

## CHAPTER 3

### COMPUTATIONAL DETAILS

#### 3.1 Developing the intermolecular potential function

Given a system of N Particles, the total configurational interaction energy  $E(v)$  can be obtained from :

$$E(v) = \sum_{i<j} V(i, j) + \sum_{i<j<k} V(i, j, k) + \dots + V(1,2,3,\dots, n) \quad (3.1)$$

where the first term in the right hand side denotes the two-body interaction, the second is the three-body, and so on until the last term which contains all the bodies of the system. The assumption that  $E(v)$  is equal to  $\sum V(i, j)$  is known as the *pairwise additive approximation* and the remaining term of the series are often referred to as *nonadditive corrections*. The basic idea is that the total configurational energy of the many particles system is approximately written as a sum of the individual interaction between the particles.

The general procedure for obtaining the *ab initio* intermolecular potential function consists of five successive steps:

- a) selection of representative geometries of the pairs,
- b) selection of a reliable basis set for the SCF calculations,
- c) performance of the SCF calculations,
- d) fitting of the computed interaction energies to a functional form, and
- e) testing the quality of the function.

In this study, the intermolecular potential function between  $C_{60}$  and lithium atom was developed, based on the *ab initio* method.

### 3.1.1 Selection of the geometries of the pairs

Due to a high symmetry of the fullerene- $C_{60}$  molecule, its point group is  $I_h$ . Therefore, only 1/8 of the spherical space around the  $C_{60}$  has been considered. Then, Li- $C_{60}$  interaction energies, where Li is positioned in the selected space, have been calculated. The optimized geometry of the  $C_{60}$ , obtained from the *ab initio* calculations using the 6-31G basis set, is shown in Fig. 3.1 and kept constant throughout. The corresponding coordinates are summarized in Table 3.1.

Specific configuration of the Li- $C_{60}$  complexes is displayed in Fig. 3.2. The four trajectories for the Li to approach the  $C_{60}$  are at the center and perpendicular to (i) the C-C single bond (bridging site between 6 and 5 membered rings, B65), (ii) the C=C double bond (bridging site between 6 and 6 membered rings, B66), (iii) the hexagon (6 membered ring, C6) and (iv) the pentagon (5 membered ring, C5). The corresponding symmetric point groups for these complexes are  $C_s$ ,  $C_{2v}$ ,  $C_{3v}$  and  $C_{5v}$ , respectively. A clear picture of the four trajectories in different views are shown in Fig. 3.3.

Each trajectory has 35 configurations, 15 inside and the rest outside the cage of the  $C_{60}$ . This leads to the total configurations of 140. Distance between the two monomers is varied up to 10 Å from the center to the surface of the ball.

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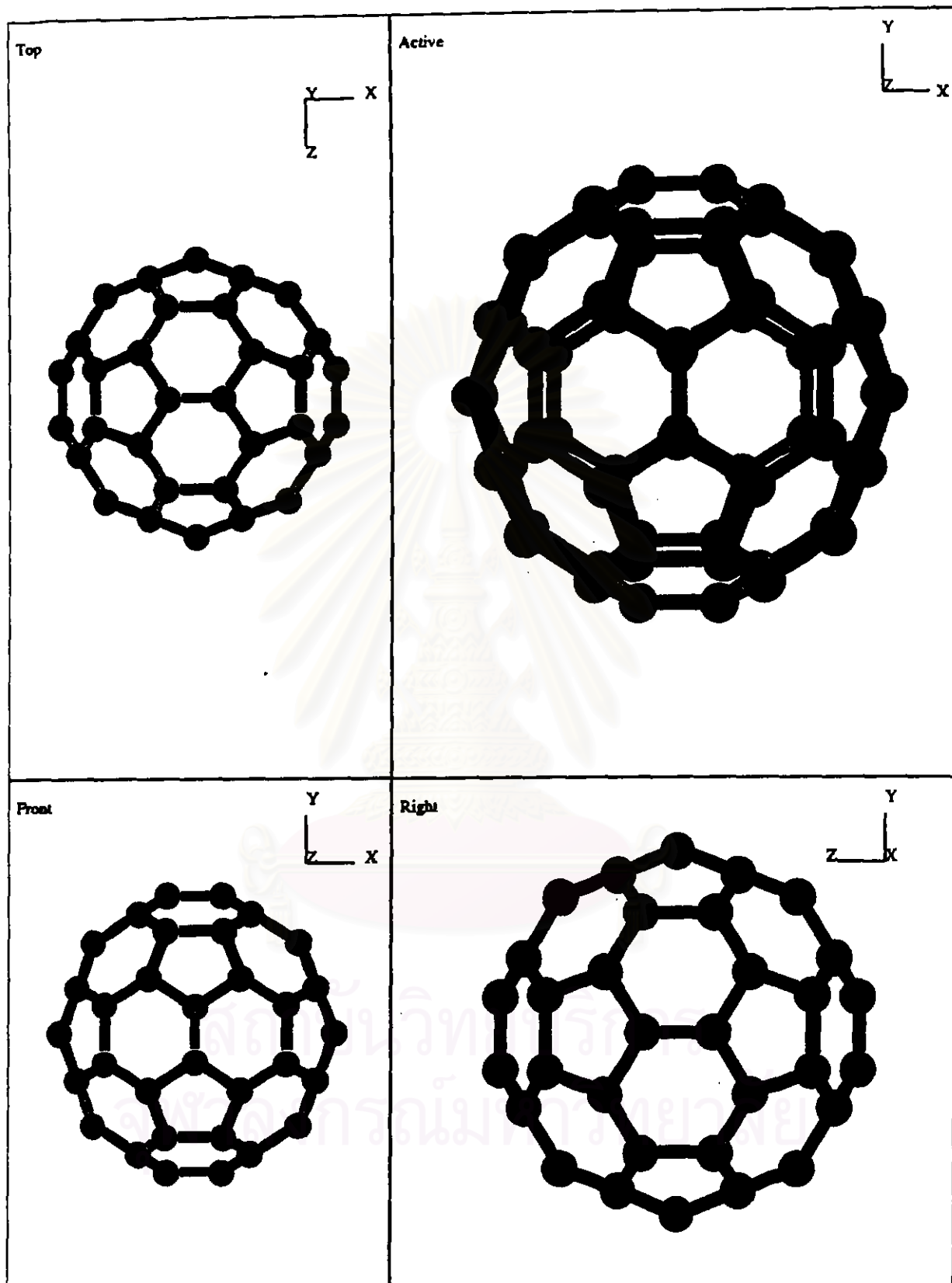


Figure 3.1 The optimized geometry of the fullerene-C<sub>60</sub>.

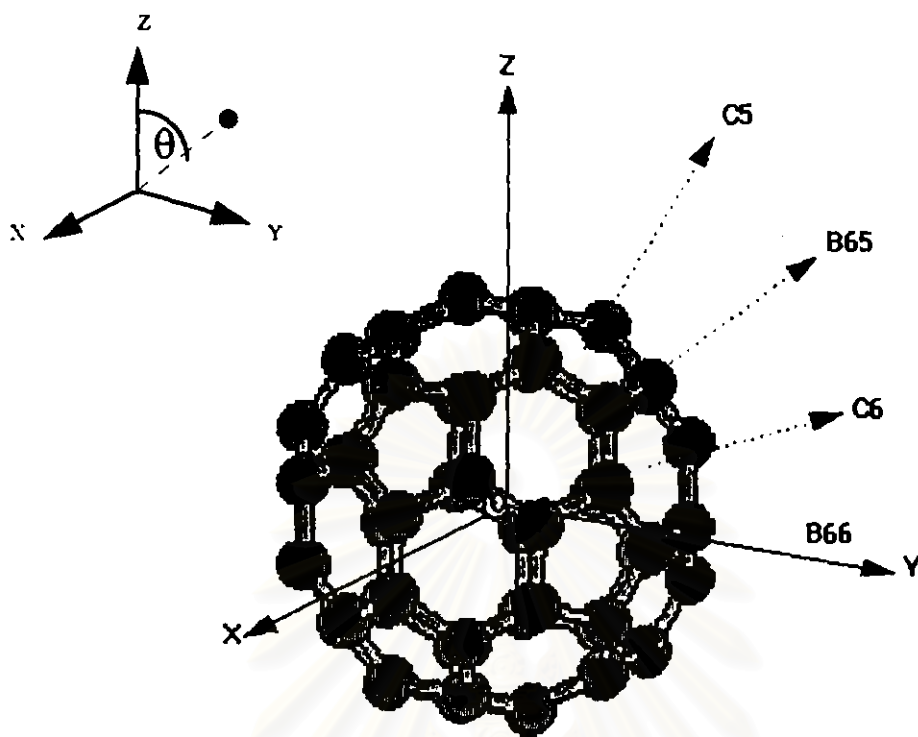
**Table 3.1** Optimized Cartesian coordinates of fullerene-C<sub>60</sub> using 6-31G basis set (in Å).

X	Y	Z
2.279810	-0.724000	2.580457
1.171457	-1.409000	3.003810
-1.171457	1.409000	-3.003810
-2.279810	0.724000	-2.580457
-0.724000	2.580457	2.279810
-1.409000	3.003810	1.171457
1.409000	-3.003810	-1.171457
0.724000	-2.580457	-2.279810
2.580457	2.279810	-0.724000
3.003810	1.171457	-1.409000
-3.003810	-1.171457	1.409000
-2.580457	-2.279810	0.724000
2.279810	0.724000	2.580457
3.003810	-1.171457	1.409000
0.000000	-0.685000	3.451266
0.724000	-2.580457	2.279810
-0.724000	2.580457	-2.279810
0.000000	0.685000	-3.451266
-3.003810	1.171457	-1.409000
-2.279810	-0.724000	-2.580457
0.724000	2.580457	2.279810
-1.171457	1.409000	3.003810
-0.685000	3.451266	0.000000
-2.580457	2.279810	0.724000
2.580457	-2.279810	-0.724000
0.685000	-3.451266	0.000000
1.171457	-1.409000	-3.003810
-0.724000	-2.580457	-2.279810
2.580457	2.279810	0.724000
1.409000	3.003810	-1.171457
3.451266	0.000000	-0.685000
2.279810	0.724000	-2.580457
-2.279810	-0.724000	2.580457
-3.451266	0.000000	0.685000
-1.409000	-3.003810	1.171457

**Table 3.1 (Continued)**

X	Y	Z
-2.580457	-2.279810	-0.724000
1.171457	1.409000	3.003810
2.580457	-2.279810	0.724000
0.000000	0.685000	3.451266
1.409000	-3.003810	1.171457
-1.409000	3.003810	-1.171457
0.000000	-0.685000	-3.451266
-2.580457	2.279810	-0.724000
-1.171457	-1.409000	-3.003810
1.409000	3.003810	1.171457
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0.685000	3.451266	0.000000
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3.003810	-1.171457	-1.409000
-0.685000	-3.451266	0.000000
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3.451266	0.000000	0.685000
1.171457	1.409000	-3.003810
-1.171457	-1.409000	3.003810
-3.451266	0.000000	-0.685000
-0.724000	-2.580457	2.279810
-3.003810	-1.171457	-1.409000

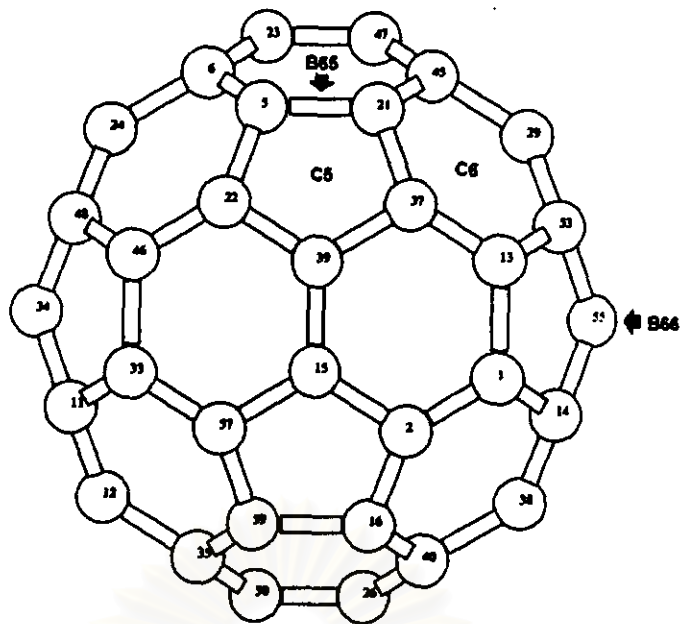
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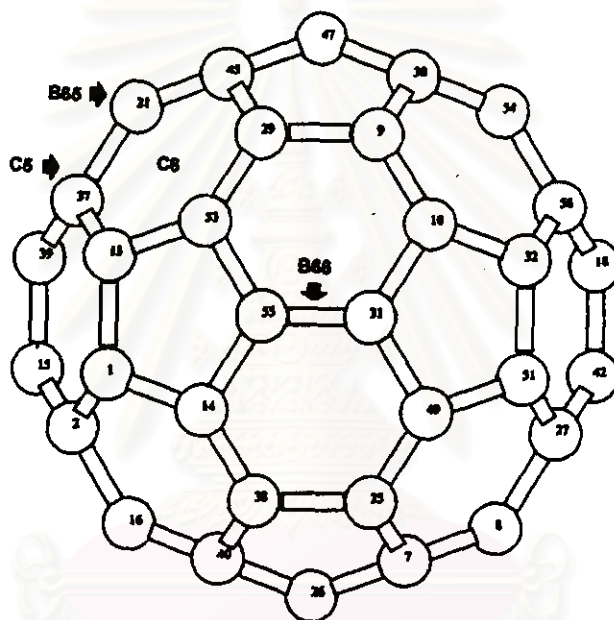
**Figure 3.2** The four trajectories of Li to approach  $C_{60}$ , the angle  $\theta$  of C5, B65, C6 and B66 are  $31.7^\circ$ ,  $48.5^\circ$ ,  $69.1^\circ$  and  $90^\circ$ , respectively.

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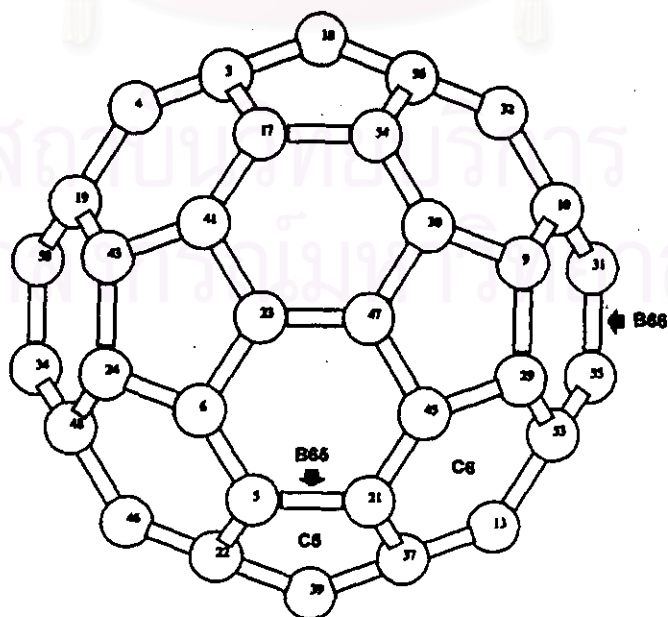
(a) Front view



(b) Right view



(c) Top view



**Figure 3.3** The four trajectories of Li to the cage of C<sub>60</sub> in different views.

### 3.1.2 Selection of a suitable basis set for the SCF calculations

To gain the best of the pair potential that represent the genuine interaction of the system, the method and the resource are the important factors those must be considered. The calculations by the *ab initio* method based on the basis sets used and the kind of Hartree-Fock method for instance UHF or ROHF. Furthermore, the restriction of time usage to affectuate the job and the capability of the obtained comtutational resources, such as the selection of the size of the basis set must compromise.

The SCF calculations were performed using STO-3G [51], 6-31G [52]-[54] and DZP [55] basis sets. An error due to the unbalance of the basis set, known as the basis set superposition error (BSSE), has been also investigated. The 6-31G basis set was finally selected (see chapter 4). The exponent of the functions and the corresponding coefficients for the tested basis sets are summarized in Appendix (I).

### 3.1.3 Performance of the SCF calculations

With the selected 6-31G basis set, the SCF calculations have been performed for 140 configurations of the selected Li-C<sub>60</sub> complexes. The interaction energies,  $\Delta E_{SCF}$ , between the buckminsterfullerene-C<sub>60</sub> (C) and the lithium atom (L) defined as the difference between the dimer energy,  $E_{CL}$ , and the sum of the isolated monomer energies ( $E_C$ ,  $E_L$ ), are, then, determined

$$\Delta E_{SCF} (\text{kcal.mol}^{-1}) = \{E_{CL} - (E_C + E_L)\} \times 627.5 \quad (3.2)$$

where  $E_{CL}$ ,  $E_C$  and  $E_L$  are in atomic units.

The SCF calculations have been carried out using Gaussian 92 program [56] on the IBM RISC 6000/530H Workstation of the Computational Chemistry



Unit Cell and the Austrian-Thai Center for Computer-Assisted Chemical Education and Research at Chulalongkorn University, Bangkok, Thailand, and on the DEC Alpha Workstation of the computing center of University of Vienna, Austria.

### 3.1.4 Fitting of the pair interaction energies to a functional form

In this step, an appropriate mathematical function is considered. Generally, the total intermolecular interaction energies between the two molecules were written as a sum of atom-atom pair potentials, each of which was considered to be a function of  $r_{ij}$  of the two atoms concerned. In the Li-C<sub>60</sub> case, the ligand is highly symmetric and all 60 atoms of C<sub>60</sub> contain atomic net charge of equal magnitude. Use of the  $r_{ij}$ , where  $i = 1 - 60$  and  $j = 1$ , would lead to complicated function. Therefore, in this specific case,  $r$  is defined as distance between center of mass of the C<sub>60</sub> and the lithium atom.

Fitting procedure was executed starting from an initial guess of the parameters and iterating until the standard deviation was minimized, where by constancy of the fitting parameters was reached.

The optimum functional form for the endohedral and the exohedral complexes are exponential growth and exponential decay models, respectively.

$$\Delta E(r) = A \exp(Br) + C \quad (\text{Endo, 3.3a})$$

$$\Delta E(r) = A \exp(-Br) + C \quad (\text{Exo, 3.3b})$$

### 3.1.5 Testing the quality of the function

To verify the quality of the potential function from fitting, the function must compromise the following criterions:

- i) Statistical value, for example standard deviation, of the fit should be lower than 5 %, [57]
- ii) Position of the fitted and the SCF functions where the minimum takes place should be identical, and
- iii) Correlation coefficient between the fitted and the SCF energies should be very close to unity.

### **3.2 The approximation of collision energy between Li and C<sub>60</sub> to form Li@C<sub>60</sub> complex**

To form endohedral complex of type Li@C<sub>60</sub> Li must has sufficient energy to penetrate the surface of C<sub>60</sub>. This phenomenon can be demonstrated using the potential energy surface.

To predict the threshold energy or collision energy ( $E_t$ ) of Li to enter to the cage of C<sub>60</sub> in different trajectories, the highest repulsive energy for each pathway, where Li is on the surface of the C<sub>60</sub>, are primarily required. As it is not possible to performed SCF calculations for those configurations due to a very short interatomic distances. Therefore, the interaction energies between Li and C<sub>60</sub> for each trajectory have been separately fitted to the analytical function of the forms:

$$V_{\text{endo}}(x) = a \exp(bx) + c \quad (3.4a)$$

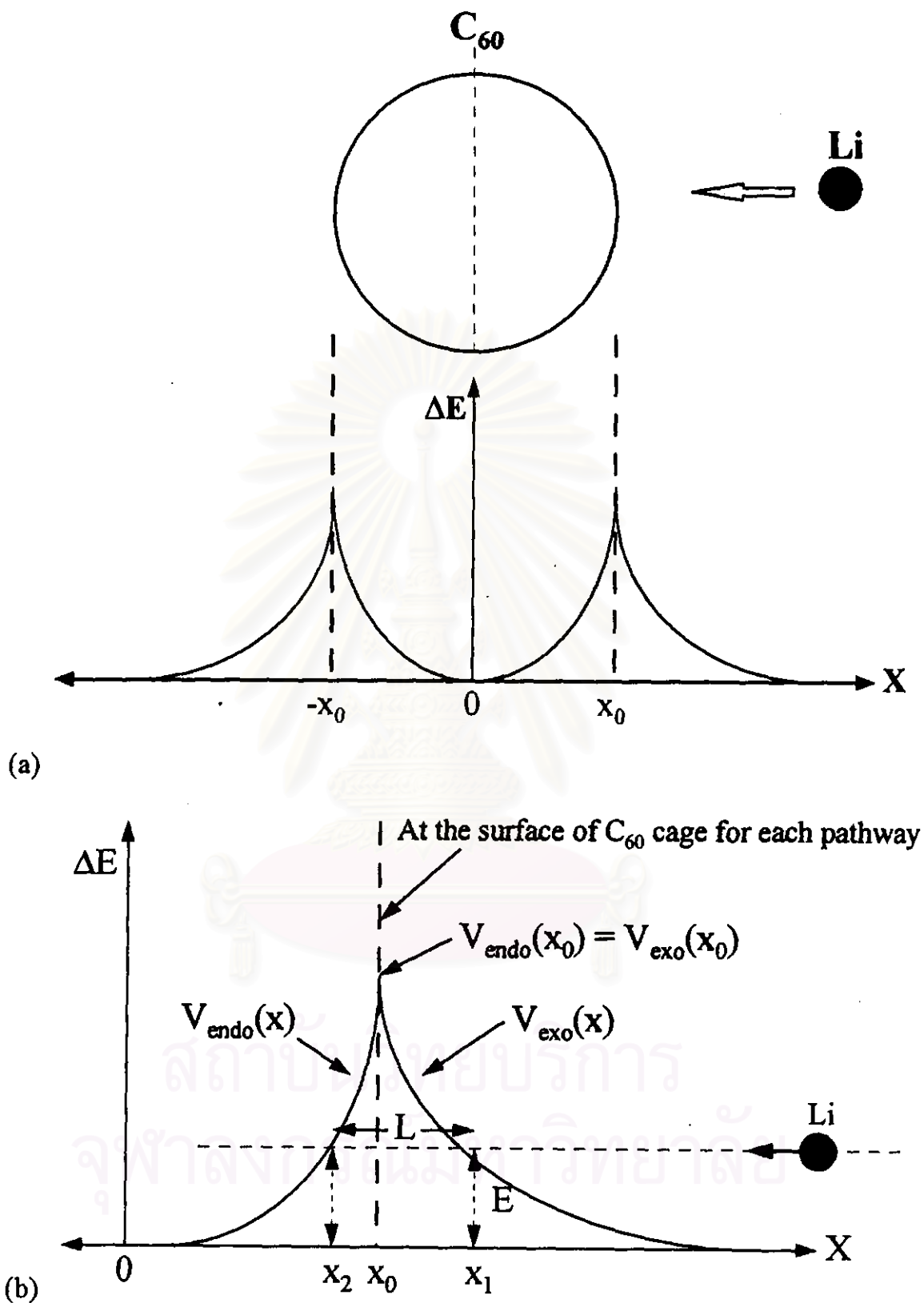
$$V_{\text{exo}}(x) = a \exp[-(x-b)/c] \quad (3.4b)$$

where  $x$  is the displacement of Li from the center of the ball,  $x_0$  is the position that yield the maximum value of  $V(x)$  on the surface of C<sub>60</sub> in each trajectory. Then,  $V_{\text{endo}}(x_0)$  (equal to  $V_{\text{exo}}(x_0)$ ) for each pathway has been extrapolated.

Length of the barrier is the distance between  $x_1$  (outside the cage) and  $x_2$  (inside the cage) where  $x_1$  and  $x_2$  are any point correspond to the high of the kinetic energy  $E$  (Fig. 3.4(a)-(b)) on the curve of  $V_{\text{exo}}(x)$  and  $V_{\text{endo}}(x)$ , respectively. The results for endohedral and exohedral complexes, are depicted in Fig. 4.5 and the optimum functional form and the corresponding parameters are also given in Table 4.3. Penetration probability of Li to enter into the cage can be evaluated using equation (2.62) for any values of the kinetic energies  $E$  of the Li.



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**Figure 3.4** (a) The tunneling of firing Li to the surface of  $C_{60}$  cage.

(b) The model of tunneling or penetration of Li at kinetic energy  $E$ .

### **3.3 Electron distribution plot**

Atomic net charge of the Li-C<sub>60</sub> complexes can be calculated from the population analysis in the SCF calculations. Variation of these data as a function of  $r$  for all C atoms has been drawn. Electron transfer, which is a typical character of this complex, as well as the most probable configuration can be determined from this plot. The plot gives tendency of finding the pathways of electron that transfer from Li to surface of C<sub>60</sub> and the most probable position of electron on the surface of C<sub>60</sub>.

### **3.4 Effect of dipole moment on stability of the Li-C<sub>60</sub> complexes**

In similarity to 3.3, change of the dipole moment of the Li-C<sub>60</sub> complexes has been also plotted. Accordingly, relation between dipole moment and stabilization energies can be analyzed.

### **3.5 Optimized structures of the Li<sub>n</sub>C<sub>60</sub> complexes**

SCF calculations have been carried out for the Li<sub>n</sub>C<sub>60</sub> complexes, where  $n = 1-6$  and 12. Distances to the  $n$  Li have been independently optimized. In addition, electronic structure as well as energy gap due to LUMO-HOMO method have been also investigated and plotted.