CHAPTER 5

RESULTS AND DISCUSSION

5.1 Selection of representative geometries of the pairs

The output of this subroutine is Cartesian coordinates of all configurations of B around A. Those will be used as an input file for subroutine *Calculate_energy*. The output file for the NH_3-Li^+ system is shown in Figure 5.1. The two values between the lines (contain Cartesian coordinates) are θ and ϕ which specify trajectory of A.

How many configurations would be enough in order to develop the potential function and how can one selects? Those are the questions which one should consider carefully and attempt to find out the solution in this step.

Basically, there are infinite numbers of Li^+ configurations around NH_3. However, it is practically possible to limit numbers of data points by varying r, θ and ϕ within a certain values depending on symmetry of both molecules. An acceptable method to limit scope of r, θ and ϕ in order to include as less data as possible but not effect quality of the function are given below.

```
alpha=0 beta=0 gamma=0 theta=60 phi=0
Li      1.039231     0.127805     0.600000
Li      1.212436     0.127805     0.700000
Li      1.385641     0.127805     0.800000
Li      1.472243     0.127805     0.850000
Li      1.558846     0.127805     0.900000




Li      3.637307     0.127805     2.100000
Li      4.503332     0.127805     2.600000
Li      5.369358     0.127805     3.100000
Li      7.101409     0.127805     4.100000
Li      8.833459     0.127805     5.100000
alpha=0 beta=0 gamma=0 theta=60 phi=30
Li      0.900000     0.647420     0.600000
Li      1.050000     0.734023     0.700000
Li      1.200000     0.820625     0.800000
Li      1.275000     0.863927     0.850000
Li      1.350000     0.907228     0.900000




Li      3.150000     1.946458     2.100000
Li      3.900000     2.379471     2.600000
Li      4.650000     2.812484     3.100000
Li      6.150000     3.678509     4.100000
Li      7.650000     4.544535     5.100000
alpha=0 beta=0 gamma=0 theta=60 phi=60
```

Figure 5.1 The output file from subroutine *Generate_Configuration* that contain the Cartesian coordinates of all configurations of molecule B.

5.1.1 Narrow scope of distance (r)

An idea to fix the minimum and maximum values of r in the development of the potential function is to include all configurations until interaction becomes zero. Such distance is approximately between 1 Å and 10 Å. The reasons behind are:

(i)   Pair interaction between the two molecules is disappears or nearly disappears at the distance longer than 10 Å.

(ii)   Size of the simulation which is normally used is approximately 20Å. That has limited the potential cut-off at ½ of box length. Distance longer than this does not satisfy periodic boundary condition.

(iii)   Pair interaction between molecules r < 1 Å is normally strong repulsive. Such configurations are surely not take place during the simulation.

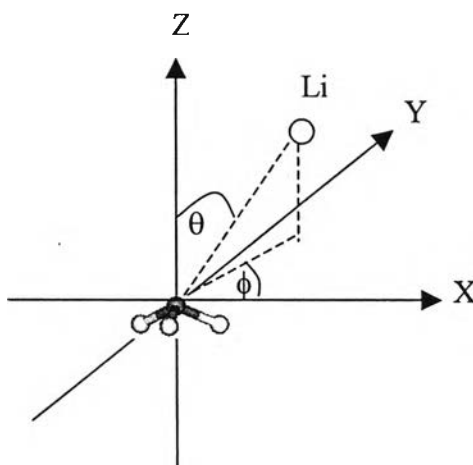**Figure 5.2** Definition of geometries variable (θ,ϕ) for the configuration of ammonia-lithium ion.

For NH_3-Li^+ system it was found that the distance shorter than 1.5 Å has lead to strong repulsion. A criteria to assign dr, interval between the two nearest data points, are:

$$1.5 \text{ Å } \leq r < 1.7 \text{ Å, } dr = 0.1 \text{ Å}$$

$$1.7 \text{ Å } \leq r < 3.0 \text{ Å, } dr = 0.05 \text{ Å}$$

$$3.0 \text{ Å } \leq r < 6.0 \text{ Å, } dr = 0.5 \text{ Å}$$

$$6.0 \text{ Å } \leq r \leq 10 \text{ Å, } dr = 2.0 \text{ Å} \qquad (5.1)$$

due to the following reasons.

Consider the plot which displays the NH_3-Li^+ interaction ($\theta = 0; \phi = 0$) as shown in Figure 5.3, the lowest interaction occurs in the range between 1.7 - 3 Å. As the distance to the minimum in the most attractive trajectory determines directly structural properties of the system, therefore, this data point as well as the nearest values have to be included in the fit. In this case, very small value of dr, 0.05 Å, has been assigned. For other ranges, dr has been given in order to follow the plot. Therefore, the values of 0.1 Å and 0.5 Å for the two sides have been proposed. For long distance, in general graph increase slowly and has slope of almost straight line, therefore dr of 2 Å has been given.

Note that the values estimated above (equation 5.1) are valid only for NH_3-Li^+ system. Therefore, suitable values have to be set by user by considering change of interaction energy as a function of r.

5.1.2 Assign scope of θ and φ

As mentioned already that number of complex configurations can be reduced by considering the symmetry of the two molecules. As in NH_3-Li^+ case (Figure 5.2) the whole space volume which specify by $0° \leq \theta \leq 180°$ and $0° \leq \phi \leq 360°$ can be reduced into $0° \leq \theta \leq 60°$ and $0° \leq \phi \leq 180°$. That is, coordinates of Li^+ have to be generated in the 1/6 of the total volume around NH_3.

To assign the intervals $\Delta\theta$ and $\Delta\phi$, the method is much simple compared to that for dr. The appropriate value in general used is $15° \leq \Delta\theta, \Delta\phi \leq 30°$. This condition can be used for any system. The narrower values of $\Delta\theta$ and $\Delta\phi$, yields the higher quality of the function. But our should keep in mind that it needs also higher computation time.

After a clear defined of r, dr, θ, $\Delta\theta$, ϕ and $\Delta\phi$, then Cartesian coordinates of B (which can be ion or monoatomic molecule) can be calculated using the following equations:

$$x = r \sin(\theta) \cos(\phi)$$
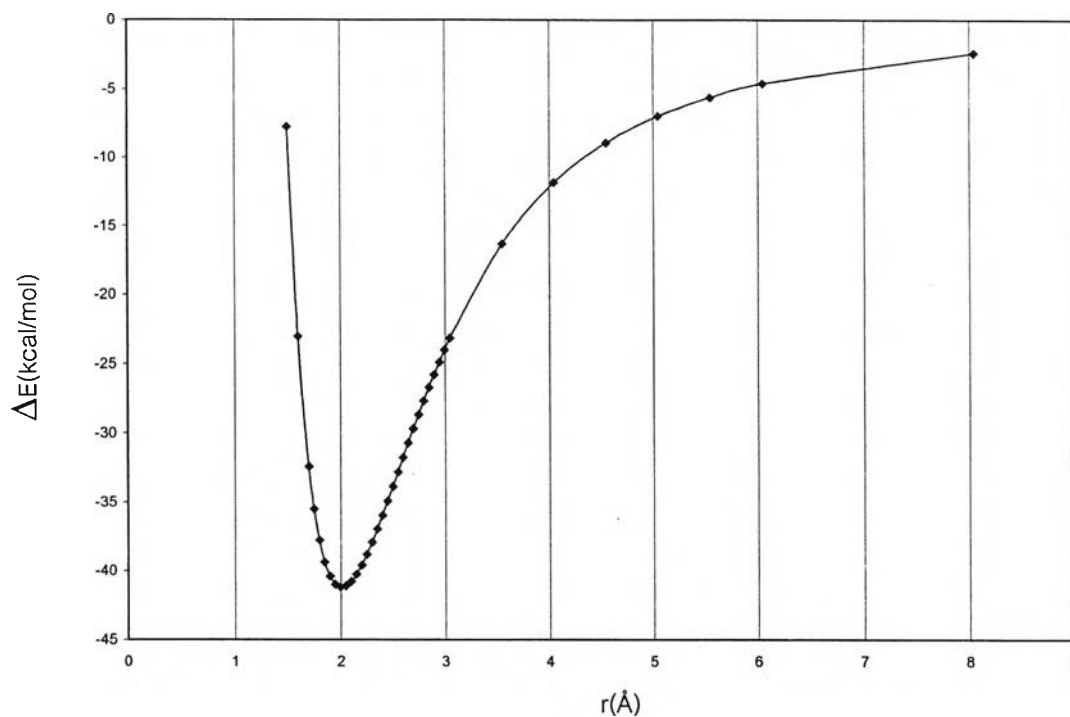$$y = r \sin(\theta) \sin(\phi)$$
$$z = r \cos(\theta) \tag{5.2}$$

Figure 5.3 NH_3-Li^+ interaction energies calculate without BSSE corrections used basis set d95** ($\theta = 0°$ and $\phi = 0°$, see Figure 5.2).

5.1.3 Specification for the NH_3-Li^+ system

Taking into account an above data on an assignments of r, dr, θ, $\Delta\theta$, ϕ and $\Delta\phi$, a conclusion for the Li^+-NH_3 system are:

- 1.5 Å $\leq$ r $\leq$ 10 Å, dr is difference for each range (equation 5.1) with this criteria, number of data points for each trajectory is 38.

- 0° $\leq\theta$ $\leq$ 180°, $\Delta\theta$ =30° and 0° $\leq\phi$ $\leq$ 60°, $\Delta\phi$ =30°. With these conditions, numbers of trajectories are given in Table 5.1.

Table 5.1 Possible trajectories around NH_3 due to the conditions: $0° \leq \theta \leq 180°$, $\Delta\theta = 30°$ and $0° \leq \phi \leq 60°$, $\Delta\phi = 30°$.

θ	φ		
	0°	30°	60°
0°	(0°,0°)	(0°,30°)	(0°,60°)
30°	(30°,0°)	(30°,30°)	(30°,60°)
60°	(60°,0°)	(60°,30°)	(60°,60°)
90°	(90°,0°)	(90°,30°)	(90°,60°)
120°	(120°,0°)	(120°,30°)	(120°,60°)
150°	(150°,0°)	(150°,30°)	(150°,60°)
180°	(180°,0°)	(180°,30°)	(180°,60°)

However, all trajectory with $\theta = 0°$ as well as $\theta = 180°$ are identical. Therefore, total numbers of different trajectories for the NH_3-Li^+ system with the above conditions are 17. Hence, total number of data points which the Cartesian coordinates have to be generated and quantum chemical calculations have to be performed are $17 \times 37 = 629$ configurations. One can estimate from here how much time require in order to compute interaction energies which have be used in the development of the potential function.

An above example can be used for any systems in which molecule B is ion or monoatomic molecule. If B is polyatomic molecule, generation process is more complicate. Detail descriptions were given in 5.3.

5.2 The *ab initio* calculations

As mentioned earlier that this routine reads coordinates of all atoms of the complex and writes them to a file which the format exactly fit to that of the Gaussian input. Quantum chemical calculations for the selected configuration has been, then performed. The Gaussian output which contains numerous informations will be automatically extracted. The only data which is required for the fitting step is the total energy. This will be used to calculate interaction energy according to equation 3.1. Therefore, then output of this subroutine are the coordinates of all configurations of B and the corresponding interaction energies. The two values specifying trajectory of A, θ and ϕ, are still given. These can be cased for future visualization. This data will be used as input file in the fitting step. The output files for the NH_3-Li^+ system were shown for two cases, without and with BSSE correction, in Figures 5.4 and 5.5, respectively.

```
alpha=0 beta=0 gamma=0 theta=60 phi=0
      .
      .
      .
  10.217         1.732051   0.127805   1.000000
   5.185         1.818654   0.127805   1.050000
   1.913         1.905256   0.127805   1.100000
  -0.131         1.991858   0.127805   1.150000
  -1.331         2.078461   0.127805   1.200000
  -1.964         2.165063   0.127805   1.250000
  -2.224         2.251666   0.127805   1.300000
  -1.726         2.598076   0.127805   1.500000
  -0.889         2.944486   0.127805   1.700000
  -0.369         3.290897   0.127805   1.900000
      .
      .
      .
alpha=0 beta=0 gamma=0 theta=60 phi=30
      .
      .
      .
 -12.849         1.425000   0.950529   0.950000
 -15.263         1.500000   0.993831   1.000000
 -16.371         1.575000   1.037132   1.050000
 -16.621         1.650000   1.080433   1.100000
 -16.318         1.725000   1.123734   1.150000
 -15.674         1.800000   1.167035   1.200000
 -14.835         1.875000   1.210337   1.250000
 -13.901         1.950000   1.253638   1.300000
 -10.227         2.250000   1.426843   1.500000
  -7.445         2.550000   1.600048   1.700000
      .
      .
      .
alpha=0 beta=0 gamma=0 theta=60 phi=60
      .
      .
      .
 -29.442         0.822724   1.552805   0.950000
 -30.529         0.866025   1.627805   1.000000
 -30.477         0.909327   1.702805   1.050000
 -29.695         0.952628   1.777805   1.100000
 -28.464         0.995929   1.852805   1.150000
 -26.980         1.039230   1.927805   1.200000
 -25.376         1.082532   2.002805   1.250000
 -23.741         1.125833   2.077805   1.300000
 -17.767         1.299038   2.377805   1.500000
 -13.284         1.472243   2.677805   1.700000
      .
      .
      .
```

Figure 5.4 The coordinates of all configurations of B and the corresponding interaction energies calculated without BSSE corrections.

```
alpha=0  beta=0  gamma=0  theta=60  phi=0
              .
              .
              .
    11.041        1.732051    0.127805    1.000000
     5.951        1.818654    0.127805    1.050000
     2.623        1.905256    0.127805    1.100000
     0.526        1.991858    0.127805    1.150000
    -0.726        2.078461    0.127805    1.200000
    -1.406        2.165063    0.127805    1.250000
    -1.712        2.251666    0.127805    1.300000
    -1.363        2.598076    0.127805    1.500000
    -0.639        2.944486    0.127805    1.700000
    -0.201        3.290897    0.127805    1.900000
              .
              .
              .
alpha=0  beta=0  gamma=0  theta=60  phi=30
              .
              .
              .
   -14.485        1.500000    0.993831    1.000000
   -15.655        1.575000    1.037132    1.050000
   -15.962        1.650000    1.080433    1.100000
   -15.712        1.725000    1.123734    1.150000
   -15.115        1.800000    1.167035    1.200000
   -14.319        1.875000    1.210337    1.250000
   -13.423        1.950000    1.253638    1.300000
    -9.866        2.250000    1.426843    1.500000
    -7.169        2.550000    1.600048    1.700000
    -5.334        2.850000    1.773253    1.900000
              .
              .
              .
alpha=0  beta=0  gamma=0  theta=60  phi=60
              .
              .
              .
   -29.584        0.866025    1.627805    1.000000
   -29.608        0.909327    1.702805    1.050000
   -28.899        0.952628    1.777805    1.100000
   -27.741        0.995929    1.852805    1.150000
   -26.326        1.039230    1.927805    1.200000
   -24.786        1.082532    2.002805    1.250000
   -23.210        1.125833    2.077805    1.300000
   -17.406        1.299038    2.377805    1.500000
   -13.001        1.472243    2.677805    1.700000
    -9.872        1.645448    2.977805    1.900000
              .
              .
              .
```

Figure 5.5 The coordinates of all configurations of B and the corresponding interaction energies calculated with BSSE corrections.

5.3 Application for NH₃-NH₃ system.

○ = Nitrogen atom of the second molecule

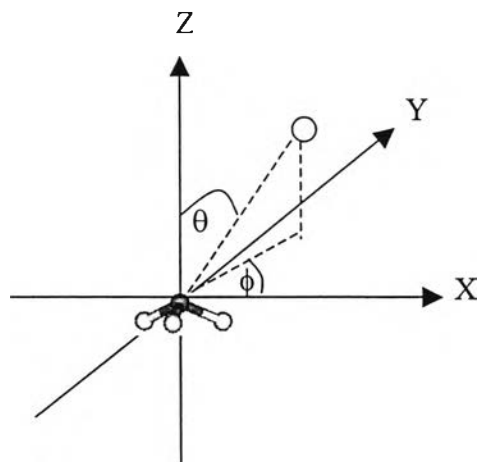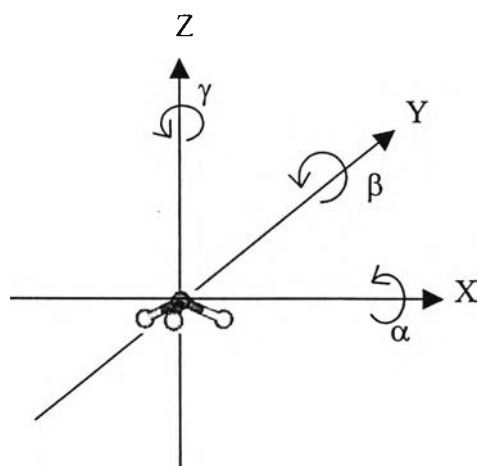**Figure 5.6** Definition of geometries variable (θ,ϕ) for the configuration of ammonia- ammonia.

Figure 5.7 Definition of geometries of ammonia, its hydrogen atoms were turned $\alpha°,\beta°$ and $\gamma°$ around x, y and z axis, respectively.

For the NH$_3$-NH$_3$ system, both NH$_3$ are treated as rigid body. The first molecule was fixed at the Cartesian coordinate system with the N atom at the origin and one of the H atom lies in the xz plan (Figure 5.6). Nitrogen atom of second molecule was placed at numerous positions within the space around the first molecule by varying r, θ and ϕ as those described in 5.1.3 where B is Li$^+$.

For each position of the second NH$_3$, numerous orientations of its hydrogen atoms have to be generated and taken into consideration in the fitting procedure. To generate such configurations, due to molecular orientation, the following steps have been performed.

Consider second NH$_3$ lying in the same orientation as the first one as shown in Figure 5.7, its hydrogen atoms were, then, turned $\Delta\alpha°$, $\Delta\beta°$ and $\Delta\gamma°$ around x, y and z axis, respectively. This Program applies the concept of Euler angles. New configuration for each orientation were calculated by

$$\begin{bmatrix} x' & y' & z' \end{bmatrix} = \begin{bmatrix} x & y & z \end{bmatrix} \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} \tag{5.3}$$

where C is the rotation matrix define as

$$C = \begin{bmatrix} \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & \sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma & \sin\beta\sin\gamma \\ -\cos\alpha\sin\gamma - \sin\alpha\cos\beta\cos\gamma & -\sin\alpha\sin\gamma + \cos\alpha\cos\beta\cos\gamma & \sin\beta\cos\gamma \\ \sin\alpha\sin\beta & -\cos\alpha\sin\beta & \cos\beta \end{bmatrix}$$

$$\tag{5.4}$$

The following values are applied for r, dr, θ, $\Delta\theta$, ϕ, $\Delta\phi$, α, $\Delta\alpha$, β, $\Delta\beta$, γ and $\Delta\gamma$ for NH_3-NH_3 system:

- $0° \leq \theta \leq 180°$, $\Delta\theta = 30°$ and $0° \leq \phi \leq 60°$, $\Delta\phi = 30°$.

- $0° \leq \alpha \leq 360°$; $0° \leq \beta \leq 360°$; $0° \leq \gamma \leq 60°$ and $\Delta\alpha = \Delta\beta = \Delta\gamma = 30°$.

- $2.4\ \text{Å} \leq r \leq 10\ \text{Å}$, dr is difference for each range:

$2.4\ \text{Å} \leq r < 3.0\ \text{Å}$, $dr = 0.2\ \text{Å}$

$3.0\ \text{Å} \leq r < 4.0\ \text{Å}$, $dr = 0.1\ \text{Å}$

$4.0\ \text{Å} \leq r < 6.0\ \text{Å}$, $dr = 0.5\ \text{Å}$

$6.0\ \text{Å} \leq r \leq 10.0\ \text{Å}$, $dr = 2.0\ \text{Å}$ (5.5).

With the above conditions, total number of trajectories are 17 and each trajectory contains 20 points. Number of orientations for each position of the second ammonia are 79. Therefore, 26,860 Cartesian coordinates have been generated and quantum chemical calculations for all configurations have been performed in order to be used to fit and improve quality of the $NH_3 - NH_3$ potential function.

For other polyatomic molecule, the above method can be also applied.