Confined Quantum Molecular Degrees of Freedom

by

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I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.
Abstract

Motivated by recent experimental measurements of the degeneracy lifting of the rotational ground state of molecular ortho-H$_2$ confined inside the fullerene cage C$_{60}$ and, more generally, motivated by the physics of confined quantum molecular degree of freedom. By using exact diagonalization we performed a detailed study on the coupled translational and rotational motion of H$_2$ based on the Van der Waals interaction model. We found that degeneracy lifting is caused by a symmetry reduction from Ih to C$_{3i}$ symmetry of C$_{60}$ in its solid state. The origin of the degeneracy lifting is found to mainly arise from the interaction between H$_2$ and its C$_{60}$ cage instead of the interaction between the H$_2$@C$_{60}$ molecule and its neighbouring molecules. The size of the splitting is extremely sensitive to the cage geometry while sitting in a relatively large linear regime. The zero point motion effect of carbon atoms does not change the size of the splitting. The analytical study also was performed by using multipole expansion on Lennard-Jones potential in order to gain a more physical perspective on confined quantum molecular degree of freedom.
Acknowledgements

The reason this paper can be completed is because I stood on the shoulders of many great people. Rain or shine these people helped me and believed in me. Through thick and thin these people never complained, never lost faith. Here I wish to acknowledge them, may their tireless support never go unnoticed.

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To Prof. Marcel Nooijen, thank you for been part of this project, and for providing me with valuable and often extremely enlightening pointers.

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To my colleague Spencer Yim. As with everything in life, a good foundation is key to success. Thank you for providing me with an extremely good foundation for my project when I first started it all. To my colleague Dmitri Iouchtchenko. Thank you for helping me with any and every computer related issues. Your support is more important to me than you could possibly imagine. I would also like to thank: Brian Yee, Cyrus Xu Cerkauskas, Xiaolong Zhang, Ce Zhou, Weiqiang Fu, Qianshi Wei, Tom Halverson, Yulia Kalugina, Matthew Schmidt and Kevin Bishop for many stimulating and enlightening conversations as well as all my colleagues in Prof. Michel Gingras and Prof. Pierre-Nicholas Roy group. Lastly, I want to thank Hunt Xu for improving the appearance of this paper, all my friends for their encouragement, and my family for their warmth and understanding.
Dedication

This is dedicated to people I love.
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Chapter 1

Introduction

The endofullurene $\text{H}_2@\text{C}_{60}$, first synthesized in 2005, has since become a classical model in the study of quantum dynamics of a single confined molecule. Recently, $\text{H}_2@\text{C}_{60}$ has drawn great attention because of the coupled translational and rotational motion of $\text{H}_2$ when confined inside $\text{C}_{60}$. In this Chapter, an outline of the fascinating features of $\text{C}_{60}$ will be presented including chemical bonding, symmetry operations, electronic states and vibrational modes of the $\text{C}_{60}$ molecule. A general introduction on the crystalline structure of crystalline $\text{C}_{60}$ will also be provided as it is the same as that of $\text{H}_2@\text{C}_{60}$. A summary on the symmetry group $\text{Pa\bar{3}}$ will be presented as it will closely relate to our work. Finally, the fundamental research motivation and objective of this work and the outline of the structure of this thesis will be discussed.
1.1 A Brief Review of $C_{60}$

1.1.1 Chemical Bonding

The Buckminsterfullerene has the chemical formula of $C_{60}$, was discovered in 1985 [34], and is a nearly spherical fullerene molecule. This molecule is also known as buckyball or soccer ball. $C_{60}$ contains 12 pentagons and 20 hexagons. This means that there are 60 vertices for the carbon atoms sharing 90 covalent bonds between them, 30 electron-rich double bonds, and 60 electron-poor single bonds [44]. The pentagon is made of 5 electron poor single bonds and the hexagon is made of 3 single bonds and 3 double bonds as shown in Figure 1.1. $C_{60}$ has a cage-like truncated icosahedron structure and has been described as the roundest molecule that can possibly exists by Curly and Smalley [19, 33]. The nucleus to nucleus diameter of $C_{60}$ molecule is around 10.1 Å and the length of a single bond that connects two hexagons is slightly larger than that of a double bond which connects two pentagons. The average bond length of a $C_{60}$ molecule is about 1.4 Å. $C_{60}$ molecule in gas phase belongs to the icosahedral (Ih) symmetry group [19, 43].

![Molecular structure of the $C_{60}$](image)

Figure 1.1: Molecular structure of the $C_{60}$

1.1.2 Icosahedral Symmetry Operations

$C_{60}$ molecule is highly symmetrical and there are many transformations that map the $C_{60}$ molecule back onto itself. These transformations are rotation around an
axis, reflection about a plane and inversion with respect to a point. All rotational axes and mirror planes must go through the centre of mass of $C_{60}$ since the centre of mass of the $C_{60}$ molecule must be unchanged under all symmetry operations. There are three kinds of rotational symmetry for a $C_{60}$ molecule as shown in Figure 1.2. One is 2-fold axis through the centres of the edges between two hexagons which is referred to as $C_2$ axis. There are 30 edges between two hexagons since each hexagon is neighboured by three other hexagons. As a result, there are 15 distinct 2-fold axes in one $C_{60}$ molecule. The second one is 3-fold axis through the centre of two facing hexagons, a rotation of 120 degrees about this axis is needed to map the molecule onto itself. Since each axis passes through two hexagons, 20 hexagons in one $C_{60}$ molecule will gives 10 different 3-fold axes which are referred to as $C_3$ axes. The third one is 5-fold rotational axis through the centre of two facing pentagons, a rotation of 72 degrees about this axis will map the molecule onto itself. 12 pentagons in $C_{60}$ molecule will give 6 different 5-fold rotational axes which are referred to as $C_5$ axes.

The reflection symmetries are in the planes that contain two edges between adjacent hexagons. There are also 15 different mirror planes. Finally, $C_{60}$ has inversion symmetry with respect to its centre of mass. It means that one can replace each carbon atoms' coordinate $(x, y, z)$ by $(-x, -y, -z)$, with the $C_{60}$ molecule mapping back onto itself. All these symmetry operations form the Ih point group. Symmetry consideration is very important when dealing with physical problems with fullerenes.
such as the electronic states or vibrational modes. The spherical harmonics are treated as natural basis functions for the full rotational group.

1.1.3 Electronic States

In this subsection, we consider the electronic states of $C_{60}$ fullerene molecules within a very simple description. Initially, $C_{60}$ was assumed to be a perfect sphere. However, qualitative treatment adapted from the quantum mechanics of one-electron hydrogen atom gives electronic structure with unpaired electrons [19, 43, 44]. This is in a contradiction with the fact that $C_{60}$ is an insulator and has no unpaired electrons. This contradiction gets resolved if the symmetry is lowered from spherical to $Ih$ since all unpaired electrons become paired under the $Ih$ symmetry. As shown in Figure 1.3, if $C_{60}$ has spherical symmetry, each carbon is single bonded to three other carbons using three of four valence electrons with the remaining one electron for each carbon moving on the sphere that is created by the 60 carbon atoms. This qualitative treatment of 60 delocalized electrons moving on a sphere results in 10 unpaired electrons. After the symmetry is lowered to $Ih$, the highest occupied molecular orbital is fivefold degenerate and the lowest unoccupied molecular orbital is threefold degeneracy. The existence of two triply degenerate states shown in Figure 1.3 is consistent with the experimental results showing that $K_3C_{60}$ is a conductor while $K_6C_{60}$ is an insulator [52].

---

Figure 1.3: Electronic energy levels of $C_{60}$ from spherical symmetry to $Ih$ symmetry [26]
1.1.4 Vibrational Modes

Symmetry consideration is also very important to characterize the nature of the vibration modes of $C_{60}$ molecule. In this subsection, we briefly summarize the symmetries of the vibrational modes for $C_{60}$ molecule. After one subtracts the translational and rotational degree of freedom, there remains 174 vibrational degrees of freedoms. However, due to the high symmetric of Ih symmetry, many vibration modes are degenerate and only 46 distinct vibrational frequencies remain. They correspond to the following symmetry decomposition [12, 13, 44]:

$$2A_{g} + 3F_{1g} + 4F_{2g} + 6G_{g} + 8H_{g} + A_{u} + 4F_{1u} + 5F_{2u} + 6G_{u} + 7H_{u}. \quad (1.1)$$

The coefficients can be explained as follows: $2A_{g}$ means that two distinct eigenfrequencies have $A_{g}$ symmetry while $3F_{1g}$ means three distinct eigenfrequencies have $F_{1g}$, etc. The lowest frequency modes of $A_{g}$ is so called the "breathing" mode and refers identical radial displacements for all 60 carbon atoms. The frequency of this mode is about $450 \text{cm}^{-1}$[12, 29] and the root-mean-square displacement at zero temperature is $0.04 \text{Å}[29]$.

1.1.5 Crystalline Structure

In this subsection, we review features of the crystalline structure of $C_{60}$ including the crystal structure of $C_{60}$ at room temperature, the structural phase transition of temperature dependence and the neighbouring orientation feature of $C_{60}$ [12]. In solid state, $C_{60}$ molecules will crystallize into face centred cubic (FCC) lattice structure. The lattice constant is $14.17 \text{Å}$ and the nearest-neighbour $C_{60}-C_{60}$ distance is $10.02 \text{Å}$ [12, 50] at room temperature and ambient pressure [12]. The $C_{60}$ molecules are located at the lattice points of a FCC lattice with one $C_{60}$ molecule per primitive FCC unit cell or four molecules per simple cubic (SC) unit cell. $C_{60}$ displays a structural phase transition as a function of temperature. At room temperature, $C_{60}$ molecules are rotating rapidly about their lattice positions. There is no orientational order and all molecules are treated as equivalent molecules. Consequently, the crystal structure of $C_{60}$ is FCC and the space group symmetry at room temperature is
Fm$\bar{3}$m as revealed by x-ray and neutron diffraction [12, 21, 15, 51]. The structural phase transition from FCC to SC structure occurs when the temperature decreases below a temperature $T_1$. This temperature is called characteristic temperature and is about 261 K. Below $T_1$, the C$_{60}$ molecules only have one degree of freedom which is the rotational motion about the four $<111>$ direction due to the strong correlation with the adjacent molecules. As a result, the lattice structure of solid C$_{60}$ is SC when the temperature is below $T_1$ and the symmetry of C$_{60}$ is Pa$\bar{3}$. Moreover, as temperature goes below $T_1$, there exists two different phase in the idealized ordered structure with respect to the relative orientation of adjacent C$_{60}$ molecules [12].

- p-phase: the electron rich double bonds faces the electron poor pentagon of the adjacent C$_{60}$ molecule
- h-phase: the electron rich double bonds faces the electron rich hexagon of the adjacent C$_{60}$ molecule

![Figure 1.4: A illustration of the p-phase and h-phase relative neighbouring C$_{60}$ molecular orientation: grey part from one cage blue part from its nearest neighbour](image)

As the temperature continues to decrease, another "phase transition" will occur at temperature $T_2$. This "phase transition" involves the transition between p-phase orientation and h-phase orientation [12, 13]. The value of $T_2$ is not determined since it differs from different properties being measured. A number of experiments such as: the velocity of sound [12, 32, 22], specific heat measurement [12, 18, 2, 47, 4], dielectric relaxation studies [12, 5] and neutron scattering measurement [12, 10], showed that this "phase transition" occurs at a temperature range of 90K-160K.
As temperature gets lower, most of the molecules tend to have a p-phase with the adjacent molecules since p-phase configuration has lower energy than that of h-phase configuration. Moreover, when $T_2 = 90K$, 87% of the intermolecular alignment are reported in lower energy p-phase and 17% of the intermolecular alignments are reported in slightly higher energy level h-phase [12]. This percentage will be maintained down to about 50K.

1.2 Background of Confined Quantum Molecule

1.2.1 A Brief Summary on General Confined Molecule

In this subsection, we present a brief summary on general endohedral compounds including several current achieved cases, the method to synthesize those compounds, and application of the endohedral compounds. Endohedral compounds are when a guest atom or molecule is trapped in the interior of a host molecule. The first endohedral compounds obtained by trapping single lanthanum atom inside carbon cage which was denoted as La@C$_{60}$[7, 16]. This notation can be explained as the following: the atom or molecule on the left of @ will be assumed to be the guest molecule and all atoms listed on the right will be assumed to be part of the cage [7]. The host molecule usually are fullerenes, such as C$_{60}$, C$_{70}$ and C$_{80}$ and in this case the endohedral compounds is also called endofullerene. The endofullerene was synthesized by a procedure named ”molecular surgery” [36, 30]. ”Molecular surgery” involves using a series of chemical reactions to open a hole on the cage, trapping the guest molecule inside and preforming another series chemical reactions to close the hole. The endofullerene H$_2$@C$_{60}$ in Figure.1.5a where a small H$_2$ molecule that is encapsulated into a fullerene cage C$_{60}$ was the first to be synthesized. [30] Similar molecules such as: H$_2$O@C$_{60}$ [35] in Figure.1.5b and HF@C$_{60}$ in Figure.1.5c have also been synthesized since[31]. One important reason that motivated people to synthesize H$_2$@C$_{60}$ endofullerene is the need to storage clear H$_2$ as it is an ideal fuel and in principle reduces or even eliminates CO$_2$ emissions[48, 42]. Moreover, in order
to reveal the fundamental properties of water molecules that exist in non-hydrogen-bonding environments, the endofullerene $\text{H}_2\text{O}@\text{C}_{60}$ is also necessary\cite{28}. All these three endofullerene displays remarkable quantum effects where the translational and rotational motion becomes coupled due to the confinement. In our project, we focused on $\text{H}_2@\text{C}_{60}$

### 1.2.2 Crystalline Structure of $\text{H}_2@\text{C}_{60}$

The crystalline structure of $\text{H}_2@\text{C}_{60}$, including the crystal structure at room temperature, the structural phase transition of temperature dependence, and the neighbouring orientation feature are all same with that of $\text{C}_{60}$. In this subsection, we will emphasis the structure feature when the lattice structure is in the symmetry group $\text{P}a\tilde{3}$ in which the point group of a single $\text{C}_{60}$ molecule is $C_{3i}$. The $C_{3i}$ operator involves the following 3-fold rotation and inversion shown in Table 1.1. For a single $\text{C}_{60}$ molecule that has $C_{3i}$ symmetry, only 10 independent carbon atoms’ positions are needed in order to obtain any carbon atoms position in one $\text{C}_{60}$ molecule. Starting with these 10 independent carbon atoms’ positions, one can apply 3-fold rotation to get 30 rotational symmetry related carbons’ position which are presented in left column of Table 1.1. Then by using inversion symmetry, one can obtain the 60 carbon atoms’ position for one $\text{C}_{60}$ molecule. The symmetry group $\text{P}a\tilde{3}$ involves the
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<tr>
<th>3-fold Rotation</th>
<th>Inversion</th>
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<tbody>
<tr>
<td>(x,y,z)</td>
<td>(-x,-y,-z)</td>
</tr>
<tr>
<td>(z,x,y)</td>
<td>(-z,-x,-y)</td>
</tr>
<tr>
<td>(y,z,x)</td>
<td>(-y,-z,-x)</td>
</tr>
</tbody>
</table>

Table 1.1: The table of general position of \( C_{3i} \) point group

following transition in the space for all the \( C_{3i} \) general positions. Let us use \((x,y,z)\) position as example as showing in Table 1.2. Similar transitions on \((z,x,y), (y,z,x)\)

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Table 1.2: The table of general position of for \((x,y,z)\) in symmetry group \( Pa\overline{3} \)

and their inversions also needs to form the full group of positions of \( Pa\overline{3} \) symmetry. In summary, the crystalline structure of \( H_2@C_{60} \) is the same as that of \( C_{60} \). In the temperature regime that relates to our projects, \( H_2@C_{60} \) is in symmetry group \( Pa\overline{3} \) in which the single \( C_{60} \) has \( C_{3i} \) symmetry.

1.2.3 Quantum Dynamics of \( H_2@C_{60} \)

The remarkable quantum effects of coupled transitional and rotational degrees of freedom will play an important role once the \( H_2 \) is trapped into the \( C_{60} \). The quantum dynamics of \( H_2 \) confined in \( C_{60} \) is even more attractive since \( H_2 \) molecules has two spin isomers, which are para-\( H_2 \) and ortho-\( H_2 \)[8]. For para-\( H_2 \), it gives the antisymmetric total spin \( (I = 0) \) isomer and has antiparallel spins, while for ortho-\( H_2 \), it gives the symmetric total spin \( (I = 1) \) isomer and has parallel spins. The Pauli exclusive principle requires that the total wave function to be antisymmetric with respect
to the exchange of nuclei due to the fact that the H nuclei spins are fermions. In
the Born-Oppenheimer approximation, if we ignore the rotation-vibration coupling,
the total wave function of the H
2
 can be written as:
\[ |\Psi\rangle = |\psi_s\rangle \cdot |\psi_{el}\rangle \cdot |\psi_{vib}\rangle \cdot |\psi_{rot}\rangle \]
which is referring to the nuclei spin, electronic, vibrational and rotational wave
functions. The vibrational and electronic wave function are symmetric with respect
to permutation of the two hydrogen molecules. Consequently, for para-H
2
, only
even rotational quantum numbers are allowed \( j = 0, 2, 4, 6... \), while for the ortho-H
2
, only odd rotational quantum number are allowed \( j = 1, 3, 5, 7... \) in order to have
an antisymmetric wave function. In our work, we will refer \( j = 1 \) state to ortho-H
2
 ground state. The spin conversion between the two isomers are extremely slow with
the absence of magnetic impurities and dopants since no measurable para-H
2
 and
ortho-H
2
 conversion in pure solids has been observed in several days at cryogenic
temperature [12]. In summary, para-H
2
 and ortho-H
2
 can be treated as two different
physical spices inside the cage C
60
.

1.3 Motivation and Objective

Due to the fascinating quantum dynamic features of the endofullerene, H
2
@C
60
 has
aroused extensive interests both in theoretical [56, 57, 53, 58, 17, 59, 14]. Numerous
experimental studies such as: nuclear magnetic resonance [6] and inelastic neutron
scattering [25, 24, 23, 54, 40] have been reported. In this section, we will present
the motivation as well as the objective of this work. The coupled translational and
rotational motion of H
2
 inside C
60
 would be effected by the potential energy surface
that H
2
 molecule experiences due to the confinement. The energy spectrum of con-
 fined H
2
 will be related to the symmetry of this potential energy surface which would
directly relate to the symmetry of C
60
. As we mentioned before, in gas phase, a
single C
60
 molecule has icosahedral (Ih) symmetry, and the rotational motion of H
2
 preserved the high degeneracy up to J=5 under Ih symmetry [13, 12]. This splitting
principle has been justified by the following theoretical works [56, 57, 53, 58]. In its
solid state, C
60
 molecules crystallize into cubic lattice with space group Pa\(\overline{3}\)[20] and
the symmetry of a single $C_{60}$ molecule will decrease from $Ih$ to $C_{3i}$. The rotational three-fold ortho-$H_2$ ground state ($j = 1$) will split into two doubly degenerate level and single nondegenerate level due to the nature of $C_{3i}$ symmetry. This splitting principle was also observed by the most recent inelastic neutron scattering experimental result in Ref.[40]. These experiments were preformed in the temperature range where $C_{60}$ has $Pa\overline{3}$ symmetry. The splitting of three-fold ortho-$H_2$ ground state ($j = 1$) was studied as a function of temperature from 40K down to 60 mK. It demonstrated that the three-fold degeneracy of ortho-$H_2$ ground state could split into a low energy nondegeneracy level and a high energy doubly degeneracy level [40]. This experiment also found that the size of this splitting would depend on orientation of the $C_{60}$ molecule. More specifically, the splitting size depend on the statistical weights of p-phase and h-phase neighbouring orientation $C_{60}$ molecules as showing in Table.1.3[40]. The ”p-phase rich” means that statistical weights of

<table>
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<th>p-phase rich</th>
<th>h-phase rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>1.089cm$^{-1}$</td>
<td>1.371cm$^{-1}$</td>
</tr>
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</table>

Table 1.3: The splitting size observed in the inelastic neutron scattering experiment[40]

p-phase orientation is larger than that of the h-phase orientation and the ”h-phase rich” means that statistical weights of h-phase orientation is larger than that of the p-phase orientation. Moreover, we will use ”$S$” to represent the splitting and use wavenumber (cm$^{-1}$) as the unit of splitting in this work as showing in Table.1.3. Here we will clarify the sign of ”$S$” due to the fact that we also found that the three-fold degeneracy can be lifted in opposite order. Therefore, we will use a positive ”$S$” to denote that the splitting had the same order as the experimental result. The sign of splitting ”$S$” have the following notation:

• $S>0$: the three-fold degeneracy of rotational ortho-$H_2$ ground state ($j = 1$) splits into a low energy nondegeneracy level and a high energy doubly degeneracy level

11
• S<0: the three-fold degeneracy of rotational ortho-H\(_2\) ground state (\(j = 1\)) splits into a high energy nondegenerate level and a low energy doubly degenerate level

These notations are illustrated in Figure.1.6

![Figure 1.6](image)

Figure 1.6: The illustration showing that the three-fold degeneracy can be lifted in opposite order: S>0 and S<0

The fundamental origin that responsible for the listing of the three-fold degeneracy is still an open problem in chemical physics. There are two possibilities and here we will use the notations used in Ref.[40]. The one possibility is that it could be caused by the interaction between H\(_2\) and its own cage. This will be refer to as "intra-cage" interaction. The other one is the interaction between H\(_2@C_{60}\) and neighbouring H\(_2@C_{60}\) molecules. This will be refer to as "inter-cage" interactions. The objective of this work is to gain insights into the role of inter-cage or intra-cage interactions in determining the energy spectrum of H\(_2\). Furthermore, the splitting size of the three-fold degeneracy of rotational ortho-H\(_2\) ground state (\(j = 1\)).

### 1.4 Outline of the Thesis

This concludes the introduction of this thesis, which was aimed to give the reader a general understanding of small molecules confined inside C\(_{60}\). The remaining part of this work consists of four chapters. Chapter 2 will introduce the model
used to accomplish our objective. The primary focus of Chapter 2 is a physical understanding of H$_2$ confined into C$_{60}$. It will start with a model of a free rotor, then add translational degree of freedom and finish by adding potential energy surface between H$_2$ and C$_{60}$. Chapter 3 will provide the numerical techniques required to investigate our problem. It will present the method of exact diagonalization, the matrix element and a discussion of the effect of the basis size truncation. Chapter 4 will display the results of applying the methods presented in Chapter 3 on the Hamiltonian of H$_2$ confined inside C$_{60}$ with the potentials discussed in Chapter 2. In order to develop a more efficient method as well as understand the physical meaning, we will introduce an analytical perspective to solve our problem in Chapter 5 and Chapter 6. Chapter 5 will introduce the analytical method on a toy model. After the validation of the toy model in Chapter 5, Chapter 6 will present the analytical method on the real model that was introduced in Chapter 2. This model leaves future direction of our work with additional further corrections on the potential between H$_2$ and C$_{60}$. With the understanding of the endofullerene H$_2@C_{60}$, the process of understanding the physical perspective of other endofullerene such as H$_2$O@C$_{60}$ or HF@C$_{60}$ would be easier. The possible directions of future work will be discussed in Chapter 7.
Chapter 2

Model

In this chapter, we start with stating all assumption basing on the quantum nature of small molecule H$_2$ trapped inside a fullerene cage C$_{60}$ and presenting the full Hamiltonian that consists of translational part, rotational part as well as interaction part. Then we will introduce each part of the Hamiltonian as well as the natural basis function. A discussion on the potential energy surface will be present. Finally, we will give a brief summary on previous studies of the potential of H$_2$ confined inside C$_{60}$. We will present the L-J potential as well as its parameters we used to physically describe the interaction between H$_2$ and its cage C$_{60}$. 

2.1 Hamiltonian

Considering the quantum nature of small molecule H$_2$ trapped inside a nano cavity C$_{60}$, there are several features that needs to be emphasized in order to simplify the Hamiltonian and solve the problem. First, C$_{60}$ is treated as a rigid cage due to fact that the H$_2$-C$_{60}$ interaction is much weaker than the lowest frequency mode of C$_{60}$ molecule [56]. The couplings between them are very weak and it is measured by the Raman and infrared spectra [11]. Second, C$_{60}$ is treated as non-rotating molecules due to the fact that the three rotational constants of C$_{60}$ are equal to 2.803 $\times$ $10^{-3}$ cm$^{-1}$ and are negligible when compared to the H$_2$-C$_{60}$ interaction [59]. Third, H$_2$ is treated as a rigid rotor, which is justified by the fact that vibrational motion of H$_2$ is coupled very weakly to the coupled translational and rotational motion [59]. With assumptions shown above, the coupled translational and rotational motion of H$_2$ inside C$_{60}$ can be described by a 5D coordinate system ($x$, $y$, $z$, $\theta$, $\phi$). Finally the 5D Hamiltonian of rigid H$_2$ trapped inside a rigid and non-rotating C$_{60}$ cage can be written as follows [59]:

$$H = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + B_\nu L^2 + V(x, y, z, \theta, \phi).$$

(2.1)

2.2 Rotational Motion

The rotational motion is described by $\theta$ and $\phi$, which specify the orientation of H$_2$ with respect to C$_{60}$ cage frame. The Hamiltonian for rotational part has the following form:

$$H_{\text{rot}} = B_\nu L^2.$$  

(2.2)

$L^2$ is the angular momentum operator of diatomic H$_2$ molecule, and is used to describe the rotational motion of H$_2$. $B_\nu$ is the rotational constant of the H$_2$ in vibrational $\nu$ state and the value is given by $B_\nu = B_{\text{eq}} - \alpha(\nu + 1/2)$ where $\alpha$ is a vibration-rotation interaction constant. The equilibrium rotational constant $B_{\text{eq}} = 59.3$ cm$^{-1}$ and the vibration-rotation constant $\alpha = 2.98$ cm$^{-1}$ are measured.
from IR spectra of H$_2$@C$_{60}$ [38]. The rotational basis function used in this work is spherical harmonic wavefunction since $|l, m\rangle$ are eigenfunction of $L^2$ simultaneously:

$$ L^2 |l, m\rangle = l(l + 1) |l, m\rangle, \quad \text{with} |l, m\rangle \equiv Y_{lm}(\theta, \phi). $$

Since this study is focused on the degeneracy lifting of ortho-H$_2$ ground state ($l = 1$) manifold, the spherical harmonic function $Y_{1m}$ under spherical coordinates ($\theta, \phi$) will be listed.

$$ Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta $$

$$ Y_{1,-1} = \sqrt{\frac{3}{4\pi}} \sin \theta e^{-i\phi} $$

$$ Y_{1,1} = -\sqrt{\frac{3}{4\pi}} \sin \theta e^{i\phi} $$

Finally, as mentioned in 1.2.3, H$_2$ can exist as two nuclear spin isomers ortho-H$_2$ and para-ceH2. Due to the fact that the conversion between the two spin isomer is extremely slow, one can treat ortho-H$_2$ and para-ceH2 as two distinct physical species. It will dramatically decrease the basis size of the full Hamiltonian and save numerous computational expenses.

### 2.3 Translational Motion

In addition to rotating, H$_2$ has translational degree of freedom and can be described by 3D coordinate system ($x, y, z$). In this system, $x, y$ and $z$ specify the centre of mass (CM) position of H$_2$ away from the geometry centre of C$_{60}$. The Hamiltonian for rotational part has the following form:

$$ H_{\text{trans}} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right). $$

In the above Equation 2.4, $-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2}$ describes the translational motion of the CM of H$_2$ along $x$ direction. $\mu$ is the reduced mass of H$_2$ inside C$_{60}$, which is given by the
mass of H$_2$ and C$_{60}$ with $\frac{m_{H_2} m_{C_{60}}}{m_{H_2} + m_{C_{60}}}$.

Due to the large mass difference between H$_2$ and C$_{60}$, the reduced mass of H$_2$ is only slightly smaller than the mass of H$_2$ (2.0160 amu). The value of 2.0104 amu will be used in this work to represent it. The 3D harmonic oscillator wave-function for translational motion of CM of H$_2$ coupled with spherical harmonics for rotational motion are used in this work in order to perform exact diagonalization on the Hamiltonian. The basis function can be written as follows:

$$\Psi(x, y, z, \theta, \phi) = \langle x, y, z, \theta, \phi \mid \langle n_x, n_y, n_z \rangle \otimes |l, m\rangle \rangle.$$  \hfill (2.5)

$|n_x, n_y, n_z\rangle$ is the 3D harmonic oscillator eigenfunction and $|n_x\rangle$ (similar with $|n_y\rangle$ and $|n_z\rangle$) can be written under the cartesian coordinate basis as follows:

$$|n_x\rangle = \phi_{n_x}(x) = \frac{1}{\sqrt{2^{n_x} n_x!}} \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} \exp \left\{ -\frac{m \omega x^2}{2 \hbar} \right\} H_n \left( \frac{\sqrt{m \omega}}{\hbar} x \right).$$ \hfill (2.6)

$H_n(x)$ is the $n$-th order Hermite polynomials. The choice of using the 3D harmonic oscillator eigenfunction basis function is motivated by the potential of the problem, and can be approximated by a harmonic potential at the vicinity of the equilibrium point.

### 2.4 The Potential Energy Surface (PES)

#### 2.4.1 Previous Studies on the PES

In order to describe the H$_2$ that trapped inside C$_{60}$, now we need to come up with an effective potential that characterizes the interaction between the trapped molecule H$_2$ and its cage C$_{60}$. A number of experimental measurements have been performed using spectroscopic techniques such as nuclear magnetic resonance spectroscopy (NMR), inelastic neutron scattering (INS), and infrared (IR) spectroscopy. An excellent review on IR, INS and NMR spectroscopy of H$_2$@C$_{60}$ at cryogenic temperature was presented by Mamone [39]. After obtaining energy levels of H$_2$@C$_{60}$ by using all three of the aforementioned spectroscopic techniques, there exist two choices to formalize the PES. One was that the PES could be obtained as a sum
of the two body interactions over all carbon and hydrogen atoms and fitted to the experimental measured spectrum to parameterize the potential. A standard two-site Lennard-Jones potential was first used to fit the energy level of H$_2$ in C$_{60}$ cage [38, 37]. To get a better fitting, a three-site LJ potential, which also accounts for the interactions between the centre of mass of H$_2$ and all carbon atoms was proposed later by fitting IR spectra [38]. This was motivated by the molecular charge distribution which was located not only at the exact nuclear positions, but also in the intermediate region between the hydrogen atoms. Consequently, the three-site potential improved the accuracy of the spectrum fitting, especially for higher energy levels. In summary, principally, a real potential energy surface that characterizes the interaction between H$_2$ and C$_{60}$ is required. However, considering the complexity of coming up with a real potential, and that since empirically parameterizing 5D Lennard-Jones(L-J) potential gives good agreements with the IR spectroscopic measurements, [38, 37], we will use a 5D parameterized L-J potential to describe the interaction between trapped H$_2$ and C$_{60}$.

2.4.2 Lennard-Jones potential

The 5D potential $V(x, y, z, \theta, \phi)$ can be written in L-J form:

$$V = \sum_{j=1}^{2} \sum_{i=1}^{60} V(r_{ij}) + w \sum_{i=1}^{60} V(r_{im})$$

(2.7)

In Equation 2.7, $r_{ij}$ is the distance between $i$-th hydrogen atom of H$_2$ and $j$-th carbon atom of C$_{60}$. $r_{im}$ is the distance between CM of H$_2$ and $j$-th carbon atom. $w$ is a dimensionless weight parameter that efficiently changes the L-J potential energy surface. In Equation 2.7, the L-J potential $V(r)$ has the following form:

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right].$$

(2.8)

In Equation 2.8, $\epsilon$ and $\sigma$ are standard L-J potential parameters, where $\epsilon$ is the depth of potential well and $\sigma$ is the finite distance where inter-particle potential equals to zero. The L-J parameters [57] used in this work are displayed in Table 2.2.
<table>
<thead>
<tr>
<th></th>
<th>$\epsilon$ (cm$^{-1}$)</th>
<th>$\sigma$ (Å)</th>
<th>$w$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
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<td>2.95</td>
<td>7.5</td>
<td>0.0</td>
</tr>
<tr>
<td>PES2</td>
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<td>3.08</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2.1: Parameters specifying potential energy surface: $\epsilon$ (cm$^{-1}$) and $\sigma$ (Å) are L-J potential parameters, $w$ is a dimensionless weight as discussed in the text. [57]

When fitting with the IR spectroscopic measurements, besides the L-J parameters, the vibrational state of H$_2$ also play an important role in the behaviours of energy spectra. As suggested by [37], H$_2$ in vibrational ground state with PES2 is better fitting with IR spectra than it in excited vibrational state. While for H$_2$ with OPES, using H$_2$ in the first vibrational excited state can explain experimental measurements better than it in vibrational ground state[38]. The PES2 with H$_2$ in first vibrational excited state and the OPES with H$_2$ in vibrational ground state are two potential energy surfaces that are motivated by PES2$\nu$0 and OPES$\nu$1 respectively. A detail explanation of vibrational quantum number $\nu$ can be found in 2.2. To get a

<table>
<thead>
<tr>
<th></th>
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<th>$\sigma$ (Å)</th>
<th>$w$</th>
<th>$\nu$</th>
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<td>OPES(\nu)1</td>
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<td>7.5</td>
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<td>3.08</td>
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</tr>
</tbody>
</table>

Table 2.2: Parameters specifying potential energy surface: $\epsilon$ (cm$^{-1}$) and $\sigma$ (Å) are L-J potential parameters, $w$ is a dimensionless weight as discussed in the text, and $\nu$ is the vibrational quantum number to specify the rotational constant $B\nu$.[57]

direct sense of the difference between the two kinds of potential energy surface, one can plot the potential with respect to the position of the centre of mass of the H$_2$ as shown in Figure 2.1. It is the plot given in [57]. The PES2 and OPES parameters generate very different well depths, and shapes of potentials that will effect the coupled translational and rotational motion of trapped H$_2$. However, as pointed out in
Figure 2.1: 1D potential $V(x)$ cuts along $x$ of H$_2$ inside C$_{60}$ of PES2 (Left) and OPES (Right): solid line and dash line stands for H$_2$ perpendicularly and parallel move along C$_2$ axis of C$_{60}$ [57], the quantum translational-rotational dynamics of H$_2$/HD/D$_2$ in C$_{60}$ on both potential energy surfaces all display the same patterns of degeneracies, which can be qualitatively understood in terms the model of the rigid rotor that is trapped inside a high symmetry cage with a large cavity. It is also shown that these features are robust, generic and independent of the details of the interaction potentials.
Chapter 3

Method

In this chapter, we introduce the methodology used to investigate the quantum rotor H$_2$ trapped inside C$_{60}$ is exact diagonalization. The reason is that the time-independent Schrödinger equation is an eigenvalue problem. Even though the real physical problem is in the infinite dimensional space, the Schrödinger equation can be formulated as an eigenvalue matrix with the approximation of truncating Hilbert space to finite dimension. We will present the matrix element basing on the Hamiltonian and the basis functions that we defined in Chapter 2. Finally, a discussion on the basis size convergence will be provide, highlighting the convergence factor we used to proceed our project.
3.1 Matrix Elements

Having defined the Hamiltonian and the basis functions in Chapter 2, it is now possible to move with evaluating the matrix elements of the Hamiltonian under the basis functions. As mentioned before, the potential used in this work has harmonic potential behaviour in the vicinity of the equilibrium point. This point will be the geometry centre of the C_{60} molecule. From these set of states, H_{2} molecule can be treated as a quantum harmonic oscillator that oscillating around the equilibrium point in the harmonic like potential well. This suggests one can rewrite the Hamiltonian in terms of 3D quantum harmonic oscillator Hamiltonian by adding the potential term $\frac{1}{2} m \omega^2 r^2$ and subtract this term in the 5D interaction potential $V(x, y, z, \theta, \phi)$ latter. The total hamiltonian will be unchanged and has the following form:

$$H = H_{\text{QHO}} + B_\nu \mathbf{L}^2 + V'(x, y, z, \theta, \phi),$$  \hspace{1cm} (3.1)

where $H_{\text{QHO}}$ and $V'(x, y, z, \theta, \phi)$ have the following form:

$$H_{\text{QHO}} = -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{1}{2} m \omega^2 r^2 \text{ and } V' = V - \frac{1}{2} m \omega^2 r^2. \hspace{1cm} (3.2)$$

Here, a parameter $\omega$ is used and represents the angular frequency of the H_{2} molecule. The value of $\omega$ can be determined by the Taylor series expansion of potential $V$ in terms of $r$ around equilibrium position ($r=0$), and more specifically by the second derivative of the potential. The value of the parameter $\omega$ will not effect the energy spectrum when using a converged basis size since the same quantities are added and subtracted. The matrix elements of $H_{\text{QHO}}$ hamiltonian are easy to evaluate since it is the diagonal in the 3D quantum harmonic oscillator basis set.

$$\langle n_x, n_y, n_z | H_{\text{QHO}} | n'_x, n'_y, n'_z \rangle = \hbar \omega \left( \frac{3}{2} + n_x + n_y + n_z \right) \delta_{n_x,n'_x} \delta_{n_y,n'_y} \delta_{n_z,n'_z}. \hspace{1cm} (3.3)$$

Similarly, the rotational part $B_\nu \mathbf{L}^2$ is diagonal in the spherical harmonic basis:

$$\langle l'm'| B_\nu \mathbf{L}^2 | l'm \rangle = l(l+1) \delta_{l,l'} \delta_{m,m'}. \hspace{1cm} (3.4)$$
We can now proceed to evaluate the matrix elements of the interaction potential, which can be done using the translational and rotational basis separately. The rotational part is as follows:

\[
\langle L'M'|V'|LM \rangle = \int_{-1}^{1} d\cos(\theta) \int_{0}^{2\pi} d\phi \langle L'M'|\theta\phi \rangle \langle \theta\phi|LM \rangle = \sum_{\alpha} \sum_{\beta} w_{\alpha} w_{\beta} Y_{L'M'}^{*}(\theta_{\alpha},\phi_{\beta}) V'(xyz,\theta_{\alpha},\phi_{\beta}) Y_{LM}(\theta_{\alpha},\phi_{\beta}).
\] (3.5)

In Equation 3.5, \( w_{\alpha} \) is Gauss-Legendre quadrature weights, which are used to evaluate the integral over the polar angle part and has the following general form:

\[
\int_{-1}^{1} f(x)dx = \sum_{i} w_{i} f(x_{i}).
\]

The \( \omega_{\beta} \) are equal spaced weights from 0 to 2\( \pi \) which is used to evaluate the integral over the azimuthal angle. The translational part needs to be calculated under the 3D quantum harmonic and it can be written as follows:

\[
\langle n'_{x}, n'_{y}, n'_{z} | V' | n_{x}, n_{y}, n_{z} \rangle = \int dx \int dy \int dz \langle n'_{x}, n'_{y}, n'_{z} | V' | xyz \rangle \langle xyz | n_{x}, n_{y}, n_{z} \rangle = \sum_{i,j,k} w_{i} w_{j} w_{k} \phi_{n'_{x}}^{*}(x_{i}) \phi_{n'_{y}}^{*}(y_{j}) \phi_{n'_{z}}^{*}(z_{k}) \ V'(x_{i}, y_{j}, z_{k}) \ \phi_{n_{x}}(x_{i}) \phi_{n_{y}}(y_{j}) \phi_{n_{z}}(z_{k}).
\] (3.6)

Again, in the above equation, \( w_{i}, w_{j} \) and \( w_{k} \) are Gauss-Laguerre quadrature weights. By combining all of the above together, one obtains all matrix elements of the Hamiltonian shown in Equation 2.1 under the basis function in Equation 2.5. After completing this, one can perform exact diagonalization on the Hamiltonian to get the full energy spectrum.

### 3.2 Basis Size Truncation

In this work, there are three convergence related factors that need to be stressed. First is the choice of the quantum oscillator frequency \( \omega \), which can be calculated...
through the second derivative of potential. The frequency used in exact diagonalization calculation is $9.673 \times 10^{-4}$ in atomic units. The second factor is the number of grid points used to get a converged value of the 5D integral. The number of grid points for the translational motion $xyz$ is 30 which means in Equation.3.6 $i, j, k = 1...30$. Similarly, for rotational motion $\theta$ and $\phi$ is 30 and 20 which means in Equation.3.5 $\alpha = 1...30$ and $\beta = 1...20$, respectively. The third factor is that based on all of the above convergency studies, a rigorous basis size convergence study must be performed. The basis for translational wavefunction is truncated at $n_x + n_y + n_z \leq 11$, and for rotational motion where only the ortho-H$_2$ wavefunction (odd J) are used is truncated at $J \leq 5$. 
In this chapter, we will present the exact diagonalizations results for H$_2@C_{60}$. Firstly, we will introduce and clarify all cases we considered to investigate the origin of the degeneracy lifting of ortho-H$_2$ ground state. Basing on the comparison between different case, we will draw an important conclusion, which is "intra-cage" interaction is the main reason of this degeneracy lifting. Then we will focus on one H$_2@C_{60}$ molecule to do the sensitivity analysis of splitting on cage geometry. Finally, we will explore the entanglement between the translational and rotational degrees of freedom using the measure known as the bipartite Von Neumann entanglement entropy.
4.1 The ”intra-cage” Interaction is the Main Reason of Splitting

The cage geometry used in this work are obtained from combining NMR [60] and X-ray[46] in [20] and measured at 11 K where all C$_{60}$ molecules are orientationally ordered. As is mentioned in Chapter 1, the symmetry group of solid C$_{60}$ is Pa$\overline{3}$ such that a single C$_{60}$ molecule has C$_{3i}$ symmetry. The all carbons’ position of a single C$_{60}$ molecule can be determined by 10 independent carbons’ coordinates since the rest of the coordinates are all C$_{3i}$ symmetry related. The coordinates that are reported in [20] is as follows:

<table>
<thead>
<tr>
<th>i</th>
<th>$X_i$</th>
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</tr>
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</tr>
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<td>-2.402</td>
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</tr>
<tr>
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<td>-1.864</td>
<td>2.516</td>
</tr>
</tbody>
</table>

Table 4.1: The C$_{60}$ geometry in orientationally ordered phase given in [20].

In order to investigate the origin of the degeneracy lifting of ortho-H$_2$ ground state, the following situations are considered and are illustrated in Figure 4.1. The symbols used in Figure 4.1 are explained as follows: A circle stands for a C$_{60}$ cage with Ih symmetry, a square stands for a C$_{60}$ in the solid with C$_{3i}$ symmetry and the two black dots connected with a solid line stands for a H$_2$ molecule. In a FCC lattice, one C$_{60}$ molecule has 12 nearest neighbour cages which are illustrated by 4 squares or
4 circles for simplicity in Figure 4.1. Here, the contribution of further neighbouring
C_{60} molecules is in the order of 0.01 compared to the nearest neighbour contribution.
It is negligible due to the fact that L-J potential has $r^{-6}$ decay. Moreover, the L-J
interaction between H$_2$ and H$_2$ is also insignificant comparing it between H$_2$ and
C_{60}, which justifies that no H$_2$ molecules was modelled inside the neighbouring C_{60}
cages.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Diagrammatic representation of a H$_2$ sitting in different cage environments.}
\end{figure}

- H$_2@Ih$: A H$_2$ inside a C$_{60}$ molecule with Ih symmetry;
- H$_2@C_{3i}$: A H$_2$ inside a C$_{60}$ molecule with C$_{3i}$ symmetry;
- H$_2@Pa\bar{3}$: A H$_2$ in a C$_{60}$ with 12 nearest neighbour C$_{60}$ cages (Pa$\bar{3}$) in the solid
  state;
- H$_2@13Ih$: A H$_2$ inside a central Ih C$_{60}$ with 12 neighbouring Ih C$_{60}$;
- H$_2@C_{3i}12Ih$: A H$_2$ inside a C$_{60}$ with C$_{3i}$ symmetry, with 12 neighbouring Ih
  C$_{60}$ cages.

In order to investigate the role of neighbour cages, the exact diagonalizations were
preformed for the above cases with all potential energy surfaces that presented in Ta-
ble 2.2. The splitting (cm$^{-1}$) of ortho-H$_2$ ground state (J=1) for PES2 with H$_2$ in its
translational ground state $\nu = 0$ were tabulated in Table 4.2. The positive splitting
denotes that the three-fold J=1 state is split into a higher doubly degenerate level
and a lower non-degenerate level and have the same ordering as the experimental
measurements in [40]. Conversely, a negative splitting denotes that the three-fold
J=1 state is split into a higher non-degenerate level and a lower doubly degenerate level as we explained in 1.3. Similarly with the PES2, the splitting (cm$^{-1}$) of ortho-

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}_2@\text{Pa}3)</th>
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<th>(\text{H}<em>2@\text{C}</em>{3\text{i}})</th>
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</tr>
</tbody>
</table>

Table 4.2: The splitting of ortho-H\(_2\)(J=1) ground state for PES2\(\nu0\)

\(\text{H}_2\) ground state (\(J=1\)) for OPES with \(\text{H}_2\) in first excited state \(\nu = 1\) and in ground state \(\nu = 0\) were tabulated in TABLE4.3 and TABEL4.4 respectively.

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}_2@\text{Pa}3)</th>
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<td>-0.0020</td>
<td>-0.0181</td>
<td>-0.0160</td>
<td>0.0000</td>
</tr>
<tr>
<td>h-phase</td>
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<td>0.0019</td>
<td>-0.0142</td>
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</tbody>
</table>

Table 4.3: The splitting of ortho-H\(_2\)(J=1) ground state for OPES\(\nu1\)

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}_2@\text{Pa}3)</th>
<th>(\text{H}_2@13\text{Ih})</th>
<th>(\text{H}<em>2@\text{C}</em>{3\text{i}}12\text{Ih})</th>
<th>(\text{H}<em>2@\text{C}</em>{3\text{i}})</th>
<th>(\text{H}_2@\text{Ih})</th>
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</thead>
<tbody>
<tr>
<td>p-phase</td>
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<td>-0.0019</td>
<td>-0.0133</td>
<td>-0.0150</td>
<td>0.0000</td>
</tr>
<tr>
<td>h-phase</td>
<td>-0.0132</td>
<td>0.0018</td>
<td>-0.0133</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: The splitting of ortho-H\(_2\)(J=1) ground state for OPES\(\nu0\)

As we mentioned in 1.1.3, the principle that the degeneracy of otrho-H\(_2\) ground state(J=1) is not lifted if the Ih symmetry of the \(\text{C}_{60}\) cage is maintained is confirmed by the fact that \(\text{H}_2@\text{Ih}\) gives no splitting at J=1 level for all potential energy surfaces considered. The splitting calculated on \(\text{H}_2\) inside a distorted cage (\(\text{H}_2@\text{C}_{3\text{i}}\)) confirms that the degeneracy of otrho-H\(_2\) ground state(J=1) is lifted if Ih symmetry is reduced to \(\text{C}_{3\text{i}}\) symmetry. The comparison between \(\text{H}_2\) sitting in a single distorted \(\text{C}_{60}\) without (\(\text{H}_2@\text{C}_{3\text{i}}\)) and with(\(\text{H}_2@\text{Pa}3\)) neighbouring cages in solid state shows that the splitting of ortho-H\(_2\) ground state(J=1) mainly caused by the \(\text{C}_{60}\) cage.
that trapped it in solid state. The fact that H₂ inside a distorted C₆₀ with other distorted C₆₀ as nearest neighbouring cages (H₂@Pa3) or with 12 Ih C₆₀ as nearest neighbouring (H₂@C₃i12Ih) gives almost the same splitting strongly suggests that the neighbouring cages’ geometry has no crucial effects on the ortho-H₂(J=1) splitting. The p-phase and h-phase nearest neighbouring cages orientation give different values for splitting in the solid state (H₂@Pa3). Whether the single cage splitting increases or decreases depends on whether it follows the same splitting ordering. For the p-phase neighbouring cages orientation, the splitting given by 12 neighbouring cages (H₂@13Ih) is negative which has the same order as with H₂ sitting in the centred single distorted C₆₀ (H₂@C₃i) such that the size of the splitting will be increased by including the neighbouring cage (H₂@C₃i12Ih). For the h-phase, the splitting given by 12 neighbouring cages has opposite order with H₂ sitting in the centred single distorted C₆₀ (H₂@C₃i) such that the magnitude of the splitting is decreased by including the neighbouring cage. The splitting is slightly different for H₂ in its vibrational ground state compared to when it is in its first excited state. In the excited state (ν = 1), it has a pairing of larger bond length of H₂ molecule and smaller rotational constant. The size of the splitting is determined by the isotropic level of the potential. By adding the third term interaction between the centre of mass of H₂ and C₆₀, the potential (OPES) become more isotropic. As a result, the splitting that is given by OPES is much smaller that those given by PES2. However, the splitting is much smaller than the experimental measurements in [40] even if when consider the PES2, which suggests that the sensitivity analysis of splitting size on single cage would be the next step.

4.2 Sensitivity Analysis of Splitting on C₆₀ geometry

The carbon position used in this work is from [20] and is summarized in Table 4.2. These coordinates, which are referred to as \{\vec{R}_i^{\exp}\}(i = 1...10) carries with experimental uncertainties which are at least in the 10⁻³Åorder of magnitude. To
explore the possible role of the experimental uncertainties, exact diagonalizations on 40 randomly distorted cages that, nevertheless, persevere of C$_{3i}$ symmetry were performed. These random distorted cages are formulated by adding random displacements taken from a normal distribution with a standard deviation of 0.001Å to the 10 independent coordinates $\{R_{\text{exp}}^i\}$ reported in [20] to get 10 independent new coordinates $\{\tilde{R}_i\}$. After this, C$_{3i}$ operators are applied onto these new coordinates to obtain a new slightly distorted cage geometry. Figure 4.2 shows how the splitting of ortho-H$_2$ ground state (J=1) varies from cage to cage in over 40 random distorted cages with same C$_{3i}$ symmetry as described above for PES2 (Left) and OPES (Right) with H$_2$ in vibrational ground state $\nu = 0$ (red circle) or first excited state $\nu = 1$ (blue square). The splitting is slightly different for H$_2$ in vibra-

Figure 4.2: The sorted splitting (S) (cm$^{-1}$) varies from cage to cage in over 40 random distorted cages with C$_{3i}$ symmetry on PES2 (Left) and OPES (Right): (a) red circle and blue square are splitting with H$_2$ in its vibrational ground state and first excited state. (b) The difference of splitting with H$_2$ in its vibrational ground state and first excited state.

ional ground state from when it was in its first excited state. This corresponds to different bond length of H$_2$ molecule and rotational constant, as discussed in 2.2. Higher vibrational state corresponds to smaller rotational constant, larger H$_2$ bond length, and larger splitting. With 0.001Å standard deviation, some geometries give
positive splitting, while some give a negative splitting. The reason that the number of cages that gives negative splitting is larger than those giving positive splitting is that start cage in [20] gives negative splitting order. This splitting extends, and is several times larger than those given by the experimental cage geometry \( \{ \vec{R}_i^{\text{exp}} \} \). This indicates that the splitting is extremely sensitive to the cage geometry. Given the sensitivity of splitting on the geometry, there are two perspective regarding the experimental measurements of splitting in [40]. One is that p-phase and h-phase nearest neighbouring orientation gives different splitting maybe due to fact that p-phase and h-phase neighbouring orientation may have different effect on the centred \( C_{60} \) cage geometry. The other one is that if it is possible to access the cage geometry that is used to measure splitting, one may compute comparable splitting with the experimental measurement given that for some random cages the splitting is close to the experimental measurements. Furthermore, we need to consider the quantum zero point translational motion of carbon atoms effect on the structure of \( C_{60} \) which has the magnitude of 0.044 Å in [29]. This will be discussed in next chapter after an analytical approach has been developed.

### 4.3 Translational and Rotational Coupling

In order to explore the effects of translational and rotational coupling on the splitting of ortho-H\(_2\) ground state \((J=1)\), calculations using different truncated basis were preformed. The splitting calculated by exact diagonalization using a converged basis is referred to as \( S_{\text{full}} \). The splitting calculated by exact diagonalization in converged rotational basis \((J \leq 5)\) coupled with translational ground state \((n_x + n_y + n_z = 0)\) is denoted as \( S_{\text{ED0}} \). The splitting calculated by exact diagonalization in ortho-H\(_2\) rotational ground state coupled with translational ground state is denoted as \( S_{\text{PT}} \). The comparison of these three calculations are shown in Figure 4.3. The effect of higher rotational level \((J > 1)\) coupling on \(J=1\) splitting are negligible. The coupling between translational ground state and ortho-H\(_2\) rotational ground state gives comparable splitting with that of those given by full calculations. To quantify the above
Figure 4.3: The comparison of splitting with different truncated basis on PES2ν0 (Left) and OPESν1 (Right): difference between $S_{\text{full}}$ and $S_{\text{ED0}}$ and difference between $S_{\text{PT}}$ and $S_{\text{ED0}}$.

coupling, the entanglement between the translational and rotational degrees of freedom has been evaluated. Our measure of entanglement is known as the bipartite Von Neumann entanglement entropy:

$$ S_r |\Phi\rangle = - \text{Tr} [\rho_r \log \rho_r] \quad \text{with} \quad \rho_r = \text{Tr}_t |\Phi\rangle \langle \Phi| $$

(4.1)

In Equation 4.1, $|\Phi\rangle$ is an eigenfunction of the Hamiltonian in Equation 2.1 and $\rho_r$ is the reduced density matrix of rotational part given by tracing out the translational part from a pure state density matrix. The results of Von Neumann entanglement entropy are showed in Table 4.5 for OPESν1 and in Table 4.6 for PES2ν0: the maximum Von Neumann entanglement entropy of the following calculation is $S_{\text{max}} = \log(\text{eigenfunction size}) = 7.6962$. The cage geometry used in the calculation is $\{\vec{R}_i^{\exp}\}$ in [20] which gives negative splitting order. The lower doubly degenerate level have same entanglement entropy which is larger than it is for the higher non-degenerate level, as was expected. The PES2 have relative larger Von Neumann entanglement entropy than OPES, which is not predicted by the translational and rotational coupling study showing in Figure 4.3. All entanglement entropy are small comparing to the maximum. The linear combination of the basis function which
Table 4.5: Von Neumann entanglement entropy of ortho-H$_2$ state calculated using OPES$\nu$1: $|\Phi = 1\rangle$ is the first eigenfunction of ortho-H$_2$ and the basis function is expressed in the form $|n_xn_yn_z; lm\rangle$

| $S_{|\Phi\rangle}^\prime$ | Linear Combination |
|---------------------|-------------------|
| $|\Phi = 1\rangle$  | 0.0111 $0.344|000; 1\bar{1}\rangle+0.851|000; 11\rangle+0.206|002; 11\rangle+0.200|020; 11\rangle+0.204|200; 11\rangle$ |
| $|\Phi = 2\rangle$  | 0.0111 $0.344|000; 11\rangle+0.851|000; 1\bar{1}\rangle+0.206|002; 1\bar{1}\rangle+0.200|200; 1\bar{1}\rangle+0.204|020; 1\bar{1}\rangle$ |
| $|\Phi = 3\rangle$  | 0.0026 $0.917|000; 10\rangle+0.212|002; 10\rangle+0.223|020; 10\rangle+0.223|200; 10\rangle$ |

Table 4.6: Von Neumann entanglement entropy of ortho-H$_2$ state calculated using PES2$\nu$0: $|\Phi = 1\rangle$ is the first eigenfunction of ortho-H$_2$

| $S_{|\Phi\rangle}^\prime$ | Linear Combination |
|---------------------|-------------------|
| $|\Phi = 1\rangle$  | 0.0247 $0.993|000; 11\rangle+0.093|000; 1\bar{1}\rangle+0.039|002; 11\rangle+0.021|020; 11\rangle+0.024|200; 11\rangle$ |
| $|\Phi = 2\rangle$  | 0.0247 $0.993|000; 1\bar{1}\rangle+0.093|000; 11\rangle+0.039|002; 1\bar{1}\rangle+0.021|200; 1\bar{1}\rangle+0.024|020; 1\bar{1}\rangle$ |
| $|\Phi = 3\rangle$  | 0.0171 $0.997|000; 10\rangle+0.039|002; 10\rangle+0.039|200; 10\rangle$ |

can be tabulated. It is showing that the basis function $|000; 1\bar{1}\rangle$ and $|000; 11\rangle$ are the main contributors in the lower doubly degenerate eigenstate and $|000; 10\rangle$ is the main contributor to the non degenerate eigenstate. The probability amplitude of the basis $|000; 10\rangle,$ $|000; 1\bar{1}\rangle$ and $|000; 11\rangle$ in PES2 is larger than them in OPES. this may explain why the splitting calculated by exact diagonalization in converged rotational basis($J \leq 5$) coupled with translational ground state $S_{ED0}$ recover more percentage of the splitting in PES2 than in OPES as shown by Figure 4.3.
Chapter 5

Analytical Approach

In this chapter, we will present how to solve our problem analytically by performing multipole expansion on the L-J potential. First, a very brief summary of multipole expansion on electric potential will be present which aims to give the reader a refresh of this general case. Then, we start with performing multipole expansion on L-J potential for pinned $\text{H}_2$ which has no translational degree of freedom comparing with that $\text{H}_2$ is trapped inside $\text{C}_{60}$. After validating the multipole expansion on L-J potential for pinned $\text{H}_2$, we will provide the multipole expansion on L-J potential for our real case which is $\text{H}_2$ trapped inside $\text{C}_{60}$ and will be referred to unpinned case in this chapter. The formalism and validation of multipole expansion on L-J potential for unpinned $\text{H}_2$ will be provide, as well as the discussion of advances of this analytical approach.
5.1 A Brief Summary of Multipole Expansion for Electric Potential

As shown in Equation 2.8, the L-J potential has $r^{-6}$ behaviours, which is similar to the Coulomb potential caused by a localized charge distribution. The Coulomb potential outside the charge distribution can be written as an expansion of spherical harmonics with properly assigned multipole moments [27]. It will be worthwhile to briefly review the formalism of the multipole expansion for Coulomb potential. Imagine that a point charge $Q$ sitting in position $\vec{R}'(R', \Theta', \Phi')$, the Coulomb potential at position $\vec{R}(R, \Theta, \Phi)$ is given by:

$$V = \frac{Q}{|\vec{R}' - \vec{R}|}. \quad (5.1)$$

One can easily generalize this expression by simply replacing the point charge into a localized charge distribution. Assuming the localized charge distribution is described by $\rho(\vec{R}')$, the Coulomb potential can be written as follows:

$$V(\vec{R}) = \int \frac{\rho(\vec{R}')}{|\vec{R}' - \vec{R}|} d\vec{R}'. \quad (5.2)$$

If the condition $|\vec{R}| \gg |\vec{R}'|$ is satisfied, one can expand $\frac{1}{|\vec{R}' - \vec{R}|}$ into a summation of Legendre polynomials:

$$\frac{1}{|\vec{R}' - \vec{R}|} = \frac{1}{\vec{R}} \sum_{l=0}^{\infty} \left( \frac{R'}{R} \right)^l P_l(\cos \gamma), \quad (5.3)$$

where $P_l(\cos \gamma)$ is the Legendre polynomials of order $l$ and $\gamma$ is the angle between $\vec{R}'$ and $\vec{R}$. The Legendre polynomials can be written as the summation of spherical harmonic functions:

$$P_l(\cos \gamma) = \frac{4\pi}{2l + 1} \sum_{m=-l}^{l} Y_{lm}^*(\Theta', \Phi') Y_{lm}(\Theta, \Phi). \quad (5.4)$$

Using Equation 5.4, the Coulomb potential due to a localized charge distribution can be written as:

$$V(\vec{R}) = \sum_{lm} \frac{4\pi}{2l + 1} \left[ \int \rho(\vec{R}')(R')^l Y_{lm}^*(\Theta', \Phi')d\vec{R}' \right] \frac{Y_{lm}(\Theta, \Phi)}{R^{l+1}}. \quad (5.5)$$
The coefficient in the square bracket in front of $\frac{Y_{lm}(\Theta, \Phi)}{R^{l+1}}$ is known as multipole moments,

$$q_{lm} = \int \rho(\vec{R}') (R')^l Y_{lm}^{*}(\Theta', \Phi') d\vec{R}'$$  \hspace{1cm} (5.6)$$

The coefficient $q_{lm}$ characterizes the properties of the charge distribution density $\rho(\vec{R}')$. $l = 0$ is called the monopole term, $l = 1$ is the dipole term which relates the electric dipole moment and $l = 2$ is the quadruple term which is related to the electric quadruple moment tensor.

5.2 Multipole Expansion on L-J of Pinned H$_2$

5.2.1 Formalism

To start with, a hydrogen molecule assumed to be pinned at the centre of C$_{60}$ molecule is considered since this is easier to deal with. Motivated by the multipole expansion for Coulomb potential using Legendre polynomials, the $r^{-6}$ and $r^{-12}$ terms of the L-J potential are expanded by using Gegenbauer polynomials. These polynomials are a generalized higher dimensional version of Legendre polynomials [3, 41]. Assuming a hydrogen atom at $\vec{r}(r, \theta, \phi)$ and $i$-th carbon atom at $\vec{R}_i(R_i, \Theta_i, \Phi_i)$, the $r^{-\lambda}$ term in the L-J potential can be written as follows:

$$\frac{1}{|\vec{R} - \vec{r}|^\lambda} = \frac{1}{R^{\lambda}} \sum_{n=0}^{\infty} \left(\frac{r}{R^n}\right) C_{n,\frac{\lambda}{2}}(\cos \gamma),$$ \hspace{1cm} (5.7)$$

where $C_{n,\frac{\lambda}{2}}(\cos \gamma)$ are Gegenbauer polynomials and, again, $\gamma$ is the angle between the $\vec{r}$ and $\vec{R}_i$. Similarly, to the Legendre polynomials, the Gegenbauer Polynomials can also be written as a summation of spherical harmonic functions by using the Addition Theorem.

$$C_{n}^{\lambda/2}(\cos \gamma) = \sum_{m=0}^{[n/2]} \sum_{k=-(n-2m)}^{n-2m} \frac{4\pi}{2(n-2m) + 1} B_{n,m}^{\lambda/2} Y_{n-2m,k}^{*}(\Theta, \Phi) Y_{n-2m,k}(\theta, \phi).$$ \hspace{1cm} (5.8)$$
The $Y_{n-2m,k}^*(\Theta, \Phi)$ and $Y_{n-2m,k}(\theta, \phi)$ terms are spherical harmonics functions both with a degree of $n - 2m$. $B_{nm}^\lambda$ is a dimensionless constant and has the following form:

$$B_{nm}^{\lambda/2} = \frac{\left(\lambda/2\right)_{n-m} \left(\lambda/2 - 1/2\right)_m (2n - 4m + 1)}{(3/2)_{n-m} m!},$$

(5.9)

where $(p)_m$ is the Pochhammer symbol and more specifically it is a rising factorial. With all of the above, the multipole expansion on L-J potential of $\text{H}_2$ molecule pinned in the geometry centre of the $C_{60}$ molecule can be written as:

$$V(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Q_{lm} Y_{l,m}(\theta, \phi)$$

(5.10)

$$Q_{lm} = 2 \sum_{k=0}^{\infty} \sum_{i=1}^{60} \frac{4\pi}{2l+1} \frac{4\epsilon}{R_i^{l+2k+12}} \left(B_{l+2k,k}^6 R_i^{l+2k+6} - B_{l+2k,k}^3 \sigma_{l+2k+2k+6}^6 \right) Y_{l,m}^*(\Theta_i, \Phi_i).$$

(5.11)

The factor 2 accounts for the 2 hydrogen atoms of $\text{H}_2$. Similarly to the multipole moments $q_{lm}$ of the Coulomb potential, $Q_{lm}$ will characterize the geometry properties of $C_{60}$ cage. A convergence study was performed in this case and, since $r \ll R$, the summation will converge very quickly. Since $k = 0$ can give 75% of the real potential and $k = 0, 1$ gives approximately 98% of the real potential, we used $l = 8$ and $k = 8$ to get very accurate potentials as well as the multipole moments $Q_{lm}$.

### 5.2.2 Validation

For a $\text{H}_2$ molecule is pinned in the geometrical centre of a $C_{60}$, only rotational degree of freedom are left to consider. The Hamiltonian only contains the rotational part and the interaction potential energy $V(\theta, \phi)$. The natural basis of this Hamiltonian is the spherical harmonic function and the matrix element has the following form:

$$\langle LM | H_{\text{pinned}} | L'M' \rangle.$$ 

(5.12)

In order to check the validity of the multipole expansion method, we compare the potential given by Equation 2.7 and that given by the multipole expansion expression. Here only the results for PES2 are presented since the interaction between
the centre of mass of H\textsubscript{2} and C\textsubscript{60} cage only gives a constant shift on the potential for pinned rotor. In Figure 5.1, we show how the potential for a pinned H\textsubscript{2} inside

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{example.pdf}
\caption{The comparison of potential dependence on \(\cos \theta\) between multipole expansion (red line) and accumulation 2-site L-J potential (blue line): Left potential gives negative splitting order and right one gives positive splitting order.}
\end{figure}

C\textsubscript{60} varies along different polar angle (\(\cos \theta\)) with averaged azimuthal angle. Our multipole expansion expression gives right results of the L-J potential for H\textsubscript{2} pinned at the centre of C\textsubscript{60} molecule. The potential shown on the left was calculated using a cage geometry that gives negative splitting and the potential showing on the right was calculated by using another cage geometry that gives positive splitting. Due to the inversion symmetry of the cage, only even multipole term will survive in the multipole expansion, moreover by choosing \(z\)-axis along \(C\textsubscript{3i}\) symmetry axis only multipole terms that has 3-fold rotational symmetry will be nonzero. The multipole term(\(Q_{lm}\)) can be tabulated in Table 5.1 for one cage geometry that gives a negative splitting and Table 5.2 for that gives positive splitting. Only results for \(l \leq 6\) are showing here since higher order terms are negligible. The sign of \(Q_{20}\) is opposite since it directly related to the ortho-H\textsubscript{2} ground state splitting.

\begin{equation}
\langle 1M' \mid V \mid 1M \rangle = \int Y_{1M'}^*(\theta, \phi)Q_{20}(\theta, \phi)Y_{20}(\theta, \phi)Y_{1,M}(\theta, \phi) \sin \theta d\theta d\phi.
\end{equation}
Furthermore, the comparison between analytical approach and numerical calculation are showing in Figure 5.2 for PES2ν0. The $S_{EDfull}$ is the splitting calculated by exact diagonalization under converged basis. The $S_{PT}$ is the splitting calculated by exact diagonalization in ortho-H$_2$ ground state (J=1), which is the first order degeneracy perturbation theory given by $\langle 1M'|V|1M \rangle$. The $S_{multipole}$ is the splitting calculated by multipole expansion by using Equation 5.13. The agreement of numerical calculation and analytical multipole expansion calculation adjusted by the insert figure(c) in Figure 5.2 and the error is in the order of $10^{-8}$. Similar with unpinned case, the higher rotational state coupling is negligible given that

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<td>-0.091</td>
</tr>
<tr>
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<td>-0.027-0.031i</td>
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<td></td>
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<tr>
<td>m=6</td>
<td></td>
<td>0.085-0.021i</td>
<td></td>
</tr>
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Table 5.1: The tabulation of multipole term($Q_{lm}$) with PES2 that gives negative splitting

<table>
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<td></td>
<td>0.088+0.021i</td>
<td></td>
</tr>
<tr>
<td>m=-3</td>
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<td>0.136+0.018i</td>
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<td>0.042</td>
<td>-0.091</td>
</tr>
<tr>
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<td>0.088-0.021i</td>
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Table 5.2: The tabulation of multipole term($Q_{lm}$) with PES2 that gives positive splitting
Figure 5.2: The comparison between analytical approach and numerical calculation for pinned rotor with PES2: The $S_{PT}$ is the splitting calculated by exact diagonalization in ortho-H$_2$ ground state (J=1), which is the first order degeneracy perturbation theory given by $\langle 1M'|V|1M \rangle$. The $S_{\text{multipole}}$ is the splitting calculated by multipole expansion by using Equation 5.13.

The difference between full calculation and perturbation is in the order of $10^{-4}$ as show in insert figure (b) in Figure 5.2. The same calculation was also conducted for OPES and it shows same qualitative behaviours which can be found in appendix. For pinned rotor, It shows that the numerical exact diagonalization agrees with the analytical approach and the splitting of ortho-H$_2$ ground state can be computed by using dipolar term $Q_{20}$ with very small error. The splitting order will determined by the sign of the dipolar term $Q_{20}$ which reflects the geometry feature of the C$_{60}$ cages. after solving the above problems for pinned case, It is time to move onto our real topic that H$_2$ confined inside C$_{60}$, which also referred as unpinned H$_2$. 
5.3 Multipole Expansion on L-J of Unpinned H$_2$

5.3.1 Formalism

Having developed the formation for the multipole expansion for the case that a H$_2$ molecule pinned at the geometry centre of C$_{60}$ which only have rotational degree of freedom. We can now consider H$_2$ with its five dimensional degrees of freedom, which are characterized by centre of mass motion $\vec{\delta}(\delta, \theta, \phi)$ and $\vec{r}(r, \theta, \phi)$. $\vec{r}$ specify the orientation of H$_2$ respect to center of mass where $r$ is half of the bond length of H$_2$. $\vec{\delta}$ specify the position of the center of mass of H$_2$. We use $\vec{R}_i(R_i, \Theta_i, \Phi_i)$ to specify the position of $i$-th carbon atom from the origin. We have the following vector relation:

$$\vec{d}_{1i} = \vec{R}_i - \vec{\delta} - \vec{r},$$
$$\vec{d}_{2i} = \vec{R}_i - \vec{\delta} + \vec{r},$$

where $\vec{d}_{1i}$ and $\vec{d}_{2i}$ refer to the vector from hydrogen atom 1 and hydrogen atom 2 to $i$-th carbon atom. The main difficulties of moving from a description of pinned H$_2$ inside C$_{60}$ to the unpinned H$_2$ inside C$_{60}$ is to deal with the translational degrees of freedom. Suggested by the numerical work in 4.3 that the coupling between translational ground state and ortho-H$_2$ rotational ground state gives comparable splitting with that of those given by full calculations, we can assume that the centre of mass motion can be described by the ground state of isotropic harmonic oscillator which has the following form:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}^{\phi}(\theta, \phi) \quad \text{with} \quad \int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1.$$  

The centre of mass of H$_2$ in the ground state have the following form:

$$\psi_{000}(\delta, \theta, \phi) = R_{00}(\delta)Y_{00}^{\phi}(\theta, \phi) = \left(\frac{2\nu^3}{\pi}\right)^{\frac{1}{4}} \sqrt{8} \exp\left\{-\nu\delta^2\right\} \frac{1}{\sqrt{4\pi}}, \quad (5.14)$$

where $\nu$ is defined as $\nu = \frac{\mu \omega}{2\hbar}$, $\mu$ is the mass of H$_2$ and $\omega$ is the angular frequency of the oscillator. We can now perform a multipole expansion of an unpinned rotor with
centre of mass in translational ground state. Firstly, the potential can be written as following given that $H_2$ is the translational ground state:

$$
\langle 000 | \hat{V} | 000 \rangle = \int_0^\infty \int_{-1}^1 \int_{0}^{2\pi} |R_{00}(\delta)|^2 \delta^2 |Y_{00}(\theta_\delta, \phi_\delta)|^2 V(|\vec{R}_i - \vec{r} - \vec{\delta}|) d\delta \ d cos \theta_\delta \ d\phi_\delta.
$$

(5.15)

Similar with the pinned rotor case, we treated $\vec{R}_i - \vec{r}$ together and expand the potential in terms of $\vec{\delta}$ since the condition $|\vec{\delta}| \ll |\vec{R}_i - \vec{r}|$ holds in this case. we got the following:

$$
V(\delta, \theta_\delta, \phi_\delta) = \sum_{l,m} \sum_{k=0}^{60} \frac{4\pi}{2l+1} \left( \frac{4\epsilon \sigma^{12} B_{l+2k,k}^6 \delta^{l+2k}}{|\vec{R}_i - \vec{r}|^{l+2k+12}} - \frac{4\epsilon \sigma^6 B_{l+2k,k}^3 \delta^{l+2k}}{|\vec{R}_i - \vec{r}|^{l+2k+6}} \right) Y_{lm}^*(\vec{R}_i - \vec{r}) Y_{lm}(\theta_\delta, \phi_\delta),
$$

(5.16)

where $\vec{R}_i - \vec{r}$ means the angle of vector $\vec{R}_i - \vec{r}$. Now, we can plug Equation 5.16 into Equation 5.15. We use the following properties of the spherical harmonic function:

$$
\frac{1}{\sqrt{4\pi}} \int_{-1}^{1} \int_{0}^{2\pi} Y_{nm}(\theta, \phi) d\cos(\theta) d\phi = \delta_{n,0}\delta_{m,0},
$$

(5.17)

where $\delta_{n,0}\delta_{m,0}$ are Kronecker delta function. This allow to simplify the expansion significantly since only the $l = 0$ and $m = 0$ terms survived. The Equation 5.15 can be rewritten as following:

$$
\langle 000 | \hat{V} | 000 \rangle = \int_0^\infty |R_{00}(\delta)|^2 \delta^2 \sum_{k=0}^{60} \left( \frac{4\epsilon \sigma^{12} B_{l+2k,k}^6 \delta^{l+2k}}{|\vec{R}_i - \vec{r}|^{l+2k+12}} - \frac{4\epsilon \sigma^6 B_{l+2k,k}^3 \delta^{l+2k}}{|\vec{R}_i - \vec{r}|^{l+2k+6}} \right) d\delta.
$$

(5.18)

Then, one find that Equation 5.18 can be further expanded again with respect to $\vec{r}$ by using Equation5.7 and Equation5.8. Now we use prime for each label:

$$
\frac{1}{|\vec{R}_i - \vec{r}|^{2k+12}} = \frac{1}{|\vec{R}_i|^{2k+12}} \sum_{l',m',k'=0}^{\infty} \frac{4\pi}{2l'+1} B_{l'+2k',k'}^{k+6} \frac{|\vec{r}|^{l'+2k'}}{|\vec{R}_i|^{l'+2k'}} Y_{l'm'}^*(\Theta_i, \Phi_i) Y_{l'm'}(\theta, \phi)
$$

(5.19)

Then the Equation 5.18 can be written as following:

$$
\langle 000 | \hat{V} | 000 \rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} A_{lm} Y_{lm}(\theta, \phi)
$$

(5.20)
with $A_{l'm'}$ has the following form and for simplicity only the repulsive part of L-J potential are presented here and we can obtain the attractive term by replacing 12 by 6 and 6 by 3:

$$A_{l'm'} = \sum_{k,k'=0}^{\infty} \sum_{i=1}^{60} \int_0^{\infty} |R_{00}(\delta)|^2 \delta^{2+2k} d\delta \frac{4\pi}{2l'+1} 4\epsilon \left( \frac{\sigma_{12}^6 B_{2k,k} B_{l'+2k',k'} |\vec{r}|^{l'+2k'}}{|\vec{R}_i|^{l'+2k'+2k+12}} \right) Y_{l'm'}^* (\Theta_i, \Phi_i) \quad (5.21)$$

The coefficient $A_{l'm'}$ is an analogue of $Q_{lm}$ which we defined for pinned rotor before. Again the factor of 2 is still needed to count in two hydrogen atoms by symmetry.

Now it is time to evaluate the integral of the translational part:

$$\int_0^{\infty} |R_{00}(\delta)|^2 \delta^{2+2k} d\delta = 8\nu \frac{(2k + 1)!!}{2^{k+2}(2\nu)^{k+1}}, \quad (5.22)$$

according to the following handy integral rules:

$$\int_0^{\infty} x^{2n} \exp \{-ax^2\} dx = \frac{(2n - 1)!!}{2^{n+1}a^n} \left( \frac{\pi}{a} \right)^{1/2}.$$

We can now put everything together to get final result for the repulsive term of the L-J potential of the interaction between one hydrogen atom and the $i$-th carbon atom:

$$A_{lm} = \sum_{k,k'=0}^{\infty} 8\nu(2k + 1)!! \frac{4\pi |\vec{r}|^{l+2k'} 4\epsilon \sigma_{12}^6 B_{2k,k} B_{l+2k',k'} |\vec{r}|^{l+2k+12}}{2^{k+2}(2\nu)^{k+1}} Y_{lm}^* (\Theta_i, \Phi_i) \quad (5.23)$$

Now the value of ortho-H$_2$ rotational ground state block ($J=1$) are easy to evaluate, since only $l' = 2$ term give nonzero value according to the properties of Clebsch-Gordan coefficients. Moreover, if the $z$-axis is align along the $C_{3i}$ symmetry axis, only $m' = 0$ term will be nonzero by the space group argument.

$$\langle 1M' | 000 \rangle V | 000 \rangle | 1M \rangle = \int Y^*_{1M'}(\theta, \phi) A_{20} Y_{20}(\theta, \phi) Y_{1,M}(\theta, \phi) \sin \theta d\theta d\phi. \quad (5.24)$$

Above is the multipole expansion for unpinned H$_2$ molecule confined into C$_{60}$ molecule with the assumption that H$_2$ is in translational ground state. We can justify our analytical result by comparing with block diagonalization calculation. For OPES, the
interaction potential between the centre of mass of $H_2$ and $C_{60}$ can be expand as following which is directly took from Equation 5.18 with $\vec{r} = 0$ and integrate over translational radius part:

$$
\langle 000 | V (| \vec{R}_i - \vec{\delta} |) | 000 \rangle = \sum_{k=0}^{\infty} \sum_{i=1}^{60} 8\nu (2k + 1)!! \left( \frac{4\epsilon \sigma^{12} B_{2k,k}^6}{|\vec{R}_i|^{2k+2}} - \frac{4\epsilon \sigma^6 B_{2k,k}^3}{|\vec{R}_i|^{2k+6}} \right) (5.25)
$$

This term is a constant and it will not lift the degeneracy or cause splitting under the assumption that $H_2$ is in translational ground state. This argument can also be justified by comparing analytical result and block diagonalization calculation with the OPES potential.

5.3.2 Validation

The L-J potential has been expanded as a summation of spherical harmonics functions under the assumption that $H_2$ is in its translational ground state. The potential calculated by multipole expansion with Equation 5.20 and Equation 5.21 is compared with it calculated by accumulated 2-site or 3-site L-J potential. The potential of PES2$\nu$0 is shown in Figure 5.3. Again, similarly with pinned case, the left

<table>
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<td></td>
<td>0.118+0.029i</td>
</tr>
<tr>
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<td>0.039-0.044i</td>
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<td>-0.039-0.044i</td>
<td>0.118-0.029i</td>
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</tbody>
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Table 5.3: The tabulation of multipole term($A_{lm}$) with PES2$\nu$0 that gives negative splitting.

potential is from a cage that gives negative splitting order and the right one is from a cage that gives positive splitting order. The multipole terms that gives the above
Figure 5.3: The comparison of potential dependence on $\cos \theta$ between multipole expansion (red line) and L-J potential (blue line) for unpinned H$_2$ with PES2ν0: Left potential gives negative splitting order and right one gives positive splitting order.

PES2 potential are tabulated in Table 5.3 for negative splitting and Table 5.4 for positive splitting. The validation of the multipole expansion can simply be justified by the comparison of splitting that calculated numerically and analytically as shown in Figure 5.4. The multipole expansion calculation that given by Equation 5.24 agrees with the block diagonal. The error is of the order of $10^{-9}$ as showing in

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Table 5.4: The tabulation of multipole term($A_{lm}$) with PES2ν1 that gives positive splitting.


the insert figure(b) in Figure 5.4.

Figure 5.4: The comparison of block diagonalization calculation and multipole expansion calculation on PES2ν0.

For OPES, the interaction potential between the centre of mass of H₂ and C₆₀ can be expand as following which is directly took from Equation 5.18 with \( \vec{r} = 0 \) and integrate over translational radius part. This term is a constant and it will not lift the degeneracy or cause splitting under the assumption that H₂ is in translational ground state. The comparison in Figure 5.5 of potential calculated by multipole expansion with Equation 5.20 and Equation 5.21 is compared with it calculated by OPES but without the interaction between centre of mass of H₂ and C₆₀ cage. The multiple moments for OPESν1 that give the above potential can be found in Table 5.5 for negative splitting order and in Table 5.6 for positive splitting order. The validation of the multipole expansion can simply be justified by the comparison of splitting that calculated numerically and analytically as shown in Figure 5.6. The fact the interaction between the centre of mass of H₂ and the cage does not affect the ortho-H₂ ground state splitting under the assumption that H₂ is in its translational ground
Figure 5.5: The comparison of potential dependence on $\cos \theta$ between multipole expansion (red line) and L-J potential (blue line) for unpinned H$_2$ with OPES$\nu$1: Left potential gives negative splitting order and right one gives positive splitting order.

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<tbody>
<tr>
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<td>0.013-0.003i</td>
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<td>0.020</td>
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<td>-0.020+0.003i</td>
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<tr>
<td>m=6</td>
<td>0.004-0.004i</td>
<td>0.004+0.004i</td>
<td>0.013-0.003i</td>
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Table 5.5: The tabulation of multipole term ($A_{lm}$) with OPES$\nu$1 that gives negative splitting state was therefore justified. For the unpinned rotor, the multipole expansion on L-J potential have been developed under the assumption that H$_2$ in its translational ground state. The analytical approach agrees with numerical results very well and the multipole moments can predict the splitting order. It also provides us a more
Table 5.6: The tabulation of multipole term \(A_{lm}\) with OPES\(\nu_1\) that gives negative splitting.

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<tbody>
<tr>
<td>(m=-6)</td>
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<td></td>
<td>0.013+0.003i</td>
</tr>
<tr>
<td>(m=-3)</td>
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<td>-0.013</td>
</tr>
<tr>
<td>(m=3)</td>
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<td></td>
</tr>
<tr>
<td>(m=6)</td>
<td>-0.020+0.003i</td>
<td>0.013-0.003i</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.6: The comparison of block diagonalization calculation and multipole expansion calculation on OPES\(\nu_1\).

efficient way to calculate the splitting compared to the exact diagonalization method.
Chapter 6

Conclusion

6.1 Conclusion of Present Work

In this work we have discussed the subject of confined quantum molecular degrees of freedom when a small molecule H\textsubscript{2} is confined inside C\textsubscript{60} fullerene molecule. We used the simplest possible Hamiltonian composed of translational term, rotational term and interaction term to encapsulate the quantum dynamics of the confined H\textsubscript{2} molecule. The interaction term can be effectively handled with L-J potential which is a simple model that approximates the interaction between H\textsubscript{2} and C\textsubscript{60}. The method we used to deal with this problem is exact diagonalization. A variety of L-J potential parameters according to experimental measurements were used to obtain the energy levels of the trapped H\textsubscript{2}. The reason for the splitting of ortho-H\textsubscript{2} ground state (J=1) has been identified to be because of the reduction from Ih symmetry to C\textsubscript{3i} symmetry, which is reflected by the interaction between H\textsubscript{2} and its C\textsubscript{60} cage instead of that between H\textsubscript{2}@C\textsubscript{60} with its neighbouring molecules. The fact that ortho-H\textsubscript{2} ground state(J=1) does not split if the Ih symmetry is maintained has been justified. The reason for the splitting of ortho-H\textsubscript{2} ground state(J=1) has been identified to be because of the reduction from Ih symmetry to C\textsubscript{3i} symmetry. It is mainly caused by the interaction between H\textsubscript{2} and its C\textsubscript{60} cage instead of that between H\textsubscript{2}@C\textsubscript{60} with its neighbouring molecules. We also found that the splitting is extremely sensitive to its
cage geometry while sitting in a relatively large linear regime. This feature suggests that the zero point motion of carbon atoms would not effect the size of the splitting. These behaviour are independent of L-J potential parameters as we expected. We also found an analytical approach to solve our problem which is doing multipole expansion on L-J potential. This analytical approach was preformed basing on the fact that the coupled motion of translational ground state and rotational ortho-ceH2 ground state(J=1) gives comparable splitting with that given by converged basis. This analytical approach gives physical understanding of energy degeneracy from symmetry perspective. We further verified that the analytical results agrees with that calculated from exact diagonalization.

Finally, a discussion of future work left for studying confined molecular degree of freedom will be present. For H$_2$@C$_{60}$, a more precise potential to better describe the interaction between H$_2$ and C$_{60}$ would be more sufficient to study the quantum dynamics of confined H$_2$ molecule. A more precise potential provide us a more accurate model to confirm the above conclusions. From the study of H$_2$@C$_{60}$, we can extend our study into other endofullerene, such as H$_2$O@C$_{60}$ and HF@C$_{60}$. Comparing with H$_2$@C$_{60}$, the only difference is that the confined molecule H$_2$O and HF are dipolar molecule and will involve the long range dipole-dipole interaction.

6.2 Future Directions

6.2.1 More Precise Potential

We begun this subsection with a discussion for obtaining more precise potential to physically describe H$_2$ trapped inside C$_{60}$. Instead of parametrizing L-J potential with the experimentally measured energy level, there exists another potential to characterize this interaction. It involves writing the potential into a series of spherical harmonics physically based on the symmetry of the system and fitting into IR spectra to obtain the coefficients of the spherical harmonics [17, 45]. However, to deal with this problem, this potential will not be sufficient due to the fact that the
splitting of ortho-H$_2$ ground state (J=1) is small and can not be measured accurately. Therefore, fitting with IR spectra to parametrize L-J potential is the only way for now to study the degeneracy lifting of ortho-H$_2$ ground state (J=1). An additional direction of future work is that instead of fitting into IR spectra one can preform Ab-initio calculation to obtain coefficients of the spherical harmonics with high accuracy.

### 6.2.2 Dipolar Molecule Confined Inside C$_{60}$

In this subsection, we will describe another potential future direction of this work. The simplest possible Hamiltonian will have one more term which is the dipolar interaction term and have the following form:

$$H_{\text{dipole-dipole}} = \frac{\mu^2}{4\pi \epsilon_0 \rho r_{nn}^3} \sum_{i>j} \hat{n}_i \cdot \hat{n}_j - 3 \hat{n}_i \cdot \hat{r}_{ij} \hat{r}_{ij} \cdot \hat{n}_j \left( \frac{r_{ij}}{r_{nn}} \right)^3. \quad (6.1)$$

In Equation 6.1, $\mu$ is the dipole moment of H$_2$O@C$_{60}$ or HF@C$_{60}$ and pointing in $\hat{n}_i$ direction. $\hat{r}_{ij}$ is the unit vector pointing from $i$-th dipole to $j$-th dipole with distance $r_{ij}$ and $r_{nn}$ is the nearest neighbour distance of H$_2$O@C$_{60}$ or HF@C$_{60}$ lattice. Of equal interest experimentally and theoretically, dipolar molecule confined inside C$_{60}$, such as H$_2$O and HF, could result in a net polarization due to the very long-range dipolar interactions. The periodic lattices of endofullerene complexes with polar molecules trapped inside the C$_{60}$ can, theoretically, exhibit ferroelectric phase transition as predicted in [9]. While experimentalists did not observe any ferroelectric phase transition [1, 31]. More theoretical efforts are needed in order to predict the collective orientation of dipolar molecule and phase transition diagrams for endofullerene complexes with polar molecules trapped inside.
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