CH504 - Computational Chemistry
Lab Assignment 1

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Question: 1

Aim:

To investigate the formation of HeH^+ by the variation of the potential energy with change in the inter-nuclear distance between H atom and He^+. Also find the optimized configuration of the given molecule.

Principle:

The Potential Energy Surface (PES) is the relation - mathematical or graphical - between the energy of the molecule (or a collection of molecule) and its geometry. The energy of a molecule depends on the atomic configuration of its constituents. Furthermore, this energy is minimum at an optimum configuration. We use geometric optimization in order to find the optimum configuration.

For a stable configuration of molecule, we find the bond length (or configuration of atoms) which has minimal energy on the PES, i.e. the point at which,

$$\frac{\partial E}{\partial q} = 0 \;, \frac{\partial^2 E}{\partial q^2} > 0$$

Files: assignment1.log
Folder details: Main Folder/ch504_42/assignment1/assignment1.log

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Observation:

HeH^+		
S.No.	Internuclear Distance (A^0)	Energy (E) in Hartee
1	0.5	-2.6316651
2	0.6	-2.7603053
3	0.7	-2.8206168
4	0.78	-2.8429209
5	1	-2.8529211
6	1.2	-2.8410973
7	1.4	-2.8284982
8	1.6	-2.8193691
9	1.8	-2.8137822

Relevant sections from output file:

HeH+

1. Energy show below is for the optimum bond length which is $0.9294 A°s$

```
1\1\GINC-ACADS\FOpt\RHF\STO-3G\H1He1(1+)\CH504_42\23-Jan-2023\0\\# HF/
STO-3G opt\\HeH+\\1,1\H,0.,0.,-0.0749818507\He,0.,0.,0.8549818507\\Ver
sion=EM64L-G09RevA.02\State=1-SG\HF=-2.8543686\RMSD=1.365e-12\RMSF=1.0
12e-04\Dipole=0.,0.,-0.8246361\Quadrupole=-0.4505091,-0.4505091,0.9010
182,0.,0.,0.\PG=C*V [C*(H1He1)]\\@
```

2. Energy show below is for bond length $= 0.78 A°s$

```
1\1\GINC-ACADS\FOpt\RHF\STO-3G\H1He1(1+)\CH504_42\23-Jan-2023\0\\# HF/
STO-3G opt\\HeH+\\1,1\H,0.,0.,-0.0749818507\He,0.,0.,0.8549818507\\Ver
sion=EM64L-G09RevA.02\State=1-SG\HF=-2.8543686\RMSD=1.365e-12\RMSF=1.0
12e-04\Dipole=0.,0.,-0.8246361\Quadrupole=-0.4505091,-0.4505091,0.9010
182,0.,0.,0.\PG=C*V [C*(H1He1)]\\@
```

3. Energy show below is for bond length $= 1.0 A°s$

```
1\1\GINC-ACADS\FOpt\RHF\STO-3G\H1He1(1+)\CH504_42\23-Jan-2023\0\\# HF/
STO-3G opt\\HeH+\\1,1\H,0.,0.,-0.0749818507\He,0.,0.,0.8549818507\\Ver
sion=EM64L-G09RevA.02\State=1-SG\HF=-2.8543686\RMSD=1.365e-12\RMSF=1.0
12e-04\Dipole=0.,0.,-0.8246361\Quadrupole=-0.4505091,-0.4505091,0.9010
182,0.,0.,0.\PG=C*V [C*(H1He1)]\\@
```

Results/Conclusions:
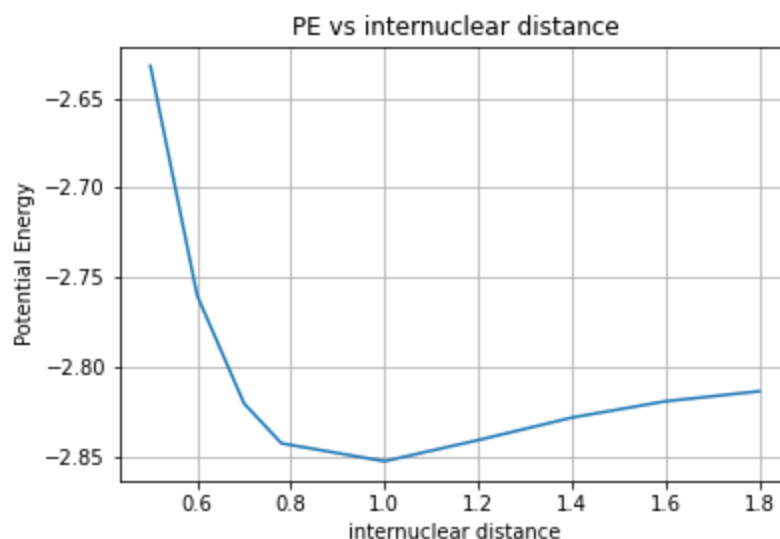
As you can observe from the above Potential Energy vs internuclear distance plot that as the distance between the two nucleus decreases the potential energy decreases upto a minima,, suggesting the bond length of HeH^+ molecule.

The bond length after using the geometric optimization turns out to be **0.9294 A^0**

Literature Comparison:

Theoretical bond length of HeH+ as per this research paper is $0.947 A^0$ which is close to the observed value with an error of 1.9%.

Extension of above concept to a new problem or situation:

The concept of geometric optimization can be used to find the most stable configuration of exotic molecules and also be used to find the cartesian coordinates of the constituents of these molecules under minimal energy state.

Furthermore, study of such exotic molecules suggest the presence of a natural environment where the molecule's chemistry can be directly observed

Question: 2

Aim:

To investigate the energy profile diagram of ethane and ethane 1,2-diol by findding the single point energy of different conformers of the aforementioned molecules.

Principle:

Consider the four atoms bonded : A-B-C-D sequentially. The **dihedral** angle or **torsional** angle is the angle between the A-B bond and the C-D bond when viewed along the B-C bond.

In conformational analysis (energetics study of different rotational conformers or rotamers), structures are represented by **Newman projection** (atoms and bonds are viewed along the axis of rotation).

staggered
$\theta = 60°$

eclipsed
$\theta = 0°$
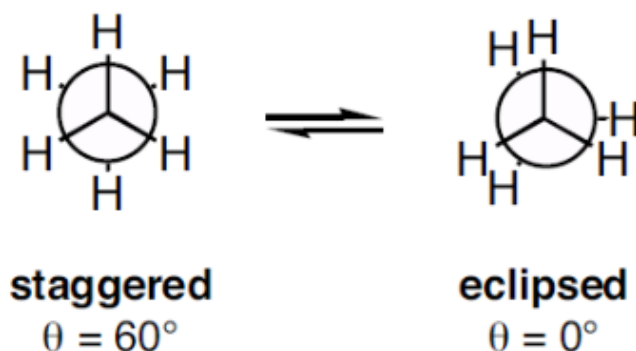
If we consider **ethane** as a reference molecule for our conformational analysis and check their Newman projection we can easily see the two extremes. The staggered conformation with the dihedral angle of 60° , where the H atoms on the 1st carbon are at maximum separation from H atoms on the 2nd carbon. In contrast stands the eclipsed conformation where the H atoms line up perfectly!

However, this perfectly lined up orientation is energetically **unfavourable** as the **negative charged electrons** in the bond repel each other strongly. This is why staggered conformation is more stable.

Hydrogen bonding is a special type of dipole-dipole attraction between molecules, not a covalent bond to a hydrogen atom. It results from the attractive force between a hydrogen atom covalently bonded to a very electronegative atom such as a **N, O, or F** atom and another very electronegative atom.

Therefore, in the case of **ethane 1,2-diol**, gauche conformers are more stable because of intramolecular H-bonding between H atom and oxygen atom of the other -OH group.

Files: ethaneθ.log, etdiolθ.log where $\theta \in \{0°, 30°, 60°, ..., 330°\}$

Folder details: ethane Main Folder/ch504_42/assignment1/q2/ethane/ to find all the log files related to ethane for its different conformers

while for **ethane 1,2-diol** Main Folder/ch504_42/assignment1/q2/ethane_diol/ to find all the log files related to ethane 1,2-diol conformers.

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Observation

For ethane:

Ethane		
S.No.	Angle of conformation	Energy (E) in Hartee
1	0	-78.2968512
2	30	-78.2998833
3	60	-78.3028682
4	90	-78.2998833
5	120	-78.2968512
6	150	-78.2998833
7	180	-78.3028682
8	210	-78.2998833
9	240	-78.2968512
10	270	-78.2998833
11	300	-78.3028682
12	330	-78.2998833

For Ethane 1,2-diol:

Ethane 1,2-diol		
S.No.	Angle of conformation	Energy (E) in Hartee
1	0	-225.9329533
2	30	-225.9385247
3	60	-225.942444
4	90	-225.9391499
5	120	-225.9353582
6	150	-225.9368473
7	180	-225.9390682
8	210	-225.9366777
9	240	-225.9353582
10	270	-225.936004
11	300	-225.9424045
12	330	-225.9346141

Relevant sections from output file:

Ethane

1. $\theta = \mathbf{0°}$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6\CH504_42\22-Jan-2023\0\\# HF/STO-3G
sp\\ethane\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\H,0,1.008807,0.,-0.356663\
H,0,-0.504403,-0.873651,-0.356667\C,0,-0.707105,1.224745,-0.500003\H,0
,-0.034565,1.807179,-1.094445\H,0,-1.547774,0.933528,-1.09445\H,0,-1.0
43377,1.807179,0.332218\\Version=EM64L-G09RevA.02\State=1-A\HF=-78.296
8512\RMSD=7.922e-09\Dipole=0.,0.,0.0000001\Quadrupole=0.0654368,-0.196
3032,0.1308665,0.2266708,-0.0925359,0.16028\PG=C01 [X(C2H6)]]\\@
```

2. $\theta = \mathbf{60°}$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6\CH504_42\22-Jan-2023\0\\# HF/STO-3G
sp\\ethane\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\H,0,1.008807,0.,-0.356663\
H,0,-0.504403,-0.873651,-0.356667\C,0,-0.707105,1.224745,-0.500003\H,0
,-0.707101,1.224745,-1.570003\H,0,-1.715912,1.224745,-0.14334\H,0,-0.2
02703,2.098396,-0.143334\\Version=EM64L-G09RevA.02\State=1-A\HF=-78.30
28682\RMSD=5.766e-09\Dipole=0.0000002,0.,0.\Quadrupole=0.0582719,-0.17
4811,0.1165391,0.2018536,-0.0824032,0.1427314\PG=C01 [X(C2H6)]]\\@
```

3. $\theta = \mathbf{120°}$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6\CH504_42\22-Jan-2023\0\\# HF/STO-3G
sp\\ethane120\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\H,0,1.008807,0.,-0.3566
63\H,0,-0.504403,-0.873651,-0.356667\C,0,-0.707105,1.224745,-0.500003\
H,0,-1.547774,0.933528,-1.09445\H,0,-1.043377,1.807179,0.332218\H,0,-0
.034565,1.807179,-1.094445\\Version=EM64L-G09RevA.02\State=1-A\HF=-78.
2968512\RMSD=7.922e-09\Dipole=0.,0.,0.0000001\Quadrupole=0.0654368,-0.
1963032,0.1308665,0.2266708,-0.0925359,0.16028\PG=C01 [X(C2H6)]]\\@
```

4. $\theta = \mathbf{180°}$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6\CH504_42\22-Jan-2023\0\\# HF/STO-3G
sp\\ethane180\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\H,0,1.008807,0.,-0.3566
63\H,0,-0.504403,-0.873651,-0.356667\C,0,-0.707105,1.224745,-0.500003\
H,0,-1.715912,1.224745,-0.14334\H,0,-0.202703,2.098396,-0.143334\H,0,-
0.707101,1.224745,-1.570003\\Version=EM64L-G09RevA.02\State=1-A\HF=-78
.3028682\RMSD=5.766e-09\Dipole=0.0000002,0.,0.\Quadrupole=0.0582719,-0
.174811,0.1165391,0.2018536,-0.0824032,0.1427314\PG=C01 [X(C2H6)]]\\@
```

Ethane 1,2-diol

1. $\theta = \mathbf{0°}$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6O2\CH504_42\23-Jan-2023\0\\# HF/STO-3
G sp\\ethanediol0\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\0,0,1.301078,0.,-0.
459995\C,0,-0.707105,1.224745,-0.500003\H,0,-0.504401,-0.873651,-0.356
669\0,0,0.160282,1.975922,-1.266666\H,0,-1.547774,0.933528,-1.09445\H,
0,-1.043377,1.807179,0.332218\H,0,1.301082,0.,-1.406995\H,0,-0.286136,
2.749144,-1.582334\\Version=EM64L-G09RevA.02\State=1-A\HF=-225.9329533
\RMSD=7.978e-09\Dipole=-0.9446859,0.1787458,-0.3075334\Quadrupole=-1.6
729845,0.986592,0.6863925,-0.6100477,-0.6043224,0.1484662\PG=C01 [X(C2
H6O2)]]\\@
```

2. $\theta = 60°$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6O2\CH5O4_42\23-Jan-2023\0\\# HF/STO-3
G sp\\ethanediol60\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\0,0,1.301078,0.,-0
.459995\C,0,-0.707105,1.224745,-0.500003\H,0,-0.504401,-0.873651,-0.35
6669\0,0,-0.7071,1.224745,-1.880003\H,0,-1.715912,1.224745,-0.14334\H,
0,-0.202703,2.098396,-0.143334\H,0,1.301082,0.,-1.406995\H,0,-1.153518
,1.997967,-2.195671\\Version=EM64L-G09RevA.02\State=1-A\HF=-225.942444
\RMSD=5.787e-09\Dipole=-0.6817766,0.4298611,-0.0904104\Quadrupole=-1.2
756926,1.2296744,0.0460182,-0.5864661,-1.1474794,-0.4435025\PG=C01 [X(
C2H6O2)]\\@
```

3. $\theta = 120°$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6O2\CH5O4_42\23-Jan-2023\0\\# HF/STO-3
G sp\\ethanediol120\\0,1\Bq\C,0,0.,0.,0.\H,0,0.,0.,1.07\0,0,1.301078,0
.,-0.459995\C,0,-0.707105,1.224745,-0.500003\H,0,-0.504401,-0.873651,-
0.356669\0,0,-1.791332,0.849156,-1.266674\H,0,-1.043377,1.807179,0.332
218\H,0,-0.034565,1.807179,-1.094445\H,0,1.301082,0.,-1.406995\H,0,-2.
237751,1.622379,-1.582342\\Version=EM64L-G09RevA.02\HF=-225.9353582\RM
SD=4.685e-09\Dipole=-0.3307218,0.5370135,-0.2786297\Quadrupole=-2.6912
624,1.5882435,1.1030189,-1.9002801,-0.9990107,-1.3172391\PG=C01 [X(C2H
6O2)]\\@
```

4. $\theta = 180°$

```
1\1\GINC-ACADS\SP\RHF\STO-3G\C2H6O2\CH5O4_42\23-Jan-2023\0\\# HF/STO-3
G sp\\ethanediol180\\0,1\C,0,0.,0.,0.\H,0,0.,0.,1.07\0,0,1.301078,0.,-
0.459995\C,0,-0.707105,1.224745,-0.500003\H,0,-0.504401,-0.873651,-0.3
56669\0,0,-2.008183,1.224745,-0.040008\H,0,-0.202703,2.098396,-0.14333
4\H,0,-0.707101,1.224745,-1.570003\H,0,1.301082,0.,-1.406995\H,0,-2.45
4602,1.997967,-0.355676\\Version=EM64L-G09RevA.02\State=1-A\HF=-225.93
90682\RMSD=4.745e-09\Dipole=-0.2519995,0.4248722,-0.6746008\Quadrupole
=-2.8066945,1.496227,1.3104675,-0.9673497,-0.2031367,0.1201944\PG=C01
[X(C2H6O2)]\\@
```

Results/Conclusions:

Energy Profile diagram (Ethane 1,2-diol)
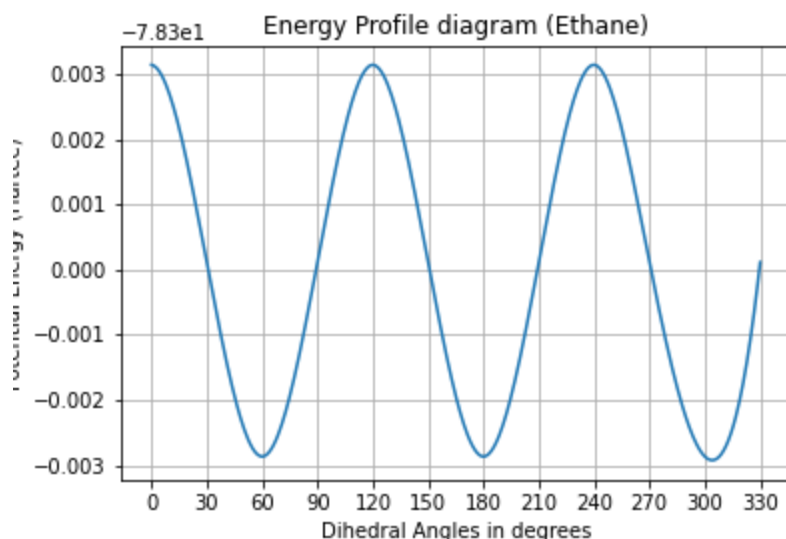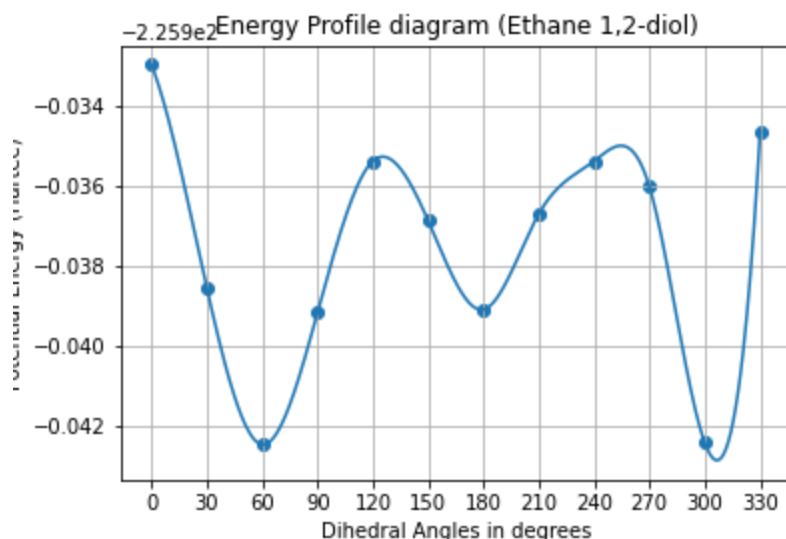
1. Most stable form of ethane is staggered conformer due to less steric hinderance as discussed previously.
2. But as you can see in the second figure, staggered conformer is not the most stable one. Instead **gauche** form with $\theta = 60°$ and $\theta = 300°$ is more stable because of intramolecular Hydrogen bonding.

Note: It is also worth mentioning that energy of the molecule also depends on the orientation of Hydrogen on oxygen atom (i.e. dihedral angle of H-O-C-C for $\theta = 300° or 60°$).

Literature Comparison:

1. As per this article, difference in energy of the most stable (staggered) and the least stable (eclipsed) is 3kcal/mol. While through simulations, we obtained the difference in energy to be $|-78.3028682 - (-78.2968512)|*627.5$ kcal/mol $= 3.775$ kcal/mol, which is close. Also, as suggested in the article and also discussed in the theory before staggered conformer is the most stable one.

2. One can find the values of total energy of the ethylene glycol (ethane 1,2-diol) in this paper. Look at the energies of g'Gt and tTt conformer where G and T represent the Gauche and Trans form along the C-C bond respectively. While g' and t represent the gauche and trans form of H-O-C-C bond respectively.

For the calculations, we dealt with g'Gt (or gGt) for the most stable conformer. The difference in energy of these two conformers is $\Delta E = |-228.955591 + 228.952761| = 0.0028$ hartee. While the value I obtained was $\Delta E = |-225.942444 + 225.9390682| = 0.0033$ hartee, which is very close.

Extension of above concept to a new problem or situation:

We know that Conformers of same molecule even though having same formula, might exhibit different chemical or physical properties. The conformational analysis can be used to predict the product selectivity, mechanisms and rate of reactions. It can be also play an important role in the rational, structure-based drug design.