Computational Chemistry and Quantum Tunneling

Key Words

  quantum chemistry, Hartree-Fock theory, density functional theory, variational principle, quantum tunneling, transition state

Object

   It is expected that students can predict the chemical trends of the inversion of amines and phosphines through calculations, and understand the theoretical backgrounds of computational chemistry and the concept of quantum tunneling.

Introduction

   Electron structure theory such as Hartree-Fock and density functional theory (DFT) have made it possible to calculate a variety of properties of molecules. They are also very useful to search the reaction pathway for a given chemical reaction which consists of the free energies of reactants, transition states, and products. Thanks to the rapid development of computer and software for computational chemistry, nowadays people in not only theoretical but also experimental chemistry laboratories use computational chemistry to investigate various molecular properties encompassing geometric structures, spectroscopic information, reaction pathways, etc, and compare them with experimental observations. One of the great advantages of accurate computational chemistry is that it would be capable of predicting molecular properties without experiments, leading to the acceleration of chemical research with inexpensive, rapid manner.

   In this experiment, reaction profiles of pyramidal inversion which involves quantum tunneling of a particle trapped in a finite potential are investigated using a modern approach of computational chemistry.

Background Information

Theory

<u>1. Hartree-Fock(HF) approximation[1,2]</u>

(McQuarrie Physical Chemistry textbook chapter 9)

The total Hamiltonian of a molecule can be written as

$$H = T_n + T_e + V_{ne} + V_{ee} + V_{nn} \qquad (1)$$

If we apply the Born-Oppenheimer approximation, the nuclear kinetic energy part T_n can be ignored. The next three terms are electronic Hamiltonian, where T_e is the kinetic energy of electrons, V_{ne} is the attraction term between nuclei and electrons, and V_{ee} is electron-electron repulsion term, respectively. V_{nn} is the nucleus-nucleus repulsion term. Then Eq. (1) can be

written as

$$H = T_e + V_{ne} + V_{ee} + V_{nn}$$

$$= -\sum_i \frac{1}{2}\nabla_i^2 - \sum_A\sum_i \frac{Z_A}{r_{iA}} + \sum_{ij}\frac{1}{r_{ij}} + \sum_{AB}\frac{Z_A Z_B}{R_{AB}} \qquad (2)$$

where the indices i, j indicate the electrons and A for nuclei, respectively. Z_A is the charge of the nucleus A.

The energy of the molecule can be evaluated,

$$E = <\Phi | H | \Phi> \qquad (3)$$

The Hartree-Fock approximation introduces a Slater determinant for wavefunction which is antisymmetric:

$$\Phi = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_1(\mathbf{x}_2) & \cdots & \chi_1(\mathbf{x}_N) \\ \chi_2(\mathbf{x}_1) & \chi_2(\mathbf{x}_2) & \cdots & \chi_2(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_N(\mathbf{x}_1) & \chi_N(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \qquad (4)$$

where $\chi_i(\mathbf{x}_j) = \phi_i(\mathbf{r}_j)\alpha_i(w_j)$ are one-electron spin orbitals and $\mathbf{x}_j = (\mathbf{r}_j, w_j)$ indicates the spatial and spin coordinates. The spin coordinate can be either α or β for up or down spin, respectively. The electronic Hamiltonian can be rewritten as the sum of one-electron part $\hat{h}_i$, i.e. core Hamiltonian and two-electron repulsion part r_{ij}^{-1},

$$H_{elec} = T_e + V_{ne} + V_{ee} = \sum_{i=1}^N \hat{h}_i + \sum_{i=1}^N\sum_{j>i}^N r_{ij}^{-1} \qquad (5)$$

where $\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \frac{Z_A}{r_{iA}}$, which consists of electron kinetic energy and electron-nucleus attraction operator.

The one-electron contribution of total energy is

$$E^{(1)} = \sum_\sigma\sum_{i=1}^N \int d\mathbf{x}_1\, \chi_i^*(\mathbf{x}_1)\hat{h}_i(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \sum_\sigma\sum_{i=1}^N h_{ii} = \sum_{i=1}^N [i\,|\,\hat{h}_i\,|\,i] \qquad (6)$$

where σ indicates the spin index and N is the number of electrons. Two-electron contribution is more complicated. It consists of Coulomb and exchange integrals J_{ij} and K_{ij}:

$$J_{ij} = \int d\mathbf{x}_1 d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\, r_{12}^{-1}\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2) = [ii\,|\,jj]$$

$$K_{ij} = \int d\mathbf{x}_1 d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\, r_{12}^{-1}\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2) = [ij\,|\,ji] \qquad (7)$$

Then the energy becomes

$$E^{(2)} = \frac{1}{2}\sum_{\sigma_i,\sigma_j}\sum_{i=1}^N\sum_{j=1}^N J_{ij} - \frac{1}{2}\sum_\sigma\sum_{i=1}^N\sum_{j=1}^N K_{ij} \qquad (8)$$

The Coulomb integral is the classical repulsive energy between two charges and the exchange integral is a stabilization energy arisen from the antisymmetric property of the wavefunction.

The exchange integral acts only between the electrons of the same spin due to the Pauli exclusion principle. Finally, the Hartree-Fock energy is

$$E_{HF} = \sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{\sigma_i,\sigma_j} \sum_{i=1}^{N} \sum_{j=1}^{N} J_{ij} - \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N} \sum_{j=1}^{N} K_{ij} \qquad (9)$$

Now the energy is minimized under orthonormality condition of spin orbitals. Using Lagrange multiplier method,

$$\delta\{E_{HF} - \sum_{i=1}^{N} \sum_{j=1}^{N} \varepsilon_{ij}(\langle i|j \rangle - \delta_{ij})\} = 0 \qquad (10)$$

where

$$\langle i|j \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(x_1)\chi_j(x_2) \qquad (11)$$

The Hartree-Fock equation as an one-electron Schrodinger-like equation can be derived by solving Eq. (10). That is,

$$[\hat{h}_1(\mathbf{r}_1) + \sum_{j \neq i}^{N}(\hat{J}_j - \hat{K}_j)]\phi_i(\mathbf{r}_1) = \sum_{j=1}^{N} \varepsilon_{ij}\phi_j(\mathbf{r}_1) \qquad (12)$$

where $\hat{J}_j, \hat{K}_j$ are the Coulomb and exchange operator.

$$\hat{J}_j\phi_i(\mathbf{r}_1) = \left\{ \int d^3\mathbf{r}_2 \phi_j^*(\mathbf{r}_2) \ r_{12}^{-1}\phi_j(\mathbf{r}_2) \right\}\phi_i(\mathbf{r}_1)$$

$$\hat{K}_j\phi_i(\mathbf{r}_1) = \left\{ \int d^3\mathbf{r}_2 \phi_j^*(\mathbf{r}_2) \ r_{12}^{-1}\phi_i(\mathbf{r}_2) \right\}\phi_j(\mathbf{r}_1) \qquad (13)$$

The parenthesis on the left-hand side of eq. (12) is called the *Fock operator*, $\hat{F}$.

2. Density functional theory (DFT)[2,3]

For the N electron system, the wave function has 3N spatial coordinates. However, regardless of the number of electrons, the electron density has only 3 spatial coordinates. Therefore the electron density rather than the wavefunction is more efficient to describe the electronic structure of molecules. DFT states that the ground energy of a system can be determined solely from the electron density by virtue of the Hohenberg-Kohn theorem:

Theorem 1 : There is one-to-one relationship between the ground state electron density ρ and the external potential v_{ext}.

Theorem 2 : For a trial density $\tilde{\rho}(\mathbf{r})$, such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int d^3r \tilde{\rho}(\mathbf{r}) = N$,

$$E_0 \leq E_v[\tilde{\rho}]. \qquad (14)$$

where $E_v[\tilde{\rho}]$ is the variational energy functional.

$$E_v[\rho] = T[\rho] + U_{ee}[\rho] + \int d^3r \rho(\mathbf{r})v_{ext}(\mathbf{r}) = F[\rho] + \int d^3r \rho(\mathbf{r})v_{ext}(\mathbf{r}) \qquad (15)$$

$T[\rho]$ is the kinetic energy functional and $U_{ee}[\rho]$ is the electron-electron repulsion energy functional.

If the functional form of $F[\rho]$, which is universal regardless of systems represented by v_{ext}, is known, in principle, one can exactly calculate the energy of the molecule, since the external potential is readily known. Unfortunately, however, the exact functional form is unknown. Kohn and Sham proposed that a non-interacting system, which produces the same electron density with that of the interacting system, gives the same energy, as the first Hohenberg-Kohn theorem tells. The kinetic energy and the electron density of the non-interacting system can be expressed in terms of one-electron orbitals like Hartree-Fock approximation (Eq. (4)),

$$T_s = -\frac{\hbar^2}{2m}\sum_{i=1}^{N} f_i < \phi_i(\mathbf{r}) | \nabla^2 | \phi_i(\mathbf{r}) > \qquad (16)$$

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} f_i \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}) \qquad (17)$$

where f_i is the occupation number. Using non-interacting kinetic energy, the universal functional $F[\rho]$ can be rewritten as

$$F[\rho] = T[\rho] + U_{ee}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \qquad (18)$$

where $J[\rho]$ is the Coulomb term,

$$J[\rho] = \frac{1}{2}\int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \qquad (19)$$

and $E_{xc}[\rho]$ is the exchange-correlation energy which includes the kinetic correlation(i.e. $T[\rho]-T_s[\rho]$). Finally, the Kohn-Sham functional becomes

$$E_{KS}[\rho] = T_s[\rho] + \int d^3r \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + \frac{1}{2}\int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho] \qquad (20)$$

Like we have done in the Hartree-Fock approximation, Eq. (10), this energy is minimized using the Lagrange multiplier method. Then we can obtain the one-electron Schrodinger-like Kohn-Sham equation which is

$$\left(-\frac{1}{2}\nabla^2 + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})\right)\phi_m(\mathbf{r}) = \varepsilon_m \phi_m(\mathbf{r}) \qquad (21)$$

where $v_{xc}(\mathbf{r})$ is the exchange-correlation potential,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \qquad (22)$$

There are many known density functionals which have different functional forms of $E_{xc}[\rho]$. Though both DFT and HF have similar features, in particular, one-electron representation of many body systems, DFT is mostly better than HF because DFT does have electron correlation term, whereas HF completely ignores it.

3. Electron density and correlation[2,3]
The one-body density matrix is

$$\rho_1(\mathbf{r},\mathbf{r}') = N\int d\mathbf{r}_2 \cdots d\mathbf{r}_N \psi^*(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)\psi(\mathbf{r}',\mathbf{r}_2,\cdots,\mathbf{r}_N) \qquad (23)$$

The diagonal elements of matrix is the electron density,

$$\rho_1(\mathbf{r},\mathbf{r}) = \rho(\mathbf{r}) = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \mid \psi(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N) \mid^2 \tag{24}$$

The total number of electron is,

$$N = \int d\mathbf{r}\rho(\mathbf{r}) \tag{25}$$

The two-body density matrix can also be defined,

$$\rho_2(\mathbf{r}_1\mathbf{r}_2,\mathbf{r}_1'\mathbf{r}_2') = \frac{N(N-1)}{2} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\psi(\mathbf{r}_1',\mathbf{r}_2',\cdots,\mathbf{r}_N) \tag{26}$$

and the diagonal elements are

$$\rho_2(\mathbf{r}\mathbf{r},\mathbf{r}'\mathbf{r}') = \rho_2(\mathbf{r},\mathbf{r}') = \frac{N(N-1)}{2} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \mid \psi(\mathbf{r},\mathbf{r}',\cdots,\mathbf{r}_N) \mid^2 \tag{27}$$

$\rho_2(\mathbf{r},\mathbf{r}')$ is the probability of finding electrons at $\mathbf{r}$ and $\mathbf{r}'$.

Now the concept of correlation is understood by using these definitions of electron density and density matrix. If there is no interaction between electrons (uncorrelated), the elements of two-body density matrix are simply the product of electron densities,

$$\rho_2(\mathbf{r},\mathbf{r}') = \frac{1}{2}\rho(\mathbf{r})\rho(\mathbf{r}') \tag{28}$$

If there exists correlation,

$$\rho_2(\mathbf{r},\mathbf{r}') = \frac{1}{2}\rho(\mathbf{r})\rho(\mathbf{r}')[1 + g(\mathbf{r},\mathbf{r}')] \tag{29}$$

where $g(\mathbf{r},\mathbf{r}')$ is the pair correlation function. It is zero if two electrons are separated at an infinite distance and different from zero when $\mathbf{r}$ is close to $\mathbf{r}'$.

Hartree-Fock contains no correlation effects, whereas in case of DFT, the correlation term can be included in the functional $E_{xc}[\rho]$.

4. Self-interaction[2]
Recall the Coulomb term in DFT, Eq. (19),

$$J[\rho] = \frac{1}{2}\int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid}. \tag{30}$$

Applying this term to one-electron system whose wave function is $\phi(\mathbf{r})$,

$$J[\mid \phi(\mathbf{r}) \mid^2] \neq 0. \tag{31}$$

Thus there exists the repulsion energy with itself, i.e. the self-interaction energy.
If one can find the exact form of $E_{xc}[\rho]$, the self-interaction energy can be completely cancelled. However, so far, it is not possible. When it comes to Hartree-Fock, there is no self-interaction, because there exists the cancellation of the self-interaction energy, $J_{ii} = K_{ii}$.

5. Basis sets[1]

(McQuarrie Physical Chemistry textbook chapter 11)

A basis set is a set of functions used to construct trial molecular orbitals according to the variational principle, which are expanded as a linear combination of certain primitive functions such as Gaussian functions.

$$\psi_i = \sum_{\mu=1}^{K} c_{\mu i} \phi_\mu \qquad (33)$$

Gaussian type basis sets rather than Slater type are often used in computations for the sake of convenience. For instance, 'X-YZG*' indicates that core orbitals are formulated by X Gaussians and valence orbitals are formulated by two atomic basis functions, one consists of Y Gaussian primitives and the other, Z primitives, respectively. '*' at the end means that polarization functions has been added. For example, 6-31G* basis sets for a carbon atom:

- Core : 1s orbital : 1-zeta function represented by 6 Gaussian functions
- Valence : 2s and 2p orbitals : 2-zeta functions represented by 3 and 1 Gaussian functions, respectively.
- Polarization : 3d orbitals have been added.

6. Quantum tunneling[5]

Let us consider an one-dimensional system whose potential is given as

$$V(x) = \begin{cases} 0 & if \ x \le -L \ \ or \ \ L \le x \\ V_1 & if \quad -L < x < L \end{cases} \qquad (34)$$

It has barrier at $-L < x < L$ whose height is $V_1 (> 0)$. Classically, if particle's total energy is less than V_1, it cannot pass through the barrier. However, a quantum particle has a probability to pass through the barrier. This phenomenon is called the quantum tunneling.
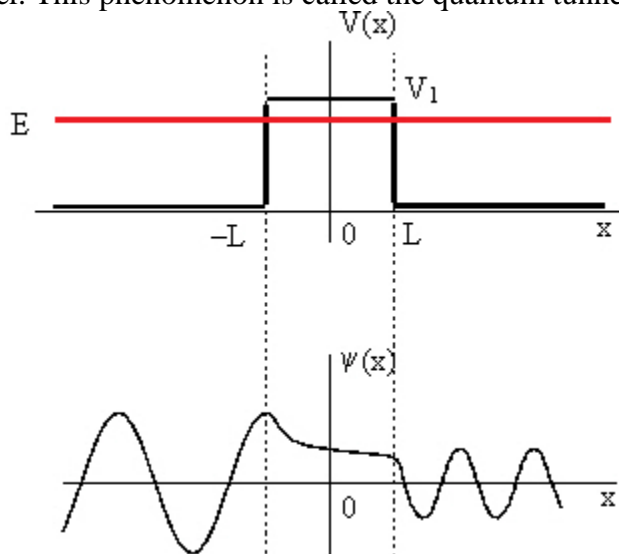
Figure 1. Quantum tunneling.

Inversion of amines or phosphines is a good example of quantum tunneling in nature. Further examples of quantum tunneling in various chemical reactions are also reported.[9]

Equipment
No special equipment for this experiment.

Pre-Laboratory Questions

1. What are pros and cons of DFT in terms of self-interaction and electron correlation compared to the HF method?
2. If we use 3-21G* basis set for calculation of the ammonia (NH_3) molecule, how many basis functions are used for calculations?
3. Explain the quantum tunneling phenomenon in terms of the Heisenberg uncertainty principle.
4. How is the inversion of amines and phosphines related to the quantum tunneling?

Materials

Reagents

No reagents.

Apparatus

Laptop provided, and the Avogadro program (It is free and you can download it easily from websites. You may practice this program before lab.[7])

Safety and Hazards

No hazards.

Experimental Procedure

Making input files of pyramidal amines and phosphines

1. Draw a molecule using Avogadro program.
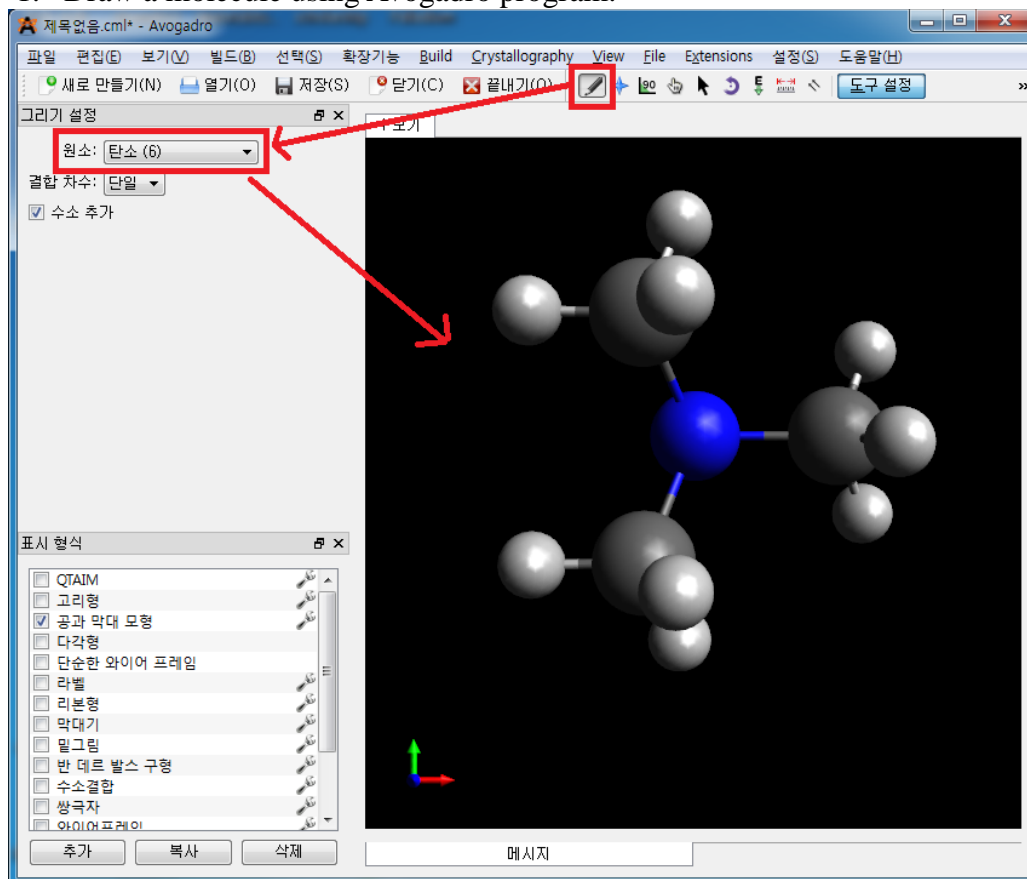
Figure 2.   Building a molecular structure.

- Click the 'pen' icon and the **Draw Settings** will appear. Choose 'Nitrogen (7)' for the element and left-click on the black viewing window (For drawing phosphine molecules, choose 'Phosphorus (15)'). The ammonia molecule will appear. Molecules can be drawn by attaching functional groups to three hydrogen atoms.

- For example, if you want to attach methyl to the hydrogen, choose 'Carbon (6)' at the element section and left-click on the hydrogen atom you want to attach.

- For the case of molecules containing benzene rings, it is more convenient to draw benzene ring first and attach groups to the terminal hydrogen of the benzene.

- The geometry of benzene is already stored. You can use it by clicking '**Build→Insert→Fragment..**'. Type '**benzene**' on the filter input box and then '**benzene.cml**' will appear. Double click it and the benzene molecule will appear on the viewing window.
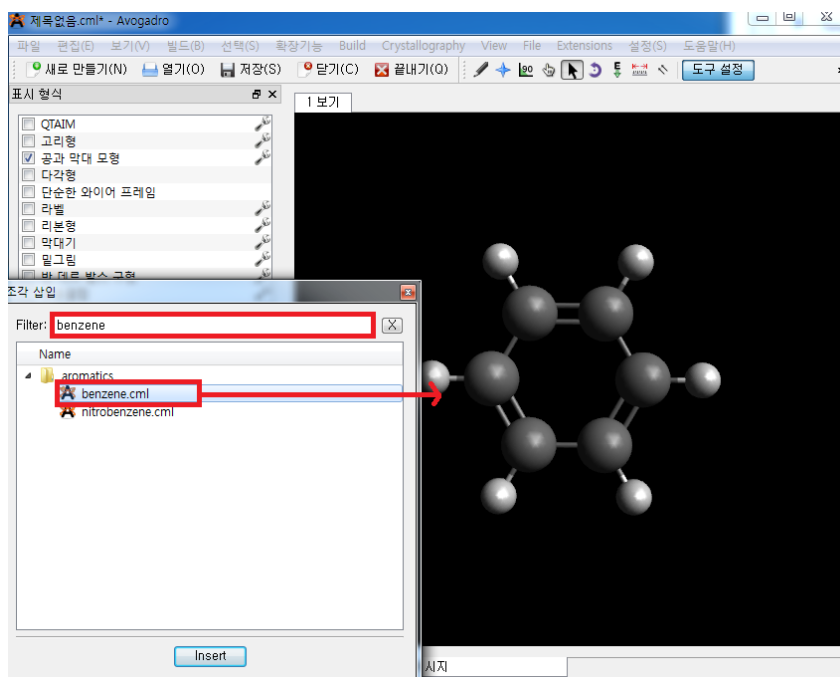
Figure 3.   Drawing the benzene molecule using saved fragments in the Avogadro program.

- If you finish drawing the molecule, press '**Ctrl**+**Alt**+**O**' to clean the geometry of the molecule. The geometry will be optimized in quantum level, but the cleaning of geometry in lower level is needed for more efficient calculation.

2. Generate the GAMESS input file using extensions of Avogadro program.
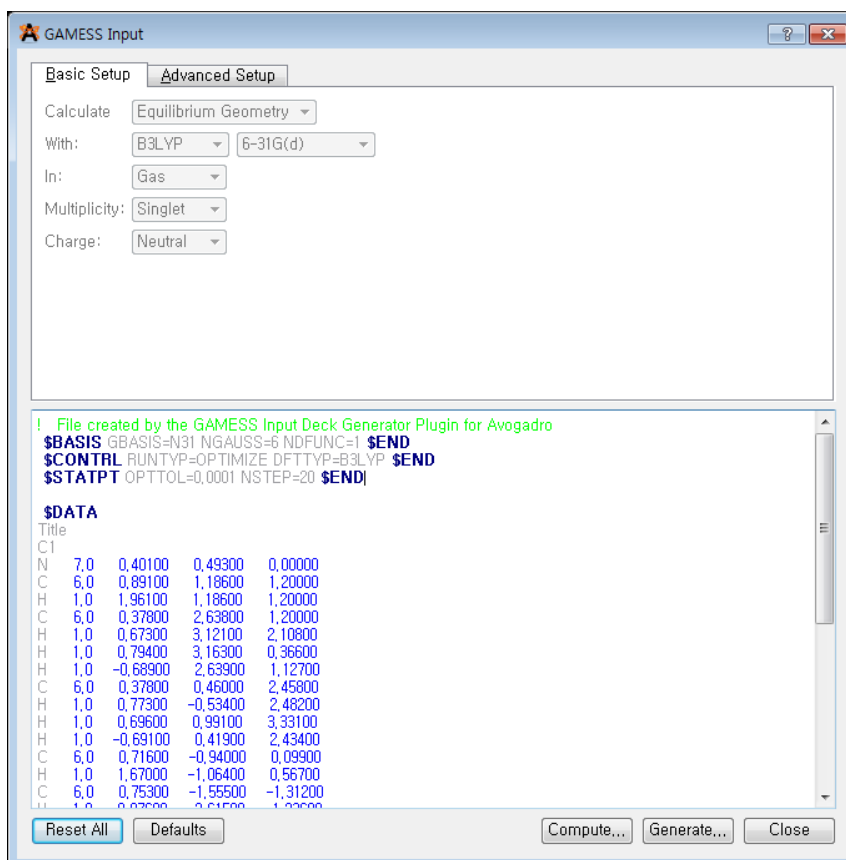   - Click **Extensions → GAMESS→Input Generator**.

Figure 4. The GAMESS input generator provided in Avogadro program.

- We are going to optimize the geometry using B3LYP density functional and 3-21g(d) basis set. Change the input lines as following:

$BASIS   GBASIS=N21   NGAUSS=3   NDFUNC=1 $END
$CONTRL   RUNTYP=OPTIMIZE   DFTTYP=B3LYP $END
$STATPT   OPTTOL=0.005   NSTEP=200 $END
$SYSTEM   MWORDS=10 $END

- DO NOT FORGET TO PUT SPACE ONCE IN FRONT OF '$' of EVERY INPUT LINE!
- If you open the new input file without closing the Avogadro program, the geometry of the previous input file remains without changing to the new geometry. Click **'Reset All'** to update the geometry.
- Do not change the $DATA block. It contains Cartesian coordinates of atoms.
- Click **'Generate'** and save the GAMESS input file (in *.inp format).

Making input files of trigonal planar transition states

1. To make the geometry of the transition state, the inverting atom and three bind atoms

should be placed at the same plane, i.e. they should form trigonal planar geometry.

- Click the 'pen' icon and the Draw Settings will appear. Choose **'Boron (5)'** for the element to make trigonal planar geometry and left-click on the viewing window to make BH_3 molecule.
- Draw remaining groups of the molecule and press 'Ctrl+Alt+O'.
- Now the boron center can be replaced with either nitrogen or phosphorous atom. Choose either 'Nitrogen (7)' or 'Phosphorus (15)' and left-click on the boron atom to replace it.
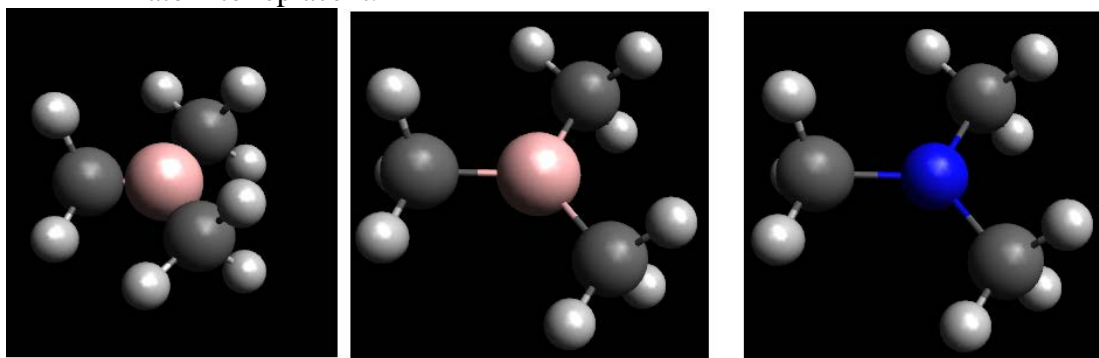
Figure 6. Drawing the geometry of the transition state. The molecule is drawn using boron center, next the geometry is cleaned, and finally replaced with the original inverting center.

2. Open the GAMESS input generator window.

- We are going to optimize the geometry in the same level of quantum theory at the previous section, with the dihedral angle FIXED, i.e. The inverting atom and three binded atoms move on same plane.
- Change the input lines as following:

$BASIS   GBASIS=N21   NGAUSS=3   NDFUNC=1 $END
$ZMAT   DLC=.T.   AUTO=.T. $END
$ZMAT   NONVDW(1)=☐, ☐, ☐, ☐ $END
$CONTRL   RUNTYP=OPTIMIZE   DFTTYP=B3LYP   NZVAR=☐ $END
$STATPT   OPTTOL=0.005   NSTEP=200 $END
$SYSTEM   MWORDS=10 $END

- The values put on the blanks should be changed according to the input molecules:
- With paying attention to the order of atoms, **NONVDW(1)** should include the indices of four atoms that form a dihedral angle that should be fixed during

geometry optimization. The indices of atoms can be seen through the Avogadro program. At the **Display Types** section, check on '**label**'. The indices of atoms will appear.
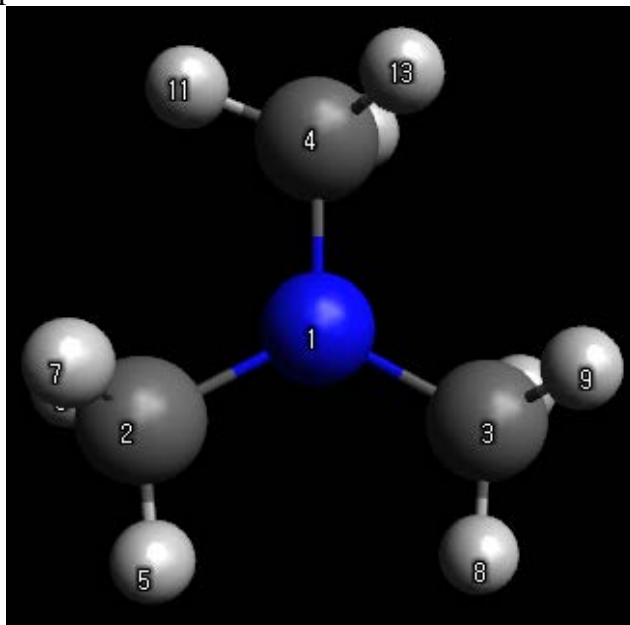

Figure 7. For this case the NONVDW(1) should be 4, 1, 2, 3.

- The value of **NZVAR** should be 3N-6, where N is the number of atoms in a molecule.

Calculation and analysis of the output file

    1. Put the GAMESS input file into the Edison chem site and call the GAMESS program. Wait until the calculation is terminated.

- Go to the Edison_chem website http://chem.edison.re.kr/ and login (ID and password will be announced by TA).
- Click '**Simulation'** and choose the software '**The General Atomic and Molecular Electronic Structure System (GAMESS)**'. Click **'Next step'**.

Figure 8. At the simulation section, find the GAMESS program and select it, and go on to the next step.

- Briefly write the name and description of the simulation at the **instance information** part, go to the **Input Port** part at the bottom.

Figure 9. Write the simulation name and description

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- Select Insert Data and insert input file made by Avogadro program

Workflow

Figure 9. Putting GAMESS input file into the EDISON system.

- Click **'Job submission status'** and the task will appear at the list. Click **'Submit job'**.

Workflow

Figure 10. Submit job to the GAMESS program.

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- Click **'Monitoring'** and check simulation status.
- There are four states : Purple color – queue, skyblue – running, green – success, and red – fail. Wait until the green button appears. If the error occurs, check the input file and fix errors.

Figure 11. The monitoring window. The running status can be checked.

- You can check running progress progress, download the ouput files and see visualizations such as electron density and molecular orbitals.
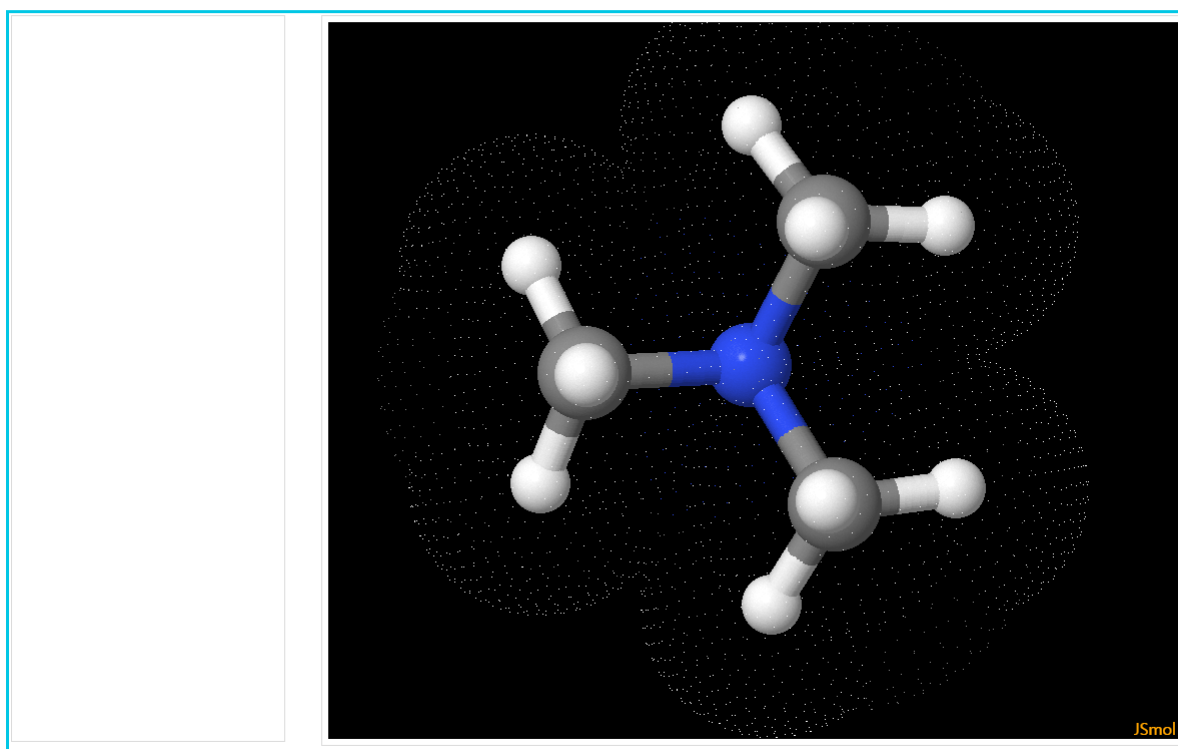
Figure 12. Visualization through Jmol program.

2. Open the log file using WordPad. Find the line containing '**TOTAL ENERGY = **'. It appears twice, and you should read the energy value of the last one. That is the calculated energy value of the optimized geometry in Hartree unit.

```
------------------
ENERGY COMPONENTS
------------------

WAVEFUNCTION NORMALIZATION =      1,0000000000

       ONE ELECTRON ENERGY =    -511,6995872013
       TWO ELECTRON ENERGY =     197,2429675868
   NUCLEAR REPULSION ENERGY =     141,0818248431
              ------------------
      TOTAL ENERGY =   -173,3747947714

ELECTRON-ELECTRON POTENTIAL ENERGY =     197,2429675868
 NUCLEUS-ELECTRON POTENTIAL ENERGY =    -684,0675607575
 NUCLEUS-NUCLEUS POTENTIAL ENERGY =     141,0818248431
              ------------------
      TOTAL POTENTIAL ENERGY =    -345,7427683276
        TOTAL KINETIC ENERGY =     172,3679735563
         VIRIAL RATIO (V/T) =      2,0058411153
```

3. Find the word **'EIGENVECTORS'** in your log file. At that section, energies of each orbital are written. Find HOMOs and write down the energy value if you need.

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Results and analysis

1. Repeat the above procedure for following six molecules : NMe_3, PMe_3, PEt_3, PMe_2F, PMe_2Ph, $PMe_2(SiH_3)$.

2. Using the information of the output files, fill in the blanks of the below tables:

Table 1. The effect of the nature of the inverting atom on the activation energy of inversion.

Compounds	$E_{pyramid}$(Hartree)	E_{planar}(Hartree)	E_a(kcal/mol)
NMe_3			
PMe_3			

Table 2. The effect of the substituent steric bulkiness on the activation energy of inversion.

Compounds	$E_{pyramid}$(Hartree)	E_{planar}(Hartree)	E_a(kcal/mol)
PMe_3			
PEt_3			

Table 3. The HOMO energy for pyramidal and planar amines and phosphines

Compounds	Pyramidal E_{HOMO}(Hartree)	Planar E_{HOMO}(Hartree)	ΔE_{HOMO} (kcal/mol)
NMe_3			
PMe_3			
PEt_3			

Table 4. The effect of the substituent electronegativity on the activation energy of inversion.

Compounds	$E_{pyramid}$(Hartree)	E_{planar}(Hartree)	E_a(kcal/mol)
PMe_3			
PMe_2F			

Table 5. The effect of conjugation on the activation energy of inversion.

Compounds	$E_{pyramid}$(Hartree)	E_{planar}(Hartree)	E_a(kcal/mol)
PMe_3			
PMe_2Ph			
$PMe_2(SiH_3)$			

Post-Laboratory Data Evaluation

1. Explain the results. Find trends of the activation energies and HOMO energy differences and explain why these trends appear.[8]

2. (A simple model of the ammonia molecule)[5]

(Cohen-Tannoudji Quantum Mechanics textbook, Complement G of Chapter 4)

For NH_3 inversion, the potential energy of the system can be represented only by one parameter, the distance x between the nitrogen atom and the plane defined by three hydrogen atoms. The plot of potential $V(x)$ with respect to x is shown on Figure 13:
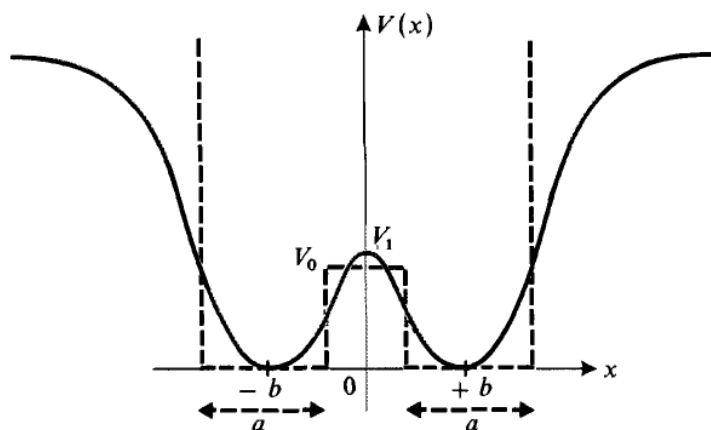

Figure 13. The potential energy V(x) of the ammonia inversion.

For the ammonia molecule, this potential can be given as

$$V(x) = 100 \times \left\{ \cos(\frac{x}{4}) - \cos A \right\}^2 \qquad (35)$$

where $A = 0.71$ for the finite potential barrier and $A = 1$ for the infinite potential barrier. You can control the height of the barrier by varing A.

By using LagChem and tdLagChem[10], confirm the following statements :

1) Infinite potential barrier

a. Show that the energy levels are two-fold degenerate.

b. Show that the states are localized at two potential wells of length a.

2) Finite potential barrier

a. Show that the energy levels are split, compared with the infinite barrier case. Show that the tunneling frequency gets higher in the higher vibration level.

b. Show that the wavefunctions do not vanish on the interval $-b + a/2 \le x \le b - a/2$.

By changing various input parameters, you can see the behavior of the wave functions according to the conditions. Refer to the manual and observe the results given by the programs.

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