. The methods that I applied were the Newton-Raphson method and the Steepest Descent Method. The reason for applying the Newton-Raphson is because of the fact that it usually takes the least amount of iterations to reach the minimum. This method is based on a Taylor series expansion of the Potential Energy Surface (PES) at the current geometry. For this method you will need to use the first derivative which is called the gradient/slope of the PES at the current geometry and the second derivative which is called the curvature.

$$X_{new} = X_{old} - \frac{PE'(X_{old})}{PE''(X_{old})}$$

Now for using Steepest Descent, the purpose for me using this method is that it does not require a second derivative. For companies this will make this approximation more cost efficient as compared to the Newton-Raphson that need two derivatives and is costly. Continuing, the Steepest Descent methods relies off of an approximation and in which the second derivative is considered to be a constant. The equation to update the geometry will be

$$X_{new} = X_{old} - \mu PE'(X_{old})$$

where μ is a constant. The gradient at each point must still be calculated here and is faster than Newton-Raphson but because of the approximation it takes more work and becomes slower in the long run. Thus, this method is first minimized in the direction in which the gradient is the largest at the initial point, once this minimum is achieved, the second minimization starts off at that point and moves in the steepest remaining direction. This continues until a minimum has been achieved from all direction within a certain tolerance.

<div align="center">Implementing Methods</div>

To be able to apply these methods and compute them using my code, I broke up each different potential energy into its own function defined in Python to be able to compute it in an easier manner. Meaning I defined C-H and H-H Bond Length, C-C-C and H-C-C Bond Angle, H-H and C-H Electrostatic, and H-H Van der Wall as their own entities and approximated their optimal values and then plugged them back into the Potential Energy equation for that interaction multiplied by the number of interactions that happens for that Energy and then added up them into one Energy at the end.

<div align="center">Validation of Methods</div>

One way that I validated the methods that I used for this project was looking into many Chemistry websites and books to look for examples of these methods being applied in theoretical and applicable examples. I was able to see the Steepest Descent and Newton-Raphson methods being used for the same type of problem that I was applying it to. As well as this I used reference articles in which people had minimized energies for similar small molecules thus my final potential energy would have to be around the same as those other molecules as they are relatively

small. Not only this but I was looking into how many iterations these examples would potentially run to see if my program was running in an efficient manner.

Results

Steepest Descent

Potential Minimized Energy	0.5856786000034494
Bond Length CH Energy	0.45052200000000087 kcal/mol
Bond Length CC Energy	0.13515660000000027 kcal/mol
Bond Angle CCC Energy	2.9633608817708482e-12 mdyne/A
Bond Length HCC Energy	4.847820244982098e-13 mdyne/A
Electrostatic CH Energy	1.1627666019477336e-27 kcal/mol
Electrostatic HH Energy	-3.7374640776891435e-28 kcal/mol
VDW Energy	-2.4801500486369745e-57 kcal/mol

Newtons-Raphson Method

Potential Minimized Energy	0.16112460000001066
Bond Length CH Energy	0.3559680000000007 kcal/mol
Bond Length CC Energy	0.13515660000000027 kcal/mol
Bond Angle CCC Energy	0.0 mdyne /A
Bond Length HCC Energy	0.0 mdyne/A
Electrostatic CH Energy	1.1627666019477336e-27 kcal/mol
Electrostatic HH Energy	-3.7374640776891435e-28 kcal/mol
VDW Energy	-0.32999999999999025 kcal/mol

The interesting thing that I found for these solutions are that between both methods some of the results are very similar to each other not including the actual minimized potential energies which are different. The potential energies between these two methods are different because for Bond Angle C-C-C and H-C-C in Newton-Raphson method it displayed it as 0 kcal/mol and this is because when the code was running it displayed the equilibrium value as if it was the approximated value after one or two iterations thus it contributed to 0 energy here. Also, the final value of the energy was in kcal/mol except for the Angles which are in mdyne/A (millidyne/Angstrom) and this is because I was not able to find a conversion into kcal/mol. The result for the molecule was supposed to be something very small as the displayed final approximations above and this is because Butane is a very small molecule. These results compare very well with the theory as the theory for the potential energy is relatively straight forward in an empirical way. These results are accurate especially for Steepest Descent compared to Newtons Method which calculate two 0 potential energies in my approximations which make it not as accurate. These approximations answer the topic of the project. The purpose was to approximate the lowest amount of potential energy by contorting the molecule Butane in a certain way and this approximation was done by approximating these values using the equilibrium values. Therefore, the criteria was met and I found all of the values to be able to compute each energy to add up to have the overall Potential Energy under the CHARMM Force Field.

Summary

An overall summary of my findings was that the Steepest Descent method had a more realistic approach and approximation to the Energy that I was looking for versus Newton-Raphson which didn't approximate one hundred percent correctly. One thing that I should also be aware of for future reference is to be able to find constants for the Bonds that are more universal when it comes to units to be able to keep them in SI units. It might've also been helpful to have used a Z-matrix which puts all of the Bond Lengths, Angles, and Torsion into a matrix and then I would've had the capacity of converting them into a Cartesian Coordinate Z-matrix but if anything, that would've been better if I had been using the Quasi-Newton Method.