國 立 交 通 大 學

應用化學系分子科學碩士班

碩 士 論 文

利用齊次方法展開求氦原子波函數之精確解

Pursuit of Exact Wave Function of Helium Using Homogeneity Expansion

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中 華 民 國 一 百 零 三 年 三 月

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中文摘要

目前，氦原子波函數的精確解仍未被完整的解出。如何制定一個有效率的方法來精確地計算出一個雙電子系統的波函數成為了量子化學領域的一個重要議題。如果這個簡單的雙電子系統問題得到解答，那將會有助於了解更進一步的多電子系統。本篇論文的主題是利用齊次方法展開來解氦原子的薛丁格方程式，為了求得精確解，我們將波函數 Ψ 展開為 $\Psi=\sum_{h=0}^{\infty}\Psi_h$，其中 Ψ_h 是在波函數之中對長度單位的次方為 h 的項。將這個展開代入氦原子的薛丁格方程式之中，便能進一步的求得在本篇論文之中所介紹的主要計算方程式 $\hat{T}\Psi_n=-\hat{V}\Psi_{n-1}+E\Psi_{n-2}$。我們利用這個主要方程式來計算 Ψ_n 在 n 值為 0、1、2 以及 3 之時。在 n 值為 0 時，方程式為 $\hat{T}\Psi_0=0$，而我們也能解出 $\Psi_0=1$，在這個部份的論文內容我們有進一步討論有關動能算符的齊次解。而 n 值為 1 時，方程式為 $\hat{T}\Psi_1=-\hat{V}\Psi_0$，而解為 $\Psi_1=-Z(r_1+r_2)+\frac{1}{2}r_{12}$。而當我們試圖更進一步的求解 n 值為 2 時，方程式為 $\hat{T}\Psi_2=-\hat{V}\Psi_1+E\Psi_0$，而它的解因為太複雜，我們便不在摘要中提及。利用我們的方法所求出之 Ψ_2 只是其中一種解，在某些情況下會有奇異點，在該章

節中我們提到利用我們的方法所求出的 Ψ_2 與 Paul Abbott 等人所找到的 Ψ_2 做討論與分析，同時在本篇論文之中我們將 Paul Abbott 等人所找到的 Ψ_2 作圖並證明了它的正確性。在後續的章節我們也利用 Ψ_2 來進一步的求解 Ψ_3，我們在此制定了一個專門用來求解單項式時的反函數表，只要能找到此張表內足夠的項，我們將能更進一步的求得精確的氦原子波函數，這項發現說明了求解氦原子的薛丁格方程式是可行並且有價值的。

Pursuit of Exact Wave Function of Helium Using Homogeneity Expansion

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Abstract

The exact wave function of helium atom has not been fully determined yet. Formulating an efficient way of describing and computing the wave functions of two-electron systems is important. Solving this fundamental problem can be useful for accurate treatment of many-electron systems. Using homogeneity expansion of the wave function to solve the Schrödinger equation is the main topic in this thesis. In order to solve the Schrödinger equation to helium atom, we assume that the wave function Ψ can be expanded as $\Psi = \sum_{h=0}^{\infty} \Psi_h$, where Ψ_h is the component of the total wave function homogeneous of order h. By substituting the expansion into Schrödinger equation, the working equation of our method, $\hat{T}\Psi_n = -\hat{V}\Psi_{n-1} + E\Psi_{n-2}$, is produced. We attempt to solve this equation to find Ψ_n with $n = 0$, 1, 2 and 3. The

first equation is $\hat{T}\Psi_0 = 0$ and its solution is $\Psi_0 = 1$. For Ψ_0, we give a short discussion of homogeneous solutions for the kinetic energy operator ($\hat{T}$) in interparticle coordinates (IC). Next, we discuss two methods of finding Ψ_1, separately for terms independent of r_{12} and terms dependent on r_{12}. By solving the equation $\hat{T}\Psi_1 = -\hat{V}\Psi_0$, we can find that $\Psi_1 = -Z(r_1 + r_2) + \frac{1}{2} r_{12}$. The equation defining Ψ_2 is $\hat{T}\Psi_2 = -\hat{V}\Psi_1 + E\Psi_0$; its solution is too complicated to quote it here. The solution Ψ_2 found by our method is a particular solution. This solution has singularities at some special points. In order to make our particular solution Ψ_2 well-behaving, we need to find homogeneous solutions to remove the singularities of Ψ_2 when $r_1 = r_2 + r_{12}$ and $r_2 = r_1 + r_{12}$. A detailed discussion of Ψ_2 found by Abbott *et al.* leads us to find homogeneous solutions we need. We also make a plot of Ψ_2 and prove that Ψ_2 is a well-behaving wave function successfully. Application of Ψ_2 for solving Ψ_3 is another important issue studied in this thesis. An inversion table for monomial terms of homogeneity one is created for finding a particular solution of Ψ_3. Enough terms in monomial tables of every homogeneity have the ability to generate particular solutions of Ψ_n with every value of n. This discovery shows that using inversion table to solve the Schrödinger equation is feasible and valuable.

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After these years, I really want to thank Prof. Henryk Witek to be my advisor and also a good teacher in chemistry, mathematics and life. I am so fortunate to be a student of such a good teacher I have ever seen. He always give me many useful suggestions when I was confused. I really learn a lot of things in this lab. All of my lab members, Chin-chai, Chien-pin, Yen-ting and Bing-hou, are really help me a lot. I am proud of saying that I am in a lovely and nice lab.

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I am really grateful to everyone who has ever helped me, inspired me, taught me or even listen to me. Thank them for being parts of my life.

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Chapter 1

Introduction

The wave functions of atoms and ions have been discussed in detail since the early days of quantum mechanics. We can completely solve Schrödinger equation for hydrogen and hydrogen-like atoms. It means that one-electron systems are understood exactly. Before we proceed to the discussion of many-electron systems, we need to know more about two-electron systems. For the systems with more than two electrons, the correlation between each two electrons is important and should be understood clearly in order to find the exact wave function of any system. Solving this fundamental problem can be useful for studying more complicated many-electron systems. Moreover, accurate wave functions of two-electron atoms are needed not only to understand the properties of three-particle system but also to describe the behavior of these systems in the presence of external fields.

However, even the wave function of helium has not yet been fully understood. It is commonly believed that helium, the second simplest of atoms, does not permit exact solution of its Schrodinger equation because of the difficulties in solving the Schrödinger equation analytically due to non-separability. This belief led to the fact that few people were trying to find the exact wave function of helium.

After over 80 years of research, we know that to formulate an efficient way of describing and computing the wave functions of two-electron systems is important. If the Schrödinger equation of a two-electron atom can be solved exactly, which means the two-electron systems are understood completely, multi-electron systems can be understood more deeply; it will also improve most of the approximation methods applied to multi-electron systems.

The history of finding the wave function of helium dates back to the beginning of quantum mechanics. It was Hylleraas who applied Schrödinger equation to the helium atom and published a series of important results in 1928[1] and 1929.[2] He introduced electron-electron distance (r_{12}) explicitly in the wave function, which was a very important and useful argument to describe the behavior of the wave function of helium. A very nearly exact approximation to the ground state wave function for the helium atom was obtained by Hylleraas. This approximation is called Hylleraas expansion. Hylleraas expansion applied to evaluate the ground state energy of helium atom produced a result correct to 3 digits. Another development of Hylleraas was the introduction of interparticle coordinates and (s,t,u) coordinates to simplify the Schrödinger equation.

In 1935, Bartlett proposed his expansion of the wave function of helium atom.[3] This expansion was the first expansion which included logarithmic terms, which is important and meaningful nowadays. He also mentioned about the importance of boundary conditions in finding an exact wave function.[4] Since then, many people tried to solve accurately the Schrödinger equation of helium atom.

In 1951, Kato demonstrated that a wave function should be well-behaving,[5] which means the wave function should be square-integrable, antisymmetric, finite and continuous everywhere and its first derivative should be also finite and continuous everywhere except for the Coulomb singular points (Kato cusp conditions). We need to use these principles to make sure our solutions are well-behaving wave functions.

In 1957, Kinoshita improved Hylleraas expansion,[6] and used 39 parameters to evaluate the energy of the helium atom, which was correct to 6 digits. Kinoshita also used a new coordinate system $(s, p = \frac{u}{s}, q = \frac{t}{u})$ to set an expansion of the wave function of helium.

There are also a lot of scientists trying to introducing new coordinates to simplify Schrödinger equation of helium. After introducing hyperspherical coordinates, Fock proposed that the exact eigenfunctions have the form of Fock expansion in 1954.[7,8] This expansion plays an important role in the research of two-electron system. Fock's research tells us that finding good coordinates is important to solve Schrödinger equation of helium.

After the publication of Fock expansion, Hylleraas proposed a new method for obtaining formal solutions by using an expansion in Legendre polynomials[9] in 1960. This research mentioned about the importance of finding homogeneous solutions; it can be considered a very important contribution for finding the exact wave function of helium.

In 1966, Frankowski and Pekeris try to add logarithmic terms in the wave function to evaluate the energy of helium.[10] The result was correct to 12 digits. At this moment, we believe that logarithmic terms are really important in the wave function.

Following Fock expansion to solve the Schrödinger equation of helium became a main topic in 1980s. There are a lot of outstanding scientists, for example, Pluvinage, who published important result of Fock expansion in order to evaluate the exact wave function and energy of helium in 1982[11] and also defined a new coordinates which called Pluvinage's coordinates. In 1986, Morgan proved pointwise convergence for every (even complex) value of E in the Schrödinger equation of helium with Fock expansion.[12]

In 1987, Gottschalk, Abbott and Maslen published papers about an important solution of parts of Fock expansion.[13,14,15] They used an expansion of the wave function by hypersperical harmonics (HHs) corresponding to homogeneity for solving the two-electron atomic Schrödinger equation. In this paper, they are successful to find $\Psi_{2,0}$ in Fock expansion, and this paper is also an important discussion of solving the following wave functions.

In 2007, Nakashima and Nakatsuji evaluated a very accurately the energy of helium atom.[16] In their result, the energy is correct to over 40 digits. The technology of very accurate approximate calculations is complete. However, the exact wave function is still not found completely. The main topic of this thesis is continuing solving the Schrödinger equation to helium by new, mathematical, and logical methods. The main methods we use and the detail we will talk in the following chapters.

Chapter 2

Theoretical Background

2.1 Schrödinger Equation of Helium Atom

Time-independent Schrödinger equation is given by

$$\hat{H}\Psi = (\hat{T} + \hat{V})\Psi = E\Psi \,. \tag{2.1}$$

Hamiltonian operator has two parts, corresponding to kinetic energy and potential energy. We can completely solve Schrödinger equation of hydrogen and hydrogen-like atoms. However, the solution to Schrödinger equation of many-electron system is still not known exactly. Before discussing many-electron system, we need to solve Schrödinger equation of two-electron system first.

The nonrelativistic many-electron Hamiltonian of an N-electron atom is given by

$$\hat{H} = \sum_{i=1}^{N}(-\frac{1}{2}\Delta_i - \frac{Z}{r_i}) + \sum_{i<j}\frac{1}{r_{ij}}, \tag{2.2}$$

where Z is the nuclear charge and $-\frac{1}{2}\Delta_i$ is the operator corresponding to the kinetic energy of the electron i. In two-electron systems, Eq. (2.2) can be written as

$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{2.3}$$

where r_1, r_2 and r_{12} are interparticle coordinates (IC) shown in **Figure 2.1**.

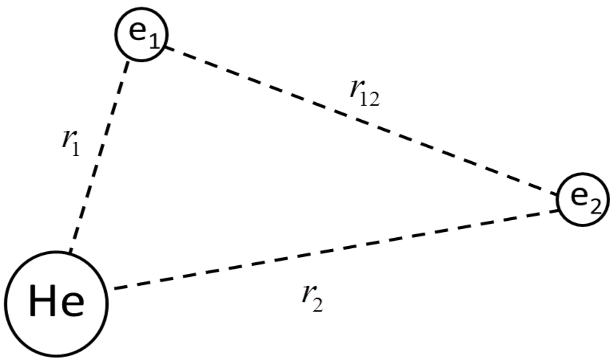


Figure 2.1
The interparticle coordinates of helium

In **Figure 2.1**, r_1 and r_2 are the electron-nucleus distances and r_{12} is the distance between the two electrons.

Therefore, we can use interparticle coordinates to describe the behavior of the wave function.

$$\Psi = \Psi^{IC}(r_1, r_2, r_{12})\,. \tag{2.4}$$

Eq. (2.1) becomes

$$(\hat{T}^{IC} + \hat{V}^{IC})\Psi^{IC} = E\Psi^{IC}\,. \tag{2.5}$$

The operators $\hat{T}^{IC}$ and $\hat{V}^{IC}$, in atomic units (a.u.) for simplicity, are given by

$$\begin{aligned}\hat{T}^{IC} = &-\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} \\ &- \frac{r_{12}^2 + r_1^2 - r_2^2}{2r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_{12}^2 - r_1^2 + r_2^2}{2r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}\,,\end{aligned} \tag{2.6}$$

$$\hat{V}^{IC} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\,. \tag{2.7}$$

Interparticle coordinates give the easiest way to understand the physical meaning of each term of the wave function of helium.

2.2 Coordinate Systems

For solving the Schrödinger equation of helium, interparticle coordinates constitute an easy to understand framework. However, the solution can be complicated in these coordinates. Discovering useful coordinates to describe and simplify the wave function is important to solve the equation systematically. Therefore, there are many different sets of coordinates which are used to evaluate and simplify the equations. These coordinates are introduced and discussed in this section.

2.2.1 Interparticle Coordinates (r_1, r_2, r_{12})

1) Definition of Interparticle coordinates (IC) is already mentioned in **Figure 2.1**

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{IC} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{2.8}$$

$$\hat{T}^{IC} = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}$$
$$-\frac{r_{12}^2 + r_1^2 - r_2^2}{2 r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_{12}^2 - r_1^2 + r_2^2}{2 r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}. \tag{2.9}$$

3) Volume Element: $8\pi^2 r_1 r_2 r_{12}$

4) Range

$$r_1 \in [0, \infty)$$
$$r_2 \in [0, \infty)$$
$$r_{12} \in \left[|r_1 - r_2|, r_1 + r_2\right]$$

2.2.2 Ratio Coordinate (r_1, ρ, r_{12})

1) Definition and Inverse Formula (Compared with IC)

$$\left\{ r_1 = r_1, \rho = \frac{r_1}{r_2}, r_{12} = r_{12} \right\}$$

$$\left\{ r_1 = r_1, r_2 = \frac{r_1}{\rho}, r_{12} = r_{12} \right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{RC}=-\frac{Z(1+\rho)}{r_1}+\frac{1}{r_{12}}, \tag{2.10}$$

$$\hat{T}^{RC}=-\frac{1}{2}\frac{\partial^2}{\partial r_1^2}-\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{2}\frac{\rho^2(\rho^2+1)}{r_1^2}\frac{\partial^2}{\partial\rho^2}-\frac{\rho}{r_1^2}\frac{\partial}{\partial\rho}-\frac{\partial^2}{\partial r_{12}^2}-\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}-\frac{\rho}{r_1}\frac{\partial^2}{\partial r_1\partial\rho}$$
$$-\frac{1}{2}\frac{r_1^2\rho^2-r_1^2+r_{12}^2\rho^2}{r_1r_{12}\rho^2}\frac{\partial^2}{\partial r_1\partial r_{12}}-\frac{1}{2}\frac{(\rho^2-1)\cdot(r_1^2\rho^2+r_1^2-r_{12}^2\rho^2)}{r_1^2r_{12}\rho}\frac{\partial^2}{\partial r_{12}\partial\rho}. \tag{2.11}$$

3) Volume Element: $\frac{8\pi^2 r_1^3 r_{12}}{\rho^3}$

4) Range

$r_1\in[0,\infty)$
$\rho\in[0,\infty)$
$r_{12}\in\left[\left|r_1-\frac{r_1}{\rho}\right|,r_1+\frac{r_1}{\rho}\right]$

2.2.3 (s,t,u) Coordinates

1) Definition and Inverse Formula (Compared with IC)

$\{s=r_1+r_2,t=r_1-r_2,u=r_{12}\}$

$\left\{r_1=\frac{s+t}{2},r_2=\frac{s-t}{2},r_{12}=u\right\}$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{(s,t,u)}=-\frac{4Zs}{s^2-t^2}+\frac{1}{u}, \tag{2.12}$$

$$\hat{T}^{(s,t,u)}=-\frac{\partial^2}{\partial s^2}-\frac{\partial^2}{\partial t^2}-\frac{\partial^2}{\partial u^2}-\frac{4s}{s^2-t^2}\frac{\partial}{\partial s}-\frac{4t}{t^2-s^2}\frac{\partial}{\partial t}-\frac{2}{u}\frac{\partial}{\partial u}$$
$$+\frac{2s(t^2-u^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial s\partial u}+\frac{2t(s^2-u^2)}{u(t^2-s^2)}\frac{\partial^2}{\partial t\partial u}. \tag{2.13}$$

3) Volume Element: $\pi^2u(s^2-t^2)$

4) Range

$s \in [0,\infty)$
$t \in (-\infty,\infty)$
$u \in [|t|, s]$

2.2.4 Spherical Polar Coordinates (r_1, r_2, θ)

1) Definition and Inverse Formula (Compared with IC)

$$\left\{ r_1 = r_1, r_2 = r_2, \theta = \arccos\left(\frac{r_1^{\ 2} + r_2^{\ 2} - r_{12}^{\ 2}}{2r_1 r_2}\right) \right\}$$

$$\left\{ r_1 = r_1, r_2 = r_2, r_{12} = \sqrt{r_1^{\ 2} + r_2^{\ 2} - 2r_1 r_2 \cos\theta} \right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{SPC} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{\sqrt{r_1^{\ 2} + r_2^{\ 2} - 2r_1 r_2 \cos\theta}}, \tag{2.14}$$

$$\hat{T}^{SPC} = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^{\ 2}} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{1}{2}\frac{\cos\theta}{\sin\theta}\frac{r_1^{\ 2} + r_2^{\ 2}}{r_1^{\ 2} r_2^{\ 2}}\frac{\partial}{\partial\theta} - \frac{1}{2}\frac{r_1^{\ 2} + r_2^{\ 2}}{r_1^{\ 2} r_2^{\ 2}}\frac{\partial^2}{\partial\theta^2}. \tag{2.15}$$

3) Volume Element: $8\pi^2 r_1^{\ 2} r_2^{\ 2} \sin\theta$

4) Range

$r_1 \in [0,\infty)$
$r_2 \in [0,\infty)$
$\theta \in [0,\pi]$

2.2.5 Hyperspherical Coordinates (r, α, θ)

1) Definition and Inverse Formula (Compared with IC)

$$\left\{ r = \sqrt{r_1^{\ 2} + r_2^{\ 2}}, \alpha = 2 \cdot \arctan\left(\frac{r_2}{r_1}\right), \theta = \arccos\left(\frac{r_1^{\ 2} + r_2^{\ 2} - r_{12}^{\ 2}}{2r_1 r_2}\right) \right\}$$

$$\left\{ r_1 = r \cdot \cos\frac{\alpha}{2}, r_2 = r \cdot \sin\frac{\alpha}{2}, r_{12} = r\sqrt{1 - \sin\alpha\cos\theta} \right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{HC} = \frac{1}{r}\left(-\frac{Z}{\cos\frac{\alpha}{2}} - \frac{Z}{\sin\frac{\alpha}{2}} + \frac{1}{\sqrt{1-\cos\theta\sin\alpha}}\right), \quad (2.16)$$

$$\hat{T}^{HC} = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{r}\left(\frac{5}{2}\cdot\frac{\partial}{\partial r}\right) - \frac{2}{r^2}\left(\frac{\partial^2}{\partial\alpha^2} + 2\cdot\frac{\cos\alpha}{\sin\alpha}\frac{\partial}{\partial\alpha}\right) - \frac{2}{r^2}\frac{1}{\sin^2\alpha}\left(\frac{\partial^2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta}\right). \quad (2.17)$$

3) Volume Element: $\pi^2 r^5 \sin^2\alpha \sin\theta$

4) Range

$r \in [0, \infty)$
$\alpha \in [0, \pi]$
$\theta \in [0, \pi]$

2.2.6 Pluvinage Coordinates (R, r_{12}, Θ)

1) Definition and Inverse Formula (Compared with IC)

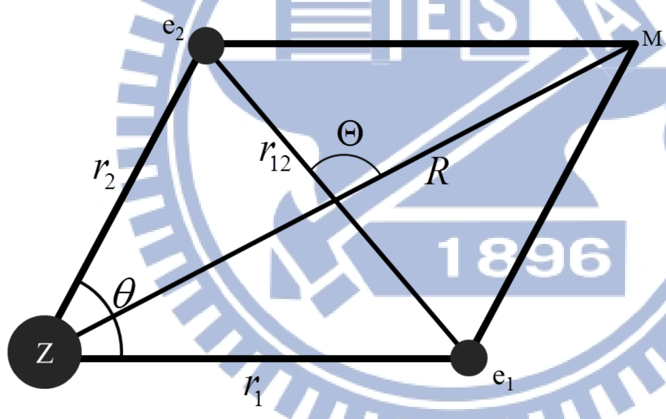


Figure 2.2
The Pluvinage's coordinates and interparticle coordinates of helium

$$\left\{R = \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2}, r_{12} = r_{12}, \Theta = \arccos\left(\frac{r_2^2 - r_1^2}{r_{12}\cdot\sqrt{2r_1^2 + 2r_2^2 - r_{12}^2}}\right)\right\}$$

$$\left\{r_1 = \frac{1}{2}\sqrt{R^2 + r_{12}^2 - 2Rr_{12}\cos\Theta}, r_2 = \frac{1}{2}\sqrt{R^2 + r_{12}^2 + 2Rr_{12}\cos\Theta}, r_{12} = r_{12}\right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{PC} = -\frac{2Z}{\sqrt{R^2 + r_{12}^2 - 2Rr_{12}\cos\Theta}} - \frac{2Z}{\sqrt{R^2 + r_{12}^2 + 2Rr_{12}\cos\Theta}} + \frac{1}{r_{12}}, \quad (2.18)$$

$$\hat{T}^{PC} = -\frac{\partial^2}{\partial R^2} - \frac{2}{R}\frac{\partial}{\partial R} - \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{R^2 + r_{12}^2}{R^2 r_{12}^2}\frac{\partial^2}{\partial\Theta^2} - \frac{R^2 + r_{12}^2}{R^2 r_{12}^2}\frac{\cos\Theta}{\sin\Theta}\frac{\partial}{\partial\Theta}. \quad (2.19)$$

3) Volume Element: $\pi^2 R^2 r_{12}{}^2 \sin\Theta$

4) Range

$$R \in [0,\infty)$$
$$r_{12} \in [0,\infty)$$
$$\Theta \in [0,\pi]$$

2.2.7 Kinoshita Coordinates (s, p, q)

1) Definition and Inverse Formula (Compared with IC)

$$\left\{ s = r_1 + r_2,\, p = \frac{r_{12}}{r_1 + r_2},\, q = \frac{r_1 - r_2}{r_{12}} \right\}$$

$$\left\{ r_1 = \frac{s\cdot(1+pq)}{2},\, r_2 = \frac{s\cdot(1-pq)}{2},\, r_{12} = sp \right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{KC} = -\frac{4Z}{s\cdot(1+pq)\cdot(1-pq)} + \frac{1}{sp}, \tag{2.20}$$

$$\begin{aligned}\hat{T}^{KC} = &-\frac{\partial^2}{\partial s^2} - \frac{4}{s(1-p^2q^2)}\frac{\partial}{\partial s} - \frac{(1-p^2)(1+p^2q^2)}{s^2(1-p^2q^2)}\frac{\partial^2}{\partial p^2} - \frac{2(1-2p^2-p^4q^2)}{s^2 p(1-p^2q^2)}\frac{\partial}{\partial p} \\ &- \frac{(1-q^2)(1+p^2q^2)}{s^2p^2(1-p^2q^2)}\frac{\partial^2}{\partial q^2} + \frac{2q(1+p^2)}{s^2p^2(1-p^2q^2)}\frac{\partial}{\partial q} \\ &+ \frac{2pq^2(1-p^2)}{s(1-p^2q^2)}\frac{\partial^2}{\partial s\partial p} + \frac{2q(1-q^2)}{s(1-p^2q^2)}\frac{\partial^2}{\partial s\partial q}.\end{aligned} \tag{2.21}$$

3) Volume Element: $\pi^2 s^5 p^2 (1-p^2q^2)$

4) Range

$$s \in [0,\infty)$$
$$p \in [0,1]$$
$$q \in [-1,1]$$

2.2.8 Perimetric Coordinates (p_1, p_2, p_3)

1) Definition and Inverse Formula (Compared with IC)

$$\{p_1=-r_1+r_2+r_{12}, p_2=r_1-r_2+r_{12}, p_3=r_1+r_2-r_{12}\}$$

$$\left\{r_1=\frac{p_2+p_3}{2}, r_2=\frac{p_1+p_3}{2}, r_{12}=\frac{p_1+p_2}{2}\right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{PerC}=-\frac{2Z(p_1+p_2+2p_3)}{(p_1+p_3)(p_2+p_3)}+\frac{2}{p_1+p_2}, \quad (2.22)$$

$$\begin{aligned}\hat{T}^{PerC}=&-\frac{2(-p_1^2+p_2^2+2p_3^2+2p_1p_2+2p_2p_3+2p_1p_3)}{(p_1+p_2)(p_2+p_3)(p_1+p_3)}\frac{\partial}{\partial p_1}\\&-\frac{2(p_1^2-p_2^2+2p_3^2+2p_1p_2+2p_2p_3+2p_1p_3)}{(p_1+p_2)(p_2+p_3)(p_1+p_3)}\frac{\partial}{\partial p_2}\\&-\frac{2p_1(p_1p_2+p_2^2+2p_1p_3+2p_2p_3+2p_3^2)}{(p_1+p_2)(p_2+p_3)(p_1+p_3)}\frac{\partial^2}{\partial p_1^2}\\&-\frac{2p_2(p_1p_2+p_1^2+2p_1p_3+2p_2p_3+2p_3^2)}{(p_1+p_2)(p_2+p_3)(p_1+p_3)}\frac{\partial^2}{\partial p_2^2}\\&-\frac{2(p_1^2+p_2^2-2p_3^2)}{(p_1+p_2)(p_2+p_3)(p_1+p_3)}\frac{\partial}{\partial p_3}-\frac{2p_3(p_1^2+p_2^2+p_1p_3+p_2p_3)}{(p_1+p_2)(p_2+p_3)(p_1+p_3)}\frac{\partial^2}{\partial p_3^2}\\&+\frac{4p_1p_3}{(p_1+p_2)(p_2+p_3)}\frac{\partial^2}{\partial p_1\partial p_3}+\frac{4p_2p_3}{(p_1+p_2)(p_1+p_3)}\frac{\partial^2}{\partial p_2\partial p_3}.\end{aligned} \quad (2.23)$$

3) Volume Element: $\frac{1}{4}\pi^2(p_1+p_2)(p_2+p_3)(p_1+p_3)$

4) Range

$p_1\in[0,\infty)$
$p_2\in[0,\infty)$
$p_3\in[0,\infty)$

2.2.9 (r,α,β) Coordinates

1) Definition and Inverse Formula (Compared with HC)

$$\{r=r,\alpha=\alpha,\beta=\arcsin(\cos\theta\sin\alpha)\}$$

$$\left\{r=r,\alpha=\alpha,\theta=\arccos\left(\frac{\sin\beta}{\sin\alpha}\right)\right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{(r,\alpha,\beta)}=-\frac{Z}{r}\left(\frac{1}{\cos\frac{\alpha}{2}}+\frac{1}{\sin\frac{\alpha}{2}}\right)+\frac{1}{r\sqrt{1-\sin\beta}}\quad, \tag{2.24}$$

$$\hat{T}^{(r,\alpha,\beta)}=-\frac{1}{2}\frac{\partial^2}{\partial r^2}-\frac{5}{2r}\frac{\partial}{\partial r}-\frac{2}{r^2}\frac{\partial^2}{\partial\alpha^2}-\frac{2}{r^2}\frac{\partial^2}{\partial\beta^2}-\frac{4}{r^2}\frac{\cos\alpha}{\sin\alpha}\frac{\partial}{\partial\alpha}+\frac{4}{r^2}\frac{\sin\beta}{\cos\beta}\frac{\partial}{\partial\beta}$$

$$-\frac{4}{r^2}\frac{\cos\alpha\sin\beta}{\sin\alpha\cos\beta}\frac{\partial^2}{\partial\alpha\partial\beta}. \tag{2.25}$$

3) Volume Element: $\pi^2 r^5\sin\alpha\cos\beta$

4) Range

$r\in[0,\infty)$

$\alpha\in[0,\pi]$

$\beta\in\left[-\frac{\pi}{2},\frac{\pi}{2}\right]$

2.2.10 (r,ε,δ) Coordinates

1) Definition and Inverse Formula (Compared with (r,α,β) coordinates)

$$\{r=r,\varepsilon=\alpha+\beta,\delta=\alpha-\beta\}$$

$$\left\{r=r,\alpha=\frac{\varepsilon+\delta}{2},\beta=\frac{\varepsilon-\delta}{2}\right\}$$

2) Definition of $\hat{V}$ and $\hat{T}$

$$\hat{V}^{(r,\varepsilon,\delta)}=-\frac{2Z\sqrt{1+\sin(\frac{\varepsilon+\delta}{2})}}{r\cdot\sin(\frac{\varepsilon+\delta}{2})}+\frac{1}{r\sqrt{1-\sin(\frac{\varepsilon-\delta}{2})}}, \tag{2.26}$$

$$\hat{T}^{(r,\varepsilon,\delta)}=-\frac{1}{2}\frac{\partial^2}{\partial r^2}-\frac{5}{2r}\frac{\partial}{\partial r}$$

$$-\frac{8}{r^2(\sin\varepsilon+\sin\delta)}[\sin\varepsilon\cdot(\frac{\cos\varepsilon}{\sin\varepsilon}\frac{\partial}{\partial\varepsilon}+\frac{\partial}{\partial\varepsilon^2})+\sin\delta\cdot(\frac{\cos\delta}{\sin\delta}\frac{\partial}{\partial\delta}+\frac{\partial}{\partial\delta^2})]. \qquad (2.27)$$

3) Volume Element: $\frac{1}{4}\pi^2 r^5(\sin\varepsilon+\sin\delta)$

4) Range

$r\in[0,\infty)$

$\varepsilon\in\left[-\frac{\pi}{2},\frac{3\pi}{2}\right]$

$\delta\in\left[-\frac{\pi}{2},\frac{3\pi}{2}\right]$

2.3 Concepts of Homogeneity

The homogeneity is a property of a mathematical function, which describes the response of a function to scaling of the argument. Homogeneity analysis is also known as dimensional scaling analysis. The dimensional scaling analysis is defined by scaling Cartesian coordinates. For example, $\begin{bmatrix} x_1 \\ x_2 \\ \dots \\ x_n \end{bmatrix}$ can be scaled to $\begin{bmatrix} \lambda x_1 \\ \lambda x_2 \\ \dots \\ \lambda x_n \end{bmatrix}$.

The formal definition of the homogeneity h is given by the equation

$$f(\lambda\vec{x})=\lambda^h\cdot f(\vec{x}) \quad ,\vec{x}\in\mathrm{R}^n. \qquad (2.28)$$

For example, if we want to find the homogeneity of a function $\frac{r_1\cdot r_2}{r_{12}}$, we can follow the definition to scale $\begin{bmatrix} r_1 \\ r_2 \\ r_{12} \end{bmatrix}\xrightarrow{\lambda}\begin{bmatrix} \lambda r_1 \\ \lambda r_2 \\ \lambda r_{12} \end{bmatrix}$. We find that the function $\frac{r_1\cdot r_2}{r_{12}}$ has the homogeneity 1 because

$$\frac{r_1\cdot r_2}{r_{12}}\xrightarrow{\lambda}\frac{(\lambda r_1)\cdot(\lambda r_2)}{(\lambda r_{12})}=\lambda^1\cdot\frac{r_1\cdot r_2}{r_{12}}. \qquad (2.29)$$

Note that the interparticle coordinates are all metric coordinates.

In hyperspherical coordinates, only r is a metric coordinate and α, θ are angular coordinates. Therefore, the definition of the homogeneity in hyperspherical coordinates becomes $\begin{bmatrix} r \\ \alpha \\ \theta \end{bmatrix} \xrightarrow{\lambda} \begin{bmatrix} \lambda r \\ \alpha \\ \theta \end{bmatrix}$, which is simpler and easier to use.

By the definition of hyperspherical coordinates, we can discuss, for an example, the homogeneity of the function $\dfrac{{r_{12}}^2}{(r_1+r_2)^2}$,

$$\frac{{r_{12}}^2}{(r_1+r_2)^2} = \frac{r^2\cdot(1-\sin\alpha\cdot\cos\theta)}{(r\cdot\cos\frac{\alpha}{2}+r\cdot\sin\frac{\alpha}{2})^2} = r^0\cdot\frac{1-\sin\alpha\cdot\cos\theta}{1+\sin\alpha} \xrightarrow{\lambda} (\lambda r)^0\cdot\frac{(1-\sin\alpha\cdot\cos\theta)}{(1+\sin\alpha)^2}. \tag{2.30}$$

It also means the function is with the homogeneity zero.

If we already know that the function φ_a has homogeneity a and the function φ_b has homogeneity b, the homogeneity of $\varphi_a\cdot\varphi_b$ is $a+b$ because

$$\varphi_a(\lambda x)\cdot\varphi_b(\lambda x) = \lambda^a\cdot\varphi_a(x)\cdot\lambda^b\cdot\varphi_b(x) = \lambda^{a+b}\cdot\varphi_a(x)\cdot\varphi_b(x). \tag{2.31}$$

To facilitate solving Schrödinger equation, one needs to discuss the homogeneity of operators. Hamiltonian ($\hat{H}$) is a partial differential operator, so we need to define the homogeneity of a differential operator. We have

$$\frac{\partial}{\partial r} \xrightarrow{\lambda} \frac{\partial}{\partial(\lambda r)} = \frac{\partial}{\partial r}\cdot\frac{\partial r}{\partial(\lambda r)} = \frac{\partial}{\partial r}\cdot\frac{1}{(\frac{\partial(\lambda r)}{\partial r})} = \frac{1}{\lambda}\cdot\frac{\partial}{\partial r} = \lambda^{-1}\cdot\frac{\partial}{\partial r}. \tag{2.32}$$

Thus, the homogeneity of the operator $\dfrac{\partial}{\partial r}$ is -1. The homogeneity of the operator $\dfrac{\partial^2}{\partial r^2}$ is -2 because of the equation

$$\frac{\partial^2}{\partial r^2} \xrightarrow{\lambda} \frac{\partial}{\partial(\lambda r)}\cdot\frac{\partial}{\partial(\lambda r)} = \lambda^{-1}\cdot\frac{\partial}{\partial r}\cdot\lambda^{-1}\cdot\frac{\partial}{\partial r} = \lambda^{-2}\cdot\frac{\partial^2}{\partial r^2}. \tag{2.33}$$

With the scaling $\begin{bmatrix} r \\ \alpha \\ \theta \end{bmatrix} \xrightarrow{\lambda} \begin{bmatrix} \lambda r \\ \alpha \\ \theta \end{bmatrix}$, the homogeneity of $\frac{\partial}{\partial \alpha}$ and $\frac{\partial}{\partial \theta}$ are clearly 0 because

$$\frac{\partial}{\partial \alpha} \xrightarrow{\lambda} \frac{\partial}{\partial \alpha} = \lambda^0 \cdot \frac{\partial}{\partial \alpha}, \tag{2.34}$$

$$\frac{\partial}{\partial \theta} \xrightarrow{\lambda} \frac{\partial}{\partial \theta} = \lambda^0 \cdot \frac{\partial}{\partial \theta}. \tag{2.35}$$

Now we are sufficiently equipped to evaluate the homogeneity of $\hat{T}$, which is written as

$$\hat{T}^{HC} = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{r}(\frac{5}{2}\cdot\frac{\partial}{\partial r}) - \frac{2}{r^2}(\frac{\partial^2}{\partial \alpha^2} + 2\cdot\frac{\cos\alpha}{\sin\alpha}\frac{\partial}{\partial \alpha}) - \frac{2}{r^2}\frac{1}{\sin^2\alpha}(\frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta}). \tag{2.36}$$

The parts of $\hat{T}$ which decide about its homogeneity are $\frac{\partial^2}{\partial r^2}$, $\frac{1}{r}(\frac{\partial}{\partial r})$ and $\frac{1}{r^2}$. We find that each component of $\hat{T}$ has the homogeneity of -2. $\hat{V}$ expressed in hyperspherical coordinates reads

$$\hat{V}^{HC} = \frac{1}{r}(-\frac{Z}{\cos\frac{\alpha}{2}} - \frac{Z}{\sin\frac{\alpha}{2}} + \frac{1}{\sqrt{1-\cos\theta\sin\alpha}}). \tag{2.37}$$

Thus, the homogeneity of $\hat{V}$ is -1. Finally, the energy (E) is just a number, which has the homogeneity of 0.

Homogeneities of some special functions, e.g., exponential, sine, and logarithm, cannot be determined easily by the original definition. Homogeneity of this type of special functions can be computed by Taylor series. Taylor series of exponential and sine are

$$e^r = \sum_{n=0}^{\infty}\frac{r^n}{n!} = 1 + r + \frac{r^2}{2!} + \frac{r^3}{3!} + \ldots, \tag{2.38}$$

$$\sin r = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} r^{2n+1} = r - \frac{r^3}{3!} + \frac{r^5}{5!} - \frac{r^7}{7!} + \dots \qquad (2.39)$$

By these equations, we find these functions have mixed homogeneities. However, logarithm cannot be expanded to Taylor series at zero. The homogeneity of this type of function can be determined by acting with the operator. The right hand side of the equation

$$\frac{\partial}{\partial r} \ln r = \frac{1}{r}. \qquad (2.40)$$

is homogeneous of degree -1. To ensure the same homogeneity on the both sides of Eq. (2.40), the homogeneity of logarithm should be equal to zero since $\frac{\partial}{\partial r}$ is homogeneous of degree -1.

If we discuss the differential of exponential, we will find out the equation

$$\frac{\partial}{\partial r} e^r = e^r. \qquad (2.41)$$

This equation will have the same homogeneity on the both sides only when exponential has the homogeneity of infinity, or exponential cannot be considered as a single value of homogeneity, which means that exponential has mixed homogeneities.

2.4 Expansion of Wave Function Based on the Concept of Homogeneity

In order to solve the Schrödinger equation, we can use the concept of homogeneity of the wave function of helium. Let us assume for a moment that the wave function of helium has the homogeneity of h. Then the Schrödinger equation

$$\hat{T}\Psi_h + \hat{V}\Psi_h = E\Psi_h \quad . \qquad (2.42)$$

The homogeneity of operators $\hat{T}$, $\hat{V}$ and E is -2, -1 and 0, respectively. Eq.

(2.42) will only hold when h is equal to infinity, or the wave function is a mixed homogeneities function.

Therefore, we can expand the wave function in terms with various homogeneities, which can be expressed as

$$\Psi = \sum_{h=0}^{\infty} \Psi_h = \Psi_0 + \Psi_1 + \Psi_2 + \Psi_3 + \ \dots . \tag{2.43}$$

Clearly, the homogeneity can change from 0 to infinity. Homogeneity of the wave functions should not be negative because the function with negative homogeneity tends to infinity when r is equal to zero. Atomic and molecular wave functions should be finite everywhere as demonstrated by Kato.

As mentioned above, the homogeneity of $\hat{T}$, $\hat{V}$ and E are -2, -1 and 0, respectively. After expanding the wave function in the homogeneity series according to Eq. (2.43) and substituting this expansion into Eq. (2.1), the equation will become

$$\hat{T}(\sum_{h=0}^{\infty} \Psi_h) + \hat{V}(\sum_{h=0}^{\infty} \Psi_h) - E(\sum_{h=0}^{\infty} \Psi_h) = 0 . \tag{2.44}$$

The homogeneity of the term $\hat{T}\Psi_h$ is $h-2$; similarly, the terms $\hat{V}\Psi_h$ and $E\Psi_h$ have homogeneities of $h-1$ and h, respectively. The homogeneity expansion of our Schrödinger equation becomes that

$$\underbrace{\hat{T}\Psi_0}_{h=-2} + \underbrace{\left(\hat{T}\Psi_1 + \hat{V}\Psi_0\right)}_{h=-1} + \sum_{n=0}^{\infty} \underbrace{(\hat{T}\Psi_{n+2} + \hat{V}\Psi_{n+1} - E\Psi_n)}_{h=n} = 0 , \tag{2.45}$$

which produces the main working equation of our method

$$\hat{T}\Psi_n = -\hat{V}\Psi_{n-1} + E\Psi_{n-2} , \tag{2.46}$$

where n varies from 0 to infinity, and Ψ_h is equal to zero when $h < 0$. The following equations are produced by Eq. (2.46) with n equal to 0, 1, 2 and 3:

$$\hat{T}\Psi_0 = 0, \tag{2.47}$$

$$\hat{T}\Psi_1 = -\hat{V}\Psi_0, \tag{2.48}$$

$$\hat{T}\Psi_2 = -\hat{V}\Psi_1 + E\Psi_0, \tag{2.49}$$

$$\hat{T}\Psi_3 = -\hat{V}\Psi_2 + E\Psi_1. \tag{2.50}$$

We will discuss these equations and solutions to them in detail in the following chapters.

The homogeneity is a useful concept applicable to solve the equation in a well-defined and ordered manner. In the next chapter we show how to solve Eq. (2.47) to find Ψ_0 and how to use this result to solve the other equations in the following chapters.

2.5 Differential Equations

A differential equation is a mathematical equation in one or several variables that relates the function and its derivatives of different orders. The differential equations in only one variable are called an ordinary differential equations (ODEs); partial differential equations (PDEs) are their equivalents several variables. Both ODEs and PDEs have two different types: linear and nonlinear. Solutions of linear differential equations can be added together to form another solution. For example, if $\hat{D}\alpha_1 f_1 = \alpha_1 g_1$ and $\hat{D}\alpha_2 f_2 = \alpha_2 g_2$, then $\hat{D}(\alpha_1 f_1 + \alpha_2 f_2) = \alpha_1 g_1 + \alpha_2 g_2$. If this equation holds for any functions f_1 and f_2, and any numbers α_1 and α_2, it means that $\hat{D}$ is a linear operator.

In this thesis, we focus on the Hamiltonian operator, which is a linear differential operator. Therefore, the main equations we will deal with in the following chapters are linear differential equations.

2.6 Particular and General Solutions to Differential Equations

Before solving Eq. (2.47), we explain the difference between particular solutions and general solutions. When we solve a partial differential equation, e.g.,

$$(\frac{\partial}{\partial x}+\frac{\partial}{\partial y})f(x,y)=x. \tag{2.51}$$

It is easy to verify that a possible solution to this equation is $f(x,y)=\frac{1}{2}x^2$. Such a solution is called a particular solution. A general solution to this differential equation should include a particular solution and a summation over all conceivable homogeneous solutions, i.e., the solutions of the equation

$$(\frac{\partial}{\partial x}+\frac{\partial}{\partial y})f_H(x,y)=0. \tag{2.52}$$

For a partial differential equation, there usually exist infinitely many homogeneous solutions. In this case, we can find out that

$$f_H(x,y)=F(-x+y), \tag{2.53}$$

where $F(-x+y)$ is a function which is with an argument $-x+y$, e.g., $(-x+y)^2$, e^{-x+y} and $\ln(-x+y)$ are all solutions of Eq. (2.52). So the general solution can be written as

$$f_{general}(x,y)=\frac{1}{2}x^2+c\cdot F(-x+y). \tag{2.54}$$

In this case, the general solution is always a solution of Eq. (2.51) for arbitrary numbers c. Therefore, we know that finding a general form of homogeneous solutions is important to get the general solution of an equation.

2.7 Elementary and Special Functions

Elementary function is a function which is built from a finite number of constants, polynomials, roots of polynomials, trigonometric functions, inverse trigonometric functions, exponentials and logarithms. Using four elementary operations (addition, subtraction, multiplication and division) on two elementary functions, we obtain another elementary function. For example, $x \cdot e^{\sin x} + \frac{\sqrt{x^2+x+1}}{\tan x} - i \cdot \ln(ix)$ is an elementary function.

The functions which are not elementary functions are called special functions here. There are two special functions we use in this thesis; their definition is given in this section. The first special function is the Lobachevsky function, which is defined as

$$L(x) = -\int_0^x \ln(\cos t)dt \,. \tag{2.55}$$

The other special function is the Heun function $HeunG(a,q;\alpha,\beta,\gamma,\delta;z)$, which is defined as a solution to the general Heun differential equation given by

$$\left[\frac{d^2}{dz^2} + \left(\frac{\gamma}{z} + \frac{\delta}{z-1} + \frac{\alpha+\beta-\gamma-\delta+1}{z-a}\right)\frac{d}{dz} + \frac{\alpha\beta z - q}{z(z-1)(z-a)}\right] HeunG(a,q;\alpha,\beta,\gamma,\delta;z) = 0 \,. \tag{2.56}$$

Chapter 3

Wave Function of Homogeneity Zero

As mentioned previously, to solve the Schrödinger equation of helium atom, we can make an expansion of wave function based on the concept of homogeneity, and solve the resulting set of equations. The first equation corresponding to the component of the wave function with homogeneity zero is given by

$$\hat{T} f_0 = 0 \tag{3.1}$$

This is a homogeneous partial differential equation. To solve it, we assume the following ansatz for f_0

$$f_0 = \sum_{j=-\infty}^{\infty} \sum_{i=-\infty}^{\infty} c_{i,j} \cdot \left(\frac{r_1}{r_{12}}\right)^i \cdot \left(\frac{r_2}{r_{12}}\right)^j \tag{3.2}$$

There are infinitely many homogeneous solutions for a partial differential equation. Therefore, this formula represents not only a single solution to Eq. (3.1) but rather a whole class of solutions. Some of homogeneous solutions represented by Eq. (3.2) are given by

$$f_0 = 0, \tag{3.3}$$

$$f_0 = 1, \tag{3.4}$$

$$f_0 = \frac{r_1^2 - r_2^2}{r_1 r_2} \tag{3.5}$$

$$f_0 = \frac{(r_1^2 + r_2^2)^2 \cdot (r_1^2 + r_2^2 - r_{12}^2)}{r_1^3 r_2^3} \tag{3.6}$$

We can get infinitely many solutions if we want, but most of them are not acceptable from physical point of view. As we know, an atomic wave function should be finite and continuous everywhere, the first derivative should be finite and continuous everywhere except the coalescence points and moreover it should be symmetric with respect to the interchange of r_1 and r_2. Among our solutions, $f_0 = 0$ and $f_0 = 1$ are the solutions which fulfill these conditions. The remaining solutions violate at least one of the aforementioned requirements.

The general physical solution Ψ_0 can be thus written as

$$\Psi_0 = c \cdot f_0 = c \tag{3.7}$$

where c is an arbitrary constant.

In this thesis, we are focus on solving the wave function of helium in the ground state. In the following part, we will evaluate other equations assuming that $\Psi_0 = 1$. If we set $\Psi_0 = 0$, the wave function represents an excited state. The details of the differences between the wave functions of the ground and excited states are given on the next page (**Table 3.1**).

ground state	first singlet excited state	first triplet excited state	other excited states			
$\hat{T}f_0 = 0 \Rightarrow f_0 = 1$	$\hat{T}f_0 = 0 \Rightarrow f_0 = 0$					
$\hat{T}f_1 = -\hat{V}f_0 = -\hat{V}$	$\hat{T}f_1 = 0 \Rightarrow f_1 = 0$					
$\hat{T}f_2 = -\hat{V}f_1 + Ef_0$	$\hat{T}f_2 = 0 \Rightarrow f_2 = r_1^2 + r_2^2 - r_{12}^2$	$\hat{T}f_2 = 0 \Rightarrow f_2 = r_1^2 - r_2^2$	$\hat{T}f_2 = 0 \Rightarrow f_2 = 0$			
$\hat{T}f_3 = -\hat{V}f_2 + Ef_1$	$\hat{T}f_3 = -\hat{V}f_2$	$\hat{T}f_3 = -\hat{V}f_2$	$\hat{T}f_3 = 0 \Rightarrow f_3 = 0$			
$\hat{T}f_4 = -\hat{V}f_3 + Ef_2$	$\hat{T}f_4 = -\hat{V}f_3 + Ef_2$	$\hat{T}f_4 = -\hat{V}f_3 + Ef_2$	$\hat{T}f_4 = 0$	$\hat{T}f_4 = 0 \Rightarrow f_4 = 0$		
$\hat{T}f_5 = -\hat{V}f_4 + Ef_3$	$\hat{T}f_5 = -\hat{V}f_4 + Ef_3$	$\hat{T}f_5 = -\hat{V}f_4 + Ef_3$	$\hat{T}f_5 = -\hat{V}f_4$	$\hat{T}f_5 = 0 \Rightarrow f_5 = 0$		
$\hat{T}f_6 = -\hat{V}f_5 + Ef_4$	$\hat{T}f_6 = -\hat{V}f_5 + Ef_4$	$\hat{T}f_6 = -\hat{V}f_5 + Ef_4$	$\hat{T}f_6 = -\hat{V}f_5 + Ef_4$	$\hat{T}f_6 = 0$	$\hat{T}f_6 = 0 \Rightarrow f_6 = 0$	...
↓	↓	↓	↓	↓	↓	↓

Table 3.1

The detail of solving wave function in the ground state and in excited states

Chapter 4

Wave Function of Homogeneity One

After solving the equation with homogeneity zero, the next equation can be determined by setting $\Psi_0 = 1$. The equation we discuss becomes

$$\hat{T}\Psi_1 = -\hat{V}\Psi_0 = Z\cdot(\frac{1}{r_1}+\frac{1}{r_2})-\frac{1}{r_{12}}. \tag{4.1}$$

To solve this equation, we can expand it into two parts. One part does not contain r_{12}, and the other part contains r_{12}^{-1}. Eq. (4.1) is then represented as

$$\hat{T}(f_{1,0}+f_{1,-1}) = g_{1,0}+g_{1,-1}, \tag{4.2}$$

where $f_{1,0}$, $f_{1,-1}$, $g_{1,0}$ and $g_{1,-1}$ are defined via

$$\hat{T}f_{1,0} = g_{1,0} = Z\cdot(\frac{1}{r_1}+\frac{1}{r_2}), \tag{4.3}$$

$$\hat{T}f_{1,-1} = g_{1,-1} = -\frac{1}{r_{12}}. \tag{4.4}$$

The general solution of Ψ_1 can be written as

$$\Psi_1 = f_{1,0}+f_{1,-1}+\sum_n c_n\cdot H_{1,n}, \tag{4.5}$$

where $H_{m,n}$ means the n-th homogeneous solution of homogeneity m.

4.1 Solving Terms Independent of r_{12}

For the terms independent of r_{12}, we can change Eq. (4.3) to ratio coordinates (RC) in order to simplify the problem. After changing to ratio coordinates, Eq. (4.3) becomes

$$\hat{T}f_{1,0}^{RC}(r_1,\rho)=g_{1,0}^{RC}=\frac{Z}{r_1}(1+\rho)\,. \tag{4.6}$$

As we know, $f_{1,0}^{RC}$ has homogeneity one, which means that it can be simplified as

$$f_{1,0}^{RC}(r_1,\rho)=r_1\cdot f_{1,0}^{RC}(\rho)\,, \tag{4.7}$$

and Eq. (4.6) becomes

$$\hat{T}(r_1\cdot f_{1,0}^{RC}(\rho))=-\frac{1}{r_1}[\,f_{1,0}^{RC}(\rho)+2\rho\cdot\frac{d}{d\rho}f_{1,0}^{RC}(\rho)+\frac{1}{2}\rho^2(1+\rho^2)\frac{d^2}{d\rho^2}f_{1,0}^{RC}(\rho)]$$

$$=\frac{Z}{r_1}(1+\rho)\,. \tag{4.8}$$

Eq. (4.8) can be treated as a simple ordinary differential equation

$$[\,f_{1,0}^{RC}(\rho)+2\rho\cdot\frac{d}{d\rho}f_{1,0}^{RC}(\rho)+\frac{1}{2}\rho^2(1+\rho^2)\frac{d^2}{d\rho^2}f_{1,0}^{RC}(\rho)]+Z(1+\rho)=0\,. \tag{4.9}$$

It is easy to find that $f_{1,0}^{RC}(\rho)=\frac{(-1+3\rho^2)}{\rho^2}\cdot C_1+\frac{(-3+\rho^2)}{\rho}\cdot C_2-Z\cdot\frac{(\rho+1)}{\rho}$, and

$$f_{1,0}^{RC}(r_1,\rho)=r_1\cdot f_{1,0}^{RC}(\rho)=r_1\cdot\frac{(-1+3\rho^2)}{\rho^2}\cdot C_1+r_1\cdot\frac{(-3+\rho^2)}{\rho}\cdot C_2-Z\cdot r_1\cdot\frac{(\rho+1)}{\rho}\,, \tag{4.10}$$

so the final form in the (r_1,r_2) coordinates reads

$$f_{1,0}^{IC}(r_1,r_2)=-Z(r_1+r_2)+3C_2\cdot r_1-3C_1\cdot r_2+C_1\cdot\frac{r_1^2}{r_2}-C_2\cdot\frac{r_2^2}{r_1}\,. \tag{4.11}$$

The two terms $\frac{r_1^2}{r_2}$ and $\frac{r_2^2}{r_1}$ have singularities when $r_2=0$ or $r_1=0$, respectively. Therefore, C_1 and C_2 should be set to zero to remove the singularities. The nonsingular solution $f_{1,0}$ reads

$$f_{1,0}=-Z(r_1+r_2)\,. \tag{4.12}$$

4.2 Expanding Functions in the Power Series of r_{12}

The solution to Eq. (4.4) can be obtained easily, if one notices a special and useful property of the operator $\hat{T}$

$$\hat{T}(f(r_1,r_2)\cdot r_{12}{}^{m}) = \hat{F}_1\cdot f(r_1,r_2)\cdot r_{12}{}^{m} + \hat{F}_2\cdot f(r_1,r_2)\cdot r_{12}{}^{m-2}, \tag{4.13}$$

where

$$\hat{F}_1 = -\frac{1}{2}\left[\frac{\partial^2}{\partial r_1{}^2} + \frac{(m+2)}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2{}^2} + \frac{(m+2)}{r_2}\frac{\partial}{\partial r_2}\right], \tag{4.14}$$

$$\hat{F}_2 = -\frac{m}{2}\left(\frac{r_1{}^2 - r_2{}^2}{r_1}\frac{\partial}{\partial r_1} + \frac{r_2{}^2 - r_1{}^2}{r_2}\frac{\partial}{\partial r_2}\right) - m(m+1). \tag{4.15}$$

If m is an odd number, both sides of Eq. (4.13) have only r_{12} terms in odd powers.

Therefore, we can assume the following ansatz for $f_{1,-1}$

$$f_{1,-1} = \sum_{k=0}^{\infty} f_{1,-1,2k+1}(r_1,r_2)\cdot r_{12}{}^{2k+1}, \tag{4.16}$$

since Eq. (4.4) has on the right hand side r_{12} in an odd power.

After substituting Eq. (4.16) into Eq. (4.4), one obtains

$$\begin{aligned}
&\hat{T}\Big(\sum_{k=0}^{\infty} f_{1,-1,2k+1}(r_1,r_2)\cdot r_{12}{}^{2k+1}\Big) + \frac{1}{r_{12}} \\
&= \sum_{k=0}^{\infty} \hat{F}_1\Big|_{m=2k+1} f_{1,-1,2k+1}\cdot r_{12}{}^{2k+1} + \sum_{k=0}^{\infty} \hat{F}_2\Big|_{m=2k+1} f_{1,-1,2k+1}\cdot r_{12}{}^{2k-1} + \frac{1}{r_{12}} \\
&= \left(\hat{F}_2\Big|_{m=1} f_{1,-1,1} + 1\right)\cdot r_{12}{}^{-1} + \sum_{k=0}^{\infty}\left(\hat{F}_1\Big|_{m=2k+1} f_{1,-1,2k+1} + \hat{F}_2\Big|_{m=2k+3} f_{1,-1,2k+3}\right)\cdot r_{12}{}^{2k+1} \\
&= \left\{\left[-\frac{1}{2}\Big(\frac{r_1{}^2 - r_2{}^2}{r_1}\frac{\partial}{\partial r_1} + \frac{r_2{}^2 - r_1{}^2}{r_2}\frac{\partial}{\partial r_2}\Big) - 2\right] f_{1,-1,1} + 1\right\}\cdot r_{12}{}^{-1} + \\
&\sum_{k=0}^{\infty}\left\{\left[-\frac{1}{2}\cdot\Big(\frac{\partial^2}{\partial r_1{}^2} + \frac{2k+3}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2{}^2} + \frac{2k+3}{r_2}\frac{\partial}{\partial r_2}\Big)\right] f_{1,-1,2k+1} + \right. \\
&\left.\left[-\frac{2k+3}{2}\cdot\left(\frac{r_1{}^2 - r_2{}^2}{r_1}\frac{\partial}{\partial r_1} + \frac{r_2{}^2 - r_1{}^2}{r_2}\frac{\partial}{\partial r_2}\right) - (2k+3)(2k+4)\right] f_{1,-1,2k+3}\right\}\cdot r_{12}{}^{2k+1} = 0,
\end{aligned} \tag{4.17}$$

where $\hat{F}_1$ and $\hat{F}_2$ is defined in Eq. (4.14) and Eq. (4.15).

In order to solve this equation step by step, we can collect different powers of r_{12}.

The first equation we can solve of Eq. (4.17) with r_{12}^{-1} reads

$$\left\{\left[-\frac{1}{2}(\frac{r_1^2-r_2^2}{r_1}\frac{\partial}{\partial r_1}+\frac{r_2^2-r_1^2}{r_2}\frac{\partial}{\partial r_2})-2\right]f_{1,-1,1}+1\right\}\cdot r_{12}^{-1}=0. \tag{4.18}$$

The solution to Eq. (4.18) is

$$f_{1,-1,1}(r_1,r_2)=\frac{r_1^2+c\cdot(r_1^2+r_2^2)}{r_1^2-r_2^2} \quad . \tag{4.19}$$

We easily see that $f_{1,-1,1}$ can have a singularity when $r_1=r_2$, and $f_{1,-1,1}$ should be symmetric with respect to the interchange of r_1 and r_2. Expanding $f_{1,-1,1}$ as a power series in (r_1-r_2) determines value of c which removes the singularity and makes this function be symmetric. After expanding, the function in Eq. (4.19) will become

$$f_{1,-1,1}=\frac{r_2(2c+1)/2}{r_1-r_2}+(\frac{3}{4}+\frac{c}{2})+\frac{2c+1}{8r_2}(r_1-r_2)+\ldots. \tag{4.20}$$

It is easy to see in Eq. (4.20) that setting $c=-\frac{1}{2}$ removes the singularity. Therefore, $f_{1,-1,1}$ becomes

$$f_{1,-1,1}(r_1,r_2)=\frac{r_1^2-\frac{1}{2}\cdot(r_1^2+r_2^2)}{r_1^2-r_2^2}=\frac{1}{2}. \tag{4.21}$$

The equation corresponding to r_{12}^{1} can be extracted from Eq. (4.17) as

$$\left\{-\frac{1}{2}(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+\frac{3}{r_1}\frac{\partial}{\partial r_1}+\frac{3}{r_2}\frac{\partial}{\partial r_2})f_{1,-1,1}(r_1,r_2)+\right.$$

$$\left.[-\frac{3}{2}\frac{(r_1^2-r_2^2)}{r_1}\cdot\frac{\partial f_{1,-1,3}(r_1,r_2)}{\partial r_1}+\frac{3}{2}\frac{(r_1^2-r_2^2)}{r_2}\cdot\frac{\partial f_{1,-1,3}(r_1,r_2)}{\partial r_2}-12f_{1,-1,3}(r_1,r_2)]\right\}\cdot r_{12}=0. \tag{4.22}$$

After substituting $f_{1,-1,1}$ from Eq. (4.21) into Eq. (4.22), we can solve for $f_{1,-1,3}$ and get

$$f_{1,-1,3}=\frac{c\cdot(r_1^2+r_2^2)}{(r_1^2-r_2^2)^2}. \tag{4.23}$$

In this case, c must equal to zero to remove the singularity when $r_1=r_2$. Therefore, we easily see that $f_{1,-1,3}=0$. By this result, we can solve the following equations:

$$\sum_{k=1}^{\infty}\left\{\left[-\frac{1}{2}\cdot(\frac{\partial^2}{\partial r_1^2}+\frac{2k+3}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_2^2}+\frac{2k+3}{r_2}\frac{\partial}{\partial r_2})\right]f_{1,-1,2k+1}+\right.$$

$$\left.\left[-\frac{2k+3}{2}\cdot\left(\frac{r_1^2-r_2^2}{r_1}\frac{\partial}{\partial r_1}+\frac{r_2^2-r_1^2}{r_2}\frac{\partial}{\partial r_2}\right)-(2k+3)(2k+4)\right]f_{1,-1,2k+3}\right\}\cdot r_{12}^{2k-1}=0. \tag{4.24}$$

If $f_{1,-1,2k+1}=0$, Eq. (4.24) becomes

$$\sum_{k=1}^{\infty}\left[-\frac{2k+3}{2}\cdot\left(\frac{r_1^2-r_2^2}{r_1}\frac{\partial}{\partial r_1}+\frac{r_2^2-r_1^2}{r_2}\frac{\partial}{\partial r_2}\right)-(2k+3)(2k+4)\right]f_{1,-1,2k+3}=0. \tag{4.25}$$

The solution of Eq. (4.25) for each k is

$$f_{1,-1,2k+3}=\frac{c\cdot(r_1^2+r_2^2)}{(r_1^2-r_2^2)^{k+2}}, \tag{4.26}$$

where $k\in N$.

As mentioned above, we know that c must equal to zero to remove the singularity when $r_1=r_2$ and also makes this function symmetric with respect to the interchange of r_1 and r_2. So we know

$$f_{1,-1,2k+1}=\begin{cases}\frac{1}{2} & when\ k=0\\ 0 & when\ k\in N\end{cases}, \tag{4.27}$$

$$f_{1,-1}=\sum_{k=0}^{\infty}f_{1,-1,2k+1}(r_1,r_2)\cdot r_{12}^{2k+1}=\frac{1}{2}r_{12}. \tag{4.28}$$

So we have solved Eq. (4.1) and the solution of Eq. (4.5) has the explicit form.

$$\Psi_1=-Z(r_1+r_2)+\frac{1}{2}r_{12}+\sum_n c_n\cdot H_{1,n}. \tag{4.29}$$

For homogeneity one, there are no well-behaving homogeneous solutions which fulfills all of the conditions of a physical wave function. So we finally obtain

$$\Psi_1 = -Z(r_1 + r_2) + \frac{1}{2} r_{12} \tag{4.30}$$

In this chapter, we introduce two general techniques of solving equations. For the equations without r_{12}, we introduce ratio coordinates to simplify the equation into an ODE (**Method 1**). For equations involving r_{12}, we expand our unknown function as a power series in r_{12}, so we can solve a family of equations in only two variables (e.g., r_1 and r_2). After collecting different powers of r_{12}, the differential equations become first-order partial differential equations (**Method 2**). Solving this kind of equations is much easier than original differential equations. By using these two techniques, we can gradually tackle the following equations arising in the theory of the wave function of the helium atom.

Chapter 5

Wave Function of Homogeneity Two

5.1 Solving the Equation and Removing Singularities

After solving $\Psi_0 = 1$ and $\Psi_1 = -Z(r_1 + r_2) + \frac{1}{2} r_{12}$, we proceed to the next equation $\hat{T}\Psi_2 = -\hat{V}\Psi_1 + E\Psi_0$ to find Ψ_2.

$$\hat{T}\Psi_2 = \frac{Z}{2}(\frac{1}{r_1} + \frac{1}{r_2}) \cdot r_{12} + [-\frac{(r_1 + r_2)^2 Z^2}{r_1 r_2} + E - \frac{1}{2}] + Z \cdot (r_1 + r_2) \cdot r_{12}^{-1}. \tag{5.1}$$

We expand Ψ_2 into three parts

$$\hat{T}\Psi_2 = \hat{T}(f_{2,1} + f_{2,0} + f_{2,-1}) = g_{2,1} + g_{2,0} + g_{2,-1}, \tag{5.2}$$

where $f_{2,1}$, $f_{2,0}$ and $f_{2,-1}$ are defined implicitly by

$$\hat{T}f_{2,1} = g_{2,1} = \frac{Z}{2}(\frac{1}{r_1} + \frac{1}{r_2}) \cdot r_{12}, \tag{5.3}$$

$$\hat{T}f_{2,0} = g_{2,0} = -\frac{(r_1 + r_2)^2 Z^2}{r_1 r_2} + E - \frac{1}{2}, \tag{5.4}$$

$$\hat{T}f_{2,-1} = g_{2,-1} = Z \cdot (r_1 + r_2) \cdot r_{12}^{-1}. \tag{5.5}$$

Since Eq. (5.4) does not contain r_{12}, we can use **Method 1** to solve this equation. For the remaining two equations, Eq. (5.3) and Eq. (5.5), we use **Method 2.**

After changing to ratio coordinates, Eq. (5.4) becomes

$$\hat{T}f_{2,0}^{RC}(r_1, \rho) = g_{2,0}^{RC}(r_1, \rho) = -Z^2(2 + \rho + \frac{1}{\rho}) + E - \frac{1}{2} \tag{5.6}$$

In this equation, we know that the function on the right hand side has homogeneity zero, and the homogeneity of $\hat{T}$ is -2. So we can assume that $f_{2,0}^{RC}(r_1,\rho)$ has homogeneity two. $\hat{T}f_{2,0}^{RC}(r_1,\rho)$ can be written as

$$\hat{T}f_{2,0}^{RC}(r_1,\rho)=\hat{T}(r_1^2\cdot f_{2,0}^{RC}(\rho))=-\left[3\rho\cdot\frac{\partial}{\partial\rho}+\frac{\rho^2(1+\rho^2)}{2}\cdot\frac{\partial^2}{\partial\rho^2}+3\right]f_{2,0}^{RC}(\rho), \tag{5.7}$$

Therefore, Eq. (5.6) can be rewritten as

$$-\left[3\rho\cdot\frac{\partial}{\partial\rho}+\frac{\rho^2(1+\rho^2)}{2}\cdot\frac{\partial^2}{\partial\rho^2}+3\right]f_{2,0}^{RC}(\rho)=-Z^2(2+\rho+\frac{1}{\rho})+E-\frac{1}{2} \tag{5.8}$$

General solution of this differential equation is given by

$$f_{2,0}^{RC}(\rho)=(1-\frac{1}{\rho^2})\cdot C_1+\frac{1-6\rho^2+\rho^4}{\rho^3}\cdot C_2+\frac{Z^2}{3}\cdot\frac{2+3\rho}{\rho^2}+\frac{1-2E}{6\rho^2} \tag{5.9}$$

After changing back to interparticle coordinates, the solution becomes

$$\begin{aligned} f_{2,0}^{IC}(r_1,r_2)&=r_1^2\cdot f_{2,0}^{RC}(\rho)+\sum_n c_n\cdot H_{2,n}\\ &=(\frac{r_2^3}{r_1}-6r_1r_2+\frac{r_1^3}{r_2})\cdot C_1+(r_1^2-r_2^2)\cdot C_2+Z^2r_1r_2+(\frac{2Z^2}{3}+\frac{1}{6}-\frac{E}{3})r_2^2\\ &\quad+\sum_n c_n\cdot H_{2,n}. \end{aligned} \tag{5.10}$$

In Eq. (5.10), we can easily see that C_1 should be set to zero to avoid singularities when r_1 or r_2 are equal to zero. The value of C_2 must be selected in a way to make the solution symmetric with respect to the $r_1 \leftrightarrow r_2$ permutation. After expanding, Eq. (5.10) becomes

$$f_{2,0}^{IC}(r_1,r_2)=C_2\cdot r_1^2+(-C_2+\frac{2Z^2}{3}-\frac{E}{3}+\frac{1}{6})\cdot r_2^2+Z^2r_1r_2+\sum_n c_n\cdot H_{2,n}. \tag{5.11}$$

This equation will be symmetric if

$$C_2=-C_2+\frac{2Z^2}{3}-\frac{E}{3}+\frac{1}{6}, \tag{5.12}$$

which can be solved to yield

$$C_2 = \frac{1}{12} + \frac{Z^2}{3} - \frac{E}{6}\,. \tag{5.13}$$

Therefore physically acceptable, $f_{2,0}^{IC}$ becomes

$$f_{2,0}^{IC} = \frac{1}{12}(r_1^2 + r_2^2)\cdot(4Z^2+1) - \frac{1}{6}(r_1^2 + r_2^2)\cdot E + Z^2 r_1 r_2 + \sum_n c_n \cdot H_{2,n}\,. \tag{5.14}$$

By solving the equation

$$\hat{T} H_{2,n} = 0\,, \tag{5.15}$$

we can find out only one symmetric solution without any singularity. It is one of the two hyperspherical harmonics of homogeneity two,

$$H_{2,1} = r_1^2 + r_2^2 - r_{12}^2\,. \tag{5.16}$$

The other hyperspherical harmonic, $H_{2,0} = r_1^2 - r_2^2$, is anti-symmetric. Therefore, we can use this homogeneous solution to simplify our result.

$$\begin{aligned} f_{2,0} &= \frac{1}{12}(r_1^2 + r_2^2)\cdot(4Z^2+1) - \frac{1}{6}(r_1^2 + r_2^2)\cdot E + Z^2 r_1 r_2 - (4Z^2+1)\cdot H_{2,1} + \sum_n c_n \cdot H_{2,n} \\ &= \frac{1}{12} r_{12}^2 \cdot (4Z^2+1) - \frac{1}{6}(r_1^2 + r_2^2)\cdot E + Z^2 r_1 r_2 + \sum_n c_n \cdot H_{2,n}\,. \end{aligned} \tag{5.17}$$

Finally, we set $c_n = 0$ for the moment to obtain the simplest form of the particular solution to Eq. (5.4),

$$f_{2,0} = \frac{1}{12} r_{12}^2 \cdot (4Z^2+1) - \frac{1}{6}(r_1^2 + r_2^2)\cdot E + Z^2 r_1 r_2\,. \tag{5.18}$$

In order to solve Eq. (5.5), we set

$$\begin{aligned} &\hat{T}(f_{2,-1}(r_1, r_2, r_{12})) - Z\cdot(r_1 + r_2)\cdot r_{12}^{-1} \\ &= \hat{T}\Big(\sum_{k=0}^{\infty} f_{2,-1,2k+1}(r_1, r_2)\cdot r_{12}^{2k+1}\Big) - Z\cdot(r_1 + r_2)\cdot r_{12}^{-1} = 0\,. \end{aligned} \tag{5.19}$$

After acting with the operator $\hat{T}$, Eq. (5.19) becomes

$$\left\{-\left[\frac{1}{2}\cdot(r_1^2-r_2^2)\cdot(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})+2\right]f_{2,-1,1}-Z\cdot(r_1+r_2)\right\}\cdot r_{12}^{-1}$$

$$+\sum_{k=1}^{\infty}\left\{\left[-\frac{1}{2}\cdot(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2})-\frac{2k+1}{2}\cdot(\frac{1}{r_1}\frac{\partial}{\partial r_1}+\frac{1}{r_2}\frac{\partial}{\partial r_2})\right]f_{2,-1,2k-1}\right.$$

$$\left.-(2k+1)\cdot\left[\frac{1}{2}\cdot(r_1^2-r_2^2)\cdot(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})+2k+2\right]f_{2,-1,2k+1}\right\}\cdot r_{12}^{2k-1}=0\,. \qquad (5.20)$$

After substituting Eq. (5.20) into Eq. (5.5), we can follow the sequence of steps defining **Method 2** to collect different powers of r_{12}, and start with solving the first equation corresponding to r_{12}^{-1}

$$-\frac{1}{2}(r_1^2-r_2^2)(\frac{1}{r_1}\cdot\frac{\partial}{\partial r_1}-\frac{1}{r_2}\cdot\frac{\partial}{\partial r_2})\cdot f_{2,-1,1}(r_1,r_2)-Z(r_1+r_2)-2\cdot f_{2,-1,1}(r_1,r_2)=0\,. \qquad (5.21)$$

The solution is

$$f_{2,-1,1}(r_1,r_2)=\frac{1}{3}\frac{-2Z(r_1^3-r_2^3)+3c\cdot(r_1^2+r_2^2)^{3/2}}{r_1^2-r_2^2}\,. \qquad (5.22)$$

We can easily see that this solution may have a singularity when $r_1=r_2$. Therefore, we can expand this function at $r_1=r_2$ by power series.

$$f_{2,-1,1}(r_1,r_2)=\frac{c\cdot\sqrt{2}\cdot r_2^2}{r_1-r_2}+r_2\cdot(c\cdot\sqrt{2}-Z)+(\frac{5\sqrt{2}}{8}c-\frac{Z}{2})\cdot(r_1-r_2)+\dots\,. \qquad (5.23)$$

Setting $c=0$ removes the singularity when $r_1=r_2$.The well-behaving function becomes

$$f_{2,-1,1}(r_1,r_2)=\frac{1}{3}\cdot\frac{-2Z(r_1^3-r_2^3)}{r_1^2-r_2^2}=-\frac{2Z}{3}\cdot\frac{r_1^2+r_1r_2+r_2^2}{r_1+r_2}\,. \qquad (5.24)$$

Next, we solve the second equation corresponding to r_{12}^{1}

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^{\,2}}+\frac{\partial^2}{\partial r_2^{\,2}}+\frac{3}{r_1}\frac{\partial}{\partial r_1}+\frac{3}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,1}(r_1,r_2)$$

$$-\frac{3}{2}(r_1^{\,2}-r_2^{\,2})\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,3}(r_1,r_2)-12\cdot f_{2,-1,3}(r_1,r_2)=0\,. \tag{5.25}$$

After substituting Eq. (5.24) into Eq. (5.25), the equation becomes

$$-\frac{3}{2}(r_1^{\,2}-r_2^{\,2})\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,3}(r_1,r_2)-12\cdot f_{2,-1,3}(r_1,r_2)$$

$$+\frac{Z}{3}\cdot\frac{11r_1^{\,2}+18r_1r_2+11r_2^{\,2}}{(r_1+r_2)^3}=0\,. \tag{5.26}$$

The solution is

$$f_{2,-1,3}(r_1,r_2)=\frac{c\cdot(r_1^{\,2}+r_2^{\,2})^{3/2}}{(r_1+r_2)^2(r_1-r_2)^2}+\frac{2Z}{9}\cdot\frac{r_1^{\,2}+3r_1r_2+r_2^{\,2}}{(r_1+r_2)^3}\,. \tag{5.27}$$

Setting $c=0$ removes the singularity when $r_1=r_2$. Therefore, the well-behaving solution is given by

$$f_{2,-1,3}(r_1,r_2)=\frac{2Z}{9}\cdot\frac{r_1^{\,2}+3r_1r_2+r_2^{\,2}}{(r_1+r_2)^3}\,. \tag{5.28}$$

We continue this process by solving the next equation corresponding to $r_{12}^{\,3}$.

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^{\,2}}+\frac{\partial^2}{\partial r_2^{\,2}}+\frac{5}{r_1}\frac{\partial}{\partial r_1}+\frac{5}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,3}(r_1,r_2)$$

$$-\frac{5}{2}(r_1^{\,2}-r_2^{\,2})\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,5}(r_1,r_2)-30\cdot f_{2,-1,5}(r_1,r_2)=0\,. \tag{5.29}$$

After substituting Eq. (5.28) into Eq. (5.29), the equation becomes

$$-\frac{5}{2}(r_1^{\,2}-r_2^{\,2})\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,5}(r_1,r_2)-30\cdot f_{2,-1,5}(r_1,r_2)$$

$$+\frac{Z}{3}\cdot\frac{9r_1^{\,2}+10r_1r_2+9r_2^{\,2}}{(r_1+r_2)^5}=0\,. \tag{5.30}$$

The solution is

$$f_{2,-1,5}(r_1,r_2)=\frac{c\cdot(r_1^2+r_2^2)^{3/2}}{(r_1+r_2)^3(r_1-r_2)^3}+\frac{2Z}{45}\cdot\frac{r_1^2+5r_1r_2+r_2^2}{(r_1+r_2)^5}. \tag{5.31}$$

Setting $c=0$ removes the singularity when $r_1=r_2$. Therefore, the solution becomes

$$f_{2,-1,5}(r_1,r_2)=\frac{2Z}{45}\cdot\frac{r_1^2+5r_1r_2+r_2^2}{(r_1+r_2)^5}. \tag{5.32}$$

In order to find a closed form of those functions, we continue this process by solving the next equation corresponding to r_{12}^5.

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+\frac{7}{r_1}\frac{\partial}{\partial r_1}+\frac{7}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,5}(r_1,r_2)$$
$$-\frac{7}{2}(r_1^2-r_2^2)\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,7}(r_1,r_2)-56\cdot f_{2,-1,7}(r_1,r_2)=0. \tag{5.33}$$

After substituting Eq. (5.32) into Eq. (5.33), the equation becomes

$$-\frac{7}{2}(r_1^2-r_2^2)\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\cdot f_{2,-1,7}(r_1,r_2)-56\cdot f_{2,-1,7}(r_1,r_2)$$
$$+\frac{Z}{5}\cdot\frac{17r_1^2+14r_1r_2+17r_2^2}{(r_1+r_2)^7}=0. \tag{5.34}$$

The solution is

$$f_{2,-1,7}(r_1,r_2)=\frac{c\cdot(r_1^2+r_2^2)^{3/2}}{(r_1+r_2)^4(r_1-r_2)^4}+\frac{2Z}{105}\cdot\frac{r_1^2+7r_1r_2+r_2^2}{(r_1+r_2)^7}. \tag{5.35}$$

Setting $c=0$ removes the singularity when $r_1=r_2$. Therefore, the solution becomes

$$f_{2,-1,7}(r_1,r_2)=\frac{2Z}{105}\cdot\frac{r_1^2+7r_1r_2+r_2^2}{(r_1+r_2)^7}. \tag{5.36}$$

Analyzing Eqs. (5.24), (5.28), (5.32) and (5.36), it is relatively easy to discover the closed form of the computed solutions for a general index $n=0,1,2,\ldots$

$$f_{2,-1,2n+1}(r_1,r_2)=\frac{2Z}{3(2n+1)(2n-1)}\cdot\frac{r_1^2+(2n+1)\cdot r_1r_2+r_2^2}{(r_1+r_2)^{2n+1}}$$

$$=\frac{2Z}{3(2n+1)(2n-1)(r_1+r_2)^{2n-1}}+\frac{2Zr_1r_2}{3(2n+1)(r_1+r_2)^{2n+1}}. \tag{5.37}$$

Therefore, we can rewrite $f_{2,-1}$,

$$f_{2,-1}(r_1,r_2,r_{12})=\sum_{n=0}^{\infty}\left(\frac{2Z}{3(2n+1)(2n-1)(r_1+r_2)^{2n-1}}+\frac{2Zr_1r_2}{3(2n+1)(r_1+r_2)^{2n+1}}\right)\cdot r_{12}^{\ 2n+1}$$

$$=-\frac{Z}{6}(r_1^2+r_2^2-r_{12}^{\ 2})\cdot\ln\left(\frac{r_1+r_2-r_{12}}{r_1+r_2+r_{12}}\right)-\frac{Z}{3}(r_1+r_2)\cdot r_{12}. \tag{5.38}$$

However, this solution have a singularity when $r_{12}=r_1+r_2$. We need a homogeneous solution to remove the singularity produced by the term $\ln(r_1+r_2-r_{12})$. It is easy to verify that the homogeneous solution

$$-\frac{Z}{6}(r_1^2+r_2^2-r_{12}^{\ 2})\cdot\left[\ln(r_1+r_2-r_{12})+\ln(r_1+r_2+r_{12})\right]+\frac{Z}{3}r_1r_2 \tag{5.39}$$

has the desired properties. After using this homogeneous solution to remove the singularity, $f_{2,-1}(r_1,r_2,r_{12})$ becomes

$$f_{2,-1}(r_1,r_2,r_{12})=-\frac{Z}{3}(r_1^2+r_2^2-r_{12}^{\ 2})\cdot\ln(r_1+r_2+r_{12})-\frac{Z}{3}(r_1+r_2)\cdot r_{12}+\frac{Z}{3}r_1r_2. \tag{5.40}$$

Solving Eq. (5.3) yields the final ingredient needed to solve Ψ_2. In order to solve Eq. (5.3), we also follow **Method 2** to set

$$\hat{T}(f_{2,1}(r_1,r_2,r_{12}))-\frac{Z}{2}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\cdot r_{12}$$

$$=\hat{T}\left(\sum_{k=0}^{\infty}f_{2,1,2k+1}(r_1,r_2)\cdot r_{12}^{\ 2k+1}\right)-\frac{Z}{2}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\cdot r_{12}=0 \tag{5.41}$$

After acting with the operator $\hat{T}$, the equation becomes

$$-\left[\frac{1}{2}\cdot(r_1^2-r_2^2)\cdot\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)+2\right]f_{2,1,1}\cdot r_{12}^{\ -1}+\left\{-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+\frac{3}{r_1}\frac{\partial}{\partial r_1}+\frac{3}{r_2}\frac{\partial}{\partial r_2}\right)f_{2,1,1}(r_1,r_2)\right.$$
$$\left.+\left[-\frac{3}{2}(r_1^2-r_2^2)\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2}\right)-12\right]f_{2,1,3}(r_1,r_2)-\frac{Z}{2}\cdot\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right\}\cdot r_{12}$$

$$+\sum_{k=2}^{\infty}\left\{\left[-\frac{1}{2}\cdot(\frac{\partial^2}{\partial r_1^{\ 2}}+\frac{\partial^2}{\partial r_2^{\ 2}})-\frac{2k+1}{2}\cdot(\frac{1}{r_1}\frac{\partial}{\partial r_1}+\frac{1}{r_2}\frac{\partial}{\partial r_2})\right]f_{2,1,2k-1}\right.$$

$$\left.-(2k+1)\cdot\left[\frac{1}{2}\cdot(r_1^{\ 2}-r_2^{\ 2})\cdot(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})+2k+2\right]f_{2,1,2k+1}\right\}\cdot r_{12}^{\ 2k-1}=0\,. \qquad (5.42)$$

After substituting Eq. (5.42) into Eq. (5.3), we can start to solve the first equation with $r_{12}^{\ -1}$

$$-\frac{1}{2}(r_1^{\ 2}-r_2^{\ 2})(\frac{1}{r_1}\cdot\frac{\partial}{\partial r_1}-\frac{1}{r_2}\cdot\frac{\partial}{\partial r_2})\cdot f_{2,1,1}(r_1,r_2)-2\cdot f_{2,1,1}(r_1,r_2)=0\,. \qquad (5.43)$$

Then we can get the solution

$$f_{2,1,1}(r_1,r_2)=\frac{c\cdot(r_1^{\ 2}+r_2^{\ 2})^{3/2}}{r_1^{\ 2}-r_2^{\ 2}}\,. \qquad (5.44)$$

In order to remove the singularity when $r_1=r_2$, we set $c=0$.The equation becomes

$$f_{2,1,1}(r_1,r_2)=\frac{0\cdot(r_1^{\ 2}+r_2^{\ 2})^{3/2}}{r_1^{\ 2}-r_2^{\ 2}}=0\,. \qquad (5.45)$$

We continue solving the next equation corresponding to $r_{12}^{\ 1}$.

$$-\frac{1}{2}(\frac{\partial^2}{\partial r_1^{\ 2}}+\frac{\partial^2}{\partial r_2^{\ 2}}+\frac{3}{r_1}\frac{\partial}{\partial r_1}+\frac{3}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,1}(r_1,r_2)$$

$$-\frac{3}{2}(r_1^{\ 2}-r_2^{\ 2})(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,3}(r_1,r_2)-12\cdot f_{2,1,3}(r_1,r_2)-\frac{Z}{2}\cdot(\frac{1}{r_1}+\frac{1}{r_2})=0\,. \qquad (5.46)$$

After substituting Eq. (5.45) into Eq. (5.46), we obtain

$$-\frac{3}{2}(r_1^{\ 2}-r_2^{\ 2})(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,3}(r_1,r_2)-12\cdot f_{2,1,3}(r_1,r_2)-\frac{Z}{2}\cdot(\frac{1}{r_1}+\frac{1}{r_2})=0\,. \qquad (5.47)$$

The solution is

$$f_{2,1,3}(r_1,r_2)=\frac{c\cdot(r_1^{\ 2}+r_2^{\ 2})^{3/2}}{(r_1-r_2)^2(r_1+r_2)^2}+\frac{Z}{9}\frac{r_1+r_2}{(r_1-r_2)^2}\,. \qquad (5.48)$$

In this equation, we can easily see that this function has a singularity when $r_1=r_2$.

In order to inspect the singularity in detail, let us expand this function as a power series in $(r_1 - r_2)$

$$f_{2,1,3}(r_1,r_2)=\frac{(\frac{\sqrt{2}}{2}c+\frac{2}{9}Z)\cdot r_2}{(r_1-r_2)^2}+\frac{\frac{\sqrt{2}}{4}c+\frac{1}{9}Z}{r_1-r_2}+\frac{3\sqrt{2}}{16}\frac{c}{r_2}-\frac{3\sqrt{2}}{32}\frac{c}{r_2^{\,2}}(r_1-r_2)+\dots\ . \tag{5.49}$$

Therefore, setting $c=-\frac{2\sqrt{2}}{9}Z$ removes the singularity. Eq. (6.48) becomes

$$f_{2,1,3}(r_1,r_2)=\frac{Z}{9}\frac{r_1+r_2}{(r_1-r_2)^2}-\frac{2\sqrt{2}Z}{9}\frac{(r_1^{\,2}+r_2^{\,2})^{3/2}}{(r_1-r_2)^2(r_1+r_2)^2}\,. \tag{5.50}$$

We continue solving the next equation corresponding to $r_{12}^{\;3}$.

$$-\frac{1}{2}(\frac{\partial^2}{\partial r_1^{\,2}}+\frac{\partial^2}{\partial r_2^{\,2}}+\frac{5}{r_1}\frac{\partial}{\partial r_1}+\frac{5}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,3}(r_1,r_2)$$

$$-\frac{5}{2}(r_1^{\,2}-r_2^{\,2})(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,5}(r_1,r_2)-30\cdot f_{2,1,5}(r_1,r_2)=0\,. \tag{5.51}$$

After substituting Eq. (5.50) into Eq. (5.51), we know

$$-\frac{5}{2}(r_1^{\,2}-r_2^{\,2})(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,5}(r_1,r_2)-30\cdot f_{2,1,5}(r_1,r_2)$$

$$+\frac{\sqrt{2}Z}{3}\cdot\frac{(13r_1^{\,4}+6r_1^{\,2}r_2^{\,2}+13r_2^{\,4})\sqrt{r_1^{\,2}+r_2^{\,2}}}{(r_1+r_2)^4(r_1-r_2)^4}-\frac{Z}{6}\cdot\frac{(r_1+r_2)(5r_1^{\,2}-6r_1r_2+5r_2^{\,2})}{(r_1-r_2)^4r_1r_2}=0\,. \tag{5.52}$$

The solution is

$$f_{2,1,5}(r_1,r_2)=\frac{Z}{15}\frac{r_1+r_2}{(r_1-r_2)^4}$$

$$+\left(\frac{c\cdot(r_1^{\,2}+r_2^{\,2})}{(r_1+r_2)^3(r_1-r_2)^3}+\frac{\sqrt{2}Z}{15}\frac{(r_1^{\,4}-13r_1^{\,2}r_2^{\,2}-4r_2^{\,2})}{(r_1+r_2)^4(r_1-r_2)^4}\right)\cdot\sqrt{r_1^{\,2}+r_2^{\,2}}\,. \tag{5.53}$$

As mentioned above, we can expand the function as a power series in $(r_1 - r_2)$

$$f_{2,1,5}(r_1,r_2)=\frac{(\frac{\sqrt{2}}{4}c+\frac{1}{12}Z)}{(r_1-r_2)^3}+\frac{\frac{3\sqrt{2}c+Z}{32r_2^{\,3}}}{r_1-r_2}-\frac{1}{192}\frac{18\sqrt{2}c+7Z}{r_2^{\,3}}+\dots \tag{5.54}$$

So setting $c=-\frac{\sqrt{2}}{6}Z$ removes the singularity when $r_1=r_2$. The function becomes

$$f_{2,1,5}(r_1,r_2)=\frac{Z}{15}\frac{r_1+r_2}{(r_1-r_2)^4}+\frac{\sqrt{2}Z}{30}\frac{(3r_1^{\,4}+26r_1^{\,2}r_2^{\,2}+3r_2^{\,2})\sqrt{r_1^{\,2}+r_2^{\,2}}}{(r_1+r_2)^4(r_1-r_2)^4}\quad . \tag{5.55}$$

Now we can continue solving the next equation corresponding to $r_{12}^{\,5}$.

$$\begin{aligned}&-\frac{1}{2}(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^{\,2}}+\frac{7}{r_1}\frac{\partial}{\partial r_1}+\frac{7}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,5}(r_1,r_2)\\&\quad-\frac{7}{2}(r_1^{\,2}-r_2^{\,2})(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,7}(r_1,r_2)-56\cdot f_{2,1,7}(r_1,r_2)=0\,.\end{aligned} \tag{5.56}$$

After substituting Eq. (5.55) into Eq. (5.56), we obtain

$$\begin{aligned}&-\frac{7}{2}(r_1^{\,2}-r_2^{\,2})(\frac{1}{r_1}\frac{\partial}{\partial r_1}-\frac{1}{r_2}\frac{\partial}{\partial r_2})\cdot f_{2,1,7}(r_1,r_2)-56\cdot f_{2,1,7}(r_1,r_2)\\&\quad+\frac{\sqrt{2}Z}{12}\cdot\frac{(121r_1^{8}+540r_1^{6}r_2^{\,2}+726r_1^{\,4}r_2^{\,4}+540r_1^{\,2}r_2^{\,8}+121r_2^{\,8})}{(r_1+r_2)^6(r_1-r_2)^6\sqrt{r_1^{\,2}+r_2^{\,2}}}=0\quad .\end{aligned} \tag{5.57}$$

The solution is

$$\begin{aligned}f_{2,1,7}(r_1,r_2)&=\frac{Z}{21}\frac{r_1+r_2}{(r_1-r_2)^6}+\frac{c\cdot(r_1^{\,2}+r_2^{\,2})^{3/2}}{(r_1+r_2)^4(r_1-r_2)^4}\\&\quad-\frac{\sqrt{2}Z}{84}\cdot\frac{(32r_1^{8}+121r_1^{6}r_2^{\,2}+206r_1^{\,4}r_2^{\,4}+121r_1^{\,2}r_2^{\,6}+\dots}{(r_1+r_2)^6(r_1-r_2)^6\sqrt{r_1^{\,2}+r_2^{\,2}}}\quad .\end{aligned} \tag{5.58}$$

And we expand this function in power series of (r_1-r_2)

$$f_{2,1,7}(r_1,r_2)=\frac{\frac{1}{64}\cdot\frac{8\sqrt{2}c-5Z}{r_2}}{(r_1-r_2)^4}-\frac{\frac{1}{128}\cdot\frac{8\sqrt{2}c-5Z}{r_2^{\,2}}}{(r_1-r_2)^3}$$

$$+\frac{\frac{5}{512}\cdot\frac{8\sqrt{2}c-5Z}{r_2^{\ 3}}}{(r_1-r_2)^2}-\frac{\frac{11}{1024}\cdot\frac{8\sqrt{2}c-5Z}{r_2^{\ 4}}}{r_1-r_2}+\frac{1}{24576}\cdot\frac{1992\sqrt{2}c-1261Z}{r_2^{\ 5}}+\dots. \qquad (5.59)$$

Therefore, setting $c=\frac{5\sqrt{2}}{16}Z$ removes the singularity. Eq. (5.58) will become

$$f_{2,1,7}(r_1,r_2)=\frac{Z}{21}\frac{r_1+r_2}{(r_1-r_2)^6}-\frac{\sqrt{2}Z}{336}\cdot\frac{(23r_1^{\ 8}+484r_1^{\ 6}r_2^{\ 2}+1034r_1^{\ 4}r_2^{\ 4}+484r_1^{\ 2}r_2^{\ 6}+23r_2^{\ 8})}{(r_1+r_2)^6(r_1-r_2)^6\sqrt{r_1^{\ 2}+r_2^{\ 2}}}. \quad (5.60)$$

Analyzing Eqs. (5.50), (5.55) and (5.60), we see that the functions are getting more and more complicated. It seems difficult to discover a closed form. In order to find a closed form, we ignore the singularities for the moment, and set $c=0$ in all of these functions obtaining

$$f_{2,1,1}=0, \qquad (5.61)$$

$$f_{2,1,3}=\frac{Z}{9}\frac{r_1+r_2}{(r_1-r_2)^2}, \qquad (5.62)$$

$$f_{2,1,5}=\frac{Z}{15}\frac{r_1+r_2}{(r_1-r_2)^4}, \qquad (5.63)$$

$$f_{2,1,7}=\frac{Z}{21}\frac{r_1+r_2}{(r_1-r_2)^6}. \qquad (5.64)$$

The closed form is easy to discover now.

$$f_{2,1,2n+1}(r_1,r_2)=\begin{cases}0 & n=0\\ \frac{Z}{6n+3}\cdot\frac{r_1+r_2}{(r_1-r_2)^{2n}} & n\in \mathrm{N}\end{cases} \qquad (5.65)$$

And $f_{2,1}$ will be

$$f_{2,1}(r_1,r_2,r_{12})=\sum_{n=0}^{\infty}f_{2,1,2n+1}(r_1,r_2)\cdot r_{12}^{\ 2n+1}$$

$$=(\sum_{n=0}^{\infty}\frac{Z}{6n+3}\cdot\frac{r_1+r_2}{(r_1-r_2)^{2n}}\cdot r_{12}^{\ 2n+1})-\frac{Z}{3}(r_1+r_2)\cdot r_{12}$$

$$= \frac{Z}{6} \cdot \ln(\frac{r_1 - r_2 + r_{12}}{-r_1 + r_2 + r_{12}}) \cdot (r_1^2 - r_2^2) - \frac{Z}{3}(r_1 + r_2) r_{12} \qquad (5.66)$$

The function given by Eq. (6.65) has singularities when $r_1 = r_2 + r_{12}$ and $r_2 = r_1 + r_{12}$. These singularities are not easy to remove. We are still trying to find homogeneous solutions to remove the singularities.

5.2 Analysis and Plotting

Since our solution for homogeneity two is not complete yet, in order to proceed to the homogeneity three terms, we discuss here briefly. The wave function which was found by J. E. Gottschalk, P. C. Abbott and E. N. Maslen. The wave function of homogeneity two in the region $r_1 \geq r_2$ can be written as

$$\begin{aligned} f(r_1, r_2) = &\frac{Z}{3} \ln(r_1 - r_2 + r_{12}) \cdot (r_1^2 - r_2^2) - \frac{Z}{3} r_{12} \cdot (r_1 + r_2) - \frac{Z}{6}(r_1^2 - r_2^2) \cdot (s_1 - \frac{s_2}{\pi}) \\ &+ \frac{Z}{6} \cdot r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} + \frac{Z}{3\pi} \cdot \ln(r_1^2 + r_2^2) \cdot (r_1^2 + r_2^2 - r_{12}^2) \\ &+ \frac{Z}{3\pi} \cdot r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} \cdot \beta - \frac{Z}{3} \ln(r_1 + r_2 + r_{12})(r_1^2 + r_2^2 - r_{12}^2) - \frac{Z}{3} \cdot r_{12} \cdot (r_1 + r_2) \\ &+ \frac{Z}{3} \cdot r_1 \cdot r_2 + \frac{1}{12} \cdot r_{12}^2 \cdot (4Z^2 + 1) - \frac{E}{6} \cdot (r_1^2 + r_2^2) + Z^2 \cdot r_1 \cdot r_2, \end{aligned} \qquad (5.67)$$

where

$$s_1 = \ln(r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} + r_1^2 - r_2^2), \qquad (5.68)$$

$$\begin{aligned} s_2 = &-\beta \cdot \ln(r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} + r_1^2 - r_2^2) + \beta \cdot \ln(r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} + r_2^2 - r_1^2) \\ &+ \alpha \cdot \ln(\frac{1 + \cos\theta}{1 - \cos\theta}) + 2\left[L(\frac{\alpha - \beta}{2}) - L(\frac{\alpha + \beta}{2}) + L(\frac{\pi - \alpha + \beta}{2}) - L(\frac{\pi - \alpha - \beta}{2}) \right], \end{aligned} \qquad (5.69)$$

$L(x)$ is Lobachevsky function (Chapter 2.7),

and α and β were defined in Chapter 2.2. [(r, α, β) coordinates].

However, this solution is valid only in the region $r_1 \geq r_2$. The complete Ψ_2 should be written as

$$\Psi_2 = \begin{cases} f(r_1, r_2) & when\ r_1 \ge r_2 \\ f(r_2, r_1) & when\ r_2 > r_1 \end{cases} . \tag{5.70}$$

To have a depth discussions and analysis of Ψ_2, we separate this solution into several parts and classify each part by our rule we defined in last section at first. We set

$$P_{2,1}(r_1,r_2) = \frac{Z}{3}\ln(r_1 - r_2 + r_{12})\cdot(r_1^2 - r_2^2) - \frac{Z}{3} r_{12}\cdot(r_1 + r_2), \tag{5.71}$$

$$P_{2,0}(r_1,r_2) = \frac{1}{12}\cdot r_{12}^2\cdot(4Z^2+1) - \frac{E}{6}\cdot(r_1^2 + r_2^2) + Z^2\cdot r_1\cdot r_2, \tag{5.72}$$

$$P_{2,-1}(r_1,r_2) = -\frac{Z}{3}\ln(r_1 + r_2 + r_{12})(r_1^2 + r_2^2 - r_{12}^2) - \frac{Z}{3}\cdot r_{12}\cdot(r_1 + r_2) + \frac{Z}{3}\cdot r_1\cdot r_2 . \tag{5.73}$$

It is easy to verify that

$$\hat{T}(P_{2,1}) = g_{2,1}, \tag{5.74}$$

$$\hat{T}(P_{2,0}) = g_{2,0}, \tag{5.75}$$

$$\hat{T}(P_{2,-1}) = g_{2,-1}. \tag{5.76}$$

Therefore, Eq. (5.67) can be written as

$$f(r_1,r_2) = P_{2,1} + P_{2,0} + P_{2,-1} + P_{else}, \tag{5.77}$$

where

$$P_{else} = -\frac{Z}{6}(r_1^2 - r_2^2)\cdot(s_1 - \frac{s_2}{\pi}) + \frac{Z}{6}\cdot r_{12}\cdot\sqrt{2r_1^2 + 2r_2^2 - r_{12}^2}$$

$$+\frac{Z}{3\pi}\cdot\ln(r_1^2 + r_2^2)\cdot(r_1^2 + r_2^2 - r_{12}^2) + \frac{Z}{3\pi}\cdot r_{12}\cdot\sqrt{2r_1^2 + 2r_2^2 - r_{12}^2}\cdot\beta . \tag{5.78}$$

Clearly, P_{else} is a homogeneous solution of homogeneity two.

Next, we can discuss each part in detail. As we mentioned, $f(r_1,r_2)$ is not the full solution of Eq. (5.1) in the (r_1,r_2) plane. The complete solution has another component, which is $f(r_2,r_1)$ when $r_2 > r_1$. We can easily find out that $P_{2,0}$ and $P_{2,-1}$ are symmetric with respect to the interchange of r_1 and r_2. But $P_{2,1}$ is not symmetric. In order to make it symmetric, the solution should be written as

$$f_{2,1} = \begin{cases} P_{2,1}(r_1,r_2) & when\ r_1 \ge r_2 \\ P_{2,1}(r_2,r_1) & when\ r_2 > r_1 \end{cases}. \tag{5.79}$$

After comparing to our solution in last section, we can find out that

$$f_{2,0} = P_{2,0}, \tag{5.80}$$

$$f_{2,-1} = P_{2,-1}. \tag{5.81}$$

Therefore, Ψ_2 can be written as

$$\Psi_2 = f_{2,0} + f_{2,-1} + \begin{cases} P_{2,1}(r_1,r_2) + P_{else}(r_1,r_2) & when\ r_1 \ge r_2 \\ P_{2,1}(r_2,r_1) + P_{else}(r_2,r_1) & when\ r_2 > r_1 \end{cases}. \tag{5.82}$$

Next, we can try to plot each part of Ψ_2.

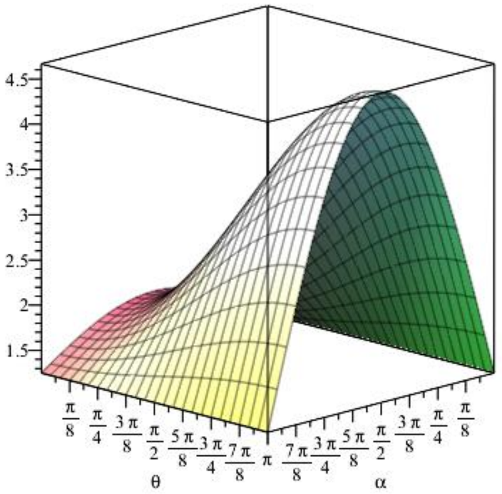


Figure 5.1
The plot of $f_{2,0}$ with
$[Z=2,\ r=1, E=1]$
in hyperspherical coordinates

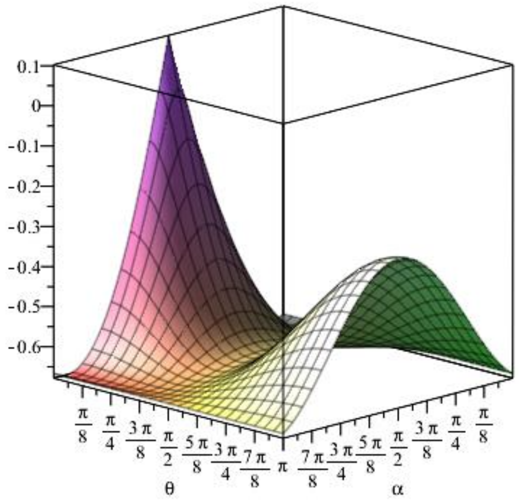


Figure 5.2
The plot of $f_{2,-1}$ with
$[Z=2,\ r=1]$
in hyperspherical coordinates

By Figure 5.1, we can find out that $f_{2,0}$ is smooth and continuous everywhere. But $f_{2,-1}$ has a cusp when $\alpha=\dfrac{\pi}{2}$ and $\theta=0$. If we consider this situation in a helium atom, we will find that it means two electrons get together at the same point, which is very unreasonable and unstable. At this point, special behaviors are acceptable and imaginable.

Then, the plot of $f_{2,1}$ is

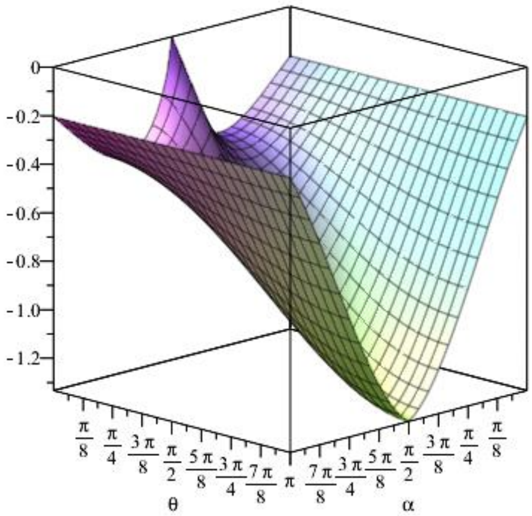


Figure 5.3
The plot of $f_{2,1}$ with
$[Z=2,\ r=1]$
in hyperspherical coordinates

By Figure 5.3, we can easily find out that this function is not differentiable at $\alpha=\frac{\pi}{2}$. To check this, we can plot $\frac{\partial}{\partial\alpha} f_{2,1}^{HC}$

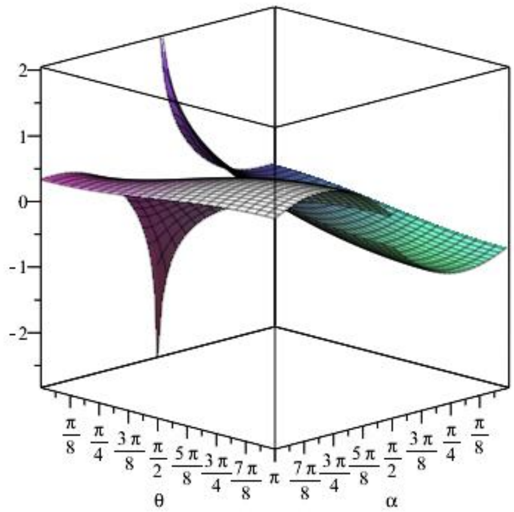


Figure 5.4
The plot of $\frac{\partial}{\partial\alpha} f_{2,1}^{HC}$ with
$[Z=2,\ r=1]$
in hyperspherical coordinates

From Figure 5.4, we know that $\frac{\partial}{\partial\alpha} f_{2,1}^{HC}$ is not continuous at $\alpha=\frac{\pi}{2}$. Therefore, we know that our $f_{2,1}$ is not acceptable from physical point of view. So that, we can assume that P_{else} term is using to remove the non-physical behavior of $f_{2,1}$. We define

$$f_{2,else}=\begin{cases} P_{else}(r_1,r_2) & when\ r_1 \ge r_2 \\ P_{else}(r_2,r_1) & when\ r_2 > r_1 \end{cases}. \qquad (6.82)$$

The plot of $f_{2,1}+f_{2,else}$ is

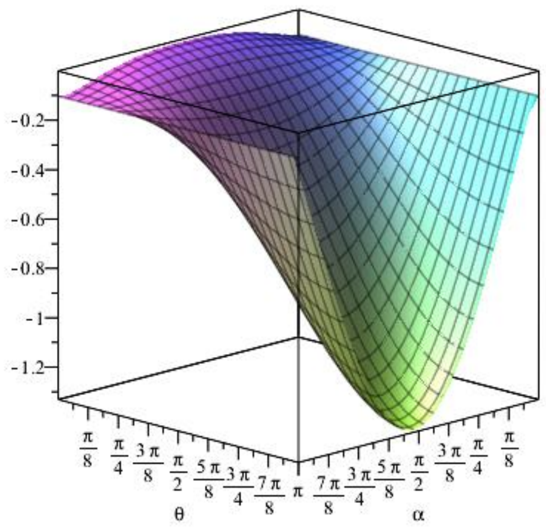


Figure 5.5
The plot of $f_{2,1}+f_{2,else}$ with $[Z=2,\ r=1]$
in hyperspherical coordinates

And the plot of $\frac{\partial}{\partial\alpha}(f_{2,1}^{HC}+f_{2,else}^{HC})$ is

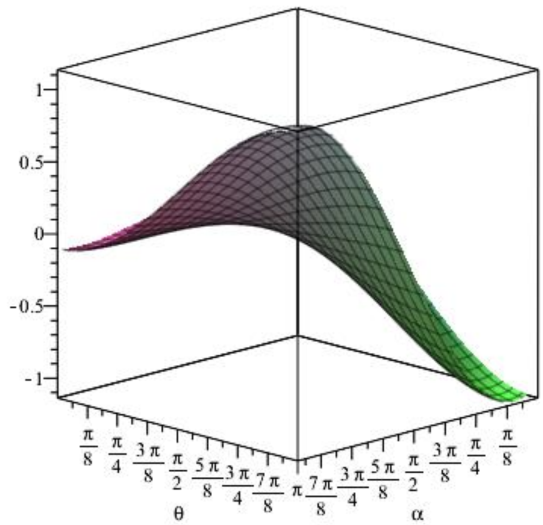


Figure 5.6
The plot of $\frac{\partial}{\partial\alpha}(f_{2,1}^{HC}+f_{2,else}^{HC})$ with $[Z=2,\ r=1]$
in hyperspherical coordinates

From Figures 5.5 and 5.6, we know that $f_{2,1}+f_{2,else}$ is a smooth and continuous function, which means $f_{2,else}$ is the homogeneous function which can really remove the non-physical behavior of $f_{2,1}$. Therefore, we can use this Ψ_2 to solve Ψ_3 in the following chapter.

Chapter 6

Wave Function of Homogeneity Three

As we discuss in the last chapter, Ψ_2 can be written as

$$\Psi_2 = f_{2,1} + f_{2,0} + f_{2,-1} + f_{2,else}. \tag{6.1}$$

The equation to solve Ψ_3 is

$$\hat{T}\Psi_3 = -\hat{V}\Psi_2 + E\Psi_1 = -\hat{V}(f_{2,1} + f_{2,0} + f_{2,-1} + f_{2,else}) + E\Psi_1. \tag{6.2}$$

Before trying to solve this equation, we separate Ψ_3 into two parts

$$\Psi_3 = f_{3,a} + f_{3,b}, \tag{6.3}$$

where

$$\hat{T}f_{3,a} = -\hat{V}(f_{2,0} + f_{2,-1}) + E\Psi_1, \tag{6.4}$$

$$\hat{T}f_{3,b} = -\hat{V}(f_{2,1} + f_{2,else}). \tag{6.5}$$

As we know, $f_{2,1}$ and $f_{2,else}$ are described in two different regions ($r_1 \geq r_2$ or $r_2 > r_1$), so solving $f_{3,a}$ will be much easier than solving $f_{3,b}$. The main method we use to find $f_{3,a}$ is making an inversion table of solving terms with homogeneity one. First, we make an ansatz.

$$t[a,b,1-a-b] = \sum_{m=-N}^{N} \sum_{n=-N}^{N} \sum_{k=1}^{4} c_{m,n,k} \cdot r_1^{\,m} r_2^{\,n} r_{12}^{\,3-m-n} \cdot sbasis_k\,, \tag{6.6}$$

where $sbasis_k = \begin{cases} 1 & k=1 \\ \ln(r_1) & k=2 \\ \ln(r_2) & k=3 \\ \ln(r_{12}) & k=4 \end{cases}$.

The elements of the inversion table are found by solving a set of linear equations for the coefficients $c_{m,n,k}$ defined by the following equation

$$\hat{T}(t[a,b,1-a-b]) = r_1^{\,a} r_2^{\,b} r_{12}^{\,1-a-b}. \tag{6.7}$$

Using this ansatz and some definite values of N, a and b, we can determine the values of the coefficients $c_{m,n,k}$.

Not every term can be found that way; the terms represented by the finite ansatz are represented by colored fields in **Figure 6.1**. Other terms require probably more complicated ansatz, possibly involving infinite summations.

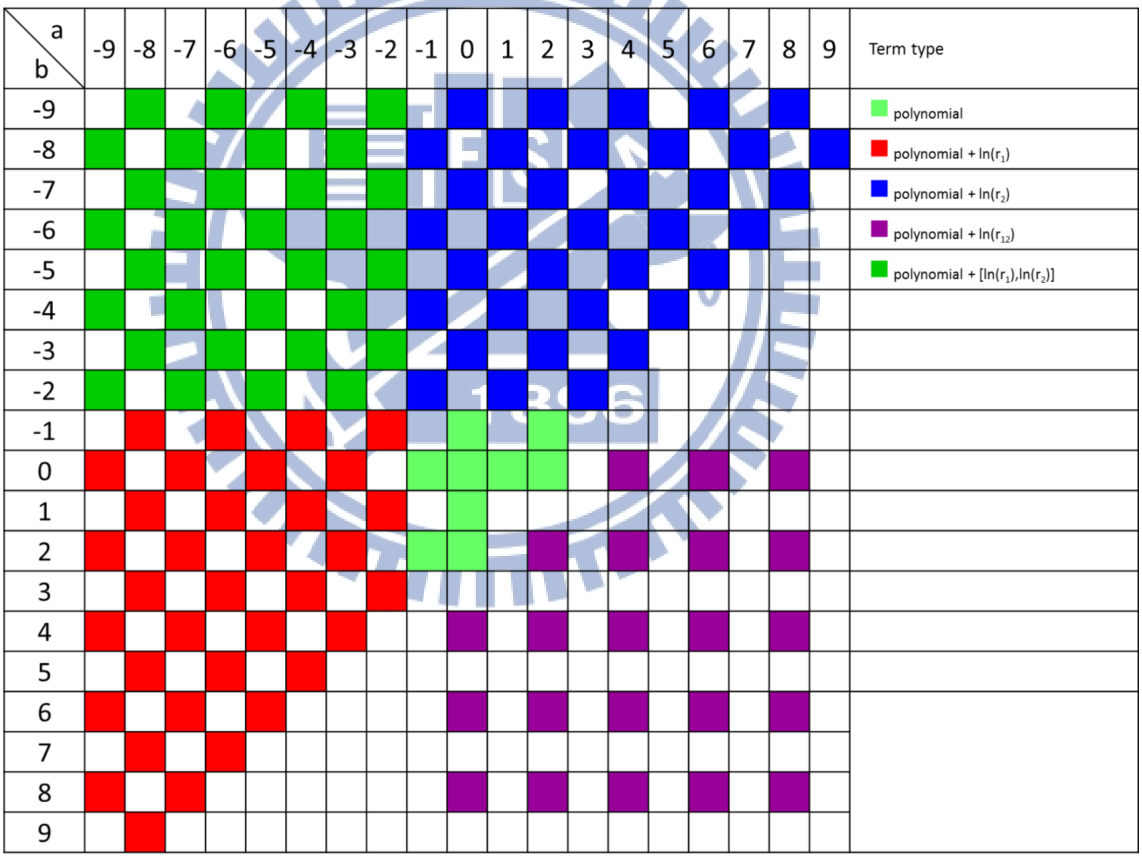


Figure 6.1
The monomial table of homogeneity 3→1

We expand our equation to see what terms are needed to solve the equation. Eq. (6.4) can be rewritten as

$$\hat{T}f_{3,a} = -\frac{Z}{6}(-6Z^2 - 2Z + 7E - 2)\cdot(r_1 + r_2) + (-Z^2 + \frac{1}{2}E - \frac{1}{12})\cdot r_{12} - \frac{Z(3Z+1)}{3}\cdot\frac{r_1 r_2}{r_{12}}$$

$$+\frac{E}{6}\cdot(\frac{r_1^{\,2}}{r_{12}} + \frac{r_2^{\,2}}{r_{12}}) - \frac{ZE}{6}\cdot(\frac{r_1^{\,2}}{r_2} + \frac{r_2^{\,2}}{r_1}) - \frac{Z^2}{3}\cdot(\frac{r_1 r_{12}}{r_2} + \frac{r_2 r_{12}}{r_1}) + \frac{Z(4Z^2+1)}{12}\cdot(\frac{r_{12}^{\,2}}{r_1} + \frac{r_{12}^{\,2}}{r_2})$$

$$-\frac{1}{3}\left[Z^2(r_1 + r_2 + \frac{r_1^{\,2}}{r_2} + \frac{r_2^{\,2}}{r_1} - \frac{r_{12}^{\,2}}{r_1} - \frac{r_{12}^{\,2}}{r_2}) + Z(r_{12} - \frac{r_1^{\,2}}{r_{12}} - \frac{r_2^{\,2}}{r_{12}})\right]\cdot\ln(r_1 + r_2 + r_{12}). \qquad (6.8)$$

About the term with $\ln(r_1 + r_2 + r_{12})$, we can use a property of $\hat{T}$, which is

$$\hat{T}(f(r_1, r_2, r_{12})\cdot\ln(r_1 + r_2 + r_{12})) = \hat{T}(f(r_1, r_2, r_{12}))\cdot\ln(r_1 + r_2 + r_{12}) + \hat{O}(f(r_1, r_2, r_{12})), \qquad (6.9)$$

where

$$\hat{O} = -\frac{r_1 - r_2 + r_{12}}{2r_1 r_{12}}\cdot\frac{\partial}{\partial r_1} - \frac{-r_1 + r_2 + r_{12}}{2r_2 r_{12}}\cdot\frac{\partial}{\partial r_2} + \frac{(r_1 - r_2)^2 - r_{12}(r_1 + r_2)}{2r_1 r_2 r_{12}}\cdot\frac{\partial}{\partial r_{12}} - \frac{r_1 + r_2}{2r_1 r_2 r_{12}}. \qquad (6.10)$$

In order to solve $f_{3,a}$, we can set

$$f_{3,a} = f_{3,a,poly} + f_{3,a,\ln}\cdot\ln(r_1 + r_2 + r_{12}), \qquad (6.11)$$

where

$$\hat{T}f_{3,a,\ln} = -\frac{1}{3}\left[Z^2(r_1 + r_2 + \frac{r_1^{\,2}}{r_2} + \frac{r_2^{\,2}}{r_1} - \frac{r_{12}^{\,2}}{r_1} - \frac{r_{12}^{\,2}}{r_2}) + Z(r_{12} - \frac{r_1^{\,2}}{r_{12}} - \frac{r_2^{\,2}}{r_{12}})\right], \qquad (6.12)$$

$$\hat{T}f_{3,a,poly} = -\frac{Z}{6}(-6Z^2 - 2Z + 7E - 2)\cdot(r_1 + r_2) + (-Z^2 + \frac{1}{2}E - \frac{1}{12})\cdot r_{12} - \frac{Z(3Z+1)}{3}\cdot\frac{r_1 r_2}{r_{12}}$$

$$+\frac{E}{6}\cdot(\frac{r_1^{\,2}}{r_{12}} + \frac{r_2^{\,2}}{r_{12}}) - \frac{ZE}{6}\cdot(\frac{r_1^{\,2}}{r_2} + \frac{r_2^{\,2}}{r_1}) - \frac{Z^2}{3}\cdot(\frac{r_1 r_{12}}{r_2} + \frac{r_2 r_{12}}{r_1}) + \frac{Z(4Z^2+1)}{12}\cdot(\frac{r_{12}^{\,2}}{r_1} + \frac{r_{12}^{\,2}}{r_2})$$

$$-\hat{O}f_{3,a,\ln}. \qquad (6.13)$$

Then, we can solve Eq. (6.12).

$$f_{3,a,\ln} = -\frac{1}{3}\left[Z^2(t[1,0,0] + t[0,1,0] + t[2,-1,0] + t[-1,2,0] - t[-1,0,2] - t[0,-1,2])\right.$$

$$\left. + Z(t[0,0,1] - t[2,0,-1] - t[0,2,-1])\right] + \text{homogeneous solutions}. \qquad (6.14)$$

For finding $f_{3,a,\ln}$, we can find out that we have every term we need by **Figure 6.1**.

The following are the functions of $t[a,b,1-a-b]$ we need in $f_{3,a,\ln}$.

$$t[1,0,0]=-\frac{1}{6}r_1^{\ 3}, \tag{6.15}$$

$$t[0,1,0]=-\frac{1}{6}r_2^{\ 3}, \tag{6.16}$$

$$t[2,-1,0]=-\frac{1}{10}\frac{r_1^{\ 4}}{r_2}, \tag{6.17}$$

$$t[-1,2,0]=-\frac{1}{10}\frac{r_2^{\ 4}}{r_1}, \tag{6.18}$$

$$t[-1,0,2]=-\frac{1}{20}\frac{r_2^{\ 4}}{r_1}-\frac{1}{2}r_1 r_{12}^{\ 2}+\frac{7}{12}r_1^{\ 3}, \tag{6.19}$$

$$t[0,-1,2]=-\frac{1}{20}\frac{r_1^{\ 4}}{r_2}-\frac{1}{2}r_2 r_{12}^{\ 2}+\frac{7}{12}r_2^{\ 3}, \tag{6.20}$$

$$t[0,0,1]=-\frac{1}{12}r_{12}^{\ 3}, \tag{6.21}$$

$$t[2,0,-1]=-\frac{3}{8}r_1^{\ 2}r_{12}-\frac{1}{8}r_2^{\ 2}r_{12}+\frac{1}{6}r_{12}^{\ 3}, \tag{6.22}$$

$$t[0,2,-1]=-\frac{1}{8}r_1^{\ 2}r_{12}-\frac{3}{8}r_2^{\ 2}r_{12}+\frac{1}{6}r_{12}^{\ 3}. \tag{6.23}$$

After using the functions of the above, $f_{3,a,\ln}$ can be written as

$$f_{3,a,\ln}=\frac{Z^2}{60}\left(\frac{r_1^{\ 4}}{r_2}+\frac{r_2^{\ 4}}{r_1}\right)+\frac{Z^2}{4}(r_1^{\ 3}+r_2^{\ 3})-\frac{Z^2}{6}(r_1+r_2)r_{12}^{\ 2}-\frac{Z}{6}(r_1^{\ 2}+r_2^{\ 2})r_{12}+\frac{5Z}{36}r_{12}^{\ 3}$$

$$+\text{homogeneous solutions} \tag{6.24}$$

By Eq. (6.24), we know we need to add some homogeneous solutions to remove the singularity from the term $\left(\frac{r_1^{\ 4}}{r_2}+\frac{r_2^{\ 4}}{r_1}\right)$. We can easily get a homogeneous solution with this term inside, which is

$$f_{3,\text{homogeneous},1} = (\frac{r_1^{\ 4}}{r_2} + \frac{r_2^{\ 4}}{r_1}) + 5 \cdot (r_1^{\ 3} + r_2^{\ 3}) - 10 \cdot (r_1^{\ 2} r_2 + r_1 r_2^{\ 2}) . \tag{6.25}$$

After adding $-\frac{Z^2}{60} \cdot f_{3,\text{homogeneous},1}$ to remove the singularity, $f_{3,a,\ln}$ becomes

$$f_{3,a,\ln} = \frac{Z^2}{6}(r_1 + r_2)(r_1^{\ 2} + r_2^{\ 2} - r_{12}^{\ 2}) - \frac{Z}{6} r_{12} (r_1^{\ 2} + r_2^{\ 2} - r_{12}^{\ 2}) - \frac{Z}{36} r_{12}^{\ 3} . \tag{6.26}$$

Now we can use $f_{3,a,\ln}$ to find $f_{3,a,poly}$. After substituting Eq. (6.26) into Eq. (6.13), the equation becomes

$$\begin{aligned} \hat{T} f_{3,a,poly} = & \frac{Z}{12} \cdot (\frac{r_1^{\ 3}}{r_2 r_{12}} + \frac{r_2^{\ 3}}{r_1 r_{12}}) + (-\frac{Z}{6} + \frac{Z^2}{3} + \frac{E}{6}) \cdot (\frac{r_1^{\ 2}}{r_{12}} + \frac{r_2^{\ 2}}{r_{12}}) + \frac{Z(3Z - 2E - 2)}{12} \cdot (\frac{r_1^{\ 2}}{r_2} + \frac{r_2^{\ 2}}{r_1}) \\ & - \frac{Z(6Z+1)}{6} \cdot \frac{r_1 r_2}{r_{12}} - \frac{Z(-12Z^2 - 7Z + 14E - 2)}{12} \cdot (r_1 + r_2) - \frac{Z(12Z+5)}{24} \cdot (\frac{r_1 r_{12}}{r_2} + \frac{r_2 r_{12}}{r_1}) \\ & + (-\frac{5Z^2}{3} + \frac{Z}{12} + \frac{E}{2} - \frac{1}{12}) \cdot r_{12} + \frac{Z(12Z^2 - 3Z + 13)}{36} \cdot (\frac{r_{12}^{\ 2}}{r_1} + \frac{r_{12}^{\ 2}}{r_2}) . \end{aligned} \tag{6.27}$$

We can solve $f_{3,a,poly}$ easily by using $t[a,b,1-a-b]$.

$$\begin{aligned} f_{3,a,poly} = & \frac{Z}{12} \cdot (t[3,-1,-1] + t[-1,3,-1]) + (-\frac{Z}{6} + \frac{Z^2}{3} + \frac{E}{6}) \cdot (t[2,0,-1] + t[0,2,-1]) \\ & + \frac{Z(3Z - 2E - 2)}{12} \cdot (t[2,-1,0] + t[-1,2,0]) - \frac{Z(6Z+1)}{6} \cdot t[1,1,-1] \\ & - \frac{Z(-12Z^2 - 7Z + 14E - 2)}{12} \cdot (t[1,0,0] + t[0,1,0]) \\ & - \frac{Z(12Z+5)}{24} \cdot (t[1,-1,1] + t[-1,1,1]) + (-\frac{5Z^2}{3} + \frac{Z}{12} + \frac{E}{2} - \frac{1}{12}) \cdot t[0,0,1] \\ & + \frac{Z(12Z^2 - 3Z + 13)}{36} \cdot (t[-1,0,2] + t[0,-1,2]) . \end{aligned} \tag{6.28}$$

By the monomial table, $f_{3,a,poly}$ can be written as

$$\begin{aligned} f_{3,a,poly} = & (-\frac{Z^2}{6} + \frac{Z}{12} - \frac{E}{12}) \cdot (r_1^{\ 2} + r_2^{\ 2}) \cdot r_{12} + (\frac{Z^2}{4} - \frac{Z}{16} + \frac{E}{72} + \frac{1}{144}) \cdot r_{12}^{\ 3} \\ & - \frac{Z(12Z^2 - 3Z + 13)}{72} \cdot (r_1 + r_2) \cdot r_{12}^{\ 2} + \frac{Z(12Z^2 - 63Z + 84E + 79)}{432} \cdot (r_1^{\ 3} + r_2^{\ 3}) \end{aligned}$$

$$+\frac{Z(-12Z^2-15Z+12E-1)}{720}\cdot(\frac{r_1^{\ 4}}{r_2}+\frac{r_2^{\ 4}}{r_1})$$

$$+\frac{Z}{12}\cdot(t[3,-1,-1]+t[-1,3,-1])-\frac{Z(12Z+5)}{24}\cdot(t[1,-1,1]+t[-1,1,1])$$

$$-\frac{Z(6Z+1)}{6}\cdot t[1,1,-1]+\text{homogeneous solutions} \qquad (6.29)$$

For $(t[3,-1,-1]+t[-1,3,-1])$, $(t[1,-1,1]+t[-1,1,1])$ and $t[1,1,-1]$ parts, we have not found the solutions in the inversion table yet.

For $f_{3,a,poly}$, we can also add $-\frac{Z(-12Z^2-15Z+12E-1)}{720}\cdot f_{3,\text{homogeneous},1}$ to remove the singularity from the term $(\frac{r_1^{\ 4}}{r_2}+\frac{r_2^{\ 4}}{r_1})$. The solution becomes

$$f_{3,a,poly}=(-\frac{Z^2}{6}+\frac{Z}{12}-\frac{E}{12})\cdot(r_1^{\ 2}+r_2^{\ 2})\cdot r_{12}+(\frac{Z^2}{4}-\frac{Z}{16}+\frac{E}{72}+\frac{1}{144})\cdot r_{12}^{\ 3}$$

$$-\frac{Z(12Z^2-3Z+13)}{72}\cdot(r_1+r_2)\cdot r_{12}^{\ 2}+\frac{Z(24Z^2-9Z+24E+41)}{216}\cdot(r_1^{\ 3}+r_2^{\ 3})$$

$$+\frac{Z(-12Z^2-15Z+12E-1)}{72}\cdot(r_1+r_2)\cdot r_1r_2$$

$$+\frac{Z}{12}\cdot(t[3,-1,-1]+t[-1,3,-1])-\frac{Z(12Z+5)}{24}\cdot(t[1,-1,1]+t[-1,1,1])$$

$$-\frac{Z(6Z+1)}{6}\cdot t[1,1,-1] \qquad (6.30)$$

Therefore, $f_{3,a}$ can be written as

$$f_{3,a}=(-\frac{Z^2}{6}+\frac{Z}{12}-\frac{E}{12})\cdot(r_1^{\ 2}+r_2^{\ 2})\cdot r_{12}+(\frac{Z^2}{4}-\frac{Z}{16}+\frac{E}{72}+\frac{1}{144})\cdot r_{12}^{\ 3}$$

$$-\frac{Z(12Z^2-3Z+13)}{72}\cdot(r_1+r_2)\cdot r_{12}^{\ 2}+\frac{Z(24Z^2-9Z+24E+41)}{216}\cdot(r_1^{\ 3}+r_2^{\ 3})$$

$$+\frac{Z(-12Z^2-15Z+12E-1)}{72}\cdot(r_1+r_2)\cdot r_1r_2$$

$$+\frac{Z}{12}\cdot(t[3,-1,-1]+t[-1,3,-1])-\frac{Z(12Z+5)}{24}\cdot(t[1,-1,1]+t[-1,1,1])$$

$$-\frac{Z(6Z+1)}{6}\cdot t[1,1,-1]$$

$$+\left[\frac{Z^2}{6}(r_1+r_2)(r_1^2+r_2^2-r_{12}^2)-\frac{Z}{6}r_{12}(r_1^2+r_2^2-r_{12}^2)-\frac{Z}{36}r_{12}^3\right]\cdot\ln(r_1+r_2+r_{12}) \quad (6.31)$$

By Eq. (6.31), we can see some terms of $f_{3,a}$ have not been solved yet. The unsolved terms and difficulties we will discuss in the next chapter.

Solving $f_{3,b}$ is much more difficult than solving $f_{3,a}$ because there are a lot of special functions in $f_{3,b}$ which make the equation very hard to solve. To continue solving next part, we need to find an easier way to simplify Ψ_2 or rewrite it by using different coordinate system. To know more about Ψ_2 and try to simplify or rewrite it become the main idea to find Ψ_3 completely. All the ideas we mentioned here we will discuss in the next chapter.

Chapter 7

Future Work and Discussions

7.1 Unsolved Terms and Difficulties

In the last chapter, we have mentioned some terms of $f_{3,a}$ have not been solved yet. These terms are $t[3,-1,-1]$, $t[-1,3,-1]$, $t[1,-1,1]$, $t[-1,1,1]$ and $t[1,1,-1]$. If we can solve those term, we will find a lot of unsolved terms in our monomial table (inversion table). After finding enough terms in our monomial table, we can use our own method to generate a particular solution of Ψ_3 easily.

In order to find those terms we have not solve yet, we know we have some equations to solve, which are

$$\hat{T}(t[3,-1,-1]) = \frac{r_1^3}{r_2 r_{12}}, \tag{7.1}$$

$$\hat{T}(t[-1,3,-1]) = \frac{r_2^3}{r_1 r_{12}}, \tag{7.2}$$

$$\hat{T}(t[1,-1,1]) = \frac{r_1 r_{12}}{r_2}, \tag{7.3}$$

$$\hat{T}(t[-1,1,1]) = \frac{r_2 r_{12}}{r_1}, \tag{7.4}$$

$$\hat{T}(t[1,1,-1]) = \frac{r_1 r_2}{r_{12}}. \tag{7.5}$$

To find these terms, we use a larger ansatz, which is

$$Ansatz = \sum_{m=-N}^{N} \sum_{n=-N}^{N} \sum_{k=1}^{8} c_{m,n,k} \cdot r_1^{\,m} r_2^{\,n} r_{12}^{\,3-m-n} \cdot sbasis_k \tag{7.6}$$

where $sbasis_k = \begin{cases} 1 & k=1 \\ \ln(r_1) & k=2 \\ \ln(r_2) & k=3 \\ \ln(r_{12}) & k=4 \\ \ln(r_1+r_2+r_{12}) & k=5 \\ \ln(-r_1+r_2+r_{12}) & k=6 \\ \ln(r_1-r_2+r_{12}) & k=7 \\ \ln(r_1+r_2-r_{12}) & k=8 \end{cases}$.

After using this generalized ansatz, we still cannot find the solutions of these terms. The main difficulty is what kinds of special functions we need to add to our $sbasis_k$ in order to solve those equations. Looking for special functions to add to our $sbasis_k$ becomes the main problem we need to overcome.

For the next part, solving $f_{3,b}$ is much more difficult than solving $f_{3,a}$. The main difficulty comes from the fact that Eq. (6.5) has two different regions, which is

$$\hat{T}f_{3,b} = -\hat{V}(f_{2,1} + f_{2,else}) = \begin{cases} -\hat{V}(P_{2,1}(r_1,r_2) + P_{else}(r_1,r_2)) & when\ r_1 \geq r_2 \\ -\hat{V}(P_{2,1}(r_2,r_1) + P_{else}(r_2,r_1)) & when\ r_2 > r_1 \end{cases}. \qquad (7.7)$$

Even if we can solve both regions completely, the function will become indifferentiable when $r_1 = r_2$. Besides, P_{else} part contains Lobachevsky function and some terms which are really difficult to be solved. In order to solve these equations easily, it is important to rewrite Ψ_2 in a simpler form. The following section is about the new coordinates we used to rewrite Ψ_2 in order to solve the equations.

7.2 Using New Coordinates to Find the Wave Function

First, we try to use (r,α,β) coordinates to rewrite $\hat{T}$. The reason why we use this coordinate system is that Ψ_2 which was found by P. C. Abbott *et al.* have β term inside. After changing to (r,α,β) coordinates, this operator becomes

$$\hat{T}^{(r,\alpha,\beta)} = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{5}{2r}\frac{\partial}{\partial r}$$

$$-\frac{2}{r^2}[(2\cot\alpha\cdot\frac{\partial}{\partial\alpha}+\frac{\partial}{\partial\alpha^2})+(-2\tan\beta\cdot\frac{\partial}{\partial\beta}+\frac{\partial}{\partial\beta^2})+2\cot\alpha\tan\beta\cdot\frac{\partial^2}{\partial\alpha\partial\beta}]. \quad (7.8)$$

Using this coordinate system can simplify $\hat{T}$ cleanly. However, we still have the mixed differential term $\frac{\partial^2}{\partial\alpha\partial\beta}$. This term include two different arguments. If we can find a coordinate system which can make $\hat{T}$ without this kind of term, the equation can be simplified in a simple form. Therefore, we use (r,ε,δ) coordinates to rewrite $\hat{T}$ and $\hat{V}$.

$$\hat{T}^{(r,\varepsilon,\delta)} = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{5}{2r}\frac{\partial}{\partial r}$$

$$-\frac{8}{r^2(\sin\varepsilon+\sin\delta)}[\sin\varepsilon\cdot(\frac{\cos\varepsilon}{\sin\varepsilon}\frac{\partial}{\partial\varepsilon}+\frac{\partial}{\partial\varepsilon^2})+\sin\delta\cdot(\frac{\cos\delta}{\sin\delta}\frac{\partial}{\partial\delta}+\frac{\partial}{\partial\delta^2})] \quad (7.9)$$

and

$$\hat{V}^{(r,\varepsilon,\delta)} = -\frac{2Z\sqrt{1+\sin(\frac{\varepsilon+\delta}{2})}}{r\cdot\sin(\frac{\varepsilon+\delta}{2})} + \frac{1}{r\sqrt{1-\sin(\frac{\varepsilon-\delta}{2})}}. \quad (7.10)$$

After using (r,ε,δ) coordinate, we can easily find out that there is no differential term with different arguments in $\hat{T}^{(r,\varepsilon,\delta)}$. Even if $\hat{V}^{(r,\varepsilon,\delta)}$ becomes much more complicated than $\hat{V}^{IC}$, we can still try to use this coordinate system to the first equation, which is

$$\hat{T}^{(r,\varepsilon,\delta)}(\Psi_0(r,\varepsilon,\delta)) = 0. \quad (7.11)$$

After we solved Eq. (7.11), we can get the solution

$$\Psi_0(r,\varepsilon,\delta) = F1(\varepsilon)\cdot F2(\delta), \quad (7.12)$$

where

$$\frac{d^2}{d\varepsilon^2}F1(\varepsilon)=c_1\frac{F1(\varepsilon)}{\sin\varepsilon}-\frac{\cos\varepsilon}{\sin\varepsilon}\frac{d}{d\varepsilon}F1(\varepsilon) \tag{7.13}$$

and

$$\frac{d^2}{d\delta^2}F2(\delta)=-c_2\frac{F2(\delta)}{\sin\delta}-\frac{\cos\delta}{\sin\delta}\frac{d}{d\delta}F2(\delta). \tag{7.14}$$

Next, we can solve Eq. (7.13) and Eq. (7.14).

$$F1(\varepsilon)=C_{\varepsilon 1}\cdot HG\varepsilon 1+C_{\varepsilon 2}\cdot\frac{(1-\sin\varepsilon)^{3/4}\cdot(1+|\sin\varepsilon|)^{1/4}}{\sqrt{\cos\varepsilon}}\cdot HG\varepsilon 2, \tag{7.15}$$

and

$$F2(\delta)=C_{\delta 1}\cdot HG\delta 1+C_{\delta 2}\cdot\frac{(1-\sin\delta)^{3/4}\cdot(1+|\sin\delta|)^{1/4}}{\sqrt{\cos\delta}}\cdot HG\delta 2, \tag{7.16}$$

where

$$HG\varepsilon 1=HeunG(2,-c_1,0,1,\frac{1}{2},1,1+\sin\varepsilon), \tag{7.17}$$

$$HG\varepsilon 2=HeunG(2,-c_1+\frac{5}{4},\frac{1}{2},\frac{3}{2},\frac{3}{2},1,1+\sin\varepsilon), \tag{7.18}$$

$$HG\delta 1=HeunG(2,c_2,0,1,\frac{1}{2},1,1+\sin\delta), \tag{7.19}$$

$$HG\delta 2=HeunG(2,c_2+\frac{5}{4},\frac{1}{2},\frac{3}{2},\frac{3}{2},1,1+\sin\delta). \tag{7.20}$$

The definition of Heun function we have already mentioned in Chapter 2.7. Nowadays, we still have not perfectly understood the properties of Heun function yet. At least we know that we find a closed form of homogeneous solutions with homogeneity zero in (r,ε,δ) coordinates. Using (r,ε,δ) coordinates to simplify our equations is an important and useful step to continue solving the wave function of helium.

7.3 Expansions of Ψ_2

From Chapter 4.2, we know that finding a wave function in an expansion of r_{12} is a useful way of solving those equations. Even if we cannot solve the full solutions now, we can still try to find the functions in expansion forms. As we know, Ψ_2 is really complicated and hard to simplify. If we can represent Ψ_2 in expansion forms, the following equations may be easier to be solved. At this chapter we will try to represent Ψ_2 in expansions of r_{12} and other arguments in different coordinate systems.

As mentioned above, we know that Ψ_2 found by Abbott *et al.* is

$$\Psi_2 = f_{2,0} + f_{2,-1} + f_{2,1} + f_{2,else} + c \cdot f_{2,H} \tag{7.21}$$

As we know, the expansions of $f_{2,0}$ and $c \cdot f_{2,H}$ are simple. The main problems of expansions of Ψ_2 are the difficulty of expanding $f_{2,-1}$ and $f_{2,1} + f_{2,else}$, which are much more complicated than the other two functions. Therefore, the following sections are about the expansions of $f_{2,-1}$ and $f_{2,1} + f_{2,else}$.

7.3.1 Expansions of $f_{2,-1}$

Now we can try to expand each function into power series of some arguments, which are r_{12}, r_1, r_2 in interparticle coordinates, s, t, u in (s,t,u) coordinates, and $\sin\alpha$, $\cos\theta$ in hyperspherical coordinates.

First, we expand $f_{2,-1}$.

$$f^{IC}_{2,-1\ (\text{series at } r_{12}=0)} = \left[-\frac{Z}{3}(r_1^2 + r_2^2)\cdot \ln(r_1 + r_2) + \frac{Z}{3} r_1 r_2 \right] + \frac{Z}{3}\ln(r_1 + r_2)\cdot r_{12}^{\ 2}$$

$$+\frac{Z}{3}\cdot(r_1^2 + r_2^2)\cdot \sum_{k=1}^{\infty}\left(\frac{1}{k}\right)\cdot\left(\frac{-r_{12}}{r_1 + r_2}\right)^k$$

$$-\frac{Z}{3}\cdot(r_1+r_2)^2\cdot\sum_{\substack{k=1\\k\neq 2}}^{\infty}\left(\frac{1}{k-2}\right)\cdot\left(\frac{-r_{12}}{r_1+r_2}\right)^k, \tag{7.22}$$

$$f^{IC}_{2,-1(\text{series at } r_1=0)}=\left[-\frac{Z}{3}(r_2{}^2-r_{12}{}^2)\cdot\ln(r_2+r_{12})-\frac{Z}{3}r_2r_{12}\right]+\frac{Z}{3}(r_2-r_{12})\cdot r_1-\frac{Z}{3}\ln(r_2+r_{12})\cdot r_1{}^2$$

$$+\frac{Z}{3}\cdot(r_2{}^2-r_{12}{}^2)\cdot\sum_{k=2}^{\infty}\left(\frac{1}{k}\right)\cdot\left(\frac{-r_1}{r_2+r_{12}}\right)^k$$

$$+\frac{Z}{3}\cdot(r_2+r_{12})^2\cdot\sum_{k=3}^{\infty}\left(\frac{1}{k-2}\right)\cdot\left(\frac{-r_1}{r_2+r_{12}}\right)^k, \tag{7.23}$$

$$f^{IC}_{2,-1(\text{series at } r_2=0)}=\left[-\frac{Z}{3}(r_1{}^2-r_{12}{}^2)\cdot\ln(r_1+r_{12})-\frac{Z}{3}r_1r_{12}\right]+\frac{Z}{3}(r_1-r_{12})\cdot r_2-\frac{Z}{3}\ln(r_1+r_{12})\cdot r_2{}^2$$

$$+\frac{Z}{3}\cdot(r_1^2-r_{12}{}^2)\cdot\sum_{k=1}^{\infty}\left(\frac{1}{k}\right)\cdot\left(\frac{-r_2}{r_1+r_{12}}\right)^k$$

$$+\frac{Z}{3}\cdot(r_1+r_{12})^2\cdot\sum_{k=3}^{\infty}\left(\frac{1}{k-2}\right)\cdot\left(\frac{-r_2}{r_1+r_{12}}\right)^k. \tag{7.24}$$

We can easily see that Eq. (8.23) and (8.24) are symmetric to each other when we interchange $r_1\leftrightarrow r_2$, which is an important property of a well-behaving wave function. In (s,t,u) coordinates,

$$f^{(s,t,u)}_{2,-1}{}_{(\text{series at } s=0)}=\left[-\frac{Z}{6}(t^2-2u^2)\cdot\ln u-\frac{Z}{12}t^2\right]-\frac{Z}{6}\frac{t^2}{u}\cdot s+\left[-\frac{Z}{6}\ln u+\frac{Z}{12}\frac{t^2-u^2}{u^2}\right]\cdot s^2$$

$$+\frac{Z}{6}\cdot(t^2-2u^2)\cdot\sum_{k=3}^{\infty}\left(\frac{1}{k}\right)\cdot\left(\frac{-s}{u}\right)^k$$

$$+\frac{Z}{6}\cdot u^2\cdot\sum_{k=3}^{\infty}\left(\frac{1}{k-2}\right)\cdot\left(\frac{-s}{u}\right)^k, \tag{7.25}$$

$$f^{(s,t,u)}_{2,-1}{}_{(\text{series at } t=0)}=\left[-\frac{Z}{6}(s^2-2u^2)\cdot\ln(s+u)-\frac{Z}{3}su+\frac{Z}{12}s^2\right]+\left[-\frac{Z}{6}\ln(s+u)-\frac{Z}{12}\right]\cdot t^2. \tag{7.26}$$

We can find out that $f_{2,-1}$ in power series at $t=0$ is not an infinite series, which is different from others.

$$f_{2,-1}^{(s,t,u)}{}_{\text{(series at u=0)}} = \left[-\frac{Z}{6}(s^2+t^2)\cdot \ln s + \frac{Z}{12}(s^2-t^2) \right] + \frac{Z}{3}\ln s \cdot u^2$$

$$+\frac{Z}{6}\cdot(s^2+t^2)\cdot\sum_{k=1}^{\infty}\left(\frac{1}{k}\right)\cdot\left(\frac{-u}{s}\right)^k$$

$$-\frac{Z}{3}\cdot s^2 \cdot \sum_{\substack{k=1\\k\neq 2}}^{\infty}\left(\frac{1}{k-2}\right)\cdot\left(\frac{-u}{s}\right)^k \tag{7.27}$$

We notice that Eq. (8.22) and (8.27) should be very similar because of $u = r_{12}$. They are the same function but present in two different coordinate systems, which are interparticle coordinates and (s,t,u) coordinates. In hypersperial coordinates,

$$f_{2,-1}^{HC}{}_{\text{(series at }\sin\alpha=0)} = -\frac{Zr^2}{3}\left[(\ln 2+\ln r)\cdot\cos\theta - \frac{1}{2}\right]\cdot\sin\alpha$$

$$-\frac{Zr^2}{3}\sum_{l=0}^{\infty}\frac{(-1)^l\cdot\left(-\frac{1}{2}\right)_l\cdot\sqrt{1+\cos\theta}\cdot{}_2F_1\left[\begin{matrix}-\frac{1}{2},\frac{3}{2}\\ \frac{1}{2}-l\end{matrix};\frac{\cos\theta}{1+\cos\theta}\right]}{l!}\cdot\sin^l\alpha$$

$$+\frac{Zr^2}{6}\cos\theta\cdot\sum_{k=1}^{\infty}\frac{(-1)^k\cdot\left(\frac{1}{2}\right)_k\cdot{}_2F_1\left[\begin{matrix}\frac{1}{2},-k\\ \frac{1}{2}-k\end{matrix};-\cos\theta\right]}{k\cdot k!}\cdot\sin^{k+1}\alpha\,, \tag{7.28}$$

$$f_{2,-1}^{HC}{}_{\text{(series at }\cos\theta=0)} = \frac{Zr^2}{6}\cdot\sin\alpha - \frac{Zr^2}{3}\cdot\ln r\cdot\sin\alpha\cdot\cos\theta$$

$$-\frac{Zr^2}{3}\cdot\sqrt{1+\sin\alpha}\cdot\sum_{k=0}^{\infty}\frac{\left(-\frac{1}{2}\right)_k\cdot\sin^k\alpha}{k!}\cdot\cos^k\theta$$

$$+\frac{Zr^2}{3}\sum_{l=0}^{\infty}\sum_{i=1}^{\infty}\frac{(-1)^i\cdot\binom{i/2}{l}}{i\cdot(1+\sin\alpha)^{i/2}}\cdot(-1)^l\cdot\sin^{l+1}\alpha\cdot\cos^{l+1}\theta \tag{7.29}$$

These two expansions are much more complicated than others. In Eq. (7.28), we can find out two hypergeometric functions and pochhammer functions. We can also see pochhammer functions and binomial coefficients in Eq. (7.29).

7.3.2 Expansions of $f_{2,1} + f_{2,else}$

Finding the expansion of $f_{2,1} + f_{2,else}$ in the power series of r_{12} is difficult because of the special functions in $f_{2,else}$. In order to find the expansion, we represent $f_{2,1} + f_{2,else}$ in five different parts:

$$f_{2,1} + f_{2,else} = f_{2,1} + \varphi_{else,a} + \varphi_{else,b} + \varphi_{else,c} + \varphi_{else,d} \,, \tag{7.30}$$

where

$$f_{2,1} = \frac{Z}{3} \ln(r_1 - r_2 + r_{12}) \cdot (r_1^2 - r_2^2) - \frac{Z}{3} r_{12} \cdot (r_1 + r_2) \,, \tag{7.31}$$

$$\varphi_{else,a} = -\frac{Z}{6} (r_1^2 - r_2^2) \cdot (s_1 - \frac{s_2}{\pi}) \,, \tag{7.32}$$

$$\varphi_{else,b} = \frac{Z}{6} \cdot r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} \,, \tag{7.33}$$

$$\varphi_{else,c} = \frac{Z}{3\pi} \cdot \ln(r_1^2 + r_2^2) \cdot (r_1^2 + r_2^2 - r_{12}^2) \,, \tag{7.34}$$

$$\varphi_{else,d} = \frac{Z}{3\pi} \cdot r_{12} \cdot \sqrt{2r_1^2 + 2r_2^2 - r_{12}^2} \cdot \arcsin(1 - \frac{r_{12}^2}{r_1^2 + r_2^2}) \,. \tag{7.35}$$

For those five functions, we only focus on the region $r_1 \geq r_2$. The functions of the other region $(r_2 > r_1)$ are interchange of $r_1 \leftrightarrow r_2$ than the original functions. The following are the expansions of $f_{2,1}$, $\varphi_{else,a}$, $\varphi_{else,b}$, $\varphi_{else,c}$ and $\varphi_{else,d}$:

$$f_{2,1} = \frac{Z}{3} \cdot \ln(r_1 - r_2) \cdot (r_1^2 - r_2^2) - \frac{Z}{3} (r_1 + r_2) \cdot r_{12} - \frac{Z}{3} (r_1^2 - r_2^2) \cdot \sum_{k=1}^{\infty} \frac{1}{k} \cdot \left(\frac{-r_{12}}{r_1 - r_2} \right)^k \,, \tag{7.36}$$

$$\varphi_{else,a} = -\frac{Z}{6} \left(r_1^2 - r_2^2 \right) \cdot \left[\ln\left(r_1^2 - r_2^2 \right) - \sum_{n=0}^{\infty} \sum_{k=1}^{\infty} \binom{k/2}{n} \frac{2^{k/2 - n} (-1)^{n+k} \left(r_1^2 + r_2^2 \right)^{k/2 - n}}{k \left(r_1^2 - r_2^2 \right)^k} r_{12}^{2n+k} \right]$$

$$+\frac{1}{3}\left[\sum_{i=0}^{\infty}\frac{\left(r_1^2-r_2^2\right)^{2i+2}\left(2r_1^2+2r_2^2-r_{12}^2\right)^{-i/2-1}r_{12}^{-2i-1}}{\pi\left(2i+1\right)}\right]\left[-\frac{1}{2}+\sum_{k=0}^{\infty}\frac{\sqrt{2}\left(1/2\right)_k r_{12}^{2k+2}}{\pi 2^k\left(r_1^2+r_2^2\right)^{k+1}\left(2k+1\right)k!}\right]$$

$$+\frac{2}{3}\left(r_1^2-r_2^2\right)\arctan\left(\frac{r_2}{r_1}\right)\sum_{n=0}^{\infty}\frac{1}{2n+1}\left(\frac{r_1^2+r_2^2-r_{12}^2}{2r_1r_2}\right)^{2k+1}$$

$$+\frac{1}{3}\frac{\left(r_1^2-r_2^2\right)^2}{r_1^2+r_2^2}\cdot\sum_{k=0}^{\infty}\sum_{i=0}^{\infty}\binom{2i+1}{k}\frac{{}_2F_1\left[\begin{matrix}1/2,\, i+1\\ 3/2\end{matrix},\left(\frac{r_1^2-r_2^2}{r_1^2+r_2^2}\right)^2\right]}{2i+1}\cdot\left(\frac{r_{12}^2}{r_1^2+r_2^2}\right)^k, \tag{7.37}$$

$$\varphi_{else,b}=\frac{Z}{6}\cdot\sum_{i=0}^{\infty}\binom{1/2}{i}\cdot(-1)^i(2r_1^2+2r_2^2)^{\frac{1}{2}-i}\cdot r_{12}^{2i+1}\quad , \tag{7.38}$$

$$\varphi_{else,c}=\frac{Z}{3\pi}\cdot\ln(r_1^2+r_2^2)\cdot(r_1^2+r_2^2)-\frac{Z}{3\pi}\cdot\ln(r_1^2+r_2^2)\cdot r_{12}^2, \tag{7.39}$$

$$\varphi_{else,d}=\frac{Z}{6}\cdot\sum_{i=0}^{\infty}\binom{1/2}{i}\cdot(-1)^i(2r_1^2+2r_2^2)^{\frac{1}{2}-i}\cdot r_{12}^{2i+1}+\frac{2Z}{9\pi}\cdot\sum_{i=0}^{\infty}(2r_1^2+2r_2^2)^{-i}\frac{1}{\binom{i+1/2}{3/2}}\cdot r_{12}^{2i+2}\quad . \tag{7.40}$$

These expansions are important results because the equation to find Ψ_3 will become

$$\hat{T}\Psi_3=\sum_{k=0}^{\infty}f_k(r_1,r_2)\cdot r_{12}^{k}\ . \tag{7.41}$$

In the future, we can use this new idea to find Ψ_3 by Eq. (7.41).

7.4 Physical meaning in special situations

After the wave function of hydrogen has been solved, hydrogen-based models are used for describing atoms. For solving Schrödinger equation of helium, a model based on hydrogenic solution is an important and easy start. However, the wave function of helium atom is very different than the wave function of hydrogen atom. One can imagine that the helium atom should reduce to a hydrogen-like model in some special situations, i.e., at the limits $r_{12}=0$, $r_1=0$ or $r_2=0$, and $r_1=\infty$ or $r_2=\infty$. The following chapter discusses the behavior of helium wave function at these limits.

7.4.1 The $r_{12}=0$ limit

When $r_{12}\to 0$ in interparticle coordinates, the helium atom becomes a composite particle consisting of nucleus with charge +2 and an electron-like particle with charge -2. In this case, the behavior of this situation is not hydrogen-like because of two reasons. First, when two electrons come together and become one particle, this particle is not a fermion anymore, which means this atom is not similar to a hydrogen atom. The behavior should not be the same as a hydrogen atom either. Second, when we assume that two electrons get together and become one particle, the kinetic energy of such an object includes translational energy. Rotational energy and vibrational energy are ignored on this assumption, which certainly is not correct. According to these two reasons, we know that the situation when $r_{12}=0$ is not hydrogen-like.

7.4.2 The $r_1=0$ or $r_2=0$ limit

When $r_1\to 0$ or $r_2\to 0$, the nucleus and an electron coalesce. If we consider that the nucleus and one of the electrons become a composite particle with charge +1, this situation should be hydrogen-like. However, we know that the two electrons in the helium atom are indistinguishable. Even if one electron becomes a part of the nucleus, the permutation symmetry of two electrons still cannot be ignored. Besides, we are solving a two-electron system, which means we need to consider the spin of electrons. For the ground state, we know that these two electrons should have different spin wave functions. For hydrogen atom, we don't need to consider the spin wave function. For these reasons, we know that helium wave function is much more complicated than hydrogen even when $r_1 = 0$ or $r_2 = 0$.

7.4.3 The $r_1 = \infty$ or $r_2 = \infty$ limit

We can imagine that the situation should become a hydrogen-like atom and one free particle when $r_1 \to \infty$ or $r_2 \to \infty$. However, because these two electrons are indistinguishable, the interaction between them still cannot be ignored. Therefore, the "free particle" is not really free, and the rest parts are also not as simple as a hydrogen atom.

Chapter 8

Conclusion

A simple method to solve particular solutions of Schrödinger equation of helium is proposed. After expanding the wave function of helium corresponding to homogeneity, the problem of finding an exact wave function of helium reduces to a series of differential equations to solve. We know that if we can find enough terms in our inversion table of monomial terms for every homogeneity, we will create a new and simple method to generate particular solutions of Ψ_h with every homogeneity h. According to our research, we know that we also are able to solve the logarithm terms by the inversion table of monomial term. By this method, we can keep solving subsequent terms until we find out the closed form of the solution. If we can find the closed form of well-behaving Ψ_h for every homogeneity h, we will finally find the exact wave function of helium. This research shows initial steps in the step-wise procedure of the pursuit of the exact wave function of helium, and it also demonstrates that solving the Schrödinger equation of helium is not hopeless.

Appendix

Expansion of Lobachevsky function

We know that there are Lobachevsky functions in Ψ_2 which are found by Abbott and Gottschalk in 1986. As mentioned above, we know that Lobachevsky functions play important roles in removing singularities and in some formula of homogeneous solutions. In this section, we will discuss about the expansion of Lobachevsky function. The definition of Lobachevsky function is

$L(x) = -\int_0^x \ln(\cos t)dt$.

The following are the Lobachevsky functions included in Ψ_2:

$$Lof = \left[L(\frac{\alpha-\beta}{2}) - L(\frac{\alpha+\beta}{2}) + L(\frac{\pi-\alpha+\beta}{2}) - L(\frac{\pi-\alpha-\beta}{2}) \right]$$

$$= -\int_0^{\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_0^{\frac{\alpha+\beta}{2}} \ln(\cos t)dt - \int_0^{\frac{\pi}{2}-\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_0^{\frac{\pi}{2}-\frac{\alpha+\beta}{2}} \ln(\cos t)dt \qquad \text{(A.1)}$$

where $\beta = \arcsin(\sin\alpha\cos\theta)$.

By simplifying, we can convert them into two integrals.

$$Lof = -\int_0^{\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_0^{\frac{\alpha+\beta}{2}} \ln(\cos t)dt - \int_0^{\frac{\pi}{2}-\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_0^{\frac{\pi}{2}-\frac{\alpha+\beta}{2}} \ln(\cos t)dt$$

$$= -\int_0^{\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_{\frac{\pi}{2}-\frac{\alpha-\beta}{2}}^0 \ln(\cos t)dt + \int_0^{\frac{\alpha+\beta}{2}} \ln(\cos t)dt - \int_{\frac{\pi}{2}-\frac{\alpha+\beta}{2}}^0 \ln(\cos t)dt$$

$$= -\int_0^{\frac{\alpha-\beta}{2}} \ln(\cos t)dt - \int_{\frac{\alpha-\beta}{2}-\frac{\pi}{2}}^0 \ln(\cos t)dt + \int_0^{\frac{\alpha+\beta}{2}} \ln(\cos t)dt + \int_{\frac{\alpha+\beta}{2}-\frac{\pi}{2}}^0 \ln(\cos t)dt$$

$$= -\int_{\frac{\alpha-\beta}{2}-\frac{\pi}{2}}^{\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_{\frac{\alpha+\beta}{2}-\frac{\pi}{2}}^{\frac{\alpha+\beta}{2}} \ln(\cos t)dt \qquad \text{(A.2)}$$

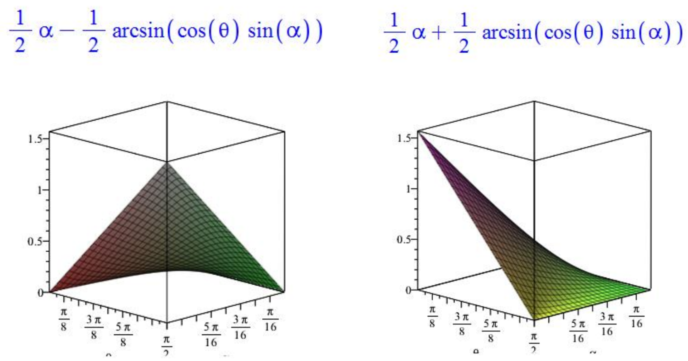
For $\int_{x-\frac{\pi}{2}}^{x} \ln(\cos t)dt$, we can convert it into polylog function.

$$-\int_{x-\frac{\pi}{2}}^{x} \ln(\cos t)dt = -\frac{1}{8}\cdot\left[4\mathrm{I}\cdot\mathrm{polylog}(2,-e^{2Ix}) - 4\mathrm{I}\cdot\mathrm{polylog}(2,e^{2Ix}) - 4\mathrm{I}x\pi - 4\pi\ln 2 + \mathrm{I}\pi^2\right],$$

(A.3)

when $x = \left[0\,,\frac{\pi}{2}\right]$.

Here we plot $\frac{\alpha+\beta}{2}$ and $\frac{\alpha-\beta}{2}$ to prove that there are both at the range $\left[0\,,\frac{\pi}{2}\right]$:



Therefore, we can use Eq. (A.3) to simplify our *Lof*:

$$Lof = -\int_{\frac{\alpha-\beta}{2}-\frac{\pi}{2}}^{\frac{\alpha-\beta}{2}} \ln(\cos t)dt + \int_{\frac{\alpha+\beta}{2}-\frac{\pi}{2}}^{\frac{\alpha+\beta}{2}} \ln(\cos t)dt$$

$$= -\frac{I}{2}\cdot\left[\pi\beta - \mathrm{polylog}(2,e^{I(\alpha-\beta)}) + \mathrm{polylog}(2,e^{I(\alpha+\beta)})\right.$$

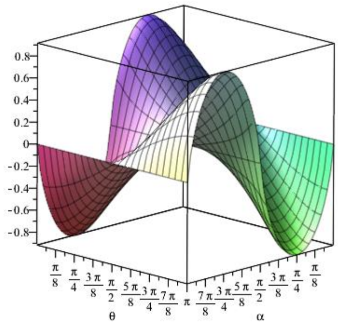
$$\left. + \mathrm{polylog}(2,-e^{I(\alpha-\beta)}) - \mathrm{polylog}(2,-e^{I(\alpha+\beta)})\right] \quad \text{(A.4)}$$

(The polylog functions sometimes are represented as $\mathrm{dilog}(x)$. In Maple, the dilog function is defined as $\mathrm{dilog}(1-x) = \mathrm{polylog}(2,x)$.)

After converting into polylog function, Maple can plot the function easily.

```
> Lof;
  plot3d(Re(Lof),alpha=0..Pi,theta=0..Pi,axes=boxed);
```

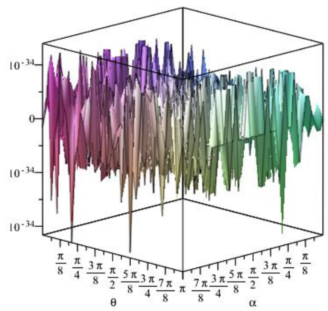
$$-\frac{1}{2} I \left(-\text{polylog}\left(2, e^{-I(-\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) + \text{polylog}\left(2, e^{I(\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) + \pi \arcsin(\cos(\theta)\sin(\alpha)) + \text{polylog}\left(2, -e^{-I(-\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) - \text{polylog}\left(2, -e^{I(\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) \right)$$



The reason we only plot the real part is that numerical evaluation of the function $\text{polylog}(2, x)$ does not give the imaginary part identically equal to zero, as it should be. Nevertheless, the imaginary part can be made arbitrary small as can be seen from the following is the plot of imaginary part of our function.

```
> Digits:=35:
  Lof;
  plot3d(Im(Lof),alpha=0..Pi,theta=0..Pi,axes=boxed);
```

$$-\frac{1}{2} I \left(-\text{polylog}\left(2, e^{-I(-\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) + \text{polylog}\left(2, e^{I(\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) + \pi \arcsin(\cos(\theta)\sin(\alpha)) + \text{polylog}\left(2, -e^{-I(-\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) - \text{polylog}\left(2, -e^{I(\alpha + \arcsin(\cos(\theta)\sin(\alpha)))}\right) \right)$$



We can also rewrite *Lof* in an easy series form:

$$Lof = -I \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{I\alpha(2n+1)} \cdot \left[e^{I\beta(2n+1)} - e^{-I\beta(2n+1)} \right] - \frac{I\beta\pi}{2} \tag{A.5}$$

By Euler's formula, Eq. (A.5) becomes:

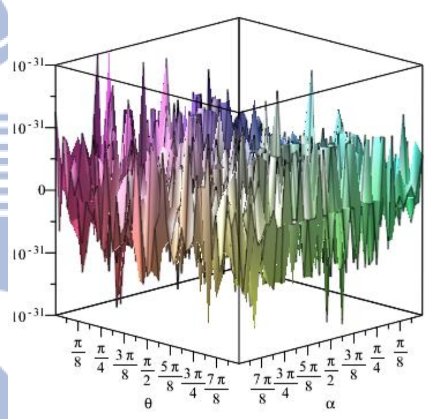
$$Lof = -I\cdot\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\left[\cos\left((2n+1)\alpha\right)+I\sin\left((2n+1)\alpha\right)\right]\cdot 2I\sin\left((2n+1)\alpha\right)-\frac{I\beta\pi}{2}$$

$$= 2\cdot\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\left[\cos\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)+I\sin\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)\right]-\frac{I\beta\pi}{2}$$

$$= 2\cdot\sum_{n=0}^{\infty}\frac{\cos\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2}+I\cdot\sum_{n=0}^{\infty}\frac{\sin\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2}-\frac{I\beta\pi}{2}$$

$$= 2\cdot\sum_{n=0}^{\infty}\frac{\cos\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2}+I\cdot\left[\left(\sum_{n=0}^{\infty}\frac{\sin\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2}\right)-\frac{\beta\pi}{2}\right] \quad \text{(A.6)}$$

Here is the plot of $\left(\sum_{n=0}^{\infty}\frac{\sin\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2}\right)-\frac{\beta\pi}{2}$:



Because the calculation only considers as finite digits, this problem causes the plot cannot really show that $\left(\sum_{n=0}^{\infty}\frac{\sin\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2}\right)-\frac{\beta\pi}{2}$ is identically equal to zero. By this result, we can simplify Eq. (A.6):

$$Lof = 2\cdot\sum_{n=0}^{\infty}\frac{\cos\left((2n+1)\alpha\right)\cdot\sin\left((2n+1)\alpha\right)}{(2n+1)^2} \quad \text{(A.7)}$$

By the definition of Chebyshev polynomials of the first kind and the second kind, we can represent Eq. (A.7) as

$$Lof = 2\cdot\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}T_{2n+1}\left(\cos\alpha\right)\cdot U_{2n}\left(\cos\beta\right)\sin\beta$$

$$= 2\sin\beta \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} T_{2n+1}(\cos\alpha) \cdot U_{2n}(\cos\beta) \tag{A.8}$$

where T_{2n+1} and U_{2n} Chebyshev polynomials of the first kind and the second kind.

Next, we are trying to find the expansion of our Lobachevsky function. We have

$$\frac{\partial}{\partial r_{12}}\left(-\int_0^x \ln(\cos t)dt\right) = -\frac{\partial x}{\partial r_{12}} \cdot \ln(\cos x) \tag{A.9}$$

Before giving an explicit series representation for the derivative of *Lof* with respect to r_{12}, let us determine some. For $\cos(x)$ we have:

$$\cos\left(\frac{\alpha+\beta}{2}\right) = \frac{1}{2(r_1^2+r_2^2)}\left[(r_1-r_2)\sqrt{2r_1^2+2r_2^2-r_{12}^2}+(r_1+r_2)r_{12}\right] \tag{A.10}$$

$$\cos\left(\frac{\alpha-\beta}{2}\right) = \frac{1}{2(r_1^2+r_2^2)}\left[(r_1+r_2)\sqrt{2r_1^2+2r_2^2-r_{12}^2}+(r_1-r_2)r_{12}\right] \tag{A.11}$$

$$\cos\left(\frac{\pi-\alpha-\beta}{2}\right) = \sin\left(\frac{\alpha+\beta}{2}\right) = \frac{1}{2(r_1^2+r_2^2)}\left[(r_1+r_2)\sqrt{2r_1^2+2r_2^2-r_{12}^2}-(r_1-r_2)r_{12}\right] \tag{A.12}$$

$$\cos\left(\frac{\pi-\alpha+\beta}{2}\right) = \sin\left(\frac{\alpha-\beta}{2}\right) = \frac{1}{2(r_1^2+r_2^2)}\left[-(r_1-r_2)\sqrt{2r_1^2+2r_2^2-r_{12}^2}+(r_1+r_2)r_{12}\right] \tag{A.13}$$

We can easily find $x = \arccos(\cos x)$ for our equations. Then $\frac{\partial x}{\partial r_{12}}$ is given as:

$$x = \frac{\alpha+\beta}{2} : \frac{\partial x}{\partial r_{12}} = -\frac{1}{\sqrt{2r_1^2+2r_2^2-r_{12}^2}} \tag{A.14}$$

$$x = \frac{\alpha-\beta}{2} : \frac{\partial x}{\partial r_{12}} = \frac{1}{\sqrt{2r_1^2+2r_2^2-r_{12}^2}} \tag{A.15}$$

$$x = \frac{\pi-\alpha-\beta}{2} : \frac{\partial x}{\partial r_{12}} = \frac{1}{\sqrt{2r_1^2+2r_2^2-r_{12}^2}} \tag{A.16}$$

$$x = \frac{\pi-\alpha+\beta}{2} : \frac{\partial x}{\partial r_{12}} = -\frac{1}{\sqrt{2r_1^2+2r_2^2-r_{12}^2}} \tag{A.17}$$

Combination of those formulas gives the derivative four integrals in *Lof* with respect to r_{12}:

$$x=\frac{\alpha+\beta}{2}:-\frac{\partial x}{\partial r_{12}}\ln(\cos x)=\frac{1}{R}\left[\ln(R(r_1-r_2)+r_{12}(r_1+r_2))-\ln(r_1^{\,2}+r_2^{\,2})-\ln 2\right] \qquad \text{(A.18)}$$

$$x=\frac{\alpha-\beta}{2}:-\frac{\partial x}{\partial r_{12}}\ln(\cos x)=-\frac{1}{R}\left[\ln(R(r_1+r_2)+r_{12}(r_1-r_2))-\ln(r_1^{\,2}+r_2^{\,2})-\ln 2\right] \qquad \text{(A.19)}$$

$$x=\frac{\pi-\alpha-\beta}{2}:-\frac{\partial x}{\partial r_{12}}\ln(\cos x)=-\frac{1}{R}\left[\ln(R(r_1+r_2)-r_{12}(r_1-r_2))-\ln(r_1^{\,2}+r_2^{\,2})-\ln 2\right] \qquad \text{(A.20)}$$

$$x=\frac{\pi-\alpha+\beta}{2}:-\frac{\partial x}{\partial r_{12}}\ln(\cos x)=\frac{1}{R}\left[\ln(-R(r_1-r_2)+r_{12}(r_1+r_2))-\ln(r_1^{\,2}+r_2^{\,2})-\ln 2\right] \qquad \text{(A.21)}$$

where $R=\sqrt{2r_1^{\,2}+2r_2^{\,2}-r_{12}^{\,2}}$

After combination, we know $\frac{\partial}{\partial r_{12}}Lof$ can be represented as four logarithms:

$$\begin{aligned}\frac{\partial}{\partial r_{12}}Lof &= -\frac{1}{R}\left\{\ln\left[R(r_1+r_2)+r_{12}(r_1-r_2)\right]-\ln\left[R(r_1+r_2)+r_{12}(r_1-r_2)\right]\right\}\\ &\quad -\frac{1}{R}\left\{\ln\left[r_{12}(r_1+r_2)+R(r_1-r_2)\right]-\ln\left[r_{12}(r_1+r_2)+R(r_1-r_2)\right]\right\}.\end{aligned} \qquad \text{(A.22)}$$

Here we can convert logarithms to inverse tangent hyperbolic functions by the conversion equation:

$$\ln(1+x)-\ln(1-x)=2\cdot\operatorname{arctanh}(x). \qquad \text{(A.23)}$$

After simplifying, the equation becomes

$$\frac{\partial}{\partial r_{12}}Lof=-\frac{2}{R}\cdot\operatorname{arctanh}\left[\frac{R(r_1-r_2)}{r_{12}(r_1+r_2)}\right]-\frac{2}{R}\cdot\operatorname{arctanh}\left[\frac{r_{12}(r_1-r_2)}{R(r_1+r_2)}\right] \qquad \text{(A.24)}$$

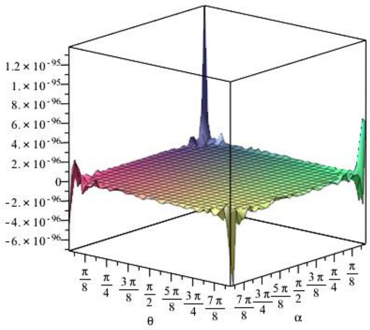
We also know how to combine two inverse tangent hyperbolic functions into one:

$$\operatorname{arctanh}(u)+\operatorname{arctanh}(v)=\operatorname{arctanh}\left(\frac{u+v}{1+uv}\right) \qquad \text{(A.25)}$$

After combining, we get the simplest form of $\frac{\partial}{\partial r_{12}}Lof$:

$$\frac{\partial}{\partial r_{12}} Lof = -\frac{2}{R} \cdot \operatorname{arctanh}\left(\frac{r_1^{2} - r_2^{2}}{R r_{12}}\right). \tag{A.26}$$

And the plot of $\frac{\partial}{\partial r_{12}} Lof - \left(-\frac{2}{R} \cdot \operatorname{arctanh}\left(\frac{r_1^{2} - r_2^{2}}{R r_{12}}\right)\right)$ is



Because the calculation only considers as finite digits, this problem causes the plot cannot really show that the difference is identically equal to zero. Therefore, we can rewrite our Lof as

$$Lof = -\int \frac{2}{R} \cdot \operatorname{arctanh}\left(\frac{r_1^{2} - r_2^{2}}{R r_{12}}\right) dr_{12}\,. \tag{A.27}$$

By this definition, we can change to (r, α, β) coordinates:

$$Lof = \int \frac{1}{\sqrt{\cos^2 \beta}} \cdot \operatorname{arctanh}\left(\frac{\cos\alpha}{\sqrt{\cos^2\beta}}\right) d(\sin\beta) = \int \frac{1}{\cos\beta} \cdot \operatorname{arctanh}\left(\frac{\cos\alpha}{\cos\beta}\right) d(\sin\beta)\,. \tag{A.28}$$

The expansion form of inverse tangent hyperbolic is:

$$\operatorname{arctanh}(x) = \sum_{n=0}^{\infty} \frac{x^{2n+1}}{2n+1}\,. \tag{A.29}$$

By this expansion form, we can rewrite Eq. (A.28):

$$Lof = \int \sum_{n=0}^{\infty} \frac{1}{2n+1} \frac{(\cos\alpha)^{2n+1}}{(\cos\beta)^{2n+2}}\, d(\sin\beta) = \int \sum_{n=0}^{\infty} \frac{1}{2n+1} \frac{(\cos\alpha)^{2n+1}}{(1-\sin^2\beta)^{n+1}}\, d(\sin\beta)$$

$$= \sum_{n=0}^{\infty} \frac{(\cos\alpha)^{2n+1}}{2n+1} \int \frac{d\sin\beta}{(1-\sin^2\beta)^{n+1}}\,. \tag{A.30}$$

After evaluating the integral, Eq. (A.30) becomes

$$Lof = \sin\beta \cdot \sum_{n=0}^{\infty} \frac{{}_2F_1\left[\begin{matrix} 1/2, n+1 \\ 3/2 \end{matrix}, \sin^2\beta\right]}{2n+1} \cdot (\cos\alpha)^{2n+1} . \tag{A.31}$$

Here we can follow the definition of hypergeometric function:

$${}_2F_1\left[\begin{matrix} a,b \\ c \end{matrix}, z\right] = \sum_{i=0}^{\infty} \frac{(a)_i (b)_i}{(c)_i\, i!} z^i . \tag{A.32}$$

Therefore, Lof becomes

$$\begin{aligned} Lof &= \sin\beta \cdot \sum_{n=0}^{\infty} \frac{1}{2n+1} \sum_{i=0}^{\infty} \frac{\left(1/2\right)_i (n+1)_i}{\left(3/2\right)_i i!} \cdot (\sin\beta)^{2i} (\cos\alpha)^{2n+1} \\ &= \sum_{n=0}^{\infty}\sum_{i=0}^{\infty} \frac{1}{2n+1} \frac{\left(1/2\right)_i (n+1)_i}{\left(3/2\right)_i i!} (\sin\beta)^{2i+1} (\cos\alpha)^{2n+1} . \end{aligned} \tag{A.33}$$

Here we can substitute $\frac{1}{2n+1} = \frac{\left(1/2\right)_n}{\left(3/2\right)_n}$, and Eq. (A.33) becomes

$$Lof = \sum_{n=0}^{\infty}\sum_{i=0}^{\infty} \frac{\left(1/2\right)_n \left(1/2\right)_i (n+1)_i}{\left(3/2\right)_n \left(3/2\right)_i i!} (\sin\beta)^{2i+1} (\cos\alpha)^{2n+1} \tag{A.34}$$

We can also substitute $\frac{(n+1)_i}{i!} = \frac{(i+n)!}{i!n!} = \frac{(1)_{i+n}}{i!n!}$:

$$Lof = \cos\alpha \sin\beta \cdot \sum_{n=0}^{\infty}\sum_{i=0}^{\infty} \frac{(1)_{n+i} \left(1/2\right)_n \left(1/2\right)_i}{\left(3/2\right)_n \left(3/2\right)_i n! i!} (\cos^2\alpha)^n (\sin^2\beta)^i \tag{A.35}$$

which is called Appell hypergeometric function F_2 :

$$Lof = \cos\alpha \sin\beta \cdot F_2\left(\begin{matrix} 1, 1/2, 1/2 \\ 3/2, 3/2 \end{matrix}; \cos^2\alpha, \sin^2\beta\right) \tag{A.36}$$

After changing into interparticle coordinates, our Lof becomes

$$Lof = \frac{\left(r_1^2 - r_2^2\right)\left(r_1^2 + r_2^2 - r_{12}^2\right)}{\left(r_1^2 + r_2^2\right)^2} F_2\left(\begin{matrix} 1, \frac{1}{2}, \frac{1}{2} \\ \frac{3}{2}, \frac{3}{2} \end{matrix}; \left(\frac{r_1^2 - r_2^2}{r_1^2 + r_2^2}\right)^2, \left(\frac{r_1^2 + r_2^2 - r_{12}^2}{r_1^2 + r_2^2}\right)^2\right) \tag{A.37}$$

which is the easiest form of *Lof*.

For the following parts, we want to find the expansion of *Lof* respect to r_{12}.

After substitute $\frac{\left(\frac{1}{2}\right)_i}{\left(\frac{3}{2}\right)_i} = \frac{1}{2i+1}$ and $\frac{(n+1)_i}{i!} = \frac{(i+1)!}{n!}$ in Eq. (A.33):

$$Lof = \sum_{n=0}^{\infty}\sum_{i=0}^{\infty} \frac{1}{2i+1} \frac{\left(\frac{1}{2}\right)_n (i+1)_n}{\left(\frac{3}{2}\right)_n n!} (\cos\alpha)^{2n+1} (\sin\beta)^{2i+1}$$

$$= \cos\alpha \cdot \sum_{i=0}^{\infty} \frac{1}{2i+1} \left(\sum_{n=0}^{\infty} \frac{\left(\frac{1}{2}\right)_n (i+1)_n}{\left(\frac{3}{2}\right)_n n!} \left(\cos^2\alpha\right)^n \right) (\sin\beta)^{2i+1} \tag{A.38}$$

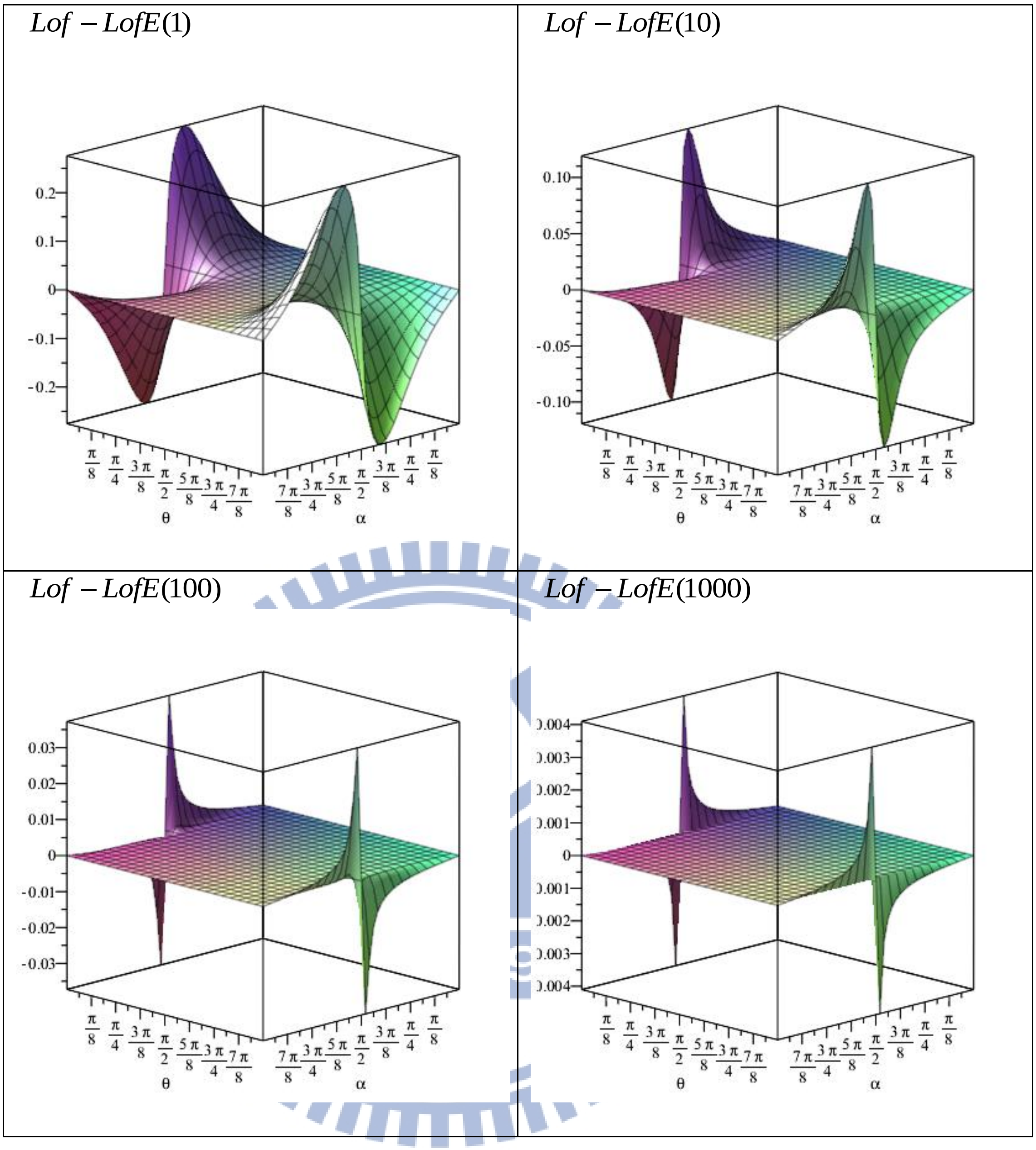
Here we can follow the definition of hypergeometric function again to simplify *Lof*:

$$Lof = \cos\alpha \cdot \sum_{i=0}^{\infty} \frac{{}_2F_1\left[\begin{matrix} \frac{1}{2}, i+1 \\ \frac{3}{2} \end{matrix}, \cos^2\alpha\right]}{2i+1} \cdot (\sin\beta)^{2i+1}. \tag{A.39}$$

To verify the validity of this expansion, we can plot both functions. Let us define $LofE(N)$, which is a fundamental series of *Lof*:

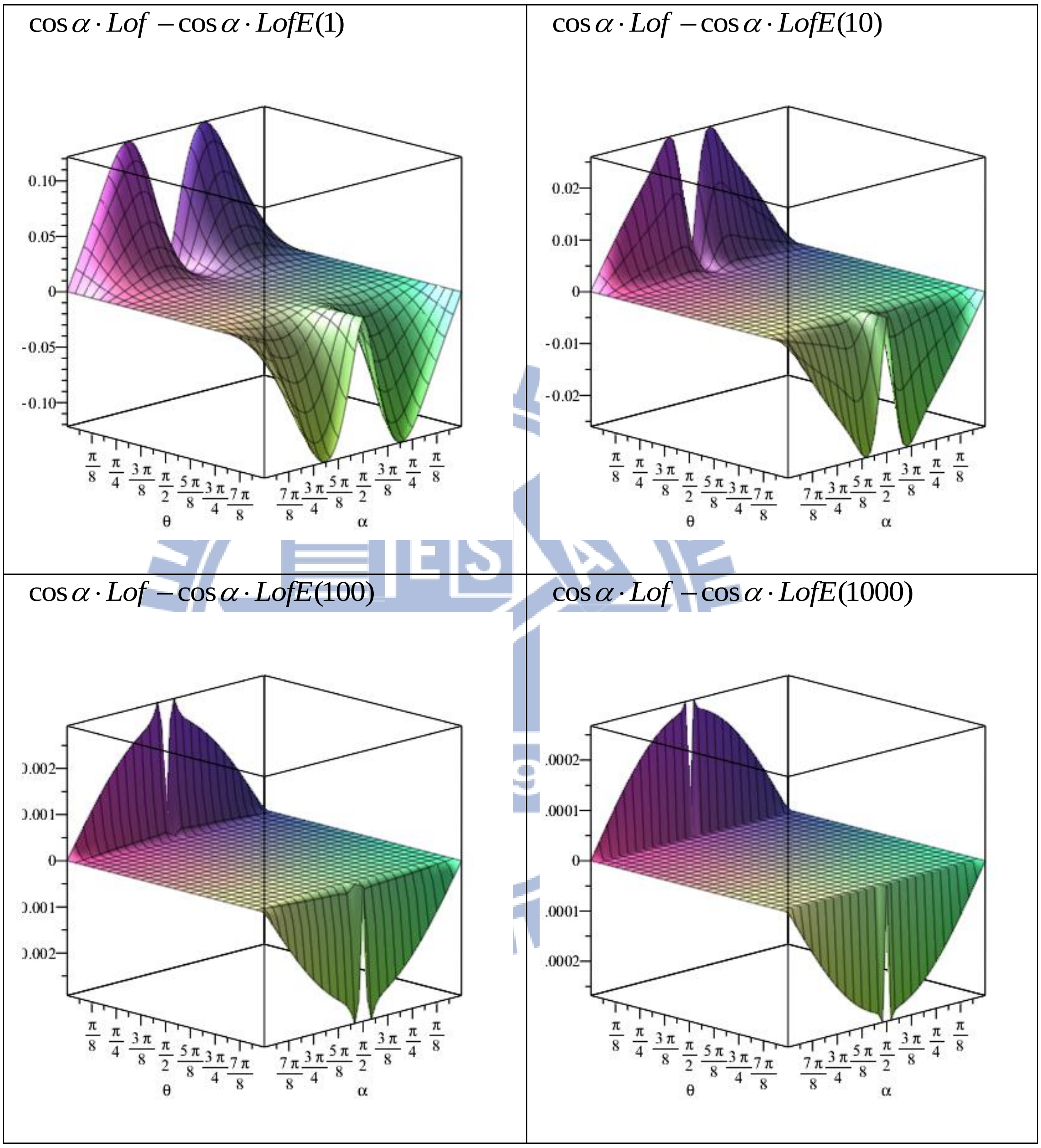
$$LofE(N) = \cos\alpha \cdot \sum_{i=0}^{N} \frac{{}_2F_1\left[\begin{matrix} \frac{1}{2}, i+1 \\ \frac{3}{2} \end{matrix}, \cos^2\alpha\right]}{2i+1} \cdot (\sin\beta)^{2i+1} \tag{A.40}$$

The following are the plots of $Lof - LofE(1)$, $Lof - LofE(10)$, $Lof - LofE(100)$ and $Lof - LofE(1000)$:



By these plots, we find that our expansion is going well when we include more terms, but there are two points $\left[\alpha = \frac{\pi}{2}, \theta = 0\right]$ and $\left[\alpha = \frac{\pi}{2}, \theta = \pi\right]$ that have problems with Riemannian sheets, which mean that we will find branch cuts if we enlarge our plots at the lines when $\left[\alpha = \frac{\pi}{2}\right]$ and $\left[\theta > \pi \; or \; \theta < 0\right]$. Fortunately, our Lof multiply one extra $\cos\alpha$ in Ψ_2 . If we compare the plots of

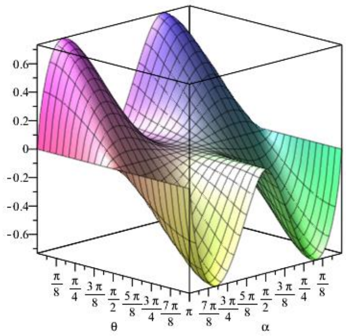
$\cos\alpha \cdot Lof - \cos\alpha \cdot LofE(1)$, $\cos\alpha \cdot Lof - \cos\alpha \cdot LofE(10)$, $\cos\alpha \cdot Lof - \cos\alpha \cdot LofE(100)$ and $\cos\alpha \cdot Lof - \cos\alpha \cdot LofE(1000)$:



The problems of branch cuts are solved here. Here we also plot $\cos\alpha \cdot Lof$ to show that $\cos\alpha \cdot Lof$ is a symmetric function.

```
> cos(alpha)*Lof;
  plot3d(cos(alpha)*Re(Lof),alpha=0..Pi,theta=0..Pi,axes=boxed);
```

$$-\frac{1}{2}\,\mathrm{I}\cos(\alpha)\,\Big(\mathrm{polylog}\big(2,-e^{-\mathrm{I}(-\alpha+\arcsin(\cos(\theta)\sin(\alpha)))}\big)+\pi\arcsin(\cos(\theta)\sin(\alpha))-\mathrm{polylog}\big(2,-e^{\mathrm{I}(\alpha+\arcsin(\cos(\theta)\sin(\alpha)))}\big)-\mathrm{polylog}\big(2,e^{-\mathrm{I}(-\alpha+\arcsin(\cos(\theta)\sin(\alpha)))}\big)+\mathrm{polylog}\big(2,e^{\mathrm{I}(\alpha+\arcsin(\cos(\theta)\sin(\alpha)))}\big)\Big)$$



Now we can try to find the expansion of *Lof* respect to r_{12} from Eq. (A.39):

$$Lof=\cos\alpha\cdot\sum_{i=0}^{\infty}\frac{{}_2F_1\left[\begin{matrix}1/2,\,i+1\\3/2\end{matrix},\cos^2\alpha\right]}{2i+1}\cdot(\sin\beta)^{2i+1}$$

$$=\cos\alpha\cdot\sum_{i=0}^{\infty}\frac{{}_2F_1\left[\begin{matrix}1/2,\,i+1\\3/2\end{matrix},\cos^2\alpha\right]}{2i+1}\cdot\left(1-\frac{r_{12}^{\;2}}{r_1^{\;2}+r_2^{\;2}}\right)^{2i+1}$$

$$=\cos\alpha\cdot\sum_{i=0}^{\infty}\frac{{}_2F_1\left[\begin{matrix}1/2,\,i+1\\3/2\end{matrix},\cos^2\alpha\right]}{2i+1}\cdot\sum_{k=0}^{\infty}(-1)^k\binom{2i+1}{k}\left(\frac{r_{12}^{\;2}}{r_1^{\;2}+r_2^{\;2}}\right)^k$$

$$=\cos\alpha\cdot\sum_{k=0}^{\infty}\sum_{i=0}^{\infty}\binom{2i+1}{k}\frac{{}_2F_1\left[\begin{matrix}1/2,\,i+1\\3/2\end{matrix},\cos^2\alpha\right]}{2i+1}\cdot(-1)^k\left(\frac{r_{12}^{\;2}}{r_1^{\;2}+r_2^{\;2}}\right)^k. \tag{A.41}$$

This is the expansion we want of *Lof* respect to r_{12}.

At first, we try to find the expansion of *Lof* by the expansion of Lobachevsky function at $x=0$, which is

$$L(x)=-\int_0^x\ln(\cos t)\,dt=-\frac{1}{2}\sum_{n=1}^{\infty}\frac{(-1)^n B_{2n}\cdot 2^{2n}(2^n+1)(2^n-1)}{n(2n+1)!}\cdot x^{2n+1}. \tag{A.42}$$

where B_n is Bernoulli number.

We also find the expansion of Lobachevsky function at $x=\frac{\pi}{2}$, which is

$$L(x)=-\int_0^x \ln(\cos t)dt$$

$$=\frac{1}{2}\pi\ln 2+[\frac{1}{2}\cdot\ln(\frac{\pi}{2}-x)^2-1]\cdot(\frac{\pi}{2}-x)+\sum_{i=1}^{\infty}\frac{(-1)^i\cdot 2^{2i}\cdot B_{2i}}{2i\cdot(2i+1)!}\cdot(\frac{\pi}{2}-x)^{2i+1} \qquad (A.43)$$

Next, we can use these two expansions to simplify our *Lof*:

$$Lof=-\int_0^{\frac{1}{2}(\alpha-\beta)}\ln(\cos t)dt-\int_0^{\frac{1}{2}(\pi-\alpha+\beta)}\ln(\cos t)dt+\int_0^{\frac{1}{2}(\alpha+\beta)}\ln(\cos t)dt+\int_0^{\frac{1}{2}(\pi-\alpha-\beta)}\ln(\cos t)dt$$

$$=\frac{1}{2}[(\alpha-\beta)\cdot\ln(\alpha-\beta)-(\alpha+\beta)\cdot\ln(\alpha+\beta)]-\beta\cdot(\ln 2+1)$$

$$-\sum_{i=1}^{\infty}(-1)^i B_{2i}(2^{2i-1}-1)\cdot\frac{(i-1)!}{(2i)!!}\cdot\alpha^{2i}\beta\cdot\sum_{n=0}^{i}\frac{2^n}{(i-n)!(2i-2n-1)!!(2n+1)!}\cdot(\frac{\beta}{\alpha})^{2n} \qquad (A.44)$$

This expansion form is too hard to simplify to the expansion form we want.

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