A molecular perspective study on lithium solvated electron solution

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**A Molecular Perspective Study on Lithium Solvated Electron
Solution**

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Abstract

Lithium based batteries plays an irreplaceable role in today's information age. The most widely used batteries nowadays are the solid lithium ion batteries(LIB), which can be found in portable devices like laptop, hand phone, calculator, and cameras and so on. However, one big disadvantage for LIB is the long charging time and restricted output power. One alternative to overcome the disadvantage is the lithium solvated electron solution battery. For the lithium solvated electron solution battery, the electrodes are composed of liquid solutions, and they can be replaced immediately after discharging process. Such design allow for rapid replenishing of the battery stack and high energy storage capacity.

In the battery, the anode is composed of lithium solvated electrons solution (Li-SES) . The Li-SES is prepared by dissolving metallic lithium in a solution of poly-aromatic hydrocarbon (such as biphenyl and naphthalene) in tetrahydrofuran (THF). And the cathode is composed of other carbon containing structures dissolved in solvent. During the discharging process, the lithium in anode will escape from the anode and recombine with the carbon structures in cathode. In this thesis, all the carbon containing structures are planar polycyclic aromatic hydrocarbons. We want to investigate the interaction mechanism between lithium and hydrocarbons.

In Chapter 1, hypothesis, investigate scope and key findings are listed. In Chapter 2, the background knowledge about lithium battery and first principle theory combined with computational methodology are shorted reviewed. The main discussion parts are Chapter 3, Chapter 4 and Chapter 5. Chapter 6 talks about the conclusion and future work.

In Chapter 3, various planar Aromatic Hydrocarbons were studied. They were characterized by different kind of shape, size, geometry, edge and show different electric and electronical properties. A new concept Clar Aromatic Sextet Per Ring

(CASPER) based on Clar Rule's was proposed to quantitatively evaluate the relationship between the shape and stability addressing various PAHs characterized by distinct shape. CASPER means the scale of aromatic π sextet stretching over the whole hydrocarbon, and in the meanwhile, it was demonstrated to be a convenient approach to assess PAHs' stability through application to various categories of PAHs. It is the shape of PAH that determine the distribution of π electron sextet and electronic orbital nature, thus furthermore determine system's physical, chemical and magnetic properties.

In chapter 4, the interaction mechanism between lithium and various polycyclic aromatic hydrocarbons was studied. A screening is carried out covering 1) naphthalene, biphenyl; 2) polyacenes from naphthalene to penance; 3) other hydrocarbons composed of six benzenes. For all the hydrocarbons, the complex geometry, binding energy, open circuit voltage, charge of lithium was studied. Referring to investigated samples, a best cathode candidate is recommended. In the final section, the electrode material is extended to a molecular with nitrogen atoms. The reaction mechanism, binding energy, geometry configuration and lithium capacity for three similar polymers are investigated.

In chapter 5, a molecular perspective study was done for lithium solvated electron solution. The possible species and complexes existing in Lithium-Tetrahydrofuran Solution were systematically studied. Their geometry configuration, contour diagram, spin distribution and binding energy will be studied and understood. The interested systems cover: 1) neutral THF cluster $(\text{THF})_n$ and negatively charged anions $(\text{THF})_n^-$; 2) complexes: $\text{Li}(\text{THF})_n$, positively charged $\text{Li}(\text{THF})_n^+$, and negatively charged $\text{Li}(\text{THF})_n^-$.

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Table of Contents

Chapter 1	Introduction	01
1.1	Hypothesis	02
1.2	Objectives and Scope	03
1.4	Findings and Outcomes	05
	References	07
Chapter 2	Literature Review	09
2.1	Lithium Solvated Electron Solution Battery	10
2.2	Theoretical Background	14
	References	20
Chapter 3	Application of Clar's Rule on Planar Hydrocarbons	41
3.1	Review on Clar's Aromatic Sextet Rule	51
3.2	Investigated Systems	29
3.3	Computational Methodology	36
3.4	Discussion and Results	53
3.5	Summary	70
	References	71
Chapter 4	Assessment of Interaction between Lithium and Polycyclic Aromatic Hydrocarbons	72
4.1	Lithium Binding with Naphthalene and Biphenyl	73
4.2	Lithium Binding with Acenes	80
4.3	Lithium Binding with other Hydrocarbons	90

4.4	Lithium Capacity Solvated Electron Solution Battery	99
	References	100

Chapter 5 A molecular Perspective Study on Lithium Tetrahydrofuran Solution

5.1	A molecular Perspective Study on Tetrahydrofuran	102
5.2	Interaction of Lithium with Tetrahydrofuran	111
	References	121

Chapter 6 Conclusions and Future Work

Abbreviations

DFT	Density Functional Theory
PAH	Polycyclic Aromatic Hydrocarbon
GNR	Graphene Nanoribbon
S-T Gap	Singlet Triplet Gap
GA	Fundamental Gap
EA	Electron Affinity
IP	Ionization Potential
CSS	Closed Shell Singlet
OSS	Open Shell Singlet
OST	Open Shell Triplet
EPMA	Electron Probe Microanalysis
FTIR	Fourier Transform Infrared Spectroscopy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
BE	Binding Energy

Chapter 1

Introduction

Lithium Solvated Electron Solution batteries have attracted enormous attention from academic and industry area due to their high energy density and fast replenishing process. In the battery, the anode is composed of lithium solvated electrons solution (Li-SES). The Li-SES is prepared by dissolving metallic lithium in a solution of poly-aromatic hydrocarbon (such as biphenyl and naphthalene) in Tetrahydrofuran (THF). And the cathode is composed of other carbon-containing structures dissolved in specified solvent. During the discharging process, the lithium in anode will escape from the anode and recombine with the carbon structures in cathode. It is necessary to investigate the interaction mechanism between lithium and various hydrocarbons.

1.1 Hypothesis

Lithium batteries are widely used in handheld consumer devices and electric vehicles for its high energy density and portability. They also produce relatively less pollution compared with traditional batteries. To improve the performance of lithium batteries, a lot of attention has been paid to their fundamental principles. Basic requirement for rechargeable batteries covers 1) long operating and cycling life time; 2) safe and green; 3) low cost; 4) high output energy efficiency. The commercial Lithium batteries being used every day are usually solid Lithium Ion Battery (LIB). LIBs are popular attributed to their low weight, high energy density, a low self-discharge rate, negligible memory effect along and long charge/discharge cycles.[1]

Most electrodes of the current LIBs are solid-based material and their charge-discharge process consists of the intercalation and de-intercalation of lithium cation across the electrodes. However, one big disadvantage for the common LIBs is their long recharging time – normally at least 6 to 8 hours. To overcome the long recycling time of LIB, one alternation is liquid redox battery. The redox batteries are having liquid catholytes and anolytes, which allows for rapid replenishment of the battery stack after electricity is exhausted. Therefore, such kind of liquid redox batteries have big potential prospect in military, aerospace and other manufacturing fields. As reported so far, some countries are investing a lot of manpower and material resources towards the liquid redox battery development. The liquid electrolyte is prepared by dissolving metallic lithium in a solution of Polycyclic Aromatic Hydrocarbon (such as biphenyl and naphthalene) in solvent Tetrahydrofuran (THF). And the mixed solution with solvated electron is called as lithium solvated electron solution (Li-SES).

The conductivity of the electrolytes plays an essential role to determine the performance of Lithium batteries. Density Functional Theory (DFT) was used to study the Lithium-PAHs structures and interaction to enhance a deeper understanding of the Lithium solvated electron solution.

Firstly, Clar's rule, a method involves clarifying chemical Kekulé resonance structure characterized by aromatic sextets was generally reviewed. Clar's rule has been proven to be amazingly effective to evaluate the stability and electronic nature of various PAHs. Sophisticated quantum mechanical calculations have been performed to explain the simple rule in detail and enable quantitative predictions. Meanwhile, experimental publications provide convincing proof to support Clar's predictions. For example, one frequently used methodology is the wide-range absorption spectra. The characteristic absorption spectra can be seen as their fingerprints, making it easy to ambiguously identify a compound as well as the inner orbital distribution. PAHs' aromaticity or stability is fundamentally determined by structures' shape effects, including symmetry, size, periphery, etc. In the chapter, a scaled index --Clar Aromatic Sextet Per Ring (CASPR) was proposed aimed to quantitatively evaluate the electron distribution within the system, and furthermore to evaluate the kinetic stability and electronic nature of PAHs.[2-4]

Secondly, a detailed molecular perspective study on possible complexes in solvated electron solutions is provided. The mechanism of lithium binding with various organic fragments solvated in Tetrahydrofuran (THF) fluids is under investigation. Density Functional Method (DFT) method is adopted to give molecular [2-4] or bital analysis of the structure and electronic properties addressing a great variety of species existing in the solutions possibly. Moreover, a good route is proposed to describe the reaction process for lithium based battery and give reasonable Open Circuit Voltage (OCV). An extended description is that two ribbons Naphthalene and Biphenyl (both of the two have two benzoin rings) are studied separately and compared. Theoretical data predicts Naphthalene in the anode will generate higher Open Circuit Voltage than Biphenyl.

Lastly, the Open Circuit Voltage during discharging process was investigated when the anode is made up of different sorts of polymers. Three molecules with similar geometry features were studied and their respective lithium-accepting capacity was discussed.

To summarize, the microscopic picture within lithium solvated electron for redox battery's electrolyte is explored from several aspects. And these simulation results and analysis will help better understand the mechanism of interaction between solution ingredients. Based on the principle of lithium redox battery, Open Circuit Voltage for various sorts of ratio or geometry is discussed. All thesis observation will enhance the understanding of electrolyte's fundamental function and can be associated with other measureable properties like electrical conductivity, viscosity or Open Circuit Voltage.

1.2 Objectives and Scope

Lithium based batteries plays an irreplaceable role in today's information age. They are widely used in in many professions, including mobile vehicles, light portable devices (like laptop, hand phone, calculator), medical treatment (like serving for artificial heart pacemaker) and so on. Lithium and Lithium based batteries are so attractive because of their unique advantages over other metal elements. The electronegativity of Lithium is 0.98 based on the Pauling scale and this makes Lithium the least electronegative metal. Meanwhile, Lithium is the lightest metal. These two fantastic properties make Lithium a promising material to be the anode for high energy density battery. Since the first assembly of primary Lithium cell in 1970s, researchers have put in a lot of efforts to improve the performance of the Lithium based batteries. At the applied level, researchers try to modify the electrodes and electrolytes of the Lithium based batteries. For example, carbonaceous materials like graphite were proposed by a group of Japanese scientists as the anode intercalation host .The problem of dendrite formation of Lithium anode was solved and the idea of Lithium ion battery was introduced. Also, a new type of electrolytes like the polymer electrolyte was introduced. At the fundamental level the coordination of Lithium ion in the electrolyte Lithium ion solvation and diffusion in organic electrolyte and a lot of others were studied. The coordination number of Lithium ion and corresponding structure minimal radius of enclosed cavity formed by the solvent molecules change with solvent species. Lithium ions favor to be solvated by organic solvent with high dielectric constant and diffuse faster in solvent with low viscosity and

so on. Researchers also build models to understand the performance of Lithium based batteries. The properties of the electrolyte play a crucial role in the performance of Lithium based batteries. The electric conductivity of the electrolyte is the key factor to determine whether the electrolyte is good or not. [5, 6]

In Chapter 3 of the thesis, a new concept – Clar Aromatic Sextet Rule Per Ring (CASPER) is introduced to quantitatively evaluate stability and electronic properties of aromatic hydrocarbons. In addition, a series of computational tests are done to justify the general rule and compare with available experimental measurement. For aromatic hydrocarbons with various geometries, size, edge and other factors, the quasi one-dimensional linear polyacenes and kindred zethrene series are simulated and compared with each other. Another comparison is addressing coronene and pyrene series, definitely two-dimensional hydrocarbons with regular extensions. Through several examples, Clar's rule are theoretically and experimentally justified and we can get information associated with Graphene Nanoribbon's stability and other properties just from Clar's rule.[7-10]

The principle and discharging reactions for the redox battery with various electrolytes are discussed. Based on the discharging reaction, a series of computation will be given to evaluate the reaction energy for different electrolytes. How Clar's rule affects the lithium-PAH binding reactions will be explored. Various planar hydrocarbons are tested and compared. This helps us to provide a best electrolyte candidate.

In the fourth chapter, three similar-looking PAHs were studied to evaluate their lithium-accepting capacity. The Open Circuit Voltage during discharging process is investigated when the anode is made up of different sorts of PAHs. For the three polymers, it can absorb up to 12 lithium atoms. However, when more lithium atoms are combined with the polymer, the changing trend for open circuit voltage will be discussed separately. There are many mid products with different geometries during the process of discharging reaction. We will also take a look inside and give a general rule.

Since it is deserved to learn more about the intrinsic physics of Lithium-Solvated Electron Solutions, it is important to study the complexes from the molecular perspective. The molecular orbital, geometry, charge density distribution and other electrical properties will be systematically investigated. From the perspective of lithium-base redox cell, THF plays the role of solvent in electrolyte. In chapter 6 of the thesis, we explore the knowledge concerning THF clustering and condition that one electron is attached to THF cluster. And then how the lithium binding with THF fragments is simulated. Same work is done for positively charged complexes whose lithium atom is ionized.

1.3 Findings and Future Work

To evaluate the stability of planar aromatic hydrocarbons, Clar's rule is applied on various structures, and the structure size, shape and edge effects are also considered. The Clar's rule help us better understand the ground state, geometry configuration, spin distribution, orbital information of structures.

The interaction mechanism between lithium and various polycyclic aromatic hydrocarbons were studied. For all the hydrocarbons, the complex geometry, binding energy, open circuit voltage, charge of lithium is studied. Referring to investigated samples, a best cathode candidate is recommended. In addition, the electrolyte material is extended to more molecules with nitrogen atoms. The reaction mechanism, binding energy, geometry configuration and lithium capacity for three similar polymers are investigated.

Future work will focus on more electrolyte candidates. The structures can be that have studied are single molecules. However, when the electrolytes are periodic nanoribbon structures, things will be totally different. Another future work is to study the ab initio molecular dynamic process for lithium solvated electron solutions. It is interesting to see the motion trail of solvated electrons. This will help in understanding the conductivity and transport properties of the solution.[11-17]

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Chapter 2

Literature Review

This chapter is composed of two main sections. In the first section, a brief review focused on lithium solvated electron solution battery is given. The development history, working principles and electrode component will be generally reviewed. In the second section, the theoretical background of the used computational methodology will be shortly reviewed. Starting from Schrodinger equation, the derivative of Hatree-Fock approximation and DFT approximation are reviewed. In this thesis, all calculations are carried by Gaussian 09 Packages with b3lyp functional at 6-31g (d, p) basis (with d and p polarization) for neutral systems. For charged systems, basis 6-31++g(d, p) are used incorporating diffusing functional.

2.1 Lithium Solvated Electron Solution Battery

2.1.1 Lithium Batteries

Nowadays lithium batteries are the main power source for the consumer electronic market with a production in the order of billions of units per year. Lithium based batteries are characterized by high specific energy, high efficiency and long lifetime, which make them the first choice for portable electronics, power tools, and hybrid/full electric vehicles.[1-4,18] The high energy efficiency also allow the wide usage in various electric grid applications, including improving the quality of energy harvested from wind, solar, geo-thermal and other renewable sources, thus contributing to more widespread use and building an energy-sustainable economy. Actually Lithium based batteries are of intense interest from both industry and government funding agencies, and research in this field has abounded in recent years. [1, 5, 19]

The electro-negativity of Lithium is 0.98 based on the Pauling scale and this makes Lithium the least electronegative metal.[1] Meanwhile, Lithium is the lightest metal element and has one of the smallest ionic radii of any single charged ion. These fantastic properties allow lithium based batteries to have high gravimetric and volumetric capacity and power density. [20]

Nowadays Lithium Ion Batteries are the first commercial choice in portable electrochemical energy storage systems within industry field considering their practical performance and economic cost. [21] Any minor improvement of performance will greatly expand the application of the battery and bring about novel technology revolution which are dependent on energy storage. Fig 2.1.1 gives a schematic description of a lithium ion battery (LIB). The battery employs graphitic carbon as anode and transition metal oxide as cathode. The discharging process involves lithium ion separation from the graphene structure of the anode and simultaneous intercalation into the layered structure of the metal oxide cathode. Meanwhile, the electrons flow through the external circuit in the same direction and therefore the current in the reverse direction. [22, 23]When the

cell is charging, the reverse reaction occurs with the lithium ions and electrons moved back into the negative electrode in a net higher energy state.

Lithium Ion Batteries (LIB) are light, compact and work with a voltage of the order of 4V with a specific energy ranging between 100Wh/kg and 150Wh/kg. In its most conventional structure, a lithium ion battery contains a graphite anode (e.g. mesocarbon microbeads, MCMB), a cathode formed by a lithium metal oxide (LiMO_2 , e.g. LiCoO_2) and an electrolyte consisting of a solution of a lithium salt (e.g. LiPF_6) in a mixed organic solvent (e.g. ethylene carbonate – dimethyl carbonate, EC-DMC) imbedded in a separator. A porous solid separator, which is not electron conducting, prevents the electrodes from touching each other and shorting out within the cell while allowing the passage of Li ions through it. In one common case based on the C/ LiPF_6 in EC-DMC/ LiMO_2 sequence and operate on a process:

involving the reversible extraction and insertion of lithium ions between the two electrodes with a concomitant removal and addition of electrons.[5, 6, 20]

Nowadays, a great deal of efforts has been spent on the research on electrode materials. Electrodes with higher rate capability, higher charge capacity, and (for cathodes) sufficiently high voltage can improve the energy and power densities of Li batteries and make them smaller and cheaper. Figure 2.1.2 is a comprehensive form to depict average electrode potential against experimentally accessible (for anodes and intercalation cathodes) or theoretical (for conversion cathodes) capacity. This allows reserachers to evaluate various anode and cathode combinations and their theoretical cell voltage, capacity, and energy density. The chart can also be used to identify suitable electrolytes, additives, and current collectors for the electrode materials of choice. The acronyms for the intercalation materials are: LCO for “lithium cobalt oxide”, LMO for “lithium manganese oxide”, NCM for “nickel cobalt manganese oxide”, NCA for “nickel cobalt aluminum oxide”, LCP for “lithium cobalt phosphate”, LFP for “lithium iron phosphate”, LFSF for “lithium iron fluorosulfate”, and LTS for “lithium titanium sulfide”. [18, 24-26]

Electrolytes are ubiquitous and indispensable in all electrochemical devices, and their basic function is independent of the much diversified chemistries and applications of these devices.[20] In this sense, the role of electrolytes in electrolytic cells, capacitors, fuel cells, or batteries would remain the same: to serve as the medium for the transfer of charges, which are in the form of ions, between a pair of electrodes. The vast majority of the electrolytes are electrolytic solution-types that consist of salts (also called “electrolyte solutes”) dissolved in solvents, either water (aqueous) or organic molecules (nonaqueous), and are in a liquid state in the service-temperature range. Because of its physical location in the electrochemical devices, that is, being sandwiched between positive and negative electrodes, the electrolyte is in close interaction with both electrodes. Therefore, when new electrode materials come into use, the need for compatible electrolytes usually arises. The interfaces between the electrolyte and the two electrodes often dictate the performance of the devices. In fact, these electrified interfaces have been the focus of interest since the dawn of modern electrochemistry and remain so in the contemporary lithium-based rechargeable battery technologies.[27]

The advantage of a Lithium Ion Battery construction is the condensed matter character of the anode and cathode, which allows a high volumetric energy density to be achieved. The drawbacks, however, are: (1) a low lithium mobility in the solid-state materials, which limits the power density (i.e., long charging and discharging time), and (2) a relatively short cycle. For an LIB-powered electric car to be competitive with gasoline cars, the charging time should be reduced to 5-10 min and the driving range should be about 500 km per charge. The driving range of a gasoline car with a full tank is about 500 km and the typical time required to fill up an empty fuel tank is not more than 10 min.[28]

However, today’s LIB technology does not allow this level of performance in a sustainable way. For instance, one of the top LIB electric vehicles available commercially is the Nissan Leaf 2013 model, which has a range of 135 km for a full battery pack and which can be charged to 80% of its full capacity with a fast charger in 30 min. LIB

performance limitations have motivated tremendous research activity aimed at increasing the energy density and power density while maintaining the calendar life to achieve over 100,000 km per battery pack lifespan. [29]

Fig 2.1.1 Approximate range of average discharge potentials and specific capacity of some of the most common (a) intercalation-type cathodes (experimental), (b) conversion-type cathodes (theoretical), (c) conversion type anodes (experimental), and (d) an overview of the average discharge potentials and specific capacities for all types of electrodes.

Fig 2.1.2 Schematic description of a lithium ion battery (LIB). The battery employs graphitic carbon as anode and transition metal oxide as cathode. The undergoing electrochemical process is lithium ion deintercalation from the graphene structure of the anode and simultaneous intercalation into the layered structure of the metal oxide cathode. For the cell, this process is discharge, since the reaction is spontaneous.

2.1.2 Redox Flow Batteries

The issues encountered in LIB-powered electric vehicles are obvious, one of which is the long charging time (30 min), which is significantly longer than the 10-min refueling time needed for gasoline vehicles. One possible solution to address these issues is the use of liquid-state electrodes in association with a solid-state electrolyte membrane such as the redox flow batteries (RFBs). The main advantage of RFBs over other conventional batteries is that they can be instantly recharged with solution exchange.[27, 30]

Attempts to incorporate both the advantages of the LIB high energy density as well as the RFB dual refueling/recharging options resulted in alkali-metal (Li or Na) half-cells utilizing liquid cathodes and semi-solid rechargeable lithium flow cells. The redox-flow half-cells use a solid anode such as metallic lithium with liquid cathodes containing

dissolved reversible redox species as the redox shuttle to the solid cathode reservoir such as the one shown in Figure 2.1.4. The semi-solid rechargeable flow cells, however, use viscous slurry-based suspensions comprised of solid electrode materials, electrolyte, and conducting carbon additives.

However, there are disadvantages in both types of cells. For semi-solid flow batteries, viscous slurry suspensions from external storage tanks are circulated through the cells during operation. For slurries containing nonconducting lithium-based oxide materials (LiFePO_4 , LiCoO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, etc.), the system requires a large quantity of carbon additives to improve their conductivity. Furthermore there is a possibility of solid particles clogging the circulatory system during operation. Finally, the flow process of the active material into and out of the cell is regulated by an external pump which requires power itself to operate. For the redox-flow half-cells utilizing an alkali metal anode, the solid anode material has to be replaced when depleted. Moreover, the presence of the alkali metal anode poses a risk due to the high reactivity of the alkali metals. A recently developed redox flow pump-assisted lithium ion cell operates with its solid anode and cathode materials stored in separate external tanks. The liquids circulating through the cell consist of redox-shuttle molecules. The tanks can be replaced once their electrode materials are fully discharged instead of recharging the whole cell, as mentioned earlier. However, it has two main shortcomings: First, critical to the working of this cell is a set of functioning pumps which themselves require a source of energy to operate. Secondly, replacing both solid electrode tanks instead of simple refueling is a cumbersome process.[1, 21, 31]

In the next section, a new kind of liquid anode cell operating at ambient temperature is introduced. Lithium-Solvated Electron Solution (Li-SES) is the active material in the liquid anode, whereas the liquid cathode consists of iodine in methanol or aqueous LiCl . The liquid anode solution has several advantages when compared to solid-state anode or slurry-based anode. First, it possesses fast ion transport capability. Secondly, it is able to achieve a physically stable anode/ceramic membrane electrolyte interface. Thirdly, as its anode is a true liquid solution instead of slurry based, the likelihood of clogging up the

pump and circulatory system is much lower. The fourth advantage lays in the metal-like property of the Li-SES itself, which means that it does not require a large amount of conducting additive to work, unlike the oxides of lithium for the slurry batteries. Next the concept of Li-SES as a liquid anode will be covered in greater detail.

Fig 2.1.4 Schematic illustration of a Li redox flow battery (RFB) with a thin LISICON separator plate between the electrodes.

2.1.4 Lithium Solvated Electron Solution

This section presents the concept of an ambient temperature liquid-based lithium anode used in a liquid cell, which is Lithium Solvated Electron Solution (Li-SES). Such a cell can be used in conjunction with a liquid-based cathode as a rechargeable Li cell with purely liquid-based refuelable electrodes.

Solvated electron solutions were first reported in the 1800s by Sir Humphrey Davy, who noted that when alkali metals dissolved in liquid ammonia, they yielded blue-colored solutions. The blue color was attributed to solvated electrons which were formed during the dissolution of the alkali metal in ammonia. Even though solvated electron solutions were often described in a variety of synthesis processes and applications over the years, there were very few reports on its application as a liquid-based anode to lithium batteries.

The concept of solvated electrons is as follows, in ammonia solution, Li atoms dissociate into cations with electrons as the anions in a process known as the Birch reaction. Alkali metals such as lithium and sodium can also form solvated electron solutions (Li-SES and Na-SES) with several other types of molecules such as organic radicals and PAHs. The solvated electrons occupy the spaces between the clusters of solvent/solute molecules surrounding them and are not strongly bound to these molecules. The resulting Li-SES is a solution and not a slurry suspension of undissolved particles like those of the slurry flow batteries.[6, 32]

In the late 1980s, Sammells and his team used liquid ammonia-based Li-SES as the liquid anode for lithium batteries. In this section, instead of using liquid ammonia, the Li-SES used were formed using simple PAHs, namely biphenyl and naphthalene. The reason PAH-based Li-SES is used as the anode instead of an ammonia-based Li-SES anode is that when a Li cell with an ammonia-based anode is discharged, the liquid ammonia changes to gas which can pose as a safety hazard (i.e., gas pressure buildup in the cell).

To prepare the PAH-based Li-SES (PAH used: biphenyl and naphthalene), anhydrous tetrahydrofuran was used as the solvent to dissolve the solid biphenyl and naphthalene to form colorless solutions before metallic lithium is added. The entire preparation process was carried out in argon atmosphere inside a glovebox at ambient temperature. The Li-SESs are denoted as $\text{Li}_x\beta(\text{THF})_n$ and $\text{Li}_y\text{N}(\text{THF})_n$ where β denotes biphenyl, N denotes naphthalene, subscripts x , y , and n represents the mole ratios of the components in the Li-SES. The electrical conductivity measurements on the Li-SES, half-cell open-circuit voltage (OCV) measurements and full-cell configuration studies are described in the following subsection.

a. Half-cell configuration and OCV measurements with Li-SES electrodes

OCV measurement of a half-cell of $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ versus Li metal using a glass ceramic lithium ion-conducting membrane (LATP), that is,

(-)Ni/Li, 1 M LiPF₆ in EC:DEC/ceramics membrane/Li_{1.0}N(THF)_{10.4}/Ni (+)

yields 0.65 V at ambient temperature. With $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$, the OCV versus Li metal is 0.68 V. Figure 2.1.5 shows the schematic diagram of the setup.

Separately, in a comparison study between the two Li-SESs, the cell configuration of (+) $\text{Ni}/\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}/\text{ceramics membrane}/\text{Li}_{1.0}\beta(\text{THF})_{10.4}/\text{Ni}$ (–) yields an OCV of 0.03 V. For this experiment, the contents of the left and right sides of the cell are simply $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ and $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$, respectively.

Figure 2.1.5 Schematic design of the cell to investigate Li-SES anode.

b. Conductivity measurement of Li-SES

The electric conductivity measurements were carried out on Li-SES samples with varying compositions of lithium, biphenyl (β), and tetrahydrofuran (THF) for $\text{Li}_x\beta(\text{THF})_n$ and lithium, naphthalene (N), and THF for $\text{Li}_y\text{N}(\text{THF})_n$ at ambient temperature condition. All measurements were conducted in a dry argon environment.

From Fig 2.1.5, for biphenyl-based Li-SES, the highest absolute conductivity at ambient temperature of 12.0 mS/cm was achieved with the solution $\text{Li}_{1.2}\beta(\text{THF})_{8.2}$ composition $\text{Li}_{1.2}\beta(\text{THF})_{8.2}$, and for naphthalene-based Li-SES, 12.4 mS/cm for the composition $\text{Li}_{0.5}\text{N}(\text{THF})_{6.2}$. A difference between these two types of Li-SES is that even though the naphthalene-based Li-SES has fewer THF solvent molecules in $\text{Li}_{0.5}\text{N}(\text{THF})_{6.2}$, it requires only a mole ratio of $\text{Li}:\text{N} = 0.5:1$ to achieve the highest conductivity of 12.4 mS/cm compared to the biphenyl-based Li-SES which requires a mole ratio of $\text{Li}:\beta = \sim 1:1$ and hence more lithium per biphenyl to achieve 12 mS/cm. Also, both types of Li-SES share the following results:

- (1) When no lithium is present in the solutions, for example $\text{Li}_0\beta(\text{THF})_n$ and $\text{Li}_0\text{N}(\text{THF})_n$, the conductivity is below the measuring range of the conductivity probe. This indicates that when only biphenyl is dissolved in THF, there is too small a number of charge carriers in the solution, if any, and so conductivity is close to 0.
- (2) Conductivity can only be measured when Li is added, which indicates that sufficient charge carriers are formed in the process of Li dissolution.

The temperature dependence of conductivity σ was studied for $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$, $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$, and $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$ solutions in the range of $7^\circ\text{C} < T < 23^\circ\text{C}$. For the $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$ composition, the $\text{Li}:\text{N}$ ratio was 0.5:1 with $[\text{Li}] = 0.5\text{ M}$ and $[\text{N}] = 1\text{ M}$ whereas for the $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$, the $\text{Li}:\text{N}$ ratio was 1:1 with $[\text{Li}] = 1\text{ M}$ and $[\text{N}] = 1\text{ M}$. Each of the three Li-SES samples was first cooled down to $\sim 7^\circ\text{C}$ before conductivity was measured inside the glovebox in an insulated glass container as the temperature slowly rose to ambient temperature over more than an hour. As shown in Fig 2.1.6, for $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$ and $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ solutions in the temperature range of $7^\circ\text{C} < T < 23^\circ\text{C}$, a metallic behavior is observed for both solutions, that is a decrease in conductivity with temperature with quasi-linear behavior. For $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$, $\sigma = 5.1\text{ mS/cm}$ at ambient temperature with a temperature coefficient of $-0.133\text{ mS}/(\text{cm K})$. For $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$, $\sigma = 8.4\text{ mS/cm}$ at ambient temperature with a temperature coefficient of $-0.087\text{ mS}/(\text{cm K})$. By contrast, for biphenyl-based Li-SES of the composition $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$, $\sigma(T)$ follows $\sigma = -0.0941T + 13.5$ (σ in mS/cm and T in $^\circ\text{C}$) with overall conductivity higher than $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ and $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$.

All three Li-SES samples showed metallic behavior (i.e., σ decreases with increasing T) similar to that of ammonia-based Li-SES. Their linear decreasing trend of conductivity with increasing sample temperature further excludes the possibility that both the biphenyl- and naphthalene-based Li-SESs behave like semiconductors or salt solutions containing ions.

Figure 2.1.6 Li-SES electrical conductivity at various PAH/THF compositions, “n,” Li/naphthalene mole ratio “y” in $\text{Li}_y\text{N}(\text{THF})_n$ compositional formulae and Li/biphenyl mole ratio “x” in $\text{Li}_x\beta(\text{THF})_n$.

Figure 2.1.7 Conductivity versus temperature for $\text{Li}_{1.0}\beta(\text{THF})_{10.4}$, $\text{Li}_{0.5}\text{N}(\text{THF})_{10.4}$, and $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$.

2.1.5 Electrolytes for Lithium-Based Rechargeable Batteries

In a battery, the chemical nature of cathode and anode, respectively, decides the energy output, while the electrolyte, in most situations, defines how fast the energy could be released by controlling the rate of mass flow within the battery. Conceptually, the electrolyte should undergo no net chemical changes during the operation of the battery, and all Faradaic processes are expected to occur within the electrodes. Therefore, in an over simplified expression, an electrolyte could be viewed as the inert component in the battery, and it must demonstrate stability against both cathode and anode surfaces. This electrochemical stability of the electrolyte, which in actual devices is usually realized in a kinetic (passivation) rather than thermodynamic manner, is of especial importance to rechargeable battery systems, but it is often challenged by the strong oxidizing and reducing nature of the cathode and the anode, respectively. The severity of this challenge is ever increasing with the pursuit of new battery systems with higher energy densities, which drives the exploration of a more oxidizing cathode and a more reducing anode as requests improvements in electrolyte stability. Ad hoc surface chemistry is often necessary for the kinetic stability of these new electrolyte/electrode interfaces. While the

potencies of electrode materials are usually quantified by the redox potential in volts against some certain reference potential, the stability of an electrolyte can also be quantified by the range in volts between its oxidative and reductive decomposition limits, which is known as the “electrochemical window”. Obviously, the redox potential of both electrode materials must fall within this electrochemical window to enable a rechargeable battery operation.

Certainly, electrochemical stability is only one of the requirements that an electrolyte should meet. A generalized list of these minimal requirements should include the following: (1) It should be a good ionic conductor and electronic insulator, so that ion transport can be facile and self-discharge can be kept to a minimum. (2) It should have a wide electrochemical window, so that electrolyte degradation would not occur within the range of the working potentials of both the cathode and the anode. (3) It should also be inert to other cell components such as cell separators, electrode substrates, and cell packaging materials. (4) It should be robust against various abuses, such as electrical, mechanical, or thermal ones. (5) Its components should be environmentally friendly. [7, 11, 12, 16, 17, 34]

Within the organic electrolyte, the interactions between Lithium and Polycyclic Aromatic Hydrocarbon are complicated and these complicated interactions lead to a series of interesting properties of the electrolyte. Many efforts were devoted to figure out the Lithium-Hydrocarbon interactions and model the charged carrier transport in the solution. The method of Density Functional Theory (DFT) is adopted to study different species of organic molecules like Naphthalene and THF are also examined. Noticing that Hoffmann [4, 35] has done a systematic work on the Lithium-Ammonia Solution system, we will follow his method of computation. The geometric structure and the molecular orbital of Lithium-Hydrocarbon are studied for different organics and with different Lithium Organic ratio. In the current stage of the research, different combination between Lithium and Naphthalene and THF are used in the computation. [36]

The dynamic reactions will enhance our understanding of the electrolytes for Lithium based batteries. The constructed model will help explain relationship between the conductivity of the Lithium solvated electron solution and properties of the solvent used which is still missing in the research related to Lithium-based batteries. Both will make a great contribution to the understanding of Lithium based batteries and searching for the optimal electrolyte as well as liquid anodes for Lithium based batteries.

In the Li-SES battery, ceramic material is usually used as electrolyte in the cell. The practical efficiency of the Li-SES anode relies on the effectiveness of the electrolyte, which also serves as a separator between the anode and cathode. [6] This electrolyte should have high alkali metal ion conductivity, low electron conductivity, chemical impermeability, good chemical stability, and thermal stability. High Li-conducting solid electrolytes based on inorganic materials are expected to be good candidates, such as the adequate ion conductivity and reliable mechanical properties have made LiPON thin film a promising electrolyte for all-solid-state thin film batteries (TFBs). It should be highlighted that the use of all-solid-state electrolyte enhances battery safety and reduces risk of leakage when compared to conventional Li-ion batteries containing flammable liquid organic electrolyte.

The LTAP (including Li, Ti, Al, and PO₄) membrane has high ion conductivity with good impermeability and thus is a promising candidate for a liquid-based Li battery based on a Li-SES anode. In such a battery system, the membrane serves as the electrolyte as well as the separator. However, the LTAP membrane was found chemically unstable in certain conditions. For example, when Li metal is directly applied to the LTAP membrane, the membrane becomes eroded and degraded due to the reduction of Ti⁴⁺ to Ti³⁺. A similar problem occurs with the LTAP membrane facing the Li-SES. Recently, such problems due to the Li metal or Li-SES have been overcome by applying a thin layer of lithium phosphorus oxynitride (LiPON). In this section, a general review of the LiPON thin film with regard to synthesis and application is presented. With the LiPON coating, the enhanced chemical stability of the LTAP membrane in the presence of Li metal and Li-SES is demonstrated.

Adequate ion conductivity and reliable mechanical properties have made LiPON thin film a promising electrolyte for all-solid-state thin film batteries (TFBs). It should be highlighted that the use of all-solid-state electrolyte enhances battery safety and reduces risk of leakage when compared to conventional Li-ion batteries containing flammable liquid organic electrolyte. Typical cathode active materials used in TFBs are oxide-based lithium intercalation compounds, for instance LiCoO_2 and LiMn_2O_4 (Bates et al., 2000). LiPON thin film was found effective in minimizing the slow self-discharge rate and maximizing cycling efficiency. As in the case of Li/LiPON/LiCoO_2 with a 2-mm-thick cathode, the self-discharge per year is less than 2% (Dudney, 2005). In a more rigorous test when a sudden discharge at a high current pulse (around 4C rate) was applied to fully charged TFBs stored at room temperature for different periods of time under open-circuit conditions, the degradation due to self-discharge was negligible.

2.2 Theoretical Background

2.2.1 The Schrödinger equation and Born-Oppenheimer Approximation

To study and predict the properties of atomic and molecular systems including solid state matter, Quantum Mechanic must be used. To describe a quantum system with N nucleons and n electrons, all information can be given by the time-independent Schrodinger equation,[37]

$$\hat{H} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n; \mathbf{R}_1, \dots, \mathbf{R}_N) = E \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n; \mathbf{R}_1, \dots, \mathbf{R}_N) \quad (2.2.1.1)$$

Where $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$ represent the spin and Cartesian coordinates of the n electrons in the molecule, and $\mathbf{R}_1, \dots, \mathbf{R}_N$ are the nuclear coordinates of the N nuclei in the molecule. The Hamiltonian operator is given by, (e-electron, n-nuclear)

$$\hat{H} = T_e + T_n + V_{en} + V_{ee} + V_{nn} \quad (2.2.1.2)$$

where the kinetic and potential energy of n electrons and N nuclei are given by,

$$\begin{aligned} T_e &= -\frac{\hbar^2}{2m_e} \sum_{\mu=1}^{N_e} \nabla_{\mu}^2 \\ T_n &= -\frac{\hbar^2}{2} \sum_{k=1}^{N_n} \frac{\nabla_k^2}{m_k} \\ V_{en} &= -\sum_{\mu=1}^{N_e} \sum_{k=1}^{N_n} \frac{Z_k e^2}{4\pi\epsilon_0 |\mathbf{r}_{\mu} - \mathbf{R}_k|} \\ V_{ee} &= \sum_{\mu=1}^{N_e} \sum_{\nu > \mu}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_{\mu} - \mathbf{r}_{\nu}|} \\ V_{nn} &= \sum_{j=1}^{N_n} \sum_{k > j}^{N_n} \frac{Z_k Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{R}_k|} \end{aligned} \quad (2.2.1.3)$$

Thus, the basic task in quantum chemistry is how to get the exact solutions of Schrödinger Equation. In principle, the exact equation can be written for any system. But in practice, the exact solution is impossible for most systems and approximation schemes

have to be employed. The most famous and accepted extensively approximation is Born-Oppenheimer approximation. [38]

Since the mass of nuclei is much larger than electron, the impact of electrons' motion on nuclei is negligible. So we can separate electron wavefunction and nuclear wavefunction respectively and solve Hamiltonian equation for electron with fixed nuclear coordinates. This is the principle of Born–Oppenheimer approximation, which is written as

$$\hat{H}_{el} \psi_{el}(\mathbf{r}) = E_{el} \psi_{el}(\mathbf{r})$$

The Hamiltonian operator, H , consists of three terms: the kinetic energy, the pair electron interaction (V_{ee}) and the interaction with the external potential (V_{ext}). That is

$$\begin{aligned} \hat{H}_{el} &= T + V_{ee} + V_{ext} \\ &= -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 + \sum_{\mu=1}^{N_e} \sum_{\nu>\mu}^{N_e} \frac{e^2}{|\mathbf{r}_\mu - \mathbf{r}_\nu|} + V_{ext} \end{aligned} \quad (2.2.1.4)$$

So, the question now entirely focuses on the how to solve the electronic equation.

2.2.2 Hatree Fock Theory

We can solve the electronic problem for the simplest atom, hydrogen, which has only one electron. However, the wave function of electron that depends explicitly on the positions of all electrons is not practical to use for many-body system. Therefore, most electron structure calculations on molecules use one-electron function composing of a spatial part and spin up or spin down part, which depend explicitly on the position of only one of the electrons. These molecular orbitals are then most commonly expressed as linear combinations of atomic orbitals, the LCAO approach. The form of these functions is known and they are computationally easy to handle.[17, 38]

Thus, the many-electron wave function can be reduced to a product of several one-electron wave functions, so called Hartree product, ϕ_{HF} . Unfortunately, this wavefunction does not fulfill the Pauli and anti-symmetry principle. Thus, the final wavefunction in the Hartree-Fock method is a Slater determinant.

$$\Psi_{\text{slater}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \dots & \chi_N(x_N) \end{vmatrix} = |\chi_1(x_1)\chi_2(x_2)\dots\chi_N(x_N)| \quad (2.2.2.1)$$

After replacing the wavefunction with Slater determinant into Born-Oppenheimer approximation equation, the Hartree-Fock equation can be obtained with exact exchange-correlation terms.

In order to get the solution of equation, the variational principle is used to give the equation some constraint.

$$\delta E(\psi) = \delta \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = 0 \quad (2.2.2.2)$$

This states that the energy of any approximate wave function is always larger than the exact energy. Thus, the best approximate wave function can be obtained by varying the expansion coefficient of spin orbitals, which are orthogonal under the constraint, until the energy expectation value, $E(\Psi)$, of the approximate wavefunction is minimized. By minimizing E_{elec} with respect to the choice of spin orbitals, the HF energy E_{HF} is obtained.

$$E^{\text{HF}} = \langle \psi_{\text{slater}} | H | \psi_{\text{slater}} \rangle = \sum_i^N \langle i | h | i \rangle + \frac{1}{2} \sum_i^N \sum_j^N (ii | jj) - (ij | ji) \quad (2.2.2.3)$$

Where

$$\langle i | h | i \rangle = \int \chi_i^*(x_1) \left(\frac{1}{2} \nabla^2 - \sum_A^M \frac{Z_A}{r_{iA}} \right) \chi_i(x_1) dx_1 \quad (2.2.2.4)$$

represents the kinetic energy and potential energy for attraction to the nuclei of the electron x_1 , and

$$(ii | jj) = \iint |\chi_i(x_1)|^2 \frac{1}{r_{12}} |\chi_j(x_2)|^2 dx_1 dx_2 \quad (2.2.2.5)$$

$$(ij | ji) = \iint \chi_i^*(x_1) \chi_j(x_1) \frac{1}{r_{12}} \chi_j^*(x_2) \chi_i(x_2) dx_1 dx_2 \quad (2.2.2.6)$$

are Coulomb and Exchange integrals, respectively, which represents the interaction between electrons.

Meanwhile, a set of HF equations are derived by using the variational principle and the set of spin orbitals:

$$f(i)\chi_i(x_1) = \varepsilon_i\chi_i(x_1) \quad (2.2.2.7)$$

where $f(i)$ is an effective one-electron operator, called the Fock operator, of the form

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i) \quad (2.2.2.8)$$

where $v^{HF}(i)$, is the average potential experienced by the i th electron due to the presence of other electrons.

$$v^{HF}(i) = \sum_j J_j(x_1) - \sum_j K_j(x_1) \quad (2.2.2.9)$$

The first term above is the Coulomb operator J , defined as:

$$J_j(x_1) = \int dx_2 |\chi_j(x_2)|^2 r_{12}^{-1} \quad (2.2.2.10)$$

which gives the average local potential at point x_1 due to the charge distribution of other electron in orbital χ_j .

The other term in equation (13) is harder to explain and does not have a simple classical analog. It arises from the antisymmetry requirement of the wave-function. It looks much like the Coulomb term, except that it exchanges spin χ_i and χ_i . Hence, we define the Exchange operator in terms of its action on an arbitrary spin orbital χ_i .

$$K_j(x_1)\chi_i(x_1) = [\int dx_2 \chi_j^*(x_2) r_{12}^{-1} \chi_i(x_2)]\chi_i(x_1) \quad (2.2.2.11)$$

Unlike the coulomb operator, the exchange operator K is a non-local operator as it depends on the value of χ_i not only on x_1 but also throughout all space. Therefore, the self-interaction induced by coulomb operator J when $i = j$ rules out by exchange operator K .

The essence of the Hartree-Fock approximation is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way.[39] Since the average potential will change as the coefficients of all other electrons change, there is no direct way of finding the correct solution. Therefore, the numerical self-consistent field method (SCF) is used. In this scheme, the HF equation is solved iteratively until the wave-function has achieved required convergence. Therefore the mean field does not change any longer, i.e. until the mean field is self-consistent.

In principle, there are infinite numbers of solutions to the Hartree-Fock equation, however, in practice, the Hartree-Fock equation is solved by introducing a finite set of orthogonal HF spin orbitals $\{\chi_k\}$ with orbital energies $\{\varepsilon_k\}$. The spatial parts of the spin orbitals can be expanded in terms of the known set of basic functions $\{\phi_k\}$. The larger and more complete set of basic functions $\{\phi_k\}$, the lower will be the expectation value $E_0 = \langle \psi | H | \psi \rangle$. Larger and larger basis sets will keep lowering the Hartree-Fock energy E_0 until a limit is reached, called the *Hartree-Fock limit*, E_0^{HF} . Therefore, any finite basis set must introduce error to HF energy.[34, 40]

Another weakness of Hartree-Fock [33, 41] equation comes from the *correlation energy*. [34] HF method takes into account the average effect of electron repulsion, but not the explicit electron-electron interaction. Within HF theory the probability of finding two electrons with different spin (electrons with same spin are forbidden due to the anti-symmetry of the Slater Determinant) at the same location is not zero. The correlation energy, E_{corr} , is defined as the energy difference between the exact energy, and the Hartree-Fock *limit*, E_0^{HF} . [42]

The correlation energy is the energy recovered by fully allowing the electrons to avoid each other. Hartree-Fock method improperly treats electron-electron interaction in an averaged way. The development of methods to determine the correlation energy is a highly active research area in conventional quantum chemistry. However, the Hartree-Fock methods finally need to solve an equation, which is still very computationally

expensive. Compared with Hartree-Fock method, DFT is quite fast and cheap, and that is the reason why DFT is quite popular for calculation now.

2.2.3 Density Functional Theory

Hartree-Fock theory is very useful for providing initial, first-level predictions for many molecular systems. However, this method has some basic deficiencies. In HF method, the energy of the molecule and all of its derivative values depend on the determination of the wave-function. The problem is that the wave-function is not a physical observable; that is, the wave-function is purely a mathematical construct. In reality, the wave-function does not exist. When squared and multiplied by the area of the molecule, the wave-function is simply a statistical probability that the electron will be at a specific place or part of the molecule. The second is that the wave-function becomes more complicated mathematically as the number of electrons increases.[43]

Llewellyn Thomas and Enrico Fermi [44] finally found that there was a one-to-one correspondence between the electron density of a molecule and the wave-function of a molecule with multiple electrons. This forms the basis for Density Functional Theory (DFT). Density functional theory is an approach to the electronic structure of atoms and molecules and states that all the ground-state properties of a system are function of the charge density. In DFT, the electron density $\rho(r)$ is the basic variable, instead of the wave function. This reduces the computational burden of treating electron – electron interaction terms, which are treated explicitly as a functional of the density.

Density Functional Theory is a microscopic first-principles theory of condensed matter physics that tries to cope with the electron-electron many-body problem via the introduction of an exchange-correlation term in the functional of the electronic density. With this theory, the properties of a many-electron system can be determined by using functional, i.e. function of another function, which in this case is the spatially dependent electron density. [34] Hence the name density functional theory comes from the use of

functional of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. [7, 9-12, 16, 17, 34, 36, 42, 45-54]

Within density functional theory, there are two fundamental theorems which is called Hohenberg-Kohn Theorems: (1) the ground state density uniquely determines the potential and thus all properties of the system, (2) there exists a density functional $F[n]$ so that the energy functional can be written in terms of external potential $v_{ext}(r)$ in the following way

$$E(\rho(\mathbf{r})) = F(n) + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} \quad (2.2.3.1)$$

The derivative of Kohn-Sham equation relies on the introduction of fictitious reference systems of non-interacting electrons which is constructed with the same electron density as the system of investigation. These electrons are moving in a complex potential that takes into account the actual forms of electron correlation and the difference between the kinetic energy functional of the reference system and the real system.

The reference system of fictitious non-interacting particles has a rigorous solution in terms of single electron wavefunctions, or molecular orbitals. These orbitals are called the Kohn-Sham orbitals. Thus, we can express the kinetic energy exactly for the reference system as the sum of the expectation value of the Laplacian for each electron.

$$T_s[\rho_s] = -\frac{1}{2} \sum_{j=1}^N \langle \chi_j | \nabla_j^2 | \chi_j \rangle \quad (2.2.3.2)$$

assumed that the density of real system, $\rho = \rho_s = \sum_{j=1}^N \sum_{\sigma} |\chi_j(\mathbf{r}, \sigma)|^2$. Then, the total

energy functional of the real system can be written as:

$$E[\rho] = T_s[\rho] + J[\rho] + V_m + Exc[\rho] \quad (2.2.3.4)$$

Where all the unknown parts are collected into the Exchange Correlation energy,

$$Exc[\rho] = T[\rho] - T_s[\rho] + E_{ee}[\rho] - J[\rho].$$

(2.2.3.5)

Now the vibrational principle is applied to get the minimum value of energy. The variables to be adjusted are the KS orbitals themselves. We write the energy functional in terms of the KS orbitals:

$$E[\rho] = -\frac{1}{2} \sum_{j=1}^N \langle \chi_j | \nabla_j^2 | \chi_j \rangle + \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N \iint \langle \chi_j \chi_i | \frac{1}{r_{12}} | \chi_j \chi_i \rangle + Exc[\rho] - \sum_{a=1}^{N_n} \sum_{j=1}^N Z_a \langle \chi_j | \frac{1}{r_{aj}} | \chi_j \rangle + \sum_{a=1}^{N_n} \sum_{b=1}^{N_n} \frac{Z_a Z_b}{r_{ab}} \quad (2.2.3.6)$$

When the derivative of expression(10) are set to zero, the K-S equation is obtained the density of the equation is same as the non-interacting fictitious system

$$\left\{ -\frac{1}{2} \nabla_j^2 - \sum_{a=1}^{N_n} \frac{Z_a}{r_{aj}} + V_{KS}(x_j) \right\} \chi_j = \epsilon_j \chi_j \quad (2.2.3.7)$$

where the effective KS potential in which the non-interacting particles move contains the classical electrostatic interaction and the Exchange-Correlation potential.

$$V_{KS}(\mathbf{r}_1) = \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{xc}(\mathbf{r}_1) \quad (2.2.3.8)$$

This result is regained within a variational context when looking for those orbitals minimizing the energy functional, subject to orthonormality conditions. Notice the Kohn-Sham equation (2.2.3.7) must be solved iteratively just as the Hartree-Fock equations. The Kohn-Sham equations are very similar to the Hartree-Fock equations. In fact, setting the exchange-correlation potential to the HF exchange potential yields the Hartree-Fock equations. However, drawing too many similarities to Hartree-Fock is dangerous. First, the Kohn-Sham orbitals are simply a way of representing the density; they are not an approximation of the wave-function. Also, HF theory is variational, providing an upper bound to the exact energy, yet DFT is only variational if the exact energy functional is used. [39, 44]

Although the final KS equation is easier to solve with only parameter r , the major problem is that the exact functional forms for the Coulomb and Exchange correlation and the correction to the kinetic energy is unknown. The price to be paid for the incorporation of electron correlation is the appearance of the exchange correlation potential V_{xc} , the form of which is unknown and for which no systematic strategy for improvement is available. The central goal of modern density functional theory is therefore to find better and better approximations to the exchange-correlation energy E_{xc} . The currently developed schemes to approximate the exchange correlation functional, $E_{xc}(\rho)$, are mainly three types: local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals. The Local Density Approximation (LDA) is widely used, where the functional depends only on the density at the coordinate where the functional is evaluated. Another approximation is Generalized Gradient Approximations (GGA), which are still local but also take into account the gradient of the density at the same coordinate. In our following calculation, we will use LDA-DFT to calculate all electronic and optical properties.

Local density approximation (LDA) is a class of approximation to the exchange-correlation (XC) energy functional in density functional theory that depends solely upon the value of the electronic density at each point in space. This approximation is based on the uniform electron gas model. [38] This model describes an idealized system of N electrons within a cubical box of volume V , in which the N electrons move on a positive background charge distribution such that the total ensemble is electrically neutral. The charge density $\rho=N/V$, can be obtained and remains constant everywhere. In this model, the E_{xc}^{LDA} can be written as

$$E_{xc}^{LDA} = \int \rho(r) \varepsilon_{xc}(\rho(r)) dr \quad (2.2.3.9)$$

$\varepsilon_{xc}(\rho(r))$ is the exchange-correlation energy per particle of a uniform electron gas of density $\rho(r)$. This energy per particle is weighted with the probability $\rho(r)$ that here is an electron at this position in space. ε_{xc} can be decomposed into exchange and correlation terms linearly, [39]

exchange and correlation terms linearly,

$$\varepsilon_{xc}(\rho(r)) = \varepsilon_x(\rho(r)) + \varepsilon_c(\rho(r)) \quad (2.2.3.10)$$

The exchange part $\varepsilon_x(\rho(r))$, is equal to the form found by Slater in his approximation of the Hartree-Fock exchange and was originally derived by Bloch and Dirac in the later 1920' s,

$$\varepsilon_x(\rho(r)) = -\frac{3}{4} \sqrt{\frac{3\rho(r)}{\pi}} \quad (2.2.3.11)$$

Substitute the $\varepsilon_x(\rho(r))$ with equation (2.37) in equation (2.36), we will get

$$E_{xc}(\rho) \cong C_x \int \rho(r)^{3/4} dr$$

There is no such explicit expression known for the correlation part ε_c . Using parameter fitting, Vosko, Wilk and Nusair obtained the expression of correlation part based on the Monte-Carlo simulation on uniform gas. [40] The currently popular LDA are SVWN and VWN5.

$$(2.2.3.12)$$

2.2.4 Introduction of Gaussian Program

As a popular computational chemistry software package, the name of Gaussian software originates from People's use of Gaussian orbitals to speed up molecular electronic structure calculations as opposed to using Slater-type orbitals, a choice made to improve performance on the limited computing capacities of computer hardware for Hartree-Fock calculations. [41-44] In Gaussian, The mathematical models used to do the computations are called FEM (Final Element Method) and Symplex method. Using matrices, this method cuts the N-dimensional space into small sub-systems that can be described by N linear equations. These equations can be solved as soon as one of them is solved.

Therefore, one must take a guess of the solution and then, recursively solve all the other ones. Once all solutions are obtained, the initial guess can be modified and the calculations repeated. This process is run until the new solution outputs the same result as in the previous iteration. This is called convergence. Because the initial guess can be very far off the real value, many thousands of iterations are often needed. The basis set selected influences, among other, the quality of the guesses, while the theoretical model influences the type of calculations that the matrices will be subjected to. The calculation stops as soon as the result converges, however convergence does not mean that the system reached its minimum. It is very likely that the minimum outputted is actually only a saddle point on the potential surface, but the program will not be aware of this. The user must be careful with this, and always perform a check of stability of the system. This is done by perturbing the "stable" system and re-calculating the minimum. If the output is the same, one can assume that the energy obtained is the total minimum.

To start a G09 job, input file is written as follows:

#X Theoretical model/Basis set Type of calculation Options

- #: mandatory sign to begin route section.
- X : specifies the amount of detail you want to acquire: X = T (terse output);
X = P (max output); X = N (normal output).
- Theoretical model: keyword that tells G09 which theoretical model to use (ex: RHF).
- Basis set: specifies the basis set to use (ex: 6-31G(d)).
- Type of calculation: specifies one or more keywords for G09 jobs to do separated by a space.
- Options: specifies additional options for this job.

Next section is usually composed of the atoms and Cartesian or Z-matrix coordinates. It is possible to calculate and input the coordinates manually, but it is much easier to obtain them through software such as Material Studio, Gaussian View or ChemBio 3D Ultra. These softwares can be used to make the input molecule.

In Gaussian job, the most referred keyword is *opt*, which means geometry optimization. The Geometry optimization procedure attempts to find the configuration of minimum

energy of the molecule. The procedure calculates the wave function and the energy at a starting geometry and then proceeds to search a new geometry of a lower energy. This is repeated until the lowest energy geometry is found. The procedure calculates the force on each atom by evaluating the gradient (first derivative) of the energy with respect to atomic positions. Sophisticated algorithms are then used at each step to select a new geometry, aiming for rapid convergence to the geometry of the lowest energy. In the final, minimum energy geometry the force on each atom is zero. It is important to recognize that this procedure will not necessarily find the global minimum, i.e. the geometry with the lowest energy. By its nature, a successive search for a minimum finds a local minimum but not necessarily the lowest. In fact, the optimization procedure stops when it finds a stationary point, i.e. a point where forces on the atoms are zero, and this may be also a saddle point (i.e. a transition structure). This will occur particularly if we restrict the symmetry of the molecule and do not allow the program to search the full space of molecular configurationally degrees of freedom. It is always a good idea to start a procedure of a geometry optimization calculation with a small basis set and a relatively poor method before we move to the basis set and method of choice for a particular problem. You can then start the final geometry optimization from the geometry selected by the simpler and less accurate approach. We can even use the second derivatives of the energy with respect to atomic coordinates (obtained during the optimization process or from a frequency run 1) to further improve the geometry optimization. Therefore, after the geometry optimization, a stability check is done to ensure achieving the ground state. The stability calculation determines whether the wavefunction computed for the molecular system is stable or not: in other words, whether there is a lower energy wavefunction corresponding to a different solution of the SCF equations. If the wavefunction is unstable, then whatever calculation you are performing is not being done on the expected /desired state of the molecule. The stability of SCF solutions for unknown systems should always be tested. Stability considerations apply and may be tested for in calculations using DFT methods as well. [41-44]

In the third chapter, we want to investigate the electronic nature of a series of Polycyclic Aromatic Hydrocarbons to get associated information concerning the aromaticity or

stability. The electronic structure optimization for the considered categories of PAHs in the thesis was performed using Gaussian 09 package of programs. All structures were optimized at the level of Beckel's 3-parameters hybrid exchange and 40] In order to clarify the ground energy state, unrestricted closed shell singlet, open shell triplet and symmetry broken open shell singlet for each PAH are simulated respectively. Unrestricted closed shell singlet optimization and restricted closed shell optimization provides the identical output data until achieving convergence criteria. In the input file of open shell triplet calculation, spin multiplicity is specified as **3** to describe a triplet state. In order to obtain symmetry broken open shell singlet solution, do the triplet simulation first and restart the program from triplet's scratch file. Initial geometry guess and orbital guess for open shell singlet simulation are read from the output file of open shell triplet relaxation in last step, along with spin multiplicity specified as **1** to describe singlet. Finally, a stability calculation with keyword ***stable=opt*** is performed to ensure a stable wavefunction. Through rigorous sight into the three possible states, the lowest energy state comes to mind naturally. [45-48]

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Chapter Three

Introduction Of Clar Aromatic Sextet Per Ring (CASPER) to evaluate the stability of PAHs

Clar's theory has thrown a giant positive influence on the historical development of Polycyclic Aromatic Hydrocarbons (PAHs) since its first publication. Under the framework of the well-known Clar's Aromatic π Sextet Rule, an intuitive Concept--Clar Aromatic Sextet Per Ring (abbreviation is CASPER) was proposed to quantitatively evaluate the relationship between the shape and stability addressing various PAHs characterized by distinct shape. CASPER means the scale of aromatic π sextet stretching over the whole hydrocarbon, and in the meanwhile, it was demonstrated to be a convenient approach to assess PAHs' stability through application to various categories of PAHs. It is the shape of PAH that determine the distribution of π electron sextet and electronic orbital nature, thus furthermore determine system's physical, chemical and magnetic properties. To justify the information in terms of Clar's rule and CASPER, structures were optimized by first principle calculation systematically. The Singlet-Triplet gap, geometry configuration, electron density of states and so forth are collected and compared with available experimental data. To further strengthen the application of CASPER to various PAH, the binding mechanism of lithium atom binding with different PAHs, including the binding energy, product's geometry and so on, are extensively studied as well.

The chapter is organized as follows. In the first subsection, an explicit review of Clar's π -aromatic sextet rule is given. Previous work in terms of Clar's rule is generally reviewed. In the meantime, CASPR, or Clar Aromatic Sextet Per Ring is introduced aimed to quantitatively weigh the scale of π electron dispensing among the whole system, and furthermore to evaluate the stability and electronic nature of PAHs. In the second section, the four investigated systems are briefly introduced. The four classes of PAHs under examination are 1) linear-shaped polyacenes; 2) Z-shaped extended zethrene series on basis of polyacenes; 3) rhombus-shaped pyrene series; and 4) hexagonal coronene series. In the third section, computational methodology performed in the study is elucidated in details. The density functional theory method has been proven to provide sufficient accuracy to analyze planar hydrocarbons terminated by hydrogen atoms. In the fourth section, preliminary DFT results are explained with respect to CASPER. With the help of CASPER, the optical, electrical and magnetic properties will be understood better. Simulation results are compared with available experimental data. Each chosen PAH series are quite representative to facilitate further enhanced exploration into more complicated PAH categories. Here specifically, the relationship between the topological shape, CASPER and stability of the four representative hydrocarbon series characterized by distinctive profiles is going to be thoroughly explored. Open shell character is discussed for those volatile PAHs. In the next chapter, mechanism of lithium binding with distinct PAHs are checked and discussed. In the final chapter, the main work is highlighted again with future work briefly mentioned.

3.1 Review of Clar's Aromatic Sextet Rule

The discovery of graphene has attracted enormous attention from people in diverse areas due to its fascinating properties and promising applications. [1-5] Polycyclic Aromatic Hydrocarbons (PAHs) are well-defined subunits from the indefinitely two-dimensional graphene sheet with hydrogen atoms attached to the peripheral carbons. The stability or the aromaticity of planar PAHs has been a hot issue for researchers for a fairly long period. To evaluate the stability of diverse compounds characterized by various shape and size, Clar's π Sextet rule has been proven to be a fundamental yet powerful tool. The

basic rule formulated by Erich Clar is based on Kekulé resonance structures. That is, if the alternating single bond and double bond is rotatable within a hexagonal benzenoid ring, like the Lewis resonance structure of benzene, the real bonding among the hexagonal ring was an extended π orbital above and below the plane. This extended π bonding is represented by a circle, and called as Clar sextet. Therefore, a Clar sextet represents electron localization within a hexagonal carbon ring. And a Kekulé resonance structure characterized by Clar aromatic sextets is called as Clar structure. [6-10]

Looking at Clar structures of manifold PAHs, bonding between carbon atoms are illuminated by Clar sextets, single bonds and double bonds. Actually one particular PAH may have several distinct Clar structures, and the number of Clar sextets varies. The Clar structure with the maximum aromatic sextets is the most important one and, the most important structure is conventionally defined as the Clar structure. In following part, if no special indication, Clar structure is the saturated configuration in Kekulé resonance form with maximum Clar sextets. (Here “saturated” means no radicals generated.) The sextet means six π electrons establishing an extended π orbital staying above and below the six-membered ring, which possesses dramatically strong localization and stability. There has been sufficient evidence to support Clar’s aromatic π -sextet rule in past decades. PAHs’ aromaticity or stability is fundamentally determined by structure’s shape, including symmetry, size and periphery etc. Depending on the shape effects, physical, chemical and optical properties varied dramatically. So far Clar’s rule has been applied to various PAHs and prodigious triumph in both academia and industry was achieved. [11-14]

PAHs can be divided into fully benzenoid PAHs and non-fully benzenoid PAHs. Fully benzenoid PAHs are constructed through cutting a graphene sheet into structures only terminated by armchair edges. Due to edge effects, all π electrons are grouped into sextets within a ring with a fixed double bonds embedded in it. In spite of fully benzenoid PAHs generally having large size, the series possess high kinetic stability and low reactivity when compared with their isomers. It is the high-density distribution of Clar aromatic sextets that contributes to their excellent stability. Neighboring Clar sextets of fully benzenoid PAHs are bridged by single bonds in conjugation with no double bond.

Therefore, at the first sight, fully benzenoid PAHs are composed of π circles and empty rings. The unique Kekulé resonance structure is due to aromatic Clar sextets being at rigidly fixed positions following Clar's rule. Experimental publications have demonstrated that optical band gaps of fully benzenoid PAHs are determined by the number of sextets rather than the size or shape. It is noteworthy that this conclusion is not applicable to other classes of PAHs. Comparing two isomers belonging to the series, it is clearly seen that higher symmetry will lead to wider optical gap, and furthermore, upper stability. Take tetrabenzanthracene (D_{2h} symmetry) and tribenzoperylene (C_{2v} symmetry) as an instance, the former compound is characterized by a higher optical energy gap and lower susceptibility to chemical reactions. For non-fully benzenoid PAHs, their bonding configuration is composed of Clar sextets, C=C double bonds and C-C single bond. Investigation of non-fully benzenoid PAHs is more complicated referring to Clar's rule. Take two isomers – anthracene **2** and phenanthrene **3** into account, both of them are established by three fused rings. Anthracene **2** is a straight-line structure assigned with only one migrating sextet merely, and the sextet can be drawn inside any of the three rings. However, phenanthrene **3** is characterized by two aromatic sextets, and possesses superior stability compared to anthracene **2**. The prediction has been proven by instinctive Experimental Resonance Energy Measurement. Material's Resonance Energy is defined as the energy difference between the real ground state energy and a hypothetical molecule containing imaginary alternate single bond and double bond within each six-membered ring. The stability of the system is identified from intuitive Resonance energy value. In this case, the value for anthracene and phenanthrene is 347 kJ/mol and 381 kJ/mol separately. [14, 16, 17, 55, 56]

Since Clar's aromatic π sextet rule was proposed several decades ago, it has been used to evaluate a great variety of PAHs. Abundant theoretical and experimental publications offer convincing evidence to support Clar's rule. In terms of sophisticated quantum mechanical calculation, Singlet-Triplet gap, ionization potential, geometry configuration, electron density of states density and many other properties, provide deep insight on system's intrinsic electronic nature. Meanwhile, certain physical, electronic and optical properties are available from corresponding experimental approaches. There are several

frequently involved experimental approaches to do evaluation. First of all, what must be mentioned is the broad-range absorption spectrum. The thermal stability can be interpreted from magnitude of optical band gap energy, and besides, α -band, p-band, β -band, fluorescence wavelength gives much insight into the nature of electronic orbital. Müllen et al. have reviewed experimental optical gap splitting, typical band wavelength, and fluorescence wavelength for numerous sorts of PAHs. [57] One thing worth to be noted is that the wavelength and intensity of spectrum are dependent on symmetry, size and edge effects. Secondly, a fairly common operation is to interpret the electron density distribution from the high-resolution image of Scanning Force Microscopy (SFM). The principle of SFM is to detect the atomic force between the probe tip and sample surface so that the contour information is acquired. A few publications have reported the successful synthesis of stable PAHs with part peripheral atoms oxidized by oxygen-containing group or other organic group in association with their SFM characterization. Gross et al. have reported the constant-height SFT image of hexabenzocoronene. The image described the distribution of Clar sextets or π electrons, which is in agreement with Clar's prediction. Toshiaki et al. have published some atomic-resolution UHV-STM current tunneling images of PAHs terminated by armchair or zigzag edges. The high resolution images enable a straight and explicit study on the localization status of aromatic π sextet. Lastly but not least, bond length and included angles are accessible from X-Ray Crystallography Diffraction (XRD) and High Resolution Neutron Powder Diffraction, as the localization and delocalization topology, stability of PAH shall be suggested in geometry information. To summarize, whether addressing fully benzenoid PAHs or non-fully benzenoid PAHs, Clar's rule has been proven to achieve extraordinary success in both theoretical and experimental area. [48, 49, 58, 59]

Some large hydrocarbons are characterized by an open shell character in the ground state. Open shell character is defined in contrast to closed shell character, to explain the reactive nature of those PAHs. In the orbital theory, closed-shell PAHs accommodate all even electrons in bonding orbitals. While for open shell PAHs, they signify two free electrons each singly occupying one orbital, which are also called one pair radicals or biradicals. Some reactive compounds can be composed of four electrons or more

electrons, called as polyradicals. [3, 4, 50, 58] Radicals have a fundamental impact on the nature of chemical bonding, and furthermore, on their physical, electronic and magnetic properties. The linear fused polyacenes have aroused particular interest from researchers concerning their chemical bonding, energetic level, geometry correlation, magnetic properties, etc. Some theoretical studies have predicted that higher order acenes are exhibiting open-shell singlet ground state with biradical or polyradical character. Carter et al have predicted that acenes longer than hexacene (including hexacene, $C_{26}H_{16}$) possess an open-shell singlet ground state by density functional theory simulation. Moreover, there was a great deal of experimental evidence to support the transition from closed shell singlet to open shell singlet as the sum of all hexagonal rings is rising. Due to the rapid increasement of reactivity, only small members size up to pentacene ($n=5$ with formula $C_{22}H_{14}$) are easily synthesized and well characterized. Larger members, such as hexacene ($n=6$ with formula $C_{26}H_{16}$) are becoming unstable under room temperature compared with smaller members. The trend from closed shell to open shell may be seen from the transition from insulator to semiconductor, and to easily decomposed species with respect to increasing conjugation length. Short life time, easily photo-oxidation under room temperature was also a kind of evidence to support the open shell character of higher-order acenes. Holger F. Bettinger et al. have reported a chemical route to synthesize pentacene, hexacene and heptacene utilizing matrix isolation technique. Image of 1H Nuclear Magnetic Resonance (1H NMR) is a detectable spectroscopy to justify PAHs to exhibit whether closed shell character or open shell character. I.e., broaden splitting lines of 1H NMR images is indicating the open-shell character, and sharp line is indicating the closed-shell configuration. The closed shell character of size up to pentacene has been proven by 1H NMR.[60] For larger compound, due to their susceptibility under ambient environment, they are synthesized either in special medium (decompose slowly in the medium) or attached with electron-withdrawn group to stabilize the electronic structure. Ascribed to experiment constraint, there is no intuitive broaden splitting curve of 1H NMR. [10, 11, 16, 17, 55, 61-64]

Until now, a great deal of imperative research progress associated with PAHs is working based on Clar's Aromatic Sextet Rule. Clar's rule, initially proposed by Clar and further

developed by Mullen, is a foundation to understand the thermal stability and electronic properties of different PAHs. The key idea in Clar's rule is Clar structure, including the localization of π sextets and the quantity of aromatic sextets. Take anthracene **2** and phenanthrene **3** as example, the armchair-structure molecular characterized by two aromatic sextets is more stable than the linear one with only one sextet, which has been proven by measured experimental resonance energy difference. [40] Another intuitive class is the quasi-one-dimensional polyacenes discussed above. There is only one migrating aromatic sextet existing in the Clar structure in spite of acene's conjugation length. However, the statistical quantity of Clar sextets allocated to each ring is decreasing versus growing conjugation length, which is corresponding to growing experimental resonance energy value. The effect of Clar sextets is to confine electrons staying within the referred ring and stabilize the whole scheme. Inspired by the two simple cases, an index aimed to quantitatively evaluate the scale of Clar aromatic sextets is proposed. It is Clar Aromatic Sextet Per Ring (CASPER), which is defined as the positive integer m divided by n ,

$$CASPER = \frac{m}{n}$$

where m is the total number of Clar sextets, while n is the total number of benzenoid fused rings. With the help of CASPER, the relationship between shape and kinetic stability shall be better performed and empathized. In the chapter, through qualitative estimation on four representative systems characterized by distinct shape, the link between CASPER and stability cooperated with extra physical and chemical properties are scrutinized as well. To elaborate the electronic nature and aromatic properties, geometry optimization is always performed to obtain the lowest energy state utilizing first principle quantum theory. Considering the simulation efficiency and accuracy, all structures are relaxed by density functional theory code. The Singlet-Triplet gap, geometry configuration, orbital distribution and many other properties are accumulated and compared with accessible experimental data. [18, 51, 60] To further emphasize the significance of CASPER concept, the mechanism of metallic lithium atom binding with PAHs is looked into carefully. The binding energy for individual chemical reaction, geometry configuration of reaction product and so forth, are studied substantially as well.

Fig 3.1.1: Clar Structure of Benzene, here the rotational disjoint single-double bond can be replaced by a Clar circle.

Fig 3.1.2: Two kinds of Clar structures of phenanthrene ($C_{14}H_{10}$), where Clar structure 1 is the more aromatic resonance one.

Fig 3.1.3: Three Clar structures of Anthracene ($C_{14}H_{10}$), each with only one single resonance sextet. The three Clar resonance structures are absolutely equivalent in statistics

Fig 3.1.4: The diagram shows the experimental heats of hydrogenation, DH_h , for three molecules, benzene, 1,3-cyclohexadiene and cyclohexene. Energy difference between benzene and cyclohexatriene is benzene's resonance energy.[59]

Table 3.1.1 Experimental Resonance Energy of several small hydrocarbons.

	Number of Clar Circles	Resonance Energy
Benzene	1	152 kJ/mol
Naphthalene	1	255 kJ/mol
Phenanthrene	2	381 kJ/mol
Anthracene	1	347 kJ/mol

[54]

Fig 3.1.5 (a) Clar Structure of Graphene Nanoribbons with armchair edges; such structures composed of aromatic sextet and empty ring are called as fully-benzenoid PAHs and indicate strong kinetic stability; (b) Tunneling current image of a nanographene fragment of oxidized graphene on Au(111) at a sample bias voltage of 50 mV. [65] For nanographene terminated by zigzag edges, the localized and migrating sextets are represented by solid and dotted circles, respectively.

3.2 Investigated Systems

Four intriguing classes of PAHs illuminated in Fig 3.2.1 are under investigation in the chapter. The four categories are 1) *n*-Polyacenes, linear strips of graphene sheet, while *n* is total number of fused benzenoid ring. The series are including naphthalene **1**, anthracene **2**, tetracene **4**, pentacene **5**, hexacene **6**; 2) zethrene series, a *Z*-shaped extension based on linear polyacenes named as zethrene **7**(or hexzethrene), heptazethrene **8**, octazethrene **9**; 3) rhombus-shaped graphene ribbons with C_{2v} symmetry named as pyrene **10**, benzo[bc,kl]coronene **11** and so forth; 4) hexagonal coronene series with chemical stoichiometry $C_{4n^2}H_{6n}$ named as coronene($n=2$) **13**, circumcoronene($n=3$) **14**, circumcircumcoronene ($n=4$) **15**. It is clearly noted that the four stereotypes in illumination scheme denote a conversion from quasi-one-dimensional arrangement to two-dimension arrangement from structure **1** to structure **10**. Referring to the shape of structures, the four categories shall be divided into two groups for study in following sections. The first group is to explore the changing rule from polyacenes to zethrene

series through adding fused rings with armchair boundary. The second group is to compare the stability between rhombus-shaped pyrene series and hexagonal coronene series. As the size of each category of PAH is extending, the variation of physical and electronical properties are studied. Meanwhile, the stability, geometry, spin configuration, orbital information and other electronical properties of large PAHs are compared with small PAHs.

Fig 3.2.1: Clar structures for investigated PAHs in the paper. Circular red filling circles are indicating aromatic Clar sextets.

3.3 Computational Methodology

The electronic structure optimization for the four considered categories of PAHs in the present paper was performed using Gaussian 09 package of programs. All structures were optimized at the level of Beckel's 3-parameters hybrid exchange and Lee-Yang-Parr correlation (B3LYP) functional combined with 6-31g (d, p) basis set. In order to clarify the ground energy state, unrestricted closed shell singlet, open shell triplet and symmetry broken open shell singlet for each PAH are simulated respectively. Unrestricted closed shell singlet optimization and restricted closed shell optimization provides the identical output data until achieving convergence criteria. In the input file of open shell triplet

calculation, spin multiplicity is specified to describe a triplet state. In order to obtain symmetry broken open shell singlet solution, do the triplet simulation first and restart the program from triplet's scratch file. Next do the open shell singlet simulation with spin multiplicity specified to describe singlet, and the initial geometry guess and orbital guess are read from the output file of open shell triplet relaxation. Finally, a stability calculation with keyword *stable=opt* is performed to ensure a stable wavefunction. Through rigorous study of the three possible states, the lowest energy state comes into view naturally.

Resonance Clar structures for investigated PAHs characterized by closed shell singlet are illustrated in Fig 3.2.1. For those hydrocarbons characterized by open shell character, resonance chemical structures decorated with radicals can be symbolized (as exemplified by hexacene in Fig 3.4.1) with supplementary one more or several more aromatic sextet rings inserted. Added a new aromatic sextet plays a role in lowering the reactivity arising from radicals and stabilizing the chemical structure. Another way to understand the radical character of reactive PAHs is from the decreasing CASPER magnitude. One noteworthy point is CASPER value can only be obtained from *normal* Clar structure (*normal* means no radical exhibited in the closed-shell Kekulé structure form). Those resonance structures with radicals are clarifying symmetry-broken open shell character. Singlet-triplet gap, defined as the result of open shell triplet energy minus closed shell singlet energy in the paper, is computed and compared with analogues within all categories of PAHs listed in Fig 3.2.1 to envisage the association between electronic stability and shape effects. Apart from S-T gap, geometry configuration, molecular orbital distribution, spin density of states and so on is inspected to look into PAHs' essential nature. Magnetic properties are explored as well for those PAHs with open shell character. All acquired data are compared with available theoretical publications and experimental papers.

To further emphasize the importance of CASPER, the mechanism of lithium binding with several representative hydrocarbons are analyzed with respect to CASPER. The binding energy, binding sites for lithium atoms and distortion of PAHs is studied. Binding energy is defined as the magnitude of total energy of products minus total energy of reactants.

The initial assumed starting position of lithium plays a vital role in determining the geometry and energy of optimization result after Li-PAH product has achieved convergence criteria. To find how CASPER of different PAHs affects the interaction mechanism, specific single lithium is always put on top of the interstitial ring zone. The relationship of electron affinity for each PAH, binding energy, and CASPER is studied, to support the significant of CASPER.

3.4 Discussion and Results

A. *n*-Polyacene and zethrene series

Applying Clar's rule to *n*-Polyacene, only one migrating Clar sextet can be drawn within the Clar structure as the ribbon length is increasing. By using b3lyp functional, our DFT calculations display a transition from closed shell singlet to open shell singlet around heptacene. That is, closed shell singlet (CSS) energy is lower than open shell singlet (OSS) energy for hexacene ($n=6$, $C_{26}H_{16}$) while CSS is higher than OSS for heptacene ($n=7$, $C_{30}H_{18}$). Referring to DFT calculations, the lowest energy state is triplet, the middle energy level is open shell singlet, and the highest energy level is the closed shell singlet. Energy order from low to high for each individual acene is listed in table [1]. This is in agreement with other published work.

The perceptive stability index, Singlet-Triplet gap splitting, is defined as:

$$\Delta E_{T-CS} = \text{Triplet Energy} - \text{Closed Shell Singlet Energy}$$

ΔE_{T-CS} of polyacenes is plotted versus the total number of fused rings n , indicating a monotonically decreasing trend. (See Fig 3.4.10) In addition, experimental data, high accuracy ab initio computational data using DMRG at basis STO-3G and cc-Pvdz, and coupled cluster theory CCSD(T)/CBS data are taken as reference. CASPER, a vital factor to gauge the effective number of Clar sextets, is equal to $1/n$ for the linear series. (n is the total number of six membered rings.) It could be deducted that the declining S-T gap is in agreement with declining CSPA value. Longer *n*-polyacenes (n is the total number of fused rings), which can be seen as linear expansion from benzene to longer strips along the horizontal direction, are characterized by only one migrating aromatic sextet. However, as the total number of fused rings is increasing, the reactivity is also increasing

monotonically. The observation from Clar's rule amazingly accords with experimental optical gap.

Fig 3.4.1 shows Clar Configuration for Naphthalene, Anthracene and Pentacene molecules. Besides, their bond length both from theoretical prediction and experimental measurement are labeled respectively. The values in black color are taken from closed shell singlet optimization. For comparison, experimental data taken from X-ray crystallographic analysis of synthesis polyacenes crystal is provided tagged by red color in brackets. Referring to Clar structures of naphthalene in Fig 3.4.1, the migrating π aromatic sextet has statistically fifty percent probability to be allocated in the left ring and fifty percent probability to be allocated in the right ring. Therefore, bond **a** is a mixture of benzene sp - sp hybridization and sp^3 - sp^3 hybridization; while bond **b** is a mixture of sp - sp hybridization and sp^2 - sp^2 hybridization. For that reason, bond **a** (1.42Å theoretically, and 1.42Å experimentally, the annotation sequence is kept in following description) should be longer than bond **b** (1.38Å, 1.38Å). Benzene carbon-carbon length is 1.4Å; C=C bond length following sp^2 - sp^2 hybridization is 1.47 Å and sp^3 - sp^3 hybridization is 1.53 Å respectively. Considering the symmetry constraint, only bond **a**, bond **b**, bond **c** and bond **d** need to be analyzed. For the rest unmentioned bond site, just find their symmetrical site and the two sites shall have the same bond length. Bond length for bond **a**, **c** and **d** are closely resembling. The maximum bond length difference for naphthalene **2** is 0.05 Å between bond **d** and bond **b**. The geometry analysis based on closed-shell Kekulé resonance structure endows deep insight into the geometry pattern. Besides, prediction from Clar structure is fairly in consistent with calculated bond length and experimentally measured bond length. Do the bond length analysis through hybridization pattern for higher-order anthracene **2** and pentacene **4**, satisfactory results are achieved as well. Take anthracene **2** as example, bond **b** (1.37Å, 1.37Å) is the shortest bond length among all bond sites, which is a consequence of sp - sp hybridization taking 1/3 portion and sp^2 - sp^2 hybridization taking 2/3 portion. Bond **a** (1.43Å, 1.43Å) is determined by the mixture of benzene sp - sp hybridization taking 1/3 portion and sp^3 - sp^3 hybridization taking 2/3 portion. That is, Clar's resonance structures explain the bond length of Naphthalene, Anthracene and Pentacene molecules quite well, and the structure

prediction from Clar structures has been demonstrated by theoretical and measured bond length. To summarize, fruitful intuitive yet valuable geometry information could be obtained from Clar's structures.

Theoretical calculation shows higher-order polyacenes are expected to display symmetry-broken open shell character at ground state. In the case of linear polyacenes, our simulation shows ground energetic state of hexacene ($n=7$) is characterized by open shell singlet along with unpairing biradicals. Longer the linear acene, more open shell diradical character exhibited. Ground energy states of long acenes beyond the transition length are characterized by open shell triplet. For PAHs always consisted of even number of electrons, an open shell system means the complete $2 \times \chi$ electrons are not perfectly double paired. That is, in the open shell system, there are two separated molecular orbitals each occupied by a single electron, and the two unpaired electrons are annotated as radicals. The chemical resonance structure of hexacene characterized by open shell singlet configuration is exemplified in Fig 3.4.2 Left. To elaborate the distribution of the two unbounding radicals of heptacene, the supplementary density distribution at open shell singlet state is also provided in Fig 3.4.2 Right. It is visible that the two free electrons adopting antiparallel spin are allocated homogenously among the middle zone, conforming to Clar Configuration. The energy difference between closed shell singlet (CS) and open-shell singlet (OS) for heptacene is found to be $\Delta E_{CS-OS} = -2.05 \text{ kcal mol}^{-1}$ and the energy difference between triple (T) and closed shell singlet (CS) is $\Delta E_{T-CS} = 10.9 \text{ kcal mol}^{-1}$. The resonance structure describing open shell character can be regarded as an extension of Clar's rule and gives an excellent explanation for corresponding disjoint nature. It is the extra aromatic sextet that compensates the energy enhanced by radicals and stabilizes the open shell structure. Computational work on the basis of B3lyp/6-31g (d, p) optimization shows the ground energy state is evolving from closed-shell singlet (CS) to open-shell singlet (OS) and to open shell triplet (T) as conjugation length is expanding. And the transition tendency has also been endorsed by previous theoretical and experimental publications.

There is intuitive sharp splitting ^1H NMR spectroscopy for hexacene demonstrating hexacene's closed shell feature at ground state. Since heptacene is quite easily collapsed or photo-oxidized under ambient conditions, heptacene derivatives with electron-withdrawn groups are synthesized for investigation. And these reported heptacene derivatives also show very reactive properties with limited life time. The reactive chemical performance can be seen as evidence to support the open shell character of heptacene and higher-order polyacenes. Bettinger et al. reported a synthetic approach with the help of isolation matrix to achieve clean pentacene, hexacene and heptacene rather than their derivatives at cryogenic temperature.[66] They discovered heptacene is considerably more thermally unstable than pentacene and hexacene. Experimental procedures to evaluate the thermal stability involve evaporating the matrix protected Argon gas carefully and monitor their UV-vis-NIR absorption spectra on a series of adjusting temperature thresholds as system is annealed gradually and then cooled back downwards. When exclusive of the protection from matrix inert gas, nonetheless in a high vacuum environment, and at room temperature, the characteristic UV-vis-NIR absorption spectrum for heptacene is missing, in contrast to stable pentacene and hexacene signal under the same conditions. The unexpected missing signal of absorption spectrum provides fair convincing evidence to support the open shell structure of heptacene with high diradical character. [34, 53, 55, 59]

Fig 3.4.1 Clar Configuration and atomic bond length (Å) for fully relaxed single Naphthalene, Anthracene and Pentacene molecules. The values in black color are taken from DFT closed shell singlet optimization. For comparison, experimental data taken from X-ray crystallographic analysis of synthesis Polyacene crystal is provided noted by red color in brackets.] (For comparison, several typical carbon-carbon bond length values are provided. Benzene C-C length: 1.4Å, sp^2 - sp^2 hybridization: 1.47 Å, sp^3 - sp^3 hybridization: 1.53: Å)

Fig 3.4.2 **Left:** Open shell resonance structure with radicals noted by red dot (**6a** and **6b**); **Right:** Spin density distribution of hexacene ($n=6$, $C_{26}H_{16}$) at the open shell singlet state with biradicals calculated by unrestricted symmetry-broken method. The two free electrons are allocated homogeneously among the middle part, in agreement with the Chemical Configuration following Clar's rule. Blue color and red color are used to discriminate two unpaired electrons.

Table 3.4.1 Computational singlet-triplet gap, singlet*-triplet gap and singlet-singlet* gap (unit: eV) for polyacenes and zethrene series.

compound	ΔE_{T-CS}	ΔE_{T-OS}	ΔE_{OS-CS}
hexacene	0.47	0.38	0.09
heptacene	0.25	0.28	-0.03
octacene	0.08	0.23	-0.15
zethrene	0.76	0.53	0.23
heptazethrene	0.42	0.32	0.10
octazethrene	0.47	0.44	0.02

Singlet* means open shell symmetry broken singlet, ΔE_{T-CS} is defined as triplet minus closed shell singlet, ΔE_{T-OS} is defined as triplet minus open shell singlet, ΔE_{OS-CS} is defined as open shell singlet minus closed shell singlet.

Zethrene molecular series, including zethrene **7** (or hexzethrene), heptazethrene **8**, octazethrene **9**, etc., Z-shaped extension based on linear polyacenes, are involving two armchair edges at bottom left position and right upper position. Through adding two fused rings to pentacene **5** at specified location, zethrene **7** is obtained. Zethrene **7** is composed of two phenalenyl moieties by head-to-head bridging way. Extension of pentacene **5** to longer acenes with triangular phenalenyls fixed gives rise to higher-order heptazethrene **8**

and octazethrene **9**. Take a careful look into zethrene **7** from the perspective of Clar resonance structure and S-T gap, the singlet triplet splitting ΔE_{T-CS} simulated to be 0.76eV for zethrene is wider than heptacene 0.47 eV.

Through analysis on the Clar resonance structure of polyacene series and zethrene series, the most intuitive yet vital conclusion is the difference of the number of Clar aromatic sext rings. For any stretching polyacene, number of Clar circles is forever equal to one; while the number for zethrene series is forever equal to 2. Likely to stretching n-Polyacene, singlet-triplet gap value is calculated for stretching n-zethrene members as well. Taking Polyacene series and zethrene series as studied objects, to justify the relationship between CASPER and aromaticity, their bonding length, spin density distribution, orbital information at Closed Shell Singlet, Open Shell Singlet and Triplet are comprehensively studied. First of all, through comparing the singlet-triplet gap of linear hexacene and Z-shaped heptazethrene, both enclosing six benzenoid rings, zethrene **7** is more stable than hexacene **6**. And this result is applicable to longer acene and zethrene series likewise. Heptazethrene is more stable than heptacene; octazethrene is more stable than octacene. The fundamental reason is attributed to zethrene's superior Clar sextets in quantity, or greater CASPER magnitude based on equivalent overall hexagonal ring number for two objects.

One intriguing finding for zethrenes is the oscillation trend for the singlet-triplet splitting magnitude ΔE_{T-CS} which is defined as open shell triplet energy minus closed shell singlet energy, see Fig 3.4.7. Gap magnitudes ΔE_{T-CS} for zethrene **7**, heptazethrene **8**, octazethrene **9** are 0.76eV, 0.42eV, 0.47 eV respectively. Therefore, two lines for S-T gap (ΔE_{T-CS}) where n is odd and even are plotted respectively. The oscillation of S-T gap owns to the variance of electron delocalization and spin contamination pattern for odd n and even n. Taking an inspection on the Clar structure of zethrene **7** at open shell singlet, one big π orbital is localized in the central part, therefore, two radicals are separated by the inter-unit and they are only residing in the head and tail triangular area. For octazetherene **8**, there is a broader aromatic π orbital composed of two fused benzenoid rings, as a consequence, distance between two radicals turns out to be wider

and their repulsion energy therefore turns to be lower. Generally, distance between two radicals for even number is longer than neighboring odd number in ahead and less repulsion energy accounts for the higher stability. Cramel et al. have reported an oscillation trend of singlet-triplet gap for [n]-cyclacenes, a hoop-like graphene nanotubes.[67] The anticipated even-odd oscillations in the S-T gaps may be attributed to the cryptoannulenic effects of *n*-cyclacenes. They reported odd *n* and even *n* cyclacenes have different HOMO and LUMO distribution.[68] To date, the reported properties of *n*-cyclacenes are only based on theoretical calculations with no experimental data available. [64] Here in the case of *n*-zethrenes, odd *n* and even *n* are characterized by similar spin density distribution for HOMO and LUMO. The oscillating ΔE_{OS-CS} for zethrenes shall be fundamentally attributed to the Clar's structures characterized by Clar sextets and radicals.

For the smallest member, zethrene, the aromaticity could by no means be recovered from closed-shell to biradical resonance form due to the lack of benzenoid space. As a result, all of the zethrene derivatives reported so far adopted a regular closed-shell configuration. The stability of the parent zethrene can be improved by either bay substitution with aryl/alkynyl (1) or peri-substitution by electron-withdrawing dicarboximide groups (2) or by both. The attempted synthesis of the parent heptazethrene and octazethrene were not successful due to their high tendency to polymerize and addition with oxygen. Kinetic blocking of the most reactive sites by TIPSE or aryl groups and thermodynamic stabilization by peri-substitution with dicarboximide groups have been used to obtain stable heptazethrene derivatives and octazethrene derivatives. Recently several publication report the successful synthesise of zethrene series and their derivatives. [10, 45, 50, 53, 55, 69] There are also theoretical predictions that the ground state of heptazethrene derivatives and octazethrene derivatives prefer to show open shell biradical character at ground state. [69] The open shell character has been demonstrated by the low electrochemical bandgap. Broadened 1H Nuclear Magnetic Resonance (NMR) and Electron paramagnetic Resonance (ESR) measurement has confirmed the magnetic properties for some kind of hepzethrene derivatives and octazethrene derivatives at room temperature. Different synthetic methods have been developed for zethrenes and their

analogues with kinetically blocked group to stabilize systems as shown in Fig 3.4.3. [10, 53] Referring to the UV-vis-NIR absorption spectra of synthesized zethrene series attached with alkynyl group in Fig 3.4.3, **3** shows a typical p-band similar to most closed-shell PAHs, while **4~9** display an obviously different pattern, with the emergence of weak absorption bands in the lower energy region (Figure 3.4.4). The origin of these bands is the presence of a low lying excited singlet state dominated by a doubly excited electronic configuration ($H, H \rightarrow L, L$). In addition, the absorption spectra of the singlet and triplet are different from each other and the shift of the singlet–triplet equilibrium can be observed in the temperature dependent absorption spectrum.

Fig 3.4.10: Singlet-Triplet Energy gap (Symmetry Broken Triplet Energy minus Closed Shell Singlet energy) (unit: eV) of linear polyacene versus the total number of aromatic rings of polyacene, calculated by b3lyp/6-31g(d, p). For comparison, the experimental data and theoretical data calculated by other ab initio methods are given. Experimental data is uncorrected for zero point vibrations, thermal vibrations, etc. Theoretical comparison CCSD(T)/CBS, DMRG/STO-3G and TAO-LDA are given.[52, 53, 70-72]

Figure 3.4.3 Chemical structures of the reported stable zethrene derivatives and the resonance structures of the two dibenzo-heptazethrene isomers. SB: singlet biradical; CS: closed-shell; y : singlet biradical character index.[10]

Figure 3.4.4 UV-vis-NIR absorption spectra of **3**~**9** corresponding to structures in Fig 3.4.3 in solution.[10]

(1) Zethrene **7** (2) Heptazethrene **8**

Closed Shell Singlet Calculation

Open Shell Singlet Calculation

X-RAY measurement

(3) Octazethrene **9**

Closed Shell Singlet Calculation

Open Shell Singlet Calculation

X-RAY measurement

Fig 3.4.5 Clar Configuration and atomic bond length (Å) for fully relaxed single zethrene **7**, heptazethrene **8** and octazethrene **9** molecules.

Fig 3.4.6 Calculated b3lyp highest Singly Occupied Molecular Orbital (SOMO) for the spin up and spin down electron respectively and spin density distribution for octazethrene **9** at symmetry broken open shell singlet state. Blue and red color contour represents electrons spin up and spin down respectively.

Fig 3.4.7 (a) Open Shell Singlet Energy Minus Closed Shell Singlet and Spin Contamination of Open Shell Singlet of n -zethrene series; (b) Open Shell Singlet energy minus Closed Shell Singlet energy compare with spin contamination of open shell singlet state ;(c) Clar Configuration for heptazethrene and octazethrene at open shell singlet.

B. Rhombus-shaped pyrene series and hexagonal coronene series

There has been a large quantity of publications focused on strip-like-shape hydrocarbons. When the planar hydrocarbons are characterized by regular two-dimensional shape, their electrical and electronic properties are still unclear and confusing. There was some computational study on the series using DFT method for coronene and pyrene series but few experimental reports for larger expansion. Successful syntheses have been achieved only for the smallest coronene ($C_{24}H_{12}$) and pyrene ($C_{16}H_{10}$). The very few experimental publications are attributed to the manufacturing difficulty to realize big benzenoid structures with smooth edges. There are four main reasons: 1) to cutting graphene sheets or open the cage fullerene C_{60} to graphene flakes, the process involve a series of chemical reactions with many byproducts generated, where the fraction of desired organic structures are very low; 2) it is very hard to separate the pure molecules due to similar chemical properties; 3) due to a series of redox reactions, the prepared samples are usually attached by derivatives rather than pure carbon hydrocarbons; 4) the expansive equipment, long manufacture period, raw material toxicity procedures and some other realistic factors also constrains the experimental results. Therefore, technical reasons restrict the fabrication of those larger fragments. [65, 73-77]

In last subsection, discussion is mainly focused on strip-like-shape hydrocarbons, and in this section, discussion will be extended to two dimensional hydrocarbons with benzenoid rings growing along horizontal and perpendicular orientation. Among so many 2D possibilities, one sort of classification deserves the exploration is the regular hexagon-shaped hydrocarbons which can be extended from coronene. Coronene, also called as superbenzene, is composed of six peri-fused benzenoid rings. The D_{6h} -symmetric hexagonal series with chemical stoichiometry ($C_{4n^2}H_{6n}$) are named as coronene ($n=2$), circumcoronene ($n=3$), circum-circum-coronene ($n=4$) and so forth. Another family is the rhombus-shaped Pyrene series, which has also attracted much attention due to its wide application in abundant area. The smallest member pyrene is composed of four fused rings following rhombus-shape arrangement. There was some computational study on the coronene and pyrene series using fast and cheap DFT coding program but few experimental reports. Referring to available experimental papers until now, the technique

development enables the successful synthesis and characterization for the smallest member-- coronene and pyrene hydrocarbon. However, no experimental publications for large polycyclic aromatic hydrocarbons with high symmetry are reported, which are because edges will collapse immediately and reconstruct significantly under ambient condition.

Following Clar's rule, for the pyrene series, number of Clar aromatic sextets is increasing as structure is expanding, which is always equal to the number of benzenoid rings on one peripheral side. For pyrene series composed of a^2 fused rings, it can be seen that total number of π aromatic sextets is defined as a , together with total number of all rings defined as a^2 . Consequently, CASPER value is equal to $1/a$ (*labelling as 0.5, 0.33, 0.25, 0.2...*), representing an exponential decreasing trend. Within Clar theory, the π electron configuration of a benzenoid hydrocarbon is presented by means of Clar formula, in which circles drawn in certain hexagons indicate that aromatic sextets are located in these hexagons. These "*full*" hexagons are then expected to have significantly greater π electron content than the other hexagons that in the jargon of theoretical chemistry are referred to as "*empty*". The latter hexagons are, of course, not really empty, and their π electron content is certainly much greater than zero. (see Fig 3.4.8.)

Table 3.4.2 Total number of π aromatic sextets, total number of fused benzenoid rings in the structures, CAPER value defined by m/n , calculated Singlet-Triplet gap defined as open shell Triplet energy minus closed shell singlet energy (unit eV) for pyrene series and coronene series.

Pyrene				Coronene			
m	n	CASPER	$\Delta E_{T-CS}/\text{eV}$	m	n	CASPER	$\Delta E_{T-CS}/\text{eV}$
2	4	0.5	2.10226	3	7	0.43	2.59679
3	9	0.33	0.89535	7	19	0.37	1.8436
4	16	0.25	0.14225	12	37	0.32	1.44651
5	25	0.20	-0.30937	19	61	0.31	0.95443
6	36	0.17		21	91	0.23	0.54831

While for hexagonal coronene series, the ratio value CASPER is no longer decreasing so dramatically when the structure is expanding dramatically. As the coronene series are

expanding, the CAPER value shifts from **0.43, 0.37, 0.32...** And structure following rhombus shape easily becomes unstable while coronene structures are always very stable even with hundreds of electrons. The third member of pyrene expanding series ($a=3$) is characterized by an open shell singlet at ground state. It can be seen that the S-T gap versus scale for coronene series has a much slower declining rate compared with rhombus-like structures. (Fig 3.4.7) Actually for coronene series, there is a mathematic rule to calculate total number of benzenoid fused rings, that is $n=3l^2+3l+1$. As predicted by the Clar configuration, hexagonal coronene series are characterized by considerably higher-density Clar aromatic sextets than rhombus-shaped pyrene series, even when coronene have far more fused benzenoid rings. The intuitive impression from the high density aromatic sextets indicated by red circles is accurately expressed by calculated CASPER value. (See Table 3.4.2) In the meantime, our calculated Singlet-Triplet gap comparison defined as open shell Triplet energy minus closed shell singlet energy (unit in eV) demonstrates coronene series are kinetically much more stable than pyrene. Experimental fundamental gap (EA-IP) for coronene is measured to be 6.82eV and the data for pyrene is 7.02eV.[78] [79, 80] In this subsection, through comparing the Clar structure and CASPER value of two representative two-dimensional shaped PAHs, it has been demonstrated that with the help of CASPER, the kinetic stability and electronic natures of manifold PAHs can be well predicted or explained.

Fig 3.4.7 Open Shell Triplet Energy minus Closed shell singlet versus total number of fused rings for hexagonal and rhombus structure hydrocarbons.(energy unit in eV)

Fig 3.4.8 The general member R_a of the homologous series of rhombus-shaped benzenoid hydrocarbons, and the labelling of its hexagons. The right-hand side diagram is the (unique) Clar formula of R_a . Recall that R_1 = benzene, R_2 = pyrene, R_3 = benzo[*bc,kl*]coronene. The *peak hexagons* of R_a are H_{1a} and H_{a1} . The other hexagons adjacent to the perimeter of R_a are referred to as its *boundary hexagons*; those not adjacent to the perimeter are the *internal hexagons*. In the unique Clar formula of R_a , the hexagons H_{1a} , $H_{2,a-1}$, $H_{3,a-2}$, ..., $H_{a-1,2}$ and $H_{a,1}$ are "full" whereas all others are "empty".

Fig 3.4.9 Clar Configuration for coronene, circum-coronene, circum-circum-coronene and so forth. As the structure is expanding, total number of horizontal hexagons on top is increasing from 2, 3, 4 and so forth.

To summarize, referring to Clar's rule and Clar configuration, we are able to get a lot of information including ground energy state, radical properties, geometry configuration,

electron delocalization and many other electronical properties. [18, 19, 31, 38, 51-53, 61, 70-72, 81] In Chapter 4, we will discuss when lithium atom is binding with hydrocarbon compound to simulate the working process of lithium battery, how will the Clar's rule of hydrocarbon compounds influence the performance of battery. Take naphthalene as example, if the anode is composed of lithium metal and cathode of naphthalene dissolved in ammonia solutions, the discharging process is a combination of lithium and naphthalene. The reaction is an Exothermic Reaction, where heat will be generated during the reaction. And the generated heat is directly correlated to the Open Circuit Voltage (OCV) of the total system. In next chapter, more information concerning the relationship between the Clar's rule and their OCV will be discussed. [3, 4, 36, 49, 50, 58, 82, 83]

3.5 Summary

In this Chapter, based on Clar's rule, a theoretical methodology to evaluate the stability of Planar Polycyclic Aromatic Hydrocarbon characterized by diverse shape, size and edges was proposed. At the beginning, Clar's rules and recent development including Müllen's work was briefly reviewed. The intuitive experimental resonance energy for selected PAHs, electron delocalization images, and, characteristic absorption and emission spectra were reviewed to validate Clar's rule. Later then, in the following sections, Clar's rule and Clar configuration together with their CASPER was applied to both quasi-one-dimensional structures and two-dimensional structures. Their electrical and optical properties, including Singlet-Triplet Gap, structure geometry, and radical properties were analyzed systematically. Available experimental data are also provided for comparison.

Through the launch of Clar Aromatic Sextet Per Ring, the electronical structures and stability can be predicted and evaluated. The ground state whether to be closed shell singlet or open shell singlet with radical can be also deducted from Clar's structure and CASPER value. The stability, orbital information, geometry, and other properties of distinct classes of PAHs are deeply explored versus CASPER index. The main findings are:

- 1) CASPER index of linear n-polyacene is equal to $1/n$, in good agreement with monotonically dropping of Singlet-Triplet Splitting gap. That is lower the CASPER in magnitude, more reactive the compound. A lot of intuitive yet valuable geometry information could be obtained from Clar's resonance structures. Higher-order polyacenes are expected to display symmetry-broken open shell character at ground state.
- 2) Z-shaped zethrene series are more stable (with CASPER equal to $2/n$) than the linear polyacenes if two compared compounds are composed of same number of hexagons, which are demonstrated by the Singlet-Triplet gap. There is an oscillation trend of the S-T gap splitting and spin contamination due to delocalization pattern of central π electrons.
- 3) The CASPER index for the rhombus-shaped pyrene series is equal to $1/a$ where a is to the number of benzenoid rings on one peripheral side. There is no general rule to give the CASPER index for the hexagonal coronene series. Calculated Singlet-Triplet gap comparison defined as open shell Triplet energy minus closed shell singlet energy demonstrates coronene series are kinetically much more stable than pyrene series.

In next chapter, the mechanism of lithium binding with PAHs within batteries will be discussed. It can be seen as an application example of CASPER based on Clar's rule to consolidate the significance of CASER. When lithium is binding with these compounds, how Clar's rule affects the binding energy and battery's performance will be studied.

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Chapter Four

Assessment of Interaction between Lithium and Polycyclic Aromatic Hydrocarbons

In this chapter, the interaction mechanism between lithium and various polycyclic aromatic hydrocarbons is studied. A screening is carried out covering 1) naphthalene, biphenyl; 2) polyacenes from naphthalene to pentacene; 3) other hydrocarbons composed of six benzenes. For all the hydrocarbons, the complex geometry, binding energy, open circuit voltage, charge of lithium is studied. Referring to investigated samples, a best cathode candidate is recommended. In the final section, the electrolyte material is extended to PAHs with nitrogen atoms. The reaction mechanism, binding energy, geometry configuration and lithium capacity for three similar materials are investigated.

4.1 Lithium Binding with Naphthalene and Biphenyl

The rechargeable lithium solvated electron solution battery has liquid anodes, which allows for rapid replenishment of the battery stack. Fig 4.1.1 gives one simple working principle: the anode is composed of metal lithium dissolved in solvent, while cathode is composed of naphthalene dissolved in solvent. The discharging process is the combination of lithium and naphthalene. [19, 31, 38, 51, 61, 81, 84]

The liquid anode is prepared by dissolving metal lithium in solvent like LiClO_4/PC . The cathode is prepared by poly-aromatic hydrocarbons dissolved in THF solvent. Actually the effective discharging reaction involves the product lithium-hydrocarbons (here is lithium-naphthalene) complexes generated in cathode. In the discharge process, there are three main steps: 1) ionized Li^+ transits from anode to cathode passing the membrane between two electrodes; 2) free electrons flow through the external circuit; 3) positively charged lithium ion, electron and naphthalene interact together. Condition is reverse for the charge process of battery. Therefore the total reaction means the transform of lithium atoms from anode to cathode and combination with organic hydrocarbons. The chemical reaction is an exothermic process with heat generated to ensure spontaneous occurrence.

At the beginning, the concentration of lithium is low compared to Naphthalene concentration. Therefore, we suppose lithium interact with Naphthalene at ratio 1:1. To find the best simulation model, three kinds of layered geometries with lithium:Nap ratio at 1:1, 2:2, 3:3 are optimized separately. (See Fig 4.1) Along with this, the Open Circuit Voltage (OCV) for each category of reaction with normalization factor is defined by

$$\text{OCV} = -\frac{G}{n * F} = -\frac{\Delta E}{n} * 0.9983$$

Where G is Gibbs Free energy in J, n represents number of electrons transferred in unit mole and F is Faraday constant $96485 \text{ J}/(\text{mol} * \text{V})$. The negative sign in the equation is to make the negative binding energy defined as product's energy minus reactants' energy for exothermic reactions become positive OCV. By means of reaction energy ΔE (in unit

eV) divided by number of electron transferred (n), open circuit voltage is achieved. Take an example for reaction with Li: Nap at ratio 3:3, value of n is equal to 3.

The geometry for lithium combined with naphthalene at ratio $n:n$ has many conditions. The ratio 1:1 with single layer structure has an OCV at 1.2414 Volt. While for the sandwich structure with ratio 2:2, many positions are available for trapping lithium atoms: 1) two lithium atoms are staying between two layers; 2) one atom stay between two layer, one is above or below Naphthalene, for this case, the two atoms can be aligned from top to bottom or staggered up and down 3) both two lithium atoms are staying outside the two layer. Fig 4.1.4 gives the several possible configurations for $\text{Li}_2(\text{Nap})_2$ and their corresponding OCV. It can be seen from the figure that the standard sandwich structure in which the two lithium atoms are staying between two layers has the maximal OCV magnitude 1.61 Volt. This means this structure is the most stable structure among all possibilities. Moreover, the case is also applicable for condition defined by 3:3 ratio. Specifically speaking, when the three Li atoms are staying inside three Naphthalene layers, it has the highest OCV (1.55 V) among all $\text{Li}_3(\text{Nap})_3$ species. (See Fig 4.1.5 for detailed explanation.) This phenomenon is reasonable since in the sandwich-like structure, lithium atoms are captured more tightly by Naphthalene molecules. If the lithium is staying outside the Naphthalene framework, there is higher possibility to escape from the position. Therefore, even normalized to the identical ratio for reactant, calculations demonstrate different layered structure will yield different normalized binding energy or open circuit voltage. It is the binding geometry and positions of lithium atoms critically determine the final open circuit voltage of reaction.

Another noteworthy issue is the practical step-by-step reactions during the discharging process. A simple model to explain reaction process is adding lithium atoms to single naphthalene molecular. From Fig 4.1.3 whose initial geometry is $\text{Li}(\text{Nap})$, the discharging process has a monotonously decreasing trend. The OCV of reaction $\text{Li} + \text{Nap} \rightarrow \text{Li}(\text{Nap})$ is calculated to be 0.5V. And in the next step $\text{Li} + \text{Li}(\text{Nap}) \rightarrow \text{Li}_2(\text{Nap})$, the OCV is simulated to be 1.24 V. The OCV of subsequent reactions is characterized by 0.87 V ($\text{Li} + \text{Li}_2(\text{Nap}) \rightarrow \text{Li}_3(\text{Nap})$), and 0.5V ($\text{Li} + \text{Li}_3(\text{Nap}) \rightarrow \text{Li}_4(\text{Nap})$). This trend is in agreement

with battery's monotonically decreasing OCV during practical discharging process. Moreover, the decreasing OCV trend can be found for process starting from geometry $\text{Li}_3(\text{Nap})_3$. However, for latter condition $\text{Li}_3(\text{Nap})_3$, it has a much high OCV value. In real case, we would like to believe the interaction complexes composed of lithium atoms and Nap molecules would like to embrace more layers for better clustering effect. Definitely thicker the layer model, more reliable simulation results provided. Considering the computational efficiency and convenience for following reaction process, it is reasonable to set up the initial product to be $\text{Li}_3(\text{Nap})_3$. If $\text{Li}_3(\text{Nap})_3$ is set up as the initial geometry, the OCV from $\text{Li}_3(\text{Nap})_3$ to $\text{Li}_4(\text{Nap})_3$ and to $\text{Li}_5(\text{Nap})_3$ in the next step is decreasing. See Fig 4.1.6 In this model, three is a pronounce change of binding energy Van Der Waals force term is added into the simulation.

To take the Van Der Waals force into account, M06 functional in G09 package is utilized for DFT method. All layer structures are optimized using M06 functional and b3lyp functional respectively. And it is observed that data obtained by M06 functional has a slightly higher OCV than b3lyp, for example, the OCV for Li-naphthalene is 0.4961V by b3lyp functional and 0.4917V by M06 functional. It seems the Van Der Waals Force interaction incorporated in Schrödinger equation plays a minor influence on the magnitude of binding energy and open circuit voltage. A computational screening covering diverse Li-Nap complexes characterized by different ratio and geometry configuration demonstrates that the magnitude of binding energy by b3lyp functional and M06 functional is very close to each other. This is principally because the Van Der Waals Force interaction potential is subtracted in the definition equation of binding energy. The distance between metallic lithium atom and naphthalene plane is estimated to be 1.62 Å if applying b3lyp functional in DFT program and 1.63 Å if applying M06 functional. Considering the estimation errors due to hexagonal ring's distortion, the variance is neglectable. The most prominent variance is the lithium charge transferred to hydrocarbon naphthalene, which is 0.22 for b3lyp and 0.33 for M06 functional. In other words, ionic positive charge of lithium in the Li-Nap complex simulated by b3lyp is less than M06 functional. And this comparison conclusion applies to other screening complexes characterized by distinct ratio. There was experimental publication showed

that OCV measurement of a half-cell of $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ versus Li metal using a glass ceramic lithium ion-conducting membrane (LATP), represented as (-)Ni/Li, 1 M LiPF_6 in EC:DEC/ceramics membrane/ $\text{Li}_{1.0}\text{N}(\text{THF})_{10.4}$ /Ni (+), yields 0.65 V open circuit voltage. OCV measurement for Li-SES full cell where anode is composed of THF/naphthalene/Li/LiI mixed solution, and cathode is composed THF/naphthalene/LiI solution, gives 1.2V at the initial point and then OCV drops linearly and keeps at -1.157V at three constant days. OCV measurement between anode THF/naphthalene/LiI/Li and cathode THF/naphthalene/LiCl is 1.103V with a constant current at -3.51mA during following 24hours. OCV measurement between anode THF/naphthalene/LiCl/Li and cathode THF/naphthalene/LiCl yields 2.177V with a constant current at -3.51mA during 24hours. The objective of of above three tests is to confirm Li ions are transferred thoroughly between anode and cathode. And the overall reaction is:

It is noticed other components in liquid electrodes will greatly influence the OCV results.

For solvated electron solution cell, the PAHs have many options. Previous paper has reported successful liquid lithium solvated electron solution which can be employed as anode in redox flow battery. The chemical component of Lithium solvated electron solution is Lithium-Naphthalene-THF mixtures or Lithium-Biphenyl-THF mixtures. Naphthalene is edge shared while biphenyl is composed of two bond-linked benzenes. From the perspective of Clar's configuration, Naphthalene has one Clar sextet while biphenyl (β) has two full Clar aromatic sextets. Geometry of naphthalene is characterized by a planar hydrocarbon while there is a slight rotation between the two bond-linked hexagons' plane of biphenyl.

At the reaction ratio set to be 1:1 for both Li: nap and Li: β with lithium atom allocated on top of one hexagonal ring, the binding complexes are fully optimized by DFT method. A set of initial geometries with the distance between lithium atom and hexagon adjusted are computed so that the most stable complex structure and highest OCV are discovered.

Reading from the most stable complex (the lowest energy state) among all possibilities, the combination of lithium-nap produces higher OCV (0.5V) than lithium- β (0.27V). For Li- β complex, position of lithium located on top of the benzenoid ring gives almost the same OCV value (0.27V) as on top of the linked bond. Experimental OCV is 1.2V for naphthalene and 0.7V for biphenyl. In the Li-SES cell, anode is prepared by dissolving lithium 1M LiClO₄/PC solution and cathode is prepared by THF/Naphthalene/LiI mixture (LiI is insoluble in the solution). Ignoring the reference's difference, our theoretical predictions are in good agreement with experimental measurement. Therefore, from the perspective of normalized binding energy or open circuit voltage, naphthalene is a better cathode candidate than biphenyl in the chemical cell. Furthermore, referring from the simulation results, the lithium charge transferred to naphthalene is 0.55 and charge transferred to biphenyl is 0.055, indicating naphthalene's superiority as an electron acceptor than biphenyl.

Experimental measurement of a half-cell of Li_{1.0}N(THF)_{10.4} versus Li metal using a glass ceramic lithium ion-conducting membrane (LATP), that is, (-)Ni/Li, 1M LiPF₆ in EC:DEC/ceramics membrane/Li_{1.0}N(THF)_{10.4}/Ni (+) yields 0.65 V at ambient temperature.[8] . [9-13] OCV 0.65V is lower than 1.2 V mentioned in last paragraph. This is reasonable since principle of the half-cell with 0.65V OCV is describing process of lithium binding with Li_{1.0}N(THF)_{10.4}.

Fig 4.1.1 Working Principle for studied Lithium Solvated Electron Solution Cell. In the discharge process, 1) ionized Li^+ transits from anode to cathode; 2) electrons flow through the external circuit; 3) positively charge lithium ion, electron and naphthalene interact together. Condition is reverse for charge process.

Fig 4.1.2 Illustration of Lithium-naphthalene and Lithium-biphenyl complexes.

Table 4.1.2 Binding Energy, Open Circuit Voltage and Charge of lithium for reaction $\text{Li} + \text{nap} \rightarrow \text{Li}(\text{nap})$ and $\text{Li} + \beta \rightarrow \text{Li}(\beta)$. Structures are optimized at B3LYP/6-31g** level.

	Li- nap	Li- β
Binding Energy /eV	-0.4969	-0.2748
Open Circuit Voltage	0.4961	0.2744
Charge of lithium	0.22	0.055
Exp OCV[85]	1.2	0.7

Fig [4.1.2] Possible Products on Cathode during discharge process.

Fig [4.1.3] Optimized geometry for $\text{Li}_2(\text{Nap})$, $\text{Li}_3(\text{Nap})$, $\text{Li}_4(\text{Nap})$ and reaction energy for each step with one lithium added in.

Fig [4.1.4] Open Circuit Voltage for reaction utilizing b3lyp/6-31** method $2\text{Li} + 2\text{Nap} \rightarrow \text{Li}_2(\text{Nap})_2$ with four possible arrangement for reaction products. Charge for Lithium ion in the complex is also provided. It can be seen the standard sandwich structure where the two lithium atoms are staying between two layers generate the highest heat energy.

Fig [4.1.5] Open Circuit Voltage utilizing b3lyp/6-31** method for reaction $3\text{Li} + 3\text{Nap} \rightarrow \text{Li}_3(\text{Nap})_3$ with four possible arrangement for reaction products. It can be seen the first structure with three lithium atoms located within the Nap framework has the highest OCV.

Fig [4.1.6] a) Output Transformation (b) Open circuit Voltage utilizing b3lyp functional and M06 functional, magnitude of the first point is from reaction $3\text{Li} + 3\text{Nap} \rightarrow \text{Li}_3(\text{Nap})_3$ for Reaction $\text{Li} + \text{Li}_{n-1}(\text{Nap})_3 \rightarrow \text{Li}_n(\text{Nap})_3$. Following are OCV data through adding lithium atoms one by one to the sandwich-like complexes.

Fig [4.1.7] OCV for reaction $\text{Li} + \text{Nap} \rightarrow \text{Li}(\text{Nap})$ (up and left); $2\text{Li} + \text{Nap} \rightarrow \text{Li}_2(\text{Nap})$ (up and right); $\text{Li} + \text{Beta} \rightarrow \text{Li}(\text{Beta})$ (down and left); $2\text{Li} + \text{Beta} \rightarrow \text{Li}_2(\text{Beta})$ calculated by M06-DFT method. Here, Nap means Naphthalene; Beta means Biphenyl.

4.2 Lithium Binding with Acenes

In last section, the discharging processes involving the lithium interacting with naphthalene biphenyls were discussed. Actually since biphenyl does not belong to a planar Graphene Nanoribbon, it is not accurate to relate binding energy to the so-called Clar structure for biphenyl. Based on the research work focused on the stability and electronical properties of manifold Polycyclic Aromatic Hydrocarbons, it seems to be promising to build up a close connection between the Clar structures and binding mechanism of PAHs with the lightest metal lithium. The binding energy or open circuit voltage is a vital factor to determine the working performance of lithium solvated electron solution battery. Aimed to find an excellent PAH material utilized in solvated electron solution battery, the binding mechanism of lithium interacting with various classes of Polycyclic Aromatic Hydrocarbon are going to be simulated systematically as well.

In this section, lithium binding with the quasi one-dimensional acenes including naphthalene, anthracene, tetracene, pentacene and hexacene will be studied. Referring to the conclusion in last chapter, there is always only one migrating Clar aromatic sextet in the Clar structure. Therefore, CASPER index, the effective scale of aromatic π sextets stretching over the whole hydrocarbon, is monotonically dropping in magnitude. The kinetic stability is also monotonically decreasing corresponding to the shift trend of CASPER. For the chemical combination of lithium and strip-like acenes, lithium atom is located in the middle part on top of the plane. For acenes composed of even hexagons, the lithium is put above one of the two central hexagons. As the ribbon length of linear acene is expanding gradually, more and more heat energy (or higher and higher OCV) will be released during the chemical reaction. Theoretical simulation by means of b3lyp/6-31g(d, p)++ theory in Gaussian program gives Naphthalene a positive electron affinity at 0.38eV. The experimental adiabatic electron affinity for naphthalene is around -0.18eV through analysis on electron transmission spectra. [81-84,86] The experimental electron affinity for consequential polyacenes from anthracene to hexacene is also negative and comes to be larger and larger in magnitude. The negative electron affinity

means these polyacenes prefer to accommodate extra electron with extra heat generated. Such a feature makes the combination of lithium and polyacenes an exothermic process.

As the linear acenes are expanding their conjugation length, binding energy for reaction lithium:acene at ratio 1:1 turns out to be larger and larger in magnitude, representing more heat energy generated after reaction. Positive charge of ionic lithium is becoming larger and larger in magnitude, which means more electrons from lithium atom are transferred to the organic hydrocarbon. The changing trend of binding energy and charge of lithium is in consistent with the electron affinity. That is, longer the acene, more negative the electron affinity, and higher Open circuit voltage. Therefore, from the perspective of binding energy, anthracene is a better candidate as cathode component than naphthalene. [9-13]

Table 4.1.1 Theoretical Vertical Electron Affinity (VEA) of acenes, Binding Energy (BE) for reaction $\text{Li} + \text{acene} \rightarrow \text{Li}(\text{acene})$, charge of lithium for $\text{Li}(\text{acene})$ complexes employing b3lyp/6-31g(d, p)++ theory in Gaussian program.

	<i>complexes</i>	<i>VEA/eV</i>	<i>BE/eV</i>	<i>CHG(Li)</i>
2	Li_naphthalene	-0.38	-0.5	0.22
3	Li_anthracene	0.43	-0.84	0.307
4	Li_tetracene	1	-1.15	0.323
5	Li_Pentacene	1.41	-1.32	0.336
6	Li_Hexacene	1.72	-1.46	0.341

4.3 Lithium binding with other Planar Aromatic Hydrocarbons

In this section, the modelling compounds would be expanded from the simplest strip-like polyacenes to more categories of aromatic hydrocarbons. Four typical structures --- hexacene g_1 , tribenz[a,h]anthracene g_2 , zethrene g_3 , and coronene g_4 are under study. These four compounds labeled as g_1 g_2 g_3 g_4 allow the wide application to practical lithium battery material attributing to the convenient access in lab. The first three compounds g_1 g_2 g_3 are composed of six aromatic hexagons while the last hexagonal coronene compound g_4 has seven fused ring. Binding energy for lithium and hexacene g_1 is calculated around -1.46eV. Tribenz[a,h]anthracene g_2 is characterized by armchair edges while zethrene is characterized by zigzag edges. In coincidence, binding energy for g_2 and g_3 are same in magnitude even though two structures are distinct in shape and electronical properties. Considering the kinetic and thermal stability in solvent, tribenz[a,h]anthracene g_2 is a better choice as electrode material than hexacene g_1 and zethrene g_3 . The stability arises from Clar's configuration that compound g_2 has three aromatic sextets while compound g_3 has two aromatic sextets, and higher density of delocalized π aromatic electrons will contribute to higher stability. In Table 4.3.1, vertical electron affinities for the four structures are given. For comparison, the binding energy for each reaction is given. And it can be realized that more negative the vertical electron affinity, higher energy released during the reaction. Comparing g_1 , g_2 and g_3 , all composed of six benzenoid fused rings; g_2 is characterized by three aromatic sextets, being the most stable structure among the three species. Compound g_2 tribenz[a,h]anthracene is have two For all the screening candidates simulated in the chapter, the combination of one coronene and one lithium atom generates the most amount of energy. The coronene has a vertical electron affinity at -4.7eV and binding energy at -4.67eV. Therefore, from this perspective; coronene is the best candidate material among all the screened hydrocarbons.

Fig 4.3.1 Illustration of lithium binding with zigzag and armchair Polycyclic Aromatic Hydrocarbons. The lithium atom is located on top of the plane, and above the central position of one hexagon. Chemical name of compound *g1* *g2* *g3* *g4* are hexacene, tribenz[a,h]anthracene, zethrene and coronene in consequence.

Table 4.3.1 Simulated Vertical Electron Affinity (VEA) for the four compounds listed in Fig 4.3.1, Binding Energy (BE) for the chemical reaction $\text{Li} + \text{g}_x \rightarrow \text{Li}(\text{g}_x)$, charge of lithium for $\text{Li}(\text{g}_x)$ complexes. (energy unit in eV) Modelling are simulated by DFT method utilizing b3lyp functional and 6-31g(d, p)++ basis embedded in Gaussian 09 program.

<i>compounds</i>	<i>VEA/eV</i>	<i>BE/eV</i>	<i>CHG(Li)</i>
<i>g1</i>	1.72	-1.46	0.341
<i>g2</i>	1.62	-0.61	0.357
<i>g3</i>	1.92	-0.61	0.326
<i>g4</i>	4.7	-4.67	0.398

4.4 Lithium Capacity for Solvated Electron Solution Battery

In addition to hydrocarbons, electrode components can be those PAHs with nitrogen atoms replacing some carbon atoms. In this section, the interaction between Li atoms and such molecules are investigated to study the effect of Li atoms on the HOMO-LUMO gap of the complex, the reaction energy of forming the binding structures and the preferred binding sites of Li atoms. We also compare the difference between the bindings of Li atoms with different molecules and try to find out a rule which could explain the different and predict the changing trend when we change the polymers.

Three polymer structures *p2*, *p4*, *p7* are presented in Fig [4.4.1]. In the figure, the gray balls, white balls and blue ball represent Carbon atoms, Hydrogen atoms and Nitrogen atom correspondingly. In Fig [4.4.1], *p2* and *p4* present a planar structure while for *p7*, it is twisted. The two wings orientate themselves in two perpendicular planes. If we replace the two wings by two Hydrogen atoms, it would become the structure of Methane. We investigated the HOMO-LUMO gap of the Li-polymer complexes to see how Li atoms would affect the gap and how the gap would be different for the three polymer molecules. The results were presented in Fig [4.4.2]. In the figure, black squares represent the results for *p2*; red triangles represent the results for *p4* and blue circles represent the results for *p7*. For the same number of Li atoms bound to the polymer molecules, we studied different possible binding geometries and compare these geometries to figure out the structure with lowest energy. The lines in the figure connect the set of data representing the most energetically favored structures among those possible binding structures between Li atoms and polymer molecules.

From Fig [4.4.2], it is noticed that the HOMO-LUMO Gap of the Li-Polymer complexes generally tend to decrease when we add more Li atoms to bind with the polymer molecules. This trend works well when the number of binding Li atoms does not exceed 6. When the number of Li atoms bound with the polymer molecules is larger than 6, the effect of these Li atoms on the HOMO-LUMO Gap of Li-polymer complexes become not so clear. For *p2*, the gap is enlarged when more Li atoms were added. While for *p4* and

p7, an oscillating gap is observed. When we examined the geometries of these Li-Polymer complexes, it was noticed the structures for Li-p2, Li-p4 and Li-p7 were quite similar except that for Li-p4, the two wings of the structure could rotate and for Li-p7, the two wings could rotate and fold. The rotating and folding behavior of the structures might lead to the different respond of the HOMO-LUMO Gap. It is also observed that the HOMO-LUMO Gap of Lixp2 is generally larger than that of Lixp4 and Lixp7. (Add some explanation)

We further investigated the interaction energy of forming the binding structures between Lithium atoms and polymer molecules through the reaction $x \text{ Li} + \text{Polymer} \rightarrow \text{Li}_x\text{-Polymer}$. The reaction energy of adding 2 additional Li atoms to the binding complex through reaction $2 \text{ Li} + \text{Li}_{(x-2)}\text{-Polymer} \rightarrow \text{Li}_x\text{-Polymer}$ were also studied. The results were presented in Fig 3.

In Fig [4.4.3], the total reaction energy of forming the binding structures through the reaction $x \text{ Li} + \text{Polymer} \rightarrow \text{Li}_x\text{-Polymer}$ ($x = 2 - 12$) was represented by the empty squares, triangles and circles with solid lines. While the reaction energy of adding 2 additional Li atoms to the biding complex using the most energetically stable structure is represented by the filled squares, triangles and circles with dotted lines. The reaction energy is negative and keep decreasing for $x = 2 - 12$, indicating that the process is exothermic. The figure also shows that when we add more Li atoms to the binding complexes, the energy released by adding Li atoms becomes smaller. This increment in reaction energy is partly accounted by the Li-Li repulsion interaction when more Li atoms were added. At some point, the reaction would increase above zero which will characterize the capacity of Li atoms for the polymer molecules.

From the figure, it is also noticed that the decreasing amount of reaction energy of forming Li-Polymer complexes become much smaller when the binding Li atoms is more than 6. It is consistent with the sharp jump in the reaction energy of adding two additional Li atom to the Li6-Polymer complex. From $x = 2$ to $x = 6$, the reaction energy of adding 2 Li atoms to the structures increases but it is kept at a similar level. This observation

suggests that for $x = 2 - 6$, the Li atoms would bind to the polymer molecules in a similar way. After that, the reaction energy experience a large increment when we add 2 more Li atoms to form Li₈-Polymer. The jump in the reaction energy implies that there might be a change in the configuration of the binding structures when the number of binding Li atoms exceeds 6. While from $x = 8$ to $x = 12$, the reaction energy is again kept at a similar level, indicating that the additional Li atoms would bind to the polymer molecules in the same way as they do in Li₈-Polymer. To explore the binding configuration further, we examined the geometries of the complexes.

In Fig [4.4.4], we presented the geometries of binding structures between Li and p2 with number of Li atoms varying from $x = 0$ to $x = 6$. From the figure, we find that each time we add more Li atoms to the p2 molecules, these Li atoms bind with the Nitrogen atoms at the empty sites. It shows that the Nitrogen atoms have a stronger affinity to Li atoms than Carbon atoms.

Similarly, the geometries of binding structures between Li and p4 and p7 with number of Li atoms varying from $x = 0$ to $x = 6$ were shown in Fig 5 and Fig 6 respectively. For all the three polymer molecules under investigation, Li atoms bind to the polymer molecules in the same way: fill up empty sites and bind with Nitrogen atoms. From $x = 0$ to $x = 6$, the binding configuration between Li atoms and polymer molecules remains unchanged which is consistent with reaction energy presented in Fig 3, the reaction energy of adding 2 additional Li atoms is kept at a similar level.

In Fig 4.4.7, it could be found out that the energy of the geometries listed on the left side of the figure is lower, indicating an energetically more stable structure. Although all Nitrogen atoms have been bound to a Li atom in the structure of Li₆p2, additional Li atoms added to the molecule still prefer to bind with the Nitrogen atoms. Also, if we compare the structure of Li₈p2 and Li₆p2, it could be found that the Li atoms in Li₈p2 are no longer in the same plane with Nitrogen atoms and Carbon atoms. The 2 added Li atoms would break the bond between Li atoms and Nitrogen atoms and form new bonds. At the binding sites with 2 Li atoms, one Li atom is located above the plane and the other

below the plane. Due to the change in the configuration of the binding Li atoms, there is a large drop in the energy released by adding these 2 Li atoms to the molecule. Reflected in Fig 3, it was a sharp jump in the reaction energy. If we add the number of Li atoms up to 10 or 12, the additional Li atoms would still prefer to break the existing Li-Nitrogen bond and bind with Nitrogen atoms at the binding site where only 1 Li atom is around. The process is the same to the process when we add 2 Li atoms to Li_6p_2 which explains the similar reaction energy level from $x = 8$ to $x = 12$.

We also examined the geometries of Li_xp_4 and Li_xp_7 when x is greater than 6. The same to the case of Li_xp_2 ($x > 6$), additional Li atoms also break the existing Li-Nitrogen bond and form new bond with the Nitrogen atoms at the binding site with only 1 Li atom around.

When more Li atoms were added to Li_6 -Polymer, the location of these Li atoms would worth a closer sight. As shown in Fig 4.1.4, Fig 4.1.5 and Fig 4.1.6, with 6 Li atoms, all the Nitrogen sites were filled with Li atoms. If any extra Li atoms come in, would they bind with the Carbon atoms or they would still prefer Nitrogen atoms and break the existing bonds to change the configuration. To figure out the answer as well as to explain the jump in the reaction energy adding 2 Li atoms to the complexes, we tried to place the Li atoms at different initial positions. The geometries for Li_8p_2 were presented in Fig 7.

Fig [4.4.1]: molecular structure of the polymers. Gray balls represent Carbon atoms; white balls represent Hydrogen atoms and blue balls represent Nitrogen atoms. a) Molecular structure of p2; b) Molecular structure of p4; c) Molecular structure of p7.

Fig [4.4.2]: The HOMO-LUMO Gap of the Li-Polymers complexes. Black squares represent Li-p2 structures; Red triangles represent Li-p4 structures; Blue circles represent Li-p7 structures. The solid lines in the figure connect the data of the most energetically stable structures.

Fig 4.4.3: The reaction energy of forming the Li-Polymer complexes and the reaction energy of adding 2 additional Li atoms the polymer molecules. Open markers with solid lines describe the total reaction energy of forming Lixp2, Lixp4 and Lixp7; filled markers with dotted lines describe the reaction of ad

Fig 4.4.4: Geometries of Lixp2 structures ($x = 0 - 6$). Pink balls represent Li atoms. It shows that Li atoms prefer to bind with Nitrogen atom in the p2 molecules.

Fig 4.4.5 Possible Geometries of Li_xP_4 ($x = 0 - 6$).

Fig 4.4.6 Possible Geometries of Li_xP_4 ($x = 0 - 6$).

Li₈p₂

Fig 4.1.7: Geometries and corresponding energy of the geometries of different binding configurations between Li atoms and p₂ molecule when Li number is 8. The structures on the left side of the figure shows the geometries and energy when Li atoms all bind to Nitrogen atoms; the structures on the right side shows the geometries and energy when 2 Li atoms bind to Carbon atoms.

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Chapter Five

A molecular Perspective Study on Lithium Tetrahydrofuran Solution

In this chapter, the possible species and complexes existing in Lithium-Tetrahydrofuran Solution were studied by a first principle method –Density Functional Theory (DFT). In the first section, we will study the information about geometry, molecular orbital, dipole moment and electron affinity both at gas phase and solvent phase. Based on the knowledge on one single THF molecular, geometry, charge distribution and reaction energy concerning neutral THF cluster $(\text{THF})_n$ and negatively charged anions $(\text{THF})_n^-$ will also be studied. In the second section, three existing species describing interaction of lithium and THF including neutral $\text{Li}(\text{THF})_n$, positively charged $\text{Li}(\text{THF})_n^+$ and negatively charged $\text{Li}(\text{THF})_n^-$ are systematically investigated. Their geometry configuration, contour diagram, spin distribution and binding energy are supplied.

5.1 A molecular Perspective Study on Tetrahydrofuran

In the lithium redox battery, THF plays a role as solvent. In this chapter, following Hoffman et al's work, we are going to investigate lithium binding with Tetrahydrofuran (THF) fluids. [2]THF, an organic compound defined by formula $(CH_2)_4O$, is often used as aprotic solvent in lithium solvated electron solution. (The chemical structure is shown in Fig 5.1.1). THF is a colorless liquid with an ether-like odor. [46] Its density is 889 kg/m^3 , lower than water. As a moderately polar solvent, THF is miscible with water and can dissolve in many polar or nonpolar organics like alcohols, ketones, etc. Our calculation gives a substantial dipole moment at 1.82D in the gas phase. Pure THF solution has a low viscosity at 0.53 cP when environmental temperature is controlled around 20 Celsius ($^{\circ}\text{C}$) degree. THF could be manufactured by Catalytic hydrogenation from furan with nickel catalyst. [3, 6, 36, 49, 50, 64, 82, 83, 89] Another popular method is through acid-catalyzed dehydration of 1,4-butanediol. [18, 51, 55, 60, 61, 81]

In gas phase, our theoretical estimation shows the single THF molecule has a positive electron affinity at 3.8395eV. This means it does not bind an extra or excess electron. P Sulzer *et al.* reported an experimental Electron Affinity of THF located around 1.25 eV in the absence of the calibration gas. The laboratory technique is using crossed electron/molecular beams to generate dissociative anions followed by mass spectrometric detection. [60] This feature is similar to NH_3 , that is, ammonia also has a positive electron affinity in the gas phase. There have been some theoretical predictions that ammonia cluster consisting of more than 30 or 35 molecules will have a positive electron affinity. [4] The characteristic property has also been proven by experiment that [1] the ammonia cluster must contain at least 13 ammonia molecules in order to bind an excess electron. [5, 8, 23, 26, 42, 54, 62, 65, 90-92]

The two highest occupied orbitals and the lowest unoccupied orbitals for THF are given in Fig 5.1.1. (Isovalue=0.02, plotted by Chemissian software). The dipole moment of a molecular is defined by the following equation

$$\vec{\mu} = \sum_i q_i \vec{r}_i \quad (3.1.1)$$

Where $\vec{\mu}$ is the final dipole moment vector, q_i is the charge of the single atom numbered by i , and $\vec{r}_i$ is the position vector of corresponding atom. Calculations are summed over all atoms in the molecular.[4, 35, 58]

Our Gaussian calculations at DFT level show THF has a substantial dipole moment at 1.82 Debye in gas phase and 2.15 D in liquid phase. In this chapter, calculations considering solvent effects is by utilizing keywords SCRF=(solvent=THF) in the input file based on Polarizable Continuum Model (PCM). [18, 51, 60, 81] This model is based upon the idea of generating multiple overlapping spheres for each of the atoms within the molecule inside of a dielectric continuum. [31, 38, 52, 53, 70-72] This method treats the continuum as a polarizable dielectric and thus is sometimes referred to as dielectric PCM (DPCM). The PCM model calculates the free energy of solvation by attempting to sum over three different terms: electrostatic energy, dispersion-repulsion energy and cavitation energy. The cavity used in the PCM is generated by a series of overlapping spheres normally defined by the van der Waals radii of the individual atoms.[26, 31, 38, 52, 53, 70-72, 93-96]

THF's geometry arrangement calculated by DFT method is in agreement with MP2 data and experimental measurement. (See table 5.1.1) Experimental geometry parameters were measured by two different techniques including X-ray crystallography and High resolution neutron powder diffraction. [9, 45, 93-98] When size of neutral cluster $(THF)_n$ is expanding, we find the cavity become larger and larger, that is, the O-O distance between each molecule become longer and longer. For $n=2-3$, the cavity is larger in solvent phase than in gas phase. The Oxygen-Oxygen distance for $(THF)_2$ is 3.34 Å in gas-phase and 6.63 Å in solution phase. For $(THF)_3$, the neighboring three oxygen distances are 3.67 Å, 4.36 Å, 6.59 Å for notation $O_1-O_2, O_2-O_3, O_3-O_1$ in gas phase and 3.88 Å, 4.67 Å, 6.74 Å in solvent phase. When molecular cluster size is increased to $(THF)_4$, the oxygen

distances are 4.18 Å, 4.0 Å, 4.27 Å, 4.20 Å noted by O₁—O₂, O₂—O₃, O₃—O₄, O₄—O₁ in gas phase and 4.06 Å, 4.35 Å, 4.52 Å, 4.28 Å in solvent phase.

As the cluster size is expanding, the solvent effect is no more obvious, which can be explained by the approaching value of neighboring Oxygen-Oxygen distance no matter in gas phases or solvent phase. (see table[3.1.1])

For THF cluster consisting of 2~4 molecules, the highest occupied molecular orbital and lowest unoccupied molecule orbital are contributed by only two THF elements. In addition, when cluster is consisted of four molecules, it can be still find that only two THF molecules make the most contributions for the HUMO and LUMO orbitals. (See Fig[4.1.3]) HUMO-LUMO gap for (THF)_n is monotonically decreasing for n from one member to three members. (See Fig [4.1.7]) However from (THF)₃ to (THF)₄, gap rises up. This is due to the fourth THF didn't interact with the other three THF members, which can be explained by the geometry of (THF)₄.

When one negative charge is introduced to THF clusters, the charge is mainly distributed within the cavity of THF clusters, which can be seen from the mapped contour spin density distribution as well as the single occupied molecular orbital (SOMO). (see Fig[4.1.5]&[4.1.6]). In (THF)₄⁻, the charge is mainly distributed among three elements, with the fourth THF only weakly associated with the cluster (THF)₃⁻. And all the observations are also applicable when solvent effects are considered. So in conclusion, the THF would like to form a team with 3 members, each team with one electron. From (THF)₄ gas phase to charged (THF)₄⁻ gas phase, the cavity become large due to the charge repulsion. From (THF)₄ gas phase to (THF)₄ solvent phase, the cavity has a slightly very minimal extension, which has been discussed before. From (THF)₄⁻ gas phase to (THF)₄⁻ solvent phase, the cavity becomes small. From (THF)₄ solvent phase to (THF)₄⁻ solvent phase, the cavity becomes large. Table [4.1.2] gives the magnitude of cluster binding energy step by step where equation is defined by (THF)_{n-1} + THF → (THF)_n and (THF)_{n-1}⁻ + THF → (THF)_n⁻ at both gas and solution phase. (Unit in eV)

Previous theoretical simulations and experimental publications have shown that liquid THF have preexisting empty space with parameters ranging from 2.5 to 5 Å therefore it is able to act as a well-prepared electron trapping center. [11-19, 31, 38, 51, 52, 55, 56, 60, 61, 70, 81] The picture for THF to accommodate electrons is sharply divergent from the process for water to solvate electrons. For water, solvated electrons need to push aside water molecules to form a cavity at around 2.5 Å, allowing electrons entering inside. Sanche [90] has used the picture to explain why THF thin film is able to trap low energy electrons at a comparatively high efficiency. At solvent phase, neutral $(\text{THF})_4$ cluster cavity has a slightly small expansion to anionic $(\text{THF})_4^-$, which can be justified from the Oxygen-Oxygen Distance form a circular shape. Consequently, our modelling result is in agreement with previous paper.

Fig 5.1.1 Chemical Structure for Tetrahydrofuran (THF). Each of the four carbons is attached by two hydrogen atoms.

Table 5.1.1 Geometry of THF calculated by Gaussian packages at b3lyp/6-31g(d,p) level, compared with MP2 and experimental data.

	B3lyp/6-31g(d,p)	MP2/6-31G(d)(5D) ^a	X-Ray ^b	HRNPD ^c
Bond Length (unit:Å)				
O—C ₁	1.42	1.4353	1.435	1.438
C ₁ —C ₂	1.54	1.5258	1.531	1.516
C ₂ —C ₃	1.55	1.528	1.531	1.101
Angular (Unit °)				
ϑ_1	112.16	109.3	109.8	109.9
ϑ_2	108.58	106.17	106.7	106.4
ϑ_3	105.34	101.12	109.9	102.6

^a MP2/6-31G(d)(5D) is taken from [5] ^b X-ray crystallography measured at 148K, taken from ref[59], ^c High resolution neutron powder diffraction at 5K, taken from ref[54]

Fig 5.1.2 The mapped contour diagrams of the two highest occupied and lowest unoccupied orbitals of Tetrahydrofuran. (Plotted by Chemission with isovalue=0.02)

Fig 5.1.3: Optimized geometry of (THF)_n (n=1-4) complexes in gas-phase.

Fig 5.1.4 Mapped contour of the highest occupied molecular orbital and lowest unoccupied molecule orbital of (THF)_n (plotted by Chemissian ,isovalue=0.02)

Table [5.1.1]: The Oxygen-Oxygen distance of neighboring THF molecules for neutral (THF)_n and charged (THF)_n⁻ clusters (n=1-4) in gas phase and liquid phase (unit in Å)

	A ₁	A ₂	A ₃	A ₄
Gas phase				

n=2	3.64			
3	3.67	4.36	6.59	
4	4.179	4.0	4.027	4.1995
Solvent phase				
n=2	6.63			
3	3.88	4.67	6.74	
4	4.06	4.35	4.52	4.28
(THF) _n ⁻ in gas phase				
n=2	10.03			
3	4.03	7.55	6.01	
4	11.25	5.76	11.40	10.57
(THF) _n ⁻ in solvent phase				
n=2	8.81			
3	4.18	6.23	7.68	
4	4.50	6.77	4.53	8.96

* A₁, A₂, A₃, A₄ represent neighboring Oxygen-Oxygen Distance. For n=2, A₁ means O₁—O₂; For n=3, A₁, A₂, A₃ means O₁—O₂, O₂—O₃, O₃—O₁; For n=4, A₁, A₂, A₃, A₄ means O₁—O₂, O₂—O₃, O₃—O₄, O₄—O₁. (O₁, O₂, O₃, O₄ represent the oxygen atoms noted in sequence.)

Fig[5.1.5] Spin density distribution of charged $(THF)_n^{-}$, calculated in gas phase.(Plotted by GaussView; Density isovalue=0.0008 for n=1, 0.0006 for n=2, 0.0004 n=3, 0.0003 for n=4)

Fig[5.1.6] Mapped surface of Singly Occupied Molecular Orbital for charged anion $(THF)_n^-$, calculated in gas phase. (Plotted by GaussView; MO isovalue=0.02 for n=1,2,3 and 0.015 for n=4)

Table[5.1.2] Binding energy of neutral $(THF)_n$ and charged $(THF)_n^-$ clusters (n=1-4) with each equation claimed in the following chart. (Unit in eV)

Formation equation	$\Delta E_{gas}/\text{eV}$	ΔE_{solv}
$THF+THF \rightarrow (THF)_2$	-0.4463	-0.2950
$THF+(THF)_2 \rightarrow (THF)_3$	-0.2041	-0.2890
$(THF)_3+THF \rightarrow (THF)_4$	-0.3728	-0.2944
<hr/>		
	$\Delta E_{gas}/\text{eV}$	ΔE_{solv}
$(THF)^- + THF \rightarrow (THF)_2^-$	-1.6953	-1.3530
$(THF)_2^- + THF \rightarrow (THF)_3^-$	-0.4572	-0.3097
$(THF)_3^- + THF \rightarrow (THF)_4^-$	-1.5565	-0.9148

Fig [5.1.7] HOMO-LUMO Gap for $(\text{THF})_n$ cluster in gas phase and solvent phase.

5.2 Interaction of Lithium with Tetrahydrofuran

5.2.1 $\text{Li}(\text{THF})_n^+$: the Solvated Lithium Cation

When lithium is dissolved in solvent THF, lithium is ionized and solvated in the solution. The Lithium cations will coordinate with THF molecules to form a first solvation shell; therefore, the cationic complexes $\text{Li}(\text{THF})_n^+$ are the dominant species present in the lithium-THF solution. It is interesting to know how many THF molecules one Li^+ prefers to have in its first coordination sphere. Fig [5.2.1] provides the optimized geometry of cationic $\text{Li}(\text{THF})_n^+$ (for $n=1-4$). When ion Li^+ is surrounded by two or three THF molecules, it shows good symmetry. When the fourth THF is added in, things become

different. The initial guessed geometry is of symmetry C_{4v} following CH_4 . After optimization, one of the Lithium-Oxygen bonds broke down and thus it yields a slightly distorted $Li(THF)_3^+$, with an isolated THF molecule nearby. The distance between cation Li^+ and the fourth THF is $4.54\text{\AA}$, much longer than the distance ($1.893\text{\AA}$) between Li^+ and other three THF molecules. Clearly, Li^+ can be coordinated up to three THF molecules in its first coordination sphere; the fourth THF is only weakly associated. This speculation is in agreement with the binding energy of equation $Li^+ + n(THF) \rightarrow Li(THF)_n^+$ ($n=1-4$). (see table [4.1.1]). It implies $Li(THF)_3^+$ is the most energetically favored structure.

For cationic complexes $Li(THF)_n^+$ (for $n=1-3$), the Li-O bond length increases slightly when the number of coordinated THF molecules increases. Part of the reason for this length increase is due to the electrostatic interaction between the positively charged Lithium cation and dipole moment of the THF molecules. When more THF molecules added to the complex, the dipole-dipole repulsion will partly offset the effect the attraction between Lithium cation Oxygen atoms in the molecules. Geometry of $Li(THF)_2^+$ is linear with O-Li-O angle being 180° , following symmetry C_{2v} . $Li(THF)_3^+$ remains to be a planar structure, following symmetry C_{3v} . That is, it forms an equilateral triangle with 120° O-Li-O angles. $Li(THF)_2^+$ and $Li(THF)_3^+$ are possessed of a nearly zero dipole moment attributed from their high symmetric geometry. The magnitude of the binding energy per THF molecule decreases with increasing n for both gas phase and solvent phase.

The isosurface and contour diagrams of the triply degenerate 3t2 HOMOs of $Li(THF)_3^+$ is presented in Figure 4.2.3. The energy gap between filled and unfilled orbital levels of the complex is calculated to be 7.49 eV, which is quite large. The binding energy in solution phase is slightly larger than that in gas phase, implying that the Polarizable Continuum Model has a slightly larger stabilizing effect on $Li(THF)_3^+$ than it does on Li^+ .

5.2.2 $Li(THF)_n$: The neutral Lithium atoms in the solution

When Lithium is added to the THF solvent, most of the Lithium is ionized and still some Lithium exists in the solution in the form of solvated Lithium atom. Similar to the case of Li(THF)_n^+ , it turns out that the most favored complex of Li(THF)_n is Li(THF)_3 when the coordination number is 3, as shown in Figure 4.2.2 and Table 4.2.3.

It is noticed that the geometries of Li(THF)_n are very similar to that of Li(THF)_n^+ , especially when $n = 3$. Compared with Li(THF)_2^+ , the Li-O bond is bent by an angle of 89° for Li(THF)_2 . Also, the Li-O bond length for solvated Lithium atom is slightly stretched when $n = 1, 2$ and the bond length is longer than that of solvated Lithium cation. It is expected. The Lithium atom is bonding with the THF molecules through covalent bond. When the Lithium atom is coordinate by only one THF molecular, the weak covalent bond is formed between the Lithium atom and the Oxygen atom. When another THF molecule is introduced, the covalent electron of Lithium atom is equally shared by the two THF molecules, thus weakening the bond strength. The bond length is longer than that of solvated Lithium cation because there is extra ion-dipole attraction for the Lithium cation case.

Li(THF)^+
Li-O :1.798Å

$\text{Li(THF)}_2^+//C_{2v}$
Li-O distance:1.812Å

$\text{Li(THF)}_3^+//C_{3v}$
Li-O distance:1.893Å

Li(THF)_4^+
Li-O distance:1.89Å & 4.54Å

Fig [5.2.1] Optimized geometry of $\text{Li}(\text{THF})_n^+$ complexes. ($n=1-4$) The gas-phase Li-O distances and Li-O-Li angles are also provided.

Fig [5.2.2] Optimized geometry of neutral $\text{Li}(\text{THF})_n$ complexes. ($n=1-4$) The gas-phase Li-O distances, Li-O-Li angles and charge of lithium are also provided. Lithium atom can be coordinated up to three THF molecules.

Fig 5.2.3(a)Contour and (b) Isosurface (Isovalue=0.04) diagrams of the three degenerate highest occupied orbitals of $\text{Li}(\text{THF})_3^+$. The plane of contour diagrams pass through three Li-O bond

Fig [5.2.4] SOMO of neutral $\text{Li}(\text{THF})_n$ ($n=1,2,3$; plotted by chemissian Isovalue=0.02)

Table [5.2.1] The binding energy for reaction $\text{Li}^+ + n(\text{THF}) \rightarrow \text{Li}(\text{THF})_n^+$ ($n=1-4$) in gas phase.

n	ΔE	$\Delta E/n$
1	-2.36	-2.36
2	-5.0006	-2.5003
3	-6.4314	-2.1438
4	-6.2287	-1.5571

Table [5.2.2] The binding energy for reaction $Li^+ + n(THF) \rightarrow Li(THF)_n^+$ (n=1-4) in solvent phase.

n	ΔE	$\Delta E/n$
1	-3.5864	-3.5864
2	-5.0006	-2.5003
3	-6.4314	-2.1438
4	-6.2287	-1.5571

Table [5.2.4] The binding energy ΔE & $\Delta E/n$ for $Li + THF \rightarrow Li(THF)_n$ in gas phase.

Equation	Bind energy (unit eV)	
	ΔE	$\Delta E/n$
$Li + THF \rightarrow Li(THF)$	-0.955	-0.955
$Li(THF) + THF \rightarrow Li(THF)_2$	-1.804	0.902
$Li(THF)_2 + THF \rightarrow Li(THF)_3$	-2.784	-
		0.928
$Li(THF)_3 + THF \rightarrow Li(THF)_4$	3.312	-
		0.783

Table [5.2.5] The binding energy ΔE & $\Delta E/n$ for $\text{Li} + \text{THF} \rightarrow \text{Li}(\text{THF})_n$ in solvent phase.

Equation	Bind energy (unit eV)	
	ΔE	$\Delta E/n$
$\text{Li} + \text{THF} \rightarrow \text{Li}(\text{THF})$	-1.143	-1.143
$\text{Li}(\text{THF}) + \text{THF} \rightarrow \text{Li}(\text{THF})_2$	-1.886	-0.943
$\text{Li}(\text{THF})_2 + \text{THF} \rightarrow \text{Li}(\text{THF})_3$	-2.555	-0.852
$\text{Li}(\text{THF})_3 + \text{THF} \rightarrow \text{Li}(\text{THF})_4$	-1.903	-0.476

Table [5.2.6] The binding energy for following reactions in gas phase and solvent phase.

Equation	Bind energy (unit eV)	
	Gas Phase	Solvent Phase
$\text{Li} + \text{THF} \rightarrow \text{Li}(\text{THF})$	-0.955	-1.143
$\text{Li} + 2\text{THF} \rightarrow \text{Li}(\text{THF})_2$	-0.849	-0.7428
$\text{Li} + 3\text{THF} \rightarrow \text{Li}(\text{THF})_3$	-0.980	-0.669
$\text{Li} + 4\text{THF} \rightarrow \text{Li}(\text{THF})_4$	-0.3483	-1.143

Table [5.2.7] Lithium-Oxygen Bond length for $\text{Li}(\text{THF})_n$ ($n=1,2,3$) after optimization with specified symmetry in both gas phase and solvent phase. (unit Å)

Molecular	Li-O Bond length(unit Å)	
	Gas Phase	Solvent Phase
$\text{Li}(\text{THF})$	1.898	1.924
$\text{Li}(\text{THF})_2$	1.964	1.95
$\text{Li}(\text{THF})_3$	1.893	1.893

Fig [5.2.5] An isosurface of somo of triangular $\text{Li}(\text{THF})_3$ from vertical view (left) and front view(right)(Isovalue=0.02 a.u.)

Fig [5.2.6] (a) Spin density distribution (Isovalue=0.004 a.u.), and (b) Contour diagram of SOMO of the triangular $\text{Li}(\text{THF})_3$. The plane of the contour diagram contains three Li-O bonds. The SOMO contains a large amount of THF homo-1 orbital. It's like pi orbital

Table [5.2.8] Dipole moment for $\text{Li}(\text{THF})_n$ and $\text{Li}(\text{THF})_n^+$ in gas phase. (unit: debye)

n	Dipole moment/(unit: debye)	
	$\text{Li}(\text{THF})_n$	$\text{Li}(\text{THF})_n^+$
1	8.5074	8.5072
2	5.5459	0.003
3	0.0254	0.0056
4	3.0259	3.226

Fig[5.2.7] Isosurface of SOMO of Li(THF)_3 (left, isovalue=0.02) and $(\text{THF})_3^-$ (middle, isovalue=0.015) and lithium 2p orbital. Here the $(\text{THF})_3^-$ has the same geometry as Li(THF)_3 but without the lithium atom in the central point.

$\text{Li} + 3\text{THF} \rightarrow \text{Li(THF)}_3$	$\text{Li}^+ + 3(\text{THF}) \rightarrow \text{Li(THF)}_3^+$
$\Delta E_{\text{gas}} = -2.615\text{eV}$	$\Delta E_{\text{gas}} = -5.8\text{eV}$
$\Delta = -2.555\text{eV}$	$\Delta E_{\text{sol}} = -6.431\text{eV}$

Fig [5.2.8] Optimized geometry for Li(THF)_3 and Li(THF)_3^+ . Our modelling results show neutral complex and cationic complex has the same geometry. In addition, reaction energy at both gas phase and solvent phase are provided.

5.3 Summary

In this chapter, a molecular perspective study was carried out to study the possible species existing in the Li-THF solution including $(\text{THF})_n$, $(\text{THF})_n^-$, Li(THF)_n , including $(\text{THF})_n$, Li(THF)_n^+ . The main findings are listed below:

- 1) The geometry configuration of neutral THF cluster or the anionic cluster in both gas phase and solution phase was studied. It was found when one negative charge is

introduced to THF clusters, the charge is mainly distributed within the cavity of THF clusters. THF would like to form a team with 3 members, each team with one electron. From $(\text{THF})_4$ gas phase to charged $(\text{THF})_4^-$ gas phase, the cavity become large due to the charge repulsion. From $(\text{THF})_4$ gas phase to $(\text{THF})_4$ solvent phase, the cavity has a slightly very minimal extension. From $(\text{THF})_4^-$ gas phase to $(\text{THF})_4^-$ solvent phase, the cavity becomes small due the solution effects.

2) The binding mechanism of lithium cations binding with THF to generate $\text{Li}(\text{THF})_n^+$ is studied as well. When lithium is dissolved in solvent THF, lithium is ionized and solvated in the solution. The Lithium cations will coordinate with THF molecules to form a first solvation shell therefore the cationic complexes $\text{Li}(\text{THF})_n^+$ is the dominant species present in the lithium-THF solution. It is noticed that $\text{Li}(\text{THF})_3^+$ is the most energetically favored structure. In addition, the binding energy in solution phase is slightly larger than that in gas phase, implying that the Polarizable Continuum Model has a slightly larger stabilizing effect on $\text{Li}(\text{THF})_n^+$ than it does on Li^+ .

3) Similar to the case of $\text{Li}(\text{THF})_n^+$, the binding mechanism and for lithium binding with THF to generate $\text{Li}(\text{THF})_n$ is studied. It turns out that the most energetically favored complex of $\text{Li}(\text{THF})_n$ is $\text{Li}(\text{THF})_3$ when the coordination number is 3. The Lithium atom is bonding with the THF molecules through covalent bond. When the Lithium atom is coordinate by only one THF molecular, the weak covalent bond is formed between the Lithium atom and the Oxygen atom. When another THF molecule is introduced, the covalent electron of Lithium atom is equally shared by the two THF molecules, thus weakening the bond strength. The bond length is longer than that of solvated Lithium cation because there is extra ion-dipole attraction for the Lithium cation case.

The preliminary study on the complexed species existing help to understand the microscopic picture of lithium solvated electron THF solution. There is still much to be done. To further

understand the system, more kinds of species existing in the solution will be studied in the near future.

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Chapter 6

Conclusions and Future work

Lithium based batteries plays an irreplaceable role in today's information age. The most widely used batteries nowadays are the solid lithium ion batteries(LIB), which can be found in portable devices like laptop, hand phone, calculator, and cameras and so on. However, one big disadvantage for LIB is the long charging time and restricted output power. One alternative to overcome the disadvantage is the lithium solvated electron solution battery. For the lithium solvated electron solution battery, the electrolytes are composed of liquid solutions, and they can be replaced immediately after discharging process. Such design allow for rapid replenishing of the battery stack and high energy storage capacity.

In the battery, the anode is composed of lithium solvated electrons solution (Li-SES) . The Li-SES is prepared by dissolving metallic lithium in a solution of poly-aromatic hydrocarbon (such as biphenyl and naphthalene) in tetrahydrofuran (THF). And the cathode is composed of other carbon containing structures dissolved in solvent. During the discharging process, the lithium in anode will escape from the anode and recombine with the carbon structures in cathode. In this thesis, all the carbon containing structures are planar polycyclic aromatic hydrocarbons. We want to investigate the interaction mechanism between lithium and hydrocarbons.

In Chapter 1, hypothesis, investigate scope and key findings are listed. In Chapter 2, the background knowledge about lithium battery and Density Functional Theory are shorted reviewed. The main discussion parts are Chapter 3, Chapter 4 and Chapter 5. Chapter 6 talks about the conclusion and future work.

In Chapter 3, various planar Aromatic Hydrocarbons were studied. They were characterized by different kind of shape, size, geometry, edge and show different electric and electronical properties. We proposed a method called as Clar Rule's to evaluate the

stability of hydrocarbons. By utilizing of Clar's rule, the ground state, geometry configuration, spin distribution, orbital information are better understood.

In chapter 4, the interaction mechanism between lithium and various polycyclic aromatic hydrocarbons was studied. A screening is carried out covering 1) naphthalene, biphenyl; 2) polyacenes from naphthalene to pence; 3) other hydrocarbons composed of six benzenes. For all the hydrocarbons, the complex geometry, binding energy, open circuit voltage, charge of lithium is studied. Referring to investigated samples, a best cathode candidate is recommended. In the final chapter, the electrolyte material is extended to polymer with nitrogen atoms. The reaction mechanism, binding energy, geometry configuration and lithium capacity for three similar polymers are investigated.

In chapter 5, a molecular perspective study was done for lithium solvated electron solution following Hoffman et al's paper. The possible species and complexes existing in Lithium-Tetrahydrofuran Solution were systematically studied. Their geometry configuration, contour diagram, spin distribution and binding energy will be studied and understood. The interested systems cover: 1) neutral THF cluster $(\text{THF})_n$ and negatively charged anions $(\text{THF})_n^-$; 2) complexes: $\text{Li}(\text{THF})_n$, positively charged $\text{Li}(\text{THF})_n^+$, and negatively charged $\text{Li}(\text{THF})_n^-$.

Our future work will focus on more electrolyte choices. The structures can be extended to bond-linked benzenes, such as Para-TerPheny or TPB. The structures we have studied are single molecules. However, when the electrolytes are periodic nanoribbon structures, things will be totally different. Another future work is to study the ab initio molecular dynamic process for lithium solvated electron solutions. We want to see the motion trail of solvated electrons. This will help us to understand the conductivity and transport properties of the solution.