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Step by Step in Fast Protein-Protein Docking Algorithms

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ABSTRACT

We present a new computational methods for computing the coefficient vectors in docking problem by using GTO and ETO orthonormal spherical polar radial basis functions. These computational techniques arise from the modeling of the molecule. Representing the molecules properties (shape and electrostatics) as three-dimensional (3D) functions in terms of GTO and ETO spherical polar radial Fourier expansion, respectively provides a straightforward way for computing the correlation between pairs of these functions. After rotating and translating the original functions, the correlation has the form of scalar products of suitably rotated and translated coefficient vectors. In this work we describe our method for computing these coefficients and finally estimating the docking problem in terms of these coefficients.

Keywords: shape complementarity (SC); electrostatic complementarity (EC); spherical harmonics; Laguerre polynomials; GTO and ETO spherical polar radial Fourier coefficients; I^{SC}-coefficients and I^{EC}-coefficients

DECLARATION

I hereby declare that this submission is my own work and that to the best of my knowledge and belief it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning except where due acknowledgment has been made in the text.

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ABBREVIATIONS

1D one-dimensional

2D two-dimensional

3D three-dimensional

5D five-dimensional

6D six-dimensional

A/ B A or B

COM centre of mass

–COOH carboxylic acid

EC electrostatic complementarity

ETO(s) exponential type orbital(s)

FFT fast Fourier transform

FRM fast rotational matching

FSOFT fast $SO(3)$ Fourier transform

FT Fourier transform

FTM fast translational matching

GTO(s) Gaussian type orbital(s)

NFFT nonequispaced fast Fourier transform

NFSOFT nonequispaced fast $SO(3)$ Fourier transform

PDB protein data bank

PPD protein-protein docking

PPI(s) protein-protein interaction(s)

SAS solvent accessible surface

SC shape complementarity

SES solvent excluded surface

SOFT $SO(3)$ Fourier transform

VDW van der Waals

VDWS van der Waals surface

wwPDB world wide protein data bank

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CHAPTER 1

INTRODUCTION

1.1. Motivation

Proteins are very important molecules in our body. They are made up of a chain of amino acids that link to each other through covalent bonds. In other words, amino acids link together by peptide bonds (covalent bonds) form a polypeptide. One or more polypeptide chains screwed into a three-dimensional (3D) shape constitute a protein. Proteins have complex shapes include various folds, loops and curves that the chemical bonds between the polypeptide chains hold the structure of the protein and make the protein's shape, see [6]. Generally four levels of protein structures are identified that distinguish of each other by the degree of complexity in the polypeptide chain.

- **Primary Structure:** Primary structure refers to the unique sequence of amino acids that are linked together to form a polypeptide or protein.
- **Secondary Structure:** Secondary structure refers to the way that the primary structure of a polypeptide chain coils or folds and gives the 3D shape of a protein and we have two types of stable secondary structures, α-helices and β-sheets.
- **Tertiary Structure:** Tertiary structure refers to the final 3D structure of the polypeptide chain of a protein.
- **Quaternary Structure:** Quaternary structure refers to the structure formed by interactions between multiple polypeptide chains or sometimes with an inorganic component to form a protein.

A 3D shape of a protein is determined by its primary structure. Each protein within the body has specific function. In other words, often protein-protein interactions (PPIs) when they constitute a complex perform the protein's function. In the following we have taken of Bailey [6, Protein Functions], a list of several types of proteins and their functions.

- Antibodies or immunoglobulin are proteins involved in defending the body from foreign objects which are called antigens. They can travel through the blood stream and are used by the immune system to identify and defend against bacteria, viruses, and other foreign invaders. An example of antibody can be find in blood types. A person with a blood type A can not receive blood type AB because blood type A produces antibodies that recognize B antigens so if a person with blood type A is transfused by blood type AB or B, then the antibodies that recognize the B antigen in the blood cause the person blood to be clotted.

- Enzymes are proteins that facilitate biochemical reactions. They are often referred to as catalysts because they speed up chemical reactions. Examples include the digestive enzymes lactase and pepsin. Lactase is essential to the complete digestion of whole milk. Pepsin is another digestive enzyme that is secreted in the stomach and helps to the digestion of protein.

- Hormonal proteins are messenger proteins which help to harmonize certain bodily activities. Examples include insulin, oxytocin and thyroid. Insulin regulates carbohydrate and fat by controlling the glucose from the blood. Thyroid controls the consumption of the body energy and sensitivity of the body to other hormones.

- Contractile proteins are proteins which participate in contractile process. Examples include actin and myosin. These proteins are responsible for muscle contraction and movement.

- Storage proteins are biological resources of amino acids and metal ions. Examples include ovalbumin and casein. Ovalbumin is the main protein found in egg white and casein is in mammalian milk.

- Transport proteins or carrier molecules are porter proteins which move molecules from one place to another place around the body. Examples include hemoglobin and serum albumin. Hemoglobin transports oxygen through the blood. Serum albumin transports water insoluble lipids (lipids are insoluble in water) in the blood stream.

So the protein's amino acid chain determines its 3D molecular structure and the protein's 3D structure determines its specific functions, see Ritchie [78].

In recent years, there is a new branch in sciences which is called proteomics. Proteomics is an interdisciplinary field and studies proteins in a large scale, particularly the protein's structure and protein's function. Proteomics relies on genome and protein information to identify proteins associated with the disease which the computer softwares use them as targets for the new drugs. If a certain protein causes a disease, its 3D structures provided the informations for designing drugs against the protein. Drugs are small molecules which in human body they bind to the disease causing protein and prevent of the activities of the disease causing protein. Often data for proteins and drugs are available but not for the interaction of them together. Genome-wide proteomics studies have provided a growing list of supposed protein-protein interactions (PPIs), but understanding the function of these predicted interaction requires additional biochemical and structural analysis, cf. Ritchie [78]. We can find good information about some known proteins in "Protein Data Bank" (PDB), ref. http://www.rcsb.org/pdb/home/home.do. The PDB archive is a bank for saving the atomic coordinates and other valuable information describing proteins and other biological macromolecules. Nowadays scientists use methods such as X-ray crystallography, nuclear magnetic resonance (NMR) spectroscopy and cryo-electron microscopy to determine the location of each atom relative to each other in the molecule, then this information is annotated and published into the archive by the "World Wide PDB" (wwPDB), see http://www.wwpdb.org/. If you look at PDB, then you can see a constantly growing list which reflects a continuous search and research in laboratories across the world. In PDB archive, we can find the structures for oncogenes, ribosomes, drug targets, and even the known viruses. However, it can be a challenge to find the information that you need, since the PDB archives has multiple structures for a given molecule, or partial structures, or structures that have been modified or inactivated from their native form. For further information refer to http://www.wwpdb.org/.

To understand and know more about PPIs help us for better understanding the molecular mechanism of diseases. Therapeutic drugs often operate by modulating or blocking PPIs and therefore PPIs represent an important class of drug targets, cf. Ritchie [78]. So the basis of new drug discovery is finding new drugs for deactivating protein involved in disease.

The problem of determining a relative motion (rotation and translation) for a pair of proteins and their compound reproducible in the nature is known as "protein-protein docking" (PPD) problem, cf. Bajaj [7]. The docking problem generally divided into two types, bound and unbound docking. In bound docking we are given a complex of two or more molecules. After artificial separation, the goal is to reconstruct the native complex, but in unbound docking we are given two molecules in their native conformation, the goal is to find the correct association. Unbound is much more difficult than bound docking because the protein involved can change conformation upon binding.

Ligands are small molecules which interact with protein's binding sites. Binding sites are areas of protein known to be active in forming of compounds. The most interesting case is the protein-ligand interactions (PLIs) and consequently protein-ligand docking (PLD).

There are two main challenges in the development of methods for protein-protein docking:

- The first is to construct a scoring function that admits the distinction between correct, nearly correct and incorrect predictions.
- The second is development an algorithm that quickly searches and scores all possible rotations and translations of proteins to be docked.

For more details see Kevin et al. [54]. Proteins intrinsically are dynamic and they can change their conformation, so solving the protein docking problem is not easy. In order to make the computations and assumptions easier, the structures of proteins are considered rigid and this essentially reduces the problem to a six-dimensional (6D) rotational-translational search space.

H. E. Fischer has an interesting theory for the rigid body protein docking which is known under the name "Key-&-Lock Theory". Roughly speaking, according to this theory, rigid body protein docking can be considered as the problem of key and lock. For opening a lock, at first we must know which key is fit and secondly which motions (rotations and translation) are required for opening the lock.

Many current protein-protein docking algorithms use fast Fourier transform (FFT) techniques, and this approach was first introduced by Katchalski-Katzir et al., cf. [51], in 1992, for computing surface complementarity (SC) and later on extended by Gabb et al., cf. [36], for surface complementarity and electrostatic complementarity (EC).

The standard way to exhaustively compute the scoring function is fast translational matching (FTM), but Wriggers and Kovacs have shown the exhaustive search in reverse order which is called fast rotational matching (FRM). In Wriggers' method the scoring function is a function of two rotations and one displacement that allows to write the scoring function as a Fourier expansion in terms of five angular variables (representing the rotations) and one linear variable for the translation, cf. [58].

1.2. Outline of the Thesis

The main aim of this work is development of computational techniques for 3D structure of molecule's properties (shape and electrostatics) and protein docking problem using efficient GTO & ETO spherical polar radial Fourier series.

Some of the mathematical ideas here were inspired of Ritchie's works. The interested readers can find protein docking material in Ritchie's papers and references therein. The rest of this preamble is structured as follows:

Chapter 2 summarizes some mathematical preliminaries related to this work, like the notions of rotations and motions in $\mathbb{R}^3$ and also Hilbert spaces and orthogonal functions specially the GTO & ETO spherical polar radial functions.

Chapter 3 presents an overview on the FTM algorithm on shape and electrostatic complementarity. FTM on shape and electrostatic complementarity is not a new and has discussed by many people, for example, Bajaj et al., see [7] and [8], and also Gabb et al., cf. [36]. Here with the inspiration of Grant-pickup's idea, cf. [41], we define a simpler model for charge density that makes the computation of the scoring function easier and hence we present a simpler and more efficient FTM algorithm for electrostatic complementarity.

Chapter 4 is the heart of this work and contains quite new computational methods for fast rotational matching (FRM) on shape and electrostatic complementarity. In the first section of this chapter we present a new computational method for computing the GTO spherical polar radial Fourier coefficients for shape complementarity and after some efforts we develop an efficient algorithm to compute these coefficients. Also we define the GTO translational coefficients I^{SC} and representing an algorithm to compute these coefficients and eventually finding an algorithm to compute the scoring function with the aid of GTO spherical polar radial Fourier coefficients, GTO translational coefficients I^{SC} and Wigner D-functions.

Analogously, in the second section of this chapter, we define the ETO spherical polar radial Fourier coefficients for two affinity functions. We present two different approaches for computing these coefficients. For computing the ETO spherical polar radial Fourier

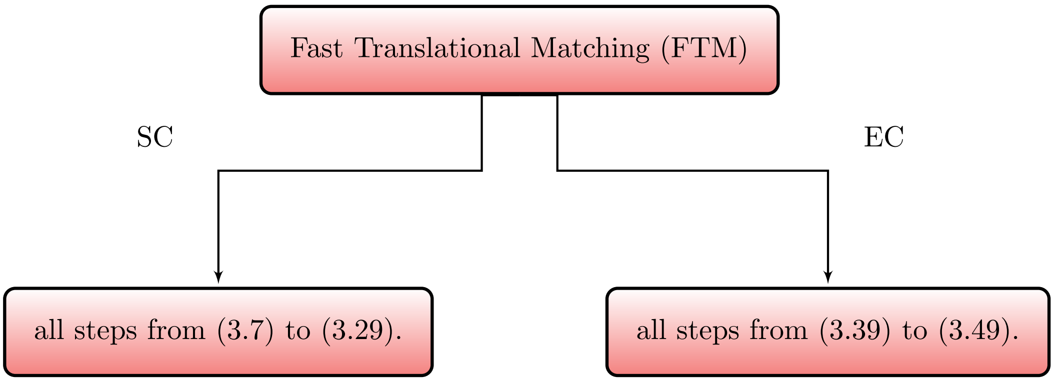


Figure 1.1.: Structure of Chapter 3, Fast Translational Matching (FTM) Algorithm on Shape Complementarity (SC) and Electrostatic Complementarity (EC).

coefficients $\hat{Q}^{\mathrm{B}}_{klm}$, we present a new computational method, but for computing $\hat{Q}^{\mathrm{A}}_{klm}$, we apply Ritchie's method. Also we define the ETO translational coefficients I^{EC} and a method for computation of them and finally describing our algorithm in terms of ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{A}}_{klm}$ and $\hat{Q}^{\mathrm{B}}_{klm}$, ETO translational coefficients I^{EC} and Wigner-D functions.

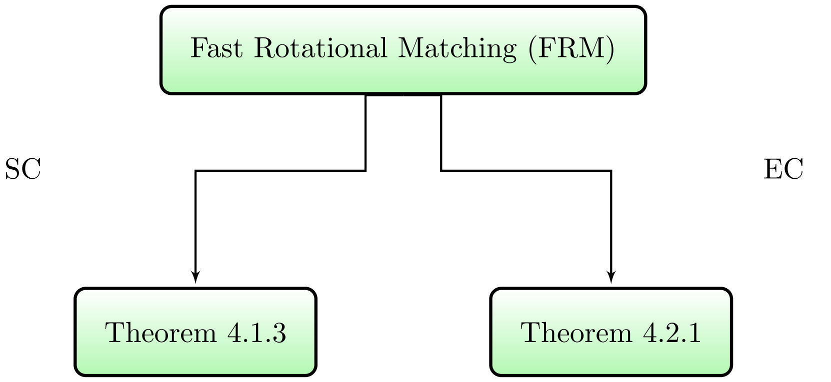


Figure 1.2.: Structure of Chapter 4, Fast Rotational Matching (FRM) Algorithm on Shape Complementarity (SC) and Electrostatic Complementarity (EC).

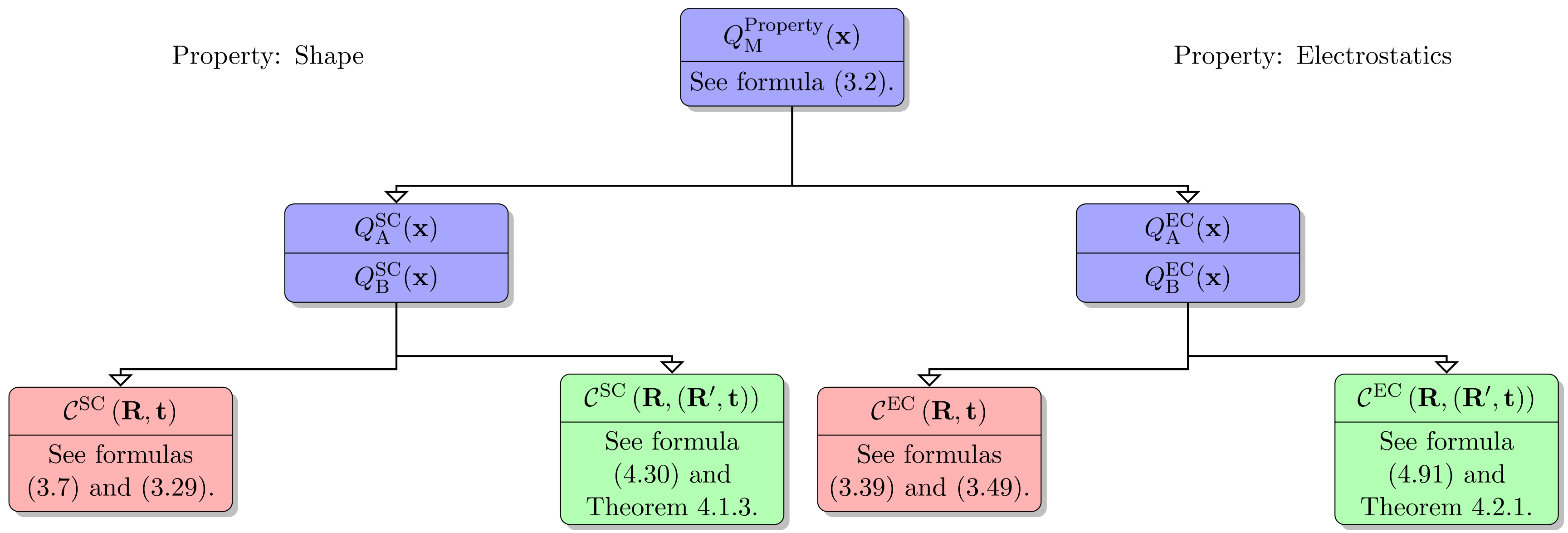


Figure 1.3.: General Structure of the Thesis. According to this figure, throughout this work, we consider only two properties, shape and electrostatics of an arbitrary molecule M. For protein-protein docking, we are given two molecules A and B with affinity functions $Q_{\mathrm{A}}^{\mathrm{SC/EC}}$ and $Q_{\mathrm{B}}^{\mathrm{SC/EC}}$. Here, the red rectangles show the fast translational matching (FTM) on surface complementarity (SC) and electrostatic complementarity (EC) which are described in **Chapter 3** and the green rectangles show the fast rotational matching (FRM) on SC and EC that are discussed with all details in **Chapter 4**.

CHAPTER 2

PRELIMINARIES

2.1. Rotation and Motion Groups

In the beginning of this section, we define the notion of a rotation of a rigid body object and in general case the rotation group. We shall pursue the rest of this section with reminding the concept of translation and also definition of motion and in general motion group. Throughout this work, all objects are rigid bodies, i.e., all deformations of theses objects will be neglected.

Definition 2.1.1 (Rotation) *A rotation is a transformation in a plane or in space that describes a movement of an object around a fixed point which is called the centre of rotation.*

In three-dimensional space $\mathbb{R}^3$, a matrix $\mathbf{R}$ describes rotation of a point (x, y, z) to a point (x', y', z') where the matrix $\mathbf{R}$ is an orthogonal 3×3 matrix with $\det(\mathbf{R}) = 1$. So with the above definition, a three-dimensional rotation about the origin $\mathbf{0} \in \mathbb{R}^3$ is a linear map

$$\begin{aligned} \Lambda_{\mathbf{R}} : \mathbb{R}^3 &\longrightarrow \mathbb{R}^3 \\ \mathbf{x} &\longmapsto \mathbf{R}\mathbf{x}, \end{aligned} \tag{2.1}$$

where $\mathbf{x} \in \mathbb{R}^3$ and $\mathbf{R}$ is an orthogonal 3×3 matrix with $\det(\mathbf{R}) = 1$.

Definition 2.1.2 (Rotation Group $SO(3)$) *The set*

$$SO(3) = \left\{ \mathbf{R} \in \mathbb{R}^{3\times 3};\ \mathbf{R}\mathbf{R}^{\mathrm{t}} = \mathbb{I} \text{ and } \det(\mathbf{R}) = 1 \right\}$$

is called special orthogonal group and it includes all the three-dimensional rotation matrices.

In this definition we can easily check that $SO(3)$ is a group and also this group is not commutative. Since $SO(3)$ is constituted of three-dimensional rotation matrices, it is also called rotation group. In the following well-known lemma we explain the intrinsic properties of a rotation.

Lemma 2.1.1 *A three-dimensional rotation preserves*

1. *the length of a vector.*
2. *the distance between two vectors.*
3. *the angles between two vectors.*
4. *the orientation of the space.*

Proof. Suppose $\mathbf{u}_1$, $\mathbf{u}_2$ and $\mathbf{u}_3$ are vectors in $\mathbb{R}^3$ and $\mathbf{R} \in SO(3)$ is an arbitrary rotation, then we have:

1. $\|\mathbf{u}_1\|_2 = \sqrt{\langle \mathbf{u}_1, \mathbf{u}_1 \rangle} = \sqrt{\mathbf{u}_1^{\mathrm{t}} \mathbf{u}_1} = \sqrt{\mathbf{u}_1^{\mathrm{t}} \mathbf{R}^{\mathrm{t}} \mathbf{R} \mathbf{u}_1} = \sqrt{\langle \mathbf{R}\mathbf{u}_1, \mathbf{R}\mathbf{u}_1 \rangle} = \|\mathbf{R}\mathbf{u}_1\|_2.$

2. The distance between two arbitrary vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ in $\mathbb{R}^3$ is given by
$$\|\mathbf{u}_1 - \mathbf{u}_2\|_2 = \sqrt{\langle \mathbf{u}_1 - \mathbf{u}_2, \mathbf{u}_1 - \mathbf{u}_2 \rangle},$$
and by the first part of this lemma, the assertion is obvious.

3. The angle between the vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ in $\mathbf{R} \in SO(3)$ is equal with
$$\cos\left(\widehat{\mathbf{u}_1, \mathbf{u}_2}\right) = \frac{\mathbf{u}_1 \cdot \mathbf{u}_2}{\|\mathbf{u}_1\|_2 \|\mathbf{u}_2\|_2},$$
but since
$$\mathbf{u}_1 \cdot \mathbf{u}_2 = \mathbf{u}_1^{\mathrm{t}} \mathbf{u}_2 = \mathbf{u}_1^{\mathrm{t}} \mathbf{R}^{\mathrm{t}} \mathbf{R} \mathbf{u}_2 = \left(\mathbf{R}\mathbf{u}_1\right)^{\mathrm{t}} \left(\mathbf{R}\mathbf{u}_2\right) = \left(\mathbf{R}\mathbf{u}_1\right) \cdot \left(\mathbf{R}\mathbf{u}_2\right),$$
hence $\cos\left(\widehat{\mathbf{u}_1, \mathbf{u}_2}\right) = \cos\left(\widehat{\mathbf{R}\mathbf{u}_1, \mathbf{R}\mathbf{u}_2}\right)$.

4. Suppose $\mathrm{U} = [\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3] \in \mathbb{R}^{3\times 3}$, then
$$\begin{aligned} \det \mathrm{U} &= \det\left([\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3]\right) \\ &= \det(\mathbf{R}) \det\left([\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3]\right) \\ &= \det\left(\mathbf{R}\left[\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3\right]\right) \\ &= \det\left([\mathbf{R}\mathbf{u}_1, \mathbf{R}\mathbf{u}_2, \mathbf{R}\mathbf{u}_3]\right), \end{aligned}$$
and hence we have the results. □

Definition 2.1.3 (Metric on $SO(3)$) *For a rotation* $\mathbf{R}$*, we denote the angle of this rotation by* $\|\mathbf{R}\|$ *which is uniquely defined by*
$$\cos(\|\mathbf{R}\|) = \frac{\operatorname{trace}(\mathbf{R}) - 1}{2} \quad \textit{and } \|\mathbf{R}\| \in [0, \pi].$$
The distance between two rotations $\mathbf{R}_1$ *and* $\mathbf{R}_2$ *of the rotation group* $SO(3)$ *is defined as the angle of the rotation* $\mathbf{R}_2 {\mathbf{R}_1}^{-1}$ *which is denoted by* $\|\mathbf{R}_2 {\mathbf{R}_1}^{-1}\|$.

There are many ways to parameterize rotations. Why we would want to use a particular parameterization (or any parameterization at all) depends entirely on its performance in applications of interest. We use the Euler angles parameterization that is defined in the following, but several other parameterizations of a rotation have been explained by Chirikjian [21, Section 5.4] and Vollrath [96, Section 2.2] in more details.

We start off with the standard definition of the rotations about the three coordinate axes:

- A rotation of α about the x-axis is defined as

$$\mathbf{R}_x(\alpha) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix}. \tag{2.2}$$

- Similarly a rotation of β about the y-axis is defined as

$$\mathbf{R}_y(\beta) = \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix}. \tag{2.3}$$

- Finally a rotation of γ about the z-axis is defined as

$$\mathbf{R}_z(\gamma) = \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{2.4}$$

Any three-dimensional rotation can be thought of a sequence of three rotations, one about each coordinate axis. We rotate first about the z-axis, then the y-axis and finally again about the z-axis. Such a sequence of rotations can be represented as the matrix product and is described in the following definition.

Definition 2.1.4 (Euler Angles) *Suppose we are given three angles α, β and γ where $\alpha,\ \gamma \in [0, 2\pi)$ and $\beta \in [0, \pi]$. If a rotation matrix is given by multiplication of three rotation matrices $\mathbf{R}_z(\alpha)$, $\mathbf{R}_y(\beta)$ and $\mathbf{R}_z(\gamma)$ by*

$$\mathbf{R}(\alpha, \beta, \gamma) := \mathbf{R}_z(\alpha)\mathbf{R}_y(\beta)\mathbf{R}_z(\gamma),$$

then the angles α, β and γ are called the Euler angles of the rotation $\mathbf{R} = \mathbf{R}(\alpha, \beta, \gamma)$.

Note that throughout this work we will use this convention for the Euler angles.

Remark 2.1.1 *In terms of Euler angles, the rotational angle of a rotation $\mathbf{R} = \mathbf{R}(\alpha, \beta, \gamma)$, in Definition 2.1.3 is*

$$\cos(\|\frac{\mathbf{R}}{2}\|) = \left(\cos\frac{\beta}{2}\cos\frac{\alpha+\gamma}{2}\right).$$

According to Definition 2.1.4, with having three Euler angles α, β and γ we can determine a rotation $\mathbf{R}(\alpha, \beta, \gamma) \in SO(3)$, but now in the following lemma is shown how one can determine the Euler angles of a three-dimensional rotation $\mathbf{R} \in SO(3)$.

Lemma 2.1.2 *If we are given a rotation matrix* $\mathbf{R} = (R_{ij})_{i,j=1,2,3}$*, then the Euler angles can be determined by*

1. *if* $|R_{33}| \neq 1$*, then*
   - $\alpha = \begin{cases} \arccos \frac{R_{13}}{\sqrt{R_{13}^2+R_{23}^2}} & \text{if } R_{23} \geq 0 \\ 2\pi - \arccos \frac{R_{13}}{\sqrt{R_{13}^2+R_{23}^2}} & \text{if } R_{23} < 0 \end{cases}$
   - $\beta = \arccos R_{33}$
   - $\gamma = \begin{cases} \arccos \frac{-R_{31}}{\sqrt{R_{31}^2+R_{32}^2}} & \text{if } R_{32} \geq 0 \\ 2\pi - \arccos \frac{R_{31}}{\sqrt{R_{31}^2+R_{32}^2}} & \text{if } R_{32} < 0 \end{cases}$
2. *if* $R_{33} = 1$*, then*
   - $\beta = 0$
   - $\alpha + \gamma = \begin{cases} \arccos R_{11} & \text{if } R_{21} \geq 0 \\ 2\pi - \arccos R_{11} & \text{if } R_{21} < 0 \end{cases}$
3. *if* $R_{33} = -1$*, then*
   - $\beta = \pi$
   - $\alpha - \gamma = \begin{cases} \arccos(-R_{11}) & \text{if } R_{21} \geq 0 \\ 2\pi - \arccos(-R_{11}) & \text{if } R_{21} < 0 \end{cases}$

Proof. See Vollrath [96, Corollary 2.2.11]. □

Now we review two lemmas of [96] to show the Euler angles are uniquely determined by its three-dimensional rotation $\mathbf{R} \in SO(3)$.

Definition 2.1.5 *Corresponding to the three unit vectors* $\mathbf{e}_x = (1,0,0)^{\mathrm{t}}$*,* $\mathbf{e}_y = (0,1,0)^{\mathrm{t}}$ *and* $\mathbf{e}_z = (0,0,1)^{\mathrm{t}}$*, we define three subgroups of the rotation group* $SO(3)$ *by*

$$\begin{aligned} \mathcal{X} &= \{\mathbf{R} \in SO(3);\ \mathbf{R}\mathbf{e}_x = \mathbf{e}_x\}, \\ \mathcal{Y} &= \{\mathbf{R} \in SO(3);\ \mathbf{R}\mathbf{e}_y = \mathbf{e}_y\}, \\ \mathcal{Z} &= \{\mathbf{R} \in SO(3);\ \mathbf{R}\mathbf{e}_z = \mathbf{e}_z\}, \end{aligned}$$

which are called respectively vanished subgroups of $SO(3)$ *along* x*-axis,* y*-axis and* z*-axis.*

Lemma 2.1.3 *Every rotation* $\mathbf{R}$ *of the vanished subgroup* $\mathcal{Z}$ *of* $SO(3)$ *fulfils*

$$\mathbf{R} = \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

for some $\gamma \in [0, 2\pi)$*.*

Proof. See Vollrath [96, Lemma 2.2.3]. □

Lemma 2.1.4 *Every rotation matrix* $\mathbf{R} = (R_{ij})_{i,j=1,2,3}$ *of* $SO(3)$ *with* $|R_{33}| \neq 1$ *uniquely determines its Euler angles.*

Proof. Suppose we are given a rotation matrix $\mathbf{R} = (R_{ij})_{i,j=1,2,3}$ with $|R_{33}| \neq 1$ which is written in terms of different Euler angles, namely

$$\mathbf{R} = \mathbf{R}_z(\alpha)\mathbf{R}_y(\beta)\mathbf{R}_z(\gamma) \text{ where } \alpha, \gamma \in [0, 2\pi) \text{ and } \beta \in [0, \pi],$$
$$\mathbf{R} = \mathbf{R}_z(\alpha')\mathbf{R}_y(\beta')\mathbf{R}_z(\gamma') \text{ where } \alpha', \gamma' \in [0, 2\pi) \text{ and } \beta' \in [0, \pi],$$

we prove $\alpha = \alpha'$, $\beta = \beta'$ and $\gamma = \gamma'$.

Since

$$\mathbf{R}_z(\alpha)\mathbf{R}_y(\beta)\mathbf{R}_z(\gamma) = \mathbf{R}_z(\alpha')\mathbf{R}_y(\beta')\mathbf{R}_z(\gamma'),$$

so we have

$$\mathbf{R}_z\left(\alpha - \alpha'\right)\mathbf{R}_y(\beta) = \mathbf{R}_y(\beta')\mathbf{R}_z\left(\gamma' - \gamma\right). \tag{2.5}$$

We multiply both sides of the equation (2.5) on the unit vector $\mathbf{e}_z$, namely

$$\mathbf{R}_z\left(\alpha - \alpha'\right)\mathbf{R}_y(\beta)\mathbf{e}_z = \mathbf{R}_y(\beta')\mathbf{R}_z\left(\gamma' - \gamma\right)\mathbf{e}_z,$$

and hence we have

$$\left(\sin\beta\cos\left(\alpha - \alpha'\right), \sin\beta\sin\left(\alpha - \alpha'\right), \cos\beta\right)^{\mathrm{t}} = \left(\sin\beta', 0, \cos\beta'\right)^{\mathrm{t}}.$$

So the corresponding pairs are equal, i.e.

$$\begin{cases} \sin\beta\cos\left(\alpha - \alpha'\right) = \sin\beta' & \text{(a)} \\ \sin\beta\sin\left(\alpha - \alpha'\right) = 0 & \text{(b)} \\ \cos\beta = \cos\beta' & \text{(c)} \end{cases} \tag{2.6}$$

According to the hypothesis $|R_{33}| \neq 1$ and hence $\mathbf{R} \notin \mathcal{X}$ and also $\mathbf{R}^{\mathrm{t}} \notin \mathcal{X}$, consequently $\cos\beta \neq 1$ and hence $\beta \in (0, \pi)$, if so then $\sin\beta \neq 0$.

- If $\cos\beta = \cos\beta'$, see (2.6)-(c), then $\beta = 2k\pi \pm \beta'$ where $k \in \mathbb{Z}$, but since $\beta \in (0, \pi)$ so $\beta = \beta'$.
- We have $\sin\beta\sin\left(\alpha - \alpha'\right) = 0$, see (2.6)-(b), but since $\sin\beta \neq 0$, therefore $\sin\left(\alpha - \alpha'\right) = 0$ and hence $\alpha - \alpha' = k\pi$ where $k \in \mathbb{Z}^+$.
- Accordingly if we replace these changes in (2.6)-(a), i.e., $\sin\beta\cos\left(k\pi\right) = \sin\beta$, then we have $\cos k\pi = 1$ and hence $k = 0$, if so since $\alpha - \alpha' = k\pi$ then $\alpha = \alpha'$.
- Now from (2.5), we have $\mathbf{R}_z\left(\gamma' - \gamma\right) = \mathbb{I}$, hence $\gamma' - \gamma = 0$. So $\gamma = \gamma'$. □

Remark 2.1.2 *Throughout this work, integration of functions $f : SO(3) \longrightarrow \mathbb{R}$ that the rotations are parameterized in terms of Euler angles are considered by*

$$\int_{SO(3)} f(\mathbf{R})\,\mathrm{d}\mathbf{R} = \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} f\left(\mathbf{R}\left(\alpha, \beta, \gamma\right)\right)\sin\beta\,\mathrm{d}\alpha\,\mathrm{d}\beta\,\mathrm{d}\gamma.$$

The volume element $\mathrm{d}\mathbf{R}$ gives the Haar measure μ of $SO(3)$ by $\mathrm{d}\mathbf{R} = \mathrm{d}\mu(\mathbf{R})$. For more details see [21, p. 256].

We know translations are also motions in a plane or in the space and hence here we recall the following definition of a translation.

Definition 2.1.6 *A translation in a plane or in space is a function that moves every point in specific direction with a constant distance, i.e.*

$$\begin{aligned}\mathcal{T}^{\mathbf{t}} : \mathbb{R}^3 &\longrightarrow \mathbb{R}^3 \\ \mathbf{x} &\longmapsto \mathbf{x} + \mathbf{t}.\end{aligned}$$

Now we know rotations and translations are motions about and along respectively point or axsis but we would like to have a mathematical definition of the notion of motion.

Definition 2.1.7 (Motion) *A motion in a plane or in space is a transformation that describes the movement of a rigid body object at first about the centre of rotation and then translates every point of the rigid body object by a fixed distance in the same direction.*

So according to this definition, a three-dimensional motion about the origin $\mathbf{0} \in \mathbb{R}^3$ is a linear map

$$\begin{aligned}\mathbb{R}^3 &\longrightarrow \mathbb{R}^3 \\ \mathbf{x} &\longmapsto \mathbf{R}\mathbf{x} + \mathbf{t},\end{aligned} \tag{2.7}$$

where $\mathbf{R} \in SO(3)$ and $\mathbf{t} \in \mathbb{R}^3$.

Definition 2.1.8 (Motion Group $SE(3)$) *The set*

$$SE(3) = \left\{(\mathbf{R}, \mathbf{t})\,;\ \mathbf{R} \in SO(3) \text{ and } \mathbf{t} \in \mathbb{R}^3\right\},$$

with the binaray operation "o" where $(\mathbf{R}_1, \mathbf{t}_1) \circ (\mathbf{R}_2, \mathbf{t}_2) = (\mathbf{R}_1\mathbf{R}_2, \mathbf{R}_2\mathbf{t}_1 + \mathbf{t}_2)$ *is called special Euclidean group and consists of all three-dimensional motions.*

Since the group $SE(3)$ consists of all motions, we call it motion group. Also note that each motion $(\mathbf{R}, \mathbf{t}) \in SE(3)$ can be written as

$$(\mathbf{R}, \mathbf{t}) = (\mathbb{I}, \mathbf{t}) \circ (\mathbf{R}, \mathbf{0}), \tag{2.8}$$

so each motion can be assumed as a rotation followed by a translation.

Definition 2.1.9 (Metric on $SE(3)$) *The distantce between two motions* $(\mathbf{R}_1, \mathbf{t}_1)$ *and* $(\mathbf{R}_2, \mathbf{t}_2)$ *of the motion group* $SE(3)$ *is defined by the metric on* $SO(3)$*, Definition 2.1.3, and metric on* $\mathbb{R}^3$ *as in the following:*

$$\|\,(\mathbf{R}_1, \mathbf{t}_1), (\mathbf{R}_2, \mathbf{t}_2)\,\| = \|\mathbf{R}_2\mathbf{R}_1^{-1}\| + \|\mathbf{t}_2 - \mathbf{t}_1\|_2.$$

We need the integration of functions on the motion group $SE(3)$ hence we remind the following remark.

Remark 2.1.3 *Throughout this work, integration of functions* $f : SE(3) \longrightarrow \mathbb{R}$ *are assumed as*

$$\int_{SE(3)} f\left((\mathbf{R}, \mathbf{t})\right) \mathrm{d}\left(\mathbf{R}, \mathbf{t}\right) = \int_{SO(3)}\int_{\mathbb{R}^3} f\left((\mathbf{R}, \mathbf{t})\right) \mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{t},$$

where $\mathrm{d}\left(\mathbf{R}, \mathbf{t}\right)$ *on* $SE(3)$ *is given by* $\mathrm{d}\mathbf{R}\mathrm{d}\mathbf{t}$ *where* $\mathrm{d}\mathbf{R}$ *and* $\mathrm{d}\mathbf{t}$ *are respectively volume element of* $SO(3)$ *and* $\mathbb{R}^3$*.*

We can represent the integration of real valued functions on $SE(3)$ in terms of various parameterizations of rotations $\mathbf{R} \in SO(3)$ and translations $\mathbf{t} \in \mathbb{R}^3$, but we will utilize the Remark 2.1.2, hence

$$\int_{SE(3)} f\left((\mathbf{R}, \mathbf{t})\right) \mathrm{d}\left(\mathbf{R}, \mathbf{t}\right) = \frac{1}{8\pi^2} \int_{\mathbb{R}^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} f\left(\mathbf{R}\left(\alpha, \beta, \gamma\right), \mathbf{t}\right) \sin\beta \,\mathrm{d}\alpha \,\mathrm{d}\beta \,\mathrm{d}\gamma \,\mathrm{d}\mathbf{t}. \tag{2.9}$$

2.2. Hypergeometric Functions

we start up this section with some elementary notions that will be used in some parts of the next chapters.

The *factorial function* is defined for nonnegative integers n where $n! = 1 \times 2 \times \ldots \times n$, and $0! = 1$. The definition of the factorial function can also be extended to noninteger arguments, i.e., the *Gamma function* denoted by "Γ" is an extension of the factorial functions of real and complex numbers except the negative integers and zero. That is, if n is a positive integer, then

$$\Gamma(n) = (n-1)! \tag{2.10}$$

and in general

$$\Gamma(n) = \int_0^{\infty} \mathrm{e}^{-t} t^{n-1} \,\mathrm{d}t. \tag{2.11}$$

Definition 2.2.1 *The hypergeometric function* ${}_pF_q\left(a_1, a_2, \ldots, a_p; b_1, b_2, \ldots, b_q; z\right)$ *is defined by*

$${}_pF_q\left(a_1, a_2, \ldots, a_p; b_1, b_2, \ldots, b_q; z\right) = \sum_{n=0}^{\infty} \frac{(a_1)_n (a_2)_n \ldots (a_p)_n}{(b_1)_n (b_2)_n \ldots (b_q)_n} \cdot \frac{z^n}{n!}$$

and $(a)_n$ *is the Pochhammer symbol which is defined by*

$$(a)_n := a(a+1)(a+2)\ldots(a+n-1),$$

where $n \in \mathbb{N}$ *and* $(a)_0 := 1$.

Note that the parameters must be such that the denominator never be zero. When one of the numerator parametrs $a_i = -N$ where N is a nonnegative integer, the hypergeometric function is a polynomial in z, for more details see Abramowitz et al. [1, p. 374-401].

2.3. Hilbert Spaces & Bases

Orthogonal functions play an important role in the theory of Hilbert spaces. We know a Hilbert space is essentially an algebraic extension of the notion of an ordinary Euclidean space. So corresponding to the axes of Euclidean space we have an infinite set of orthogonal basis functions and hence corresponding to a coordinate vector in Euclidean space, each point in the Hilbert space is described as a linear combination of basis functions, cf. Ritchie [78].

In this section we shall seek to summarize some ideas of algebra and linear algebra. To do this, we at first recall some elementary properties of vectors.

Two vectors U and V are called orthogonal if the dot product of them be zero. The dot product of two vectors $U = (u_1, u_2, \dots, u_n)$ and $V = (v_1, v_2, \dots, v_n)$ is defined as

$$U \cdot V = \sum_{i=0}^{n} u_i v_i.$$

In particular we would like to generalize the notion of vector orthogonality to functions. We think of a function space that the value of each function being specified by substituting a particular value of x, taken from some interval (a, b). In such case we can define two functions $U(x)$ and $V(x)$ are orthogonal in (a, b), if

$$\int_a^b U(x)V(x)\,\mathrm{d}x = 0.$$

A vector U is called a unit vector or normalized vector, if $U \cdot \overline{U} = 1$. Extending the concept, we say that the function $U(x)$ is orthonormal or normalized, if

$$\int_a^b |U(x)|^2\,\mathrm{d}x = 1.$$

Now we recall a notion that throughout this work will be used.

Definition 2.3.1 *Suppose $f(x)$ is a real or complex valued measurable function for which*

$$\int_{-\infty}^{\infty} |f(x)|^2\,\mathrm{d}x < \infty,$$

then the function f is called square integrable function on the real line and we denote it by $f \in L^2(\mathbb{R})$.

The interval of an integration can also be bounded such as $[0, 1]$. The square integrable functions form an inner product space whose inner product is given by

$$\langle f, g\rangle = \int_{-\infty}^{\infty} f(x)\overline{g(x)}\,\mathrm{d}x. \tag{2.12}$$

So, square integrability is the same as saying $\langle f, f\rangle < \infty$.

Definition 2.3.2 *A sequence $\{f_n\}_{n\in\mathbb{N}}$ is a Schauder basis (or simply a basis) for a Hilbert space H, if each element of H can be written uniquely as an infinite linear combination of the set $\{f_n\}_{n\in\mathbb{N}}$, i.e., given $f \in H$, there must exist unique coefficients $c_n(f)$, such that*

$$f = \sum_{n=1}^{\infty} c_n(f) f_n.$$

In addition, if $\{f_n\}_{n\in\mathbb{N}}$ is an orthonormal sequence, then we call this set as an orthonormal basis, or complete orthonormal sequence.

Note that we are only considering a countable set of basis vectors, i.e. separable Hilbert spaces. If we try and have uncountably many then we run into trouble trying to define $\sum_n c_n(f)f_n$. It can be shown that square integrable functions form a complete metric space under the metric induced by the inner product, therefore the space of square integrable functions is a Hilbert space because the space is complete under the metric induced by inner product. We consider two facts about square integrable functions and Hilbert spaces:

- Every square integrable function can be expanded in terms of Fourier like series.
- Every Hilbert space admits an orthogonal basis, and each vector in this Hilbert space can be expanded in terms of this orthonormal basis.

It turns out that the first of these facts is the special case of the second one, for example, the trigonometric functions $\{\mathrm{e}^{\mathrm{i}nx}\}_{n\in\mathbb{Z}}$ can be considered as an orthonormal basis of the space of square integrable functions and then the Fourier expansion of an arbitrary square integrable function is the same as its Hilbert space expansion in terms of orthonormal basis.

Lemma 2.3.1 (Parseval's Lemma) *If $f(x)$ and $g(x)$ be in $L^2(\mathbb{T})$ of period 2π with Fourier series*

$$f(x) = \sum_{k=-\infty}^{\infty} \hat{f}_k \mathrm{e}^{2\pi\mathrm{i}x.k}$$

and

$$g(x) = \sum_{k=-\infty}^{\infty} \hat{g}_k \mathrm{e}^{2\pi\mathrm{i}x.k},$$

then

$$\frac{1}{2\pi}\int_{-\pi}^{\pi} f(x)\overline{g(x)}\,\mathrm{d}x = \sum_{k=-\infty}^{\infty} \hat{f}_k\overline{\hat{g}_k}.$$

In the following lemma, we can see the Fourier expansion of the correlation of two functions in $L^2(\mathbb{T}^3)$.

Lemma 2.3.2 *Suppose we are given $f(\mathbf{x}) = \sum_{\mathbf{k}\in\mathbb{Z}^3} \hat{f}_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}.\mathbf{k}}$ and $g(\mathbf{x}) = \sum_{\mathbf{k}\in\mathbb{Z}^3} \hat{g}_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}.\mathbf{k}}$. If*

$$\mathcal{C}(\mathbf{t}) = \int_{\mathbb{T}^3} f(\mathbf{x})g(\mathbf{t}+\mathbf{x})\,\mathrm{d}\mathbf{x},$$

where $\mathbf{t}\in\mathbb{R}^3$, be the correlation of these two functions, then the Fourier coefficients of the correlation are

$$\hat{\mathcal{C}}(\mathbf{t}) = \sum_{\mathbf{k}\in\mathbb{Z}^3} \hat{f}_{\mathbf{k}}\hat{g}_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{t}.\mathbf{k}}.$$

Now we recall and introduce some orthogonal polynomials that are related to our work and will be used in the next chapters.

2.3.1. Legendre Polynomials

Legendre polynomials $\mathrm{P}_l(x)$ are defined here, using the Rodrigues formula

$$\mathrm{P}_l(x) = \frac{1}{2^l l!} \frac{\mathrm{d}^l}{\mathrm{d}x^l} \left(x^2 - 1\right)^l. \tag{2.13}$$

Also these polynomials are known as the solutions of the Legendre differential equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\left(1 - x^2\right) \frac{\mathrm{d}}{\mathrm{d}x}\mathrm{P}_l(x)\right] + l\,(l+1)\,\mathrm{P}_l(x) = 0,$$

for $x \in [-1, 1]$, where $l = 0, 1, 2, \ldots$. The Legendre polynomials satisfy the orthogonality condition

$$\int_{-1}^{1} \mathrm{P}_l(x)\mathrm{P}_m(x)\,\mathrm{d}x = \frac{2}{2l+1}\delta_{l,m}. \tag{2.14}$$

For more details see Chirikjian [21, 3.2.1].

2.3.2. Associated Legendre Functions

The *associated Legendre functions* $\mathrm{P}_l^m(x)$ can be calculated from the Legendre polynomials as

$$\mathrm{P}_l^m(x) = (-1)^m \left(1 - x^2\right)^{m/2} \frac{\mathrm{d}^m}{\mathrm{d}x^m} \left(\mathrm{P}_l(x)\right), \tag{2.15}$$

where $l = 0,\ 1,\ 2,\ \ldots$ and $0 \le |m| \le l$.

It is easy to see that $\mathrm{P}_l^0(x) = \mathrm{P}_l(x)$. In the following lemma, we present another representation for the associated Legendre functions that will be used in our work.

Lemma 2.3.3 *Associated Legendre functions* $\mathrm{P}_l^m(x)$ *with the integer indices* l *and* m*, where* $0 \le |m| \le l$*, have the following representation*

$$\mathrm{P}_l^m(x) = 2^{-l} \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(-1)^{t+m}\,(2l-2t)!}{(l-m-2t)!\,(l-t)!t!} \left(1 - x^2\right)^{m/2} x^{l-m-2t}.$$

Proof. Substituting the Rodrigues formula (2.13) in the associated Legendre polynomials (2.15) gives

$$\mathrm{P}_l^m(x) = \frac{(-1)^m}{2^l l!} \left(1 - x^2\right)^{m/2} \frac{\mathrm{d}^{l+m}}{\mathrm{d}x^{l+m}} \left(x^2 - 1\right)^l.$$

Hence according to this equation, the extension range of m can be $-l \le m \le l$. Using the binomial expansion of $\left(x^2 - 1\right)^l$, gives

$$\begin{aligned}\frac{\mathrm{d}^{l+m}}{\mathrm{d}x^{l+m}} \left(x^2 - 1\right)^l &= \frac{\mathrm{d}^{l+m}}{\mathrm{d}x^{l+m}} \left(\sum_{t=0}^{l} \binom{l}{t} (-1)^t (x^2)^{l-t}\right) \\ &= \sum_{t=0}^{l} \frac{(-1)^t l!}{t!(l-t)!} \frac{\mathrm{d}^{l+m}}{\mathrm{d}x^{l+m}} x^{2l-2t}\end{aligned}$$

and since

$$\frac{\mathrm{d}^{l+m}}{\mathrm{d}x^{l+m}} x^{2l-2t} = \begin{cases} \frac{(2l-2t)!}{(l-m-2t)!} x^{l-m-2t} & \text{if } l-m-2t \geq 0 \\ 0 & \text{otherwise.} \end{cases}$$

So we have $l - m - 2t \geq 0$ and hence $l - m \geq 2t$, consequently $\frac{l-m}{2} \geq t$. Also since t is defined for positive integers therefore the range of t is $0 \leq t \leq \lfloor \frac{l-m}{2} \rfloor$. $\square$

The associated Legendre functions are orthogonal, i.e.

$$\int_{-1}^{1} \mathrm{P}_k^m(x) \mathrm{P}_l^m(x) \, \mathrm{d}x = \frac{2\,(l+m)!}{(2l+1)\,(l-m)!} \delta_{k,l}, \tag{2.16}$$

where $0 \leq |m| \leq l, k$. For any fixed $m \in [-l, l]$, the associated Legendre functions form an orthonormal basis for $L^2\,([-1,1])$, i.e.

$$P_l^m(x) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \mathrm{P}_l^m(x), \tag{2.17}$$

this means, any function on the interval $[-1, 1]$ can be expanded in terms of normalized associated Legendre functions as

$$f(x) = \sum_{l=|m|}^{\infty} \hat{f}_{lm} P_l^m(x), \tag{2.18}$$

where

$$\hat{f}_{lm} = \int_{-1}^{1} f(x) P_l^m(x) \, \mathrm{d}x, \tag{2.19}$$

are called the associated Legendre (Fourier) coefficients, cf. Chirikjian [21, p. 45].

Note that during this work, we will always use the normalized associated Legendre functions (2.17), *otherwise we will mention it.*

2.3.3. Spherical Harmonics

Associated Legendre functions play a vital role in definition of spherical harmonics. Here, using the normalized associated Legendre functions defined in (2.17), we have the following definition for spherical harmonics.

$$Y_l^m\,(\theta, \phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \mathrm{P}_l^m\,(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\phi}, \tag{2.20}$$

where l and m are integers such that $l \geq m \geq 0$ and θ is the colatitudinal coordinate with $\theta \in [0, \pi]$ and ϕ as azimuthal (latitudinal) coordinate with $\phi \in [0, 2\pi)$.

Remark 2.3.1 *Note that in the definition of spherical harmonics $Y_l^m\,(\theta, \phi)$, l and m are considered positive integers where $l \geq m \geq 0$. The negative order spherical harmonics $Y_l^{-m}\,(\theta, \phi)$ are rotated about z-axis by $90\,°/m$ with respect to the positive order ones. This comes from the point that in the associated Legendre functions $P_l^m(x)$ where l, and*

m are refered to the degree and order and $l \geq m \geq 0$ and since the differential equation inside the associated Legendre functions (2.15) *is clearly invariant under a change in sign of m, the function for negative m is proportional to those of positive m, i.e.*

$$P_l^{-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x). \tag{2.21}$$

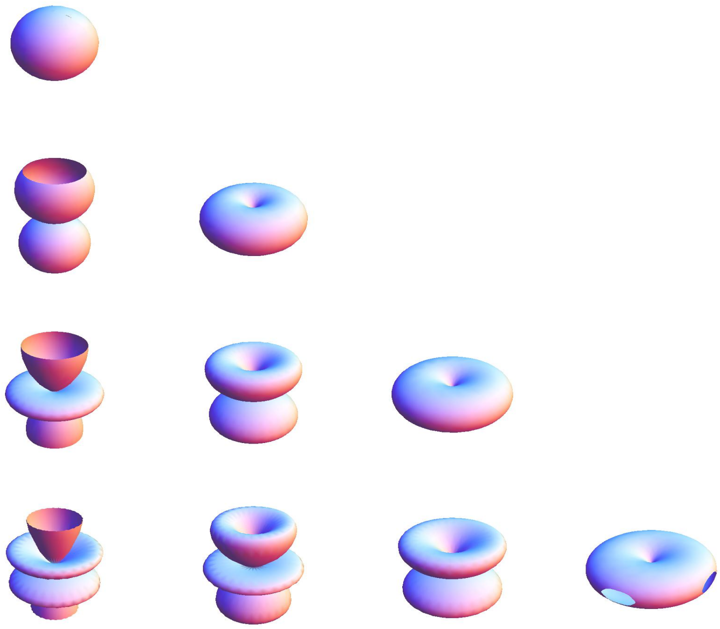


Figure 2.1.: This is a figure of spherical harmonics $Y_l^m(\theta, \phi)$, for $l = 0,\ 1,\ 2,\ 3$ (top to bottom) and $m = 0,\ 1,\ 2,\ 3$ (left to right). The negative order spherical harmonics $Y_l^m(\theta, \phi)$ are rotated about the z-axis by $90°/m$ with respect to the positive order ones.

Lemma 2.3.4 *The spherical harmonics for integer indices l and m where $l \geq |\, m \,| \geq 0$ have the following representation*

$$Y_l^m(\theta, \phi) = 2^{-l} \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!} (\sin\theta)^m (\cos\theta)^{l-m-2t} \mathrm{e}^{\mathrm{i}m\phi}.$$

Proof. The assertion is clear by using the spherical harmonics, see (2.20), and Lemma 2.3.3. □

The unit sphere $\mathbb{S}^2$ in $\mathbb{R}^3$ is a two-dimensional surface denoted by

$$\mathbb{S}^2 := (\theta, \phi) \quad \text{where} \quad \theta \in [0, \pi] \text{ and } \phi \in [0, 2\pi). \tag{2.22}$$

Functions on the sphere can be viewed as functions on $\mathbb{S}^1 \times [0, \pi]$. Hence the volume element is viewed as the product of volume element for $\mathbb{S}^1$ and $[0, \pi]$, namely

$$w(\theta, \phi) = w(\theta) \cdot w(\phi) = \sin\theta \cdot 1.$$

We know $\left\{e^{im\phi}\right\}_{m\in\mathbb{Z}}$ is an orthonormal basis for $L^2(\mathbb{S}^1)$. Also from the previous section we know associated Legendre functions form an orthogonal basis for $L^2\left([-1,1],\mathrm{d}x\right)$. By change of coordinates $x = \cos\theta$, the normalized associated Legendre functions (2.17) form an orthonormal basis for the Hilbert space $L^2\left([0,\pi],\ \sin\theta\mathrm{d}\theta\right)$ and hence altogether the set

$$\{\, Y_l^m\left(\theta,\phi\right);\ l,\ |m|\in\mathbb{N}_0,\ (\theta,\phi)\in[0,\pi]\times[0,2\pi)\}\,, \tag{2.23}$$

of spherical harmonics forms an orthonormal basis for the Hilbert space $L^2(\mathbb{S}^2)$, see Chirikjian [21, p. 100], i.e.

$$\int_0^\pi\int_0^{2\pi} Y_l^m\left(\theta,\phi\right)\, Y_{l'}^{m'}\left(\theta,\phi\right)\sin\theta\,\mathrm{d}\phi\,\mathrm{d}\theta = \delta_{l,l'}\delta_{m,m'},$$

therefore any function in $L^2(\mathbb{S}^2)$ can be expanded uniquely in terms of spherical harmonic Fourier series as

$$f\left(\theta,\phi\right) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\hat{f}_{lm}\, Y_l^m\left(\theta,\phi\right), \tag{2.24}$$

where

$$\hat{f}_{lm} = \int_{\mathbb{S}^2} f\left(\theta,\phi\right)\overline{Y_l^m\left(\theta,\phi\right)}\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi, \tag{2.25}$$

are called spherical (harmonic) Fourier coefficients.

Spherical harmonics have many theoretical and practical applications, particularly in the computation of atomic orbital electron configurations which is pretty much related to our work and will be applied in the next chapters.

Here we recall the Laplace operator. The Laplace operator is a second order differential operator in the 3-dimensional Euclidean space $\mathbb{R}^3$, defined as the divergence $(\triangledown\cdot)$ of the gradient $(\triangledown f)$. Thus if f is a twice differentiable real valued function, then the Laplacian of f is defined by

$$\triangle f = \triangledown^2 f = \triangledown\cdot\triangledown f, \tag{2.26}$$

where

$$\triangledown = \left(\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z}\right). \tag{2.27}$$

Given a scalar field $\Phi(\mathbf{x})$, the Laplace equation is

$$\triangledown^2\Phi(\mathbf{x}) = 0,$$

where in Cartesian coordinates

$$\triangledown^2 = \left(\frac{\partial^2}{\partial x^2},\frac{\partial^2}{\partial y^2},\frac{\partial^2}{\partial z^2}\right)$$

and in spherical coordinate system

$$\triangledown^2 = \frac{1}{r}\left(\frac{\partial^2}{\partial r^2}\right)r + \frac{1}{r^2}\Lambda^2, \tag{2.28}$$

where Λ^2 is the Legendrian operator defined by

$$\Lambda^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \tag{2.29}$$

The angular part of Laplace's equation has solutions

$$\Lambda^2 Y_l^m(\theta,\phi) = -l(l+1)\, Y_l^m(\theta,\phi)\,, \tag{2.30}$$

cf. Ritchie [78, equations 2.67, 2.68, 2.69 & p. 19] or Chirikjian [21, equation 4.22, p. 92].

2.3.4. Laguerre Polynomials

Laguerre polynomials $L_n(x)$ may be defined by Rodrigues formula

$$L_n(x) = \frac{\mathrm{e}^x}{n!}\frac{\mathrm{d}^n}{\mathrm{d}x^n}\left(\mathrm{e}^{-x}x^n\right). \tag{2.31}$$

These polynomials are solutions of the differential equation

$$xy'' + \left(1-x^2\right)y' + ny = 0,$$

for $x \in \mathbb{R}^+$. The Laguerre polynomials satisfy the orthogonality conditions

$$\int_0^\infty L_m(x)L_n(x)\mathrm{e}^{-x}\mathrm{d}x = (n!)^2\delta_{m,n}. \tag{2.32}$$

For more details see Chirikjian [21, p. 48-49].

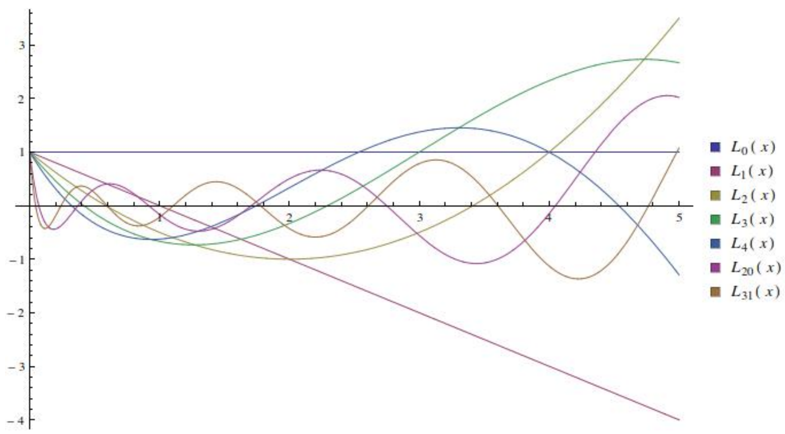
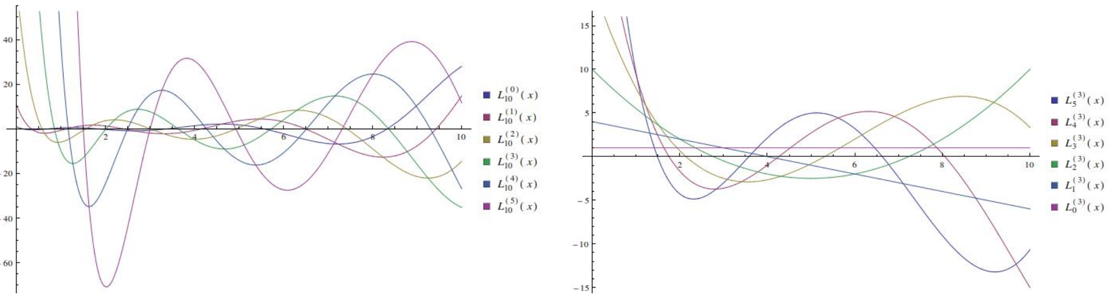


Figure 2.2.: The Laguerre polynomials $L_n(x)$ for $n = 0,\ 1,\ 2,\ 3,\ 4,\ 20,\ 31$.

2.3.5. Associated Laguerre Polynomials

The *associated (or generalized) Laguerre polynomials* $L_n^{(\alpha)}(x)$ are defined by the Rodrigues formula

$$L_n^{(\alpha)}(x) = \frac{\mathrm{e}^x x^{-\alpha}}{n!}\frac{\mathrm{d}^n}{\mathrm{d}x^n}\left(\mathrm{e}^{-x}x^{n+\alpha}\right). \tag{2.33}$$



(a) The associated Laguerre polynomials $L_n^{(\alpha)}(x)$, for $n = 10$ and $\alpha = 0, 1, 2, 3, 4, 5$.

(b) The associated Laguerre polynomials $L_n^{(\alpha)}(x)$, for $\alpha = 3$ and $n = 0, 1, 2, 3, 4, 5$.

Figure 2.3.: Associated Laguerre Polynomials

Lemma 2.3.5 (Leibniz Rule) *If we have n-times differentiable functions f and g, then the n-th derivative of the product $f \cdot g$ is given by*

$$(f \cdot g)^{(n)} = \sum_{j=0}^{n} \binom{n}{j} f^{(j)} g^{(n-j)},$$

where $\binom{n}{j}$ is the binomial coefficient.

For more detail refer to the Olver [69, p. 318]. Applying the Leibniz rule for differentiation of products gives the following representation of associated Laguerre polynomials

$$L_n^{(\alpha)}(x) = \sum_{j=0}^{n} \frac{1}{j!} \binom{n+\alpha}{n-j} (-x)^j. \tag{2.34}$$

Setting $\alpha = 0$ results $L_n^{(0)}(x) = L_n(x)$, see Figure (2.6a). These polynomials are the solution of the differential equation

$$xy'' + (\alpha + 1 - x)\, y' + ny = 0.$$

The set

$$\left\{ L_n^{(\alpha)}(x);\ n \in \mathbb{N},\ \alpha \in \mathbb{R} \right\}, \tag{2.35}$$

of associated Laguerre polynomials forms an orthogonal basis for $L^2(\mathbb{R}^+)$ with respect to the weight function $\mathrm{e}^{-x} x^{\alpha}$, i.e.

$$\int_0^{\infty} L_n^{(\alpha)}(x) L_m^{(\alpha)}(x) \mathrm{e}^{-x} x^{\alpha}\, \mathrm{d}x = \frac{\Gamma(n + \alpha + 1)}{n!} \delta_{n,m}. \tag{2.36}$$

2.3.6. GTO & ETO Radial Basis Functions

We identify two weighted versions of the associated Laguerre polynomials which are called in general, radial basis functions.

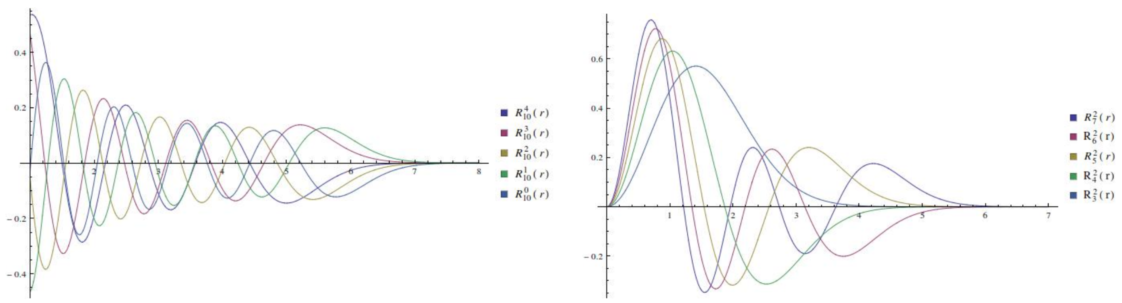
Definition 2.3.3 *We define*

$$R_k^l(r) = \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})}}\mathrm{e}^{-\frac{r^2}{2}} r^l L_{k-l-1}^{(l+\frac{1}{2})}(r^2),$$

for $r \in \mathbb{R}_0^+$ and $k,\ l \in \mathbb{N}_0$ where $k > l$, as the GTO radial basis functions.

Since these functions have a Gaussian pre factor and spherical harmonics basis functions are often called Gaussian type orbitals (GTO) in the quantum chemistry literature, see Ritchie [78, p. 24]. Applying the formula (2.34) for associated Laguerre polynomials in (2.3.3), brings the following representation

$$R_k^l(r) = \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})}}\mathrm{e}^{-\frac{r^2}{2}} r^l \sum_{j'=0}^{k-l-1} \frac{1}{j'!}\binom{k-\frac{1}{2}}{k-l-1-j'}(-r^2)^{j'}. \tag{2.37}$$



(a) The GTO radial functions $R_k^l(r)$, for $k = 10$ and $l = 0,\ 1,\ 2,\ 3,\ 4$.

(b) The GTO radial functions $R_k^l(r)$, for $l = 2$ and $k = 3,\ 4,\ 5,\ 6,\ 7$.

Figure 2.4.: GTO Radial Functions

Now in the following lemma, we show the orthogonality of the GTO radial functions with respect to the weight function r^2.

Lemma 2.3.6 *For each $r \in \mathbb{R}_0^+$ and $k, l \in \mathbb{N}_0$ where $k > l$, we have*

$$\int_0^\infty R_k^l(r) R_{k'}^l(r) r^2 \,\mathrm{d}r = \delta_{k,k'}.$$

Proof. Applying Definition 2.3.3, causes to have

$$\int_0^\infty R_k^l(r) R_{k'}^l(r) r^2 \,\mathrm{d}r = \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})} \times \frac{2(k'-l-1)!}{\Gamma(k'+\frac{1}{2})}} \times \int_0^\infty \mathrm{e}^{-r^2} r^{2l} L_{k-l-1}^{l+1/2}(r^2) L_{k'-l-1}^{l+1/2}(r^2) r^2 \,\mathrm{d}r.$$

Substituting the variable r^2 by x, gives

$$\int_0^\infty R_k^l(r) R_{k'}^l(r) r^2 \,\mathrm{d}r = \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})} \times \frac{2(k'-l-1)!}{\Gamma(k'+\frac{1}{2})}} \times \int_0^\infty \mathrm{e}^{-x} x^l L_{k-l-1}^{l+1/2}(x) L_{k'-l-1}^{l+1/2}(x) x \,\frac{\mathrm{d}x}{2\sqrt{x}}.$$

Hence,

$$\begin{aligned}\int_0^\infty \mathrm{e}^{-x} x^l L_{k-l-1}^{l+1/2}(x) L_{k'-l-1}^{l+1/2}(x) x \frac{\mathrm{d}x}{2\sqrt{x}} &= \frac{1}{2}\int_0^\infty \mathrm{e}^{-x} L_{k-l-1}^{l+1/2}(x) L_{k'-l-1}^{l+1/2}(x) x^{l+1/2}\,\mathrm{d}x \\ &= \frac{\Gamma\left(k-l-1+l+1/2+1\right)}{2(k-l-1)!}\delta_{k-l-1,k'-l-1} \\ &= \frac{\Gamma\left(k+1/2\right)}{2(k-l-1)!}\delta_{k,k'}. \ \square\end{aligned}$$

In analogy to the GTO radial basis functions, we define another orthogonal radial basis functions.

Definition 2.3.4 *We define*

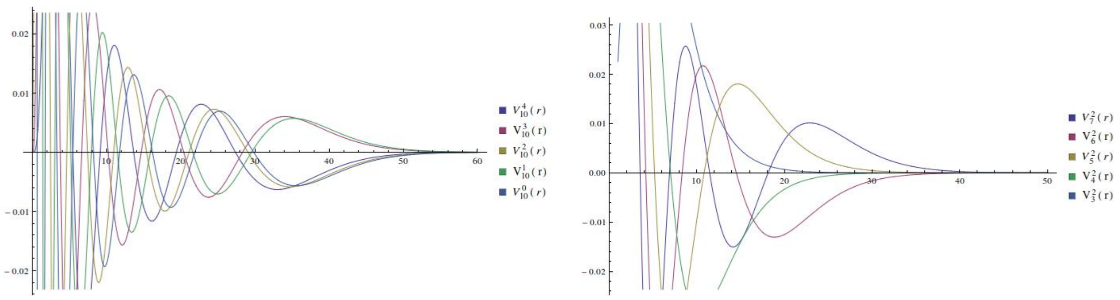
$$V_k^l(r) = \sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)}}\mathrm{e}^{-\frac{r}{2}} r^l L_{k-l-1}^{(2l+2)}(r),$$

for $r \in \mathbb{R}_0^+$ *and* $k,\ l \in \mathbb{N}_0$ *where* $k > l$*, as the ETO radial functions.*

These functions in quantum mechanics correspond to certain Coulomb potential problems and in quantum chemistry are often called exponential type orbitals (ETO) to represent the electrostatic properties of proteins, see Ritchie [78, 2.101, p. 25].

Using the associated Laguerre polynomials in (2.34), we have the following representation for ETO radial basis functions

$$V_k^l(r) = \sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)}}\mathrm{e}^{-\frac{r}{2}} r^l \sum_{j'=0}^{k-l-1} \frac{1}{j'!}\binom{k+l+1}{k-l-1-j'}(-r)^{j'}. \tag{2.38}$$



(a) The ETO radial functions $V_k^l(r)$, for $k = 10$ and $l = 0,\ 1,\ 2,\ 3,\ 4$.

(b) The ETO radial functions $V_k^l(r)$, for $l = 2$ and $k = 3,\ 4,\ 5,\ 6,\ 7$.

Figure 2.5.: ETO Radial Functions

Now in the following lemma, we show the ETO radial functions are orthogonal with respect to a weight function r^2.

Lemma 2.3.7 *We have*

$$\int_0^\infty V_k^l(r)\, V_{k'}^l(r) r^2\,\mathrm{d}r = \delta_{k,k'},$$

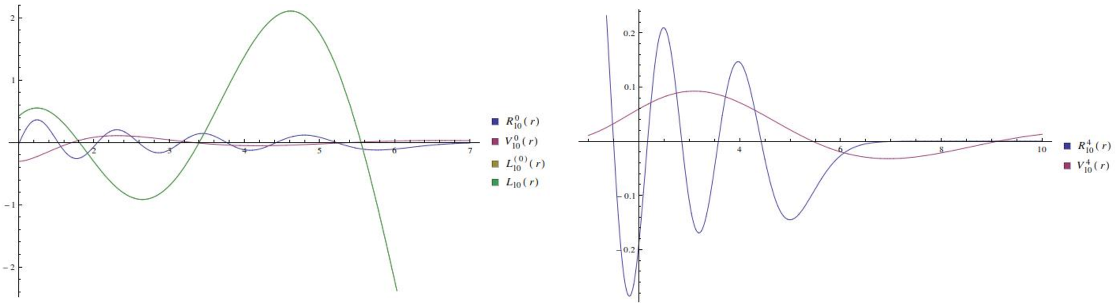
where $r \in \mathbb{R}_0^+$*,* $l,\ k,\ k' \in \mathbb{N}_0$ *and* $k,\ k' > l$*.*

Proof. By (2.38), we have

$$\int_0^\infty V_k^l(r)\, V_{k'}^l(r) r^2\, \mathrm{d}r = \sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)} \times \frac{(k'-l-1)!}{\Gamma(k'+l+2)}} \times \int_0^\infty \mathrm{e}^{-r} r^{2l} L_{k-l-1}^{(2l+2)}(r) L_{k'-l-1}^{(2l+2)}(r) r^2\, \mathrm{d}r.$$

Now using the orthogonality of associated Laguerre polynomials in (2.36), gives

$$\int_0^\infty \mathrm{e}^{-r} r^{2l+2} L_{k-l-1}^{(2l+2)}(r) L_{k'-l-1}^{(2l+2)}(r)\, \mathrm{d}r = \frac{\Gamma(k+l+2)}{(k-l-1)!} \delta_{k,k'}. \ \Box$$



(a) Comparison of the functions $R_{10}^0(r)$, $V_{10}^0(r)$, $L_{10}^{(0)}(r)$ & $L_{10}(r)$.

(b) In the above figure, we can see $R_{10}^4(r)$ and $V_{10}^4(r)$.

Figure 2.6.: Comparision of the GTO and ETO radial functions.

2.3.7. GTO & ETO Spherical Polar Radial Basis Functions

In this section, we introduce GTO and ETO spherical polar radial functions. To prove the GTO and ETO spherical polar radial functions yield an orthonormal basis for $L^2(\mathbb{R}^3)$, we shall briefly review some basic concepts related to the theory of Hilbert space. We are not trying to give a complete development but rather review the basic lemmas and theorems mostly without proof and finally we are able to prove that these functions constitute bases for square integrable functions on $\mathbb{R}^3$.

In the following lemma, we remind the "Bessel's inequality" which will be used in the proof of the next lemma. You can find a proof for the Bessel's inequality in Robinson's book [84, Corollary 5.11]

Lemma 2.3.8 (Bessel's inequality) *If $\{f_n\}_{n\in\mathbb{N}}$ is an orthonormal set in an inner product space* X*, then for any $f \in$* X*, we have*

$$\sum_{n=1}^{\infty} |\langle f, f_n\rangle|^2 \leq \|f\|^2 .$$

In the following lemma, the necessary and sufficient condition for the convergence of an orthonormal set in a Hilbert space is explained.

Lemma 2.3.9 *Let H be a Hilbert space and $\{f_n\}_{n\in\mathbb{N}}$ be an orthonormal set in H. Then the series $\sum_{n=1}^{\infty} c_n f_n$ converges, if and only if, $\sum_{n=1}^{\infty} |c_n|^2 < \infty$.*

Proof. Suppose $\{f_n\}_{n\in\mathbb{N}}$ be an orthonormal set in the Hilbert space H and $f = \sum_{n=1}^{\infty} c_n f_n$. For the natural numbers $k \leq n$, we have

$$\langle \sum_{n=1}^{\infty} c_n f_n, f_k \rangle = \sum_{n=1}^{\infty} c_n \langle f_n, f_k \rangle = f_k.$$

Letting $n \to \infty$ and using the continuity of the inner product, we obtain

$$\langle f, f_k \rangle = \lim_{n\to\infty} c_k = c_k.$$

Hence by Bessel's inequality, we have

$$\sum_{k=1}^{\infty} |c_k|^2 = \sum_{k=1}^{\infty} |\langle f, f_k \rangle|^2 \leq \|f\|^2 < \infty.$$

Conversely, we assume $\sum_{n=1}^{\infty} |c_n|^2 < \infty$. We set $f_n = \sum_{i=1}^{n} c_i f_i$. By Pythagoras' Theorem for $n > m$ in $\mathbb{N}$, we have

$$\|f_n - f_m\|^2 = \left\| \sum_{i=m+1}^{n} c_i f_i \right\|^2 = \sum_{i=m+1}^{n} |c_i|^2 .$$

By the assumption $\sum_{i=1}^{\infty} |c_i|^2 < \infty$, the sequence of partial sums is Cauchy and so we can make the right hand side arbitrary small, hence $\{f_n\}_{n\in\mathbb{N}}$ is a Cauchy sequence in a Hilbert space H and it converges to some point of H. □

Corollary 2.3.1 *Let H be a Hilbert space and $\{f_n\}_{n\in\mathbb{N}}$ be an orthonormal set in H, then for any $f \in H$, the series $\sum_{n=1}^{\infty} \langle f, f_n \rangle f_n$ converges.*

This leads us to the following proposition of the Robinson's book [84, Proposition 5.14]:

Proposition 2.3.1 *Let $\{f_n\}_{n\in\mathbb{N}}$ be an orthonormal set in a Hilbert space H, then the following assertions are equivalent.*

1. *$\langle f, f_n \rangle = 0$, for all $n \in \mathbb{N}$ implies that $f = 0$.*

2. *$\{f_n\}_{n\in\mathbb{N}}$ is an orthonormal basis for H.*

3. *$f = \sum_{n=1}^{\infty} \langle f, f_n \rangle f_n$, for all $f \in H$.*

4. $\|f\|^2 = \sum_{n=1}^{\infty} |\langle f, f_n\rangle|^2$, *for all* $f \in H$.

Now we identify an orthonormal basis for $L^2(\mathbb{R}^3)$. The first point in our work here is transferring the Cartesian coordinate system to spherical coordinate system, in other words, each point $\mathbf{x} \in \mathbb{R}^3$ is written as

$$\mathbf{x} = r\mathbf{u}; \qquad r = \|\mathbf{x}\|_2 \text{ and } \mathbf{u} = (\theta, \phi) \in \mathbb{S}^2, \tag{2.39}$$

where $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi)$. For the functions $f(\mathbf{x})$ and $g(\mathbf{x})$ of the Hilbert space $L^2(\mathbb{R}^3)$, we have

$$\text{For all } f, g \in L^2(\mathbb{R}^3); \qquad \langle f, g\rangle = \int_{\mathbb{R}^+}\int_{\mathbb{S}^2} f(r\mathbf{u})\overline{g(r\mathbf{u})}r^2 \,\mathrm{d}\mathbf{u}\,\mathrm{d}r. \tag{2.40}$$

Lemma 2.3.10 *The set* $\left\{R_k^l(r)\, Y_l^m(\mathbf{u});\ k,\ l,\ |m| \in \mathbb{N}_0,\ k > l \geq |m| \geq 0\right\}$ *where* $R_k^l(r)$*s are the GTO radial basis functions and* $Y_l^m(\mathbf{u})$*s are spherical harmonics form an orthonormal basis for* $L^2(\mathbb{R}^3)$.

Proof. At first we show this is an orthonormal set. We have

$$\begin{aligned}
\langle R_k^l(r)\, Y_l^m(\mathbf{u}), R_{k'}^{l'}(r)\, Y_{l'}^{m'}(\mathbf{u})\rangle &= \int_0^\infty \int_{\mathbb{S}^2} R_k^l(r)\, Y_l^m(\mathbf{u}) \cdot R_{k'}^{l'}(r)\, \overline{Y_{l'}^{m'}(\mathbf{u})}\, r^2 \,\mathrm{d}\mathbf{u}\,\mathrm{d}r \\
&= \int_0^\infty R_k^l(r) R_{k'}^{l'}(r) \left(\int_{\mathbb{S}^2} Y_l^m(\mathbf{u})\, \overline{Y_{l'}^{m'}(\mathbf{u})}\,\mathrm{d}\mathbf{u}\right) r^2 \,\mathrm{d}r \\
&= \int_0^\infty R_k^l(r) R_{k'}^{l'}(r) \left(\delta_{l,l'}\delta_{m,m'}\right) r^2 \,\mathrm{d}r \\
&= \delta_{k,k'}\delta_{l,l'}\delta_{m,m'}.
\end{aligned}$$

So the set $\left\{R_k^l(r)\, Y_l^m(\mathbf{u})\right\}_{klm}$ is an orthonormal set in the Hilbert space $L^2(\mathbb{R}^3)$ and by the 1sh part of Proposition 2.3.1, we prove this is an orthonormal basis for $L^2(\mathbb{R}^3)$. If we assume for all integers k, l and m where $k > l \geq |m| \geq 0$,

$$\langle f(r\mathbf{u}), R_k^l(r)\, Y_l^m(\mathbf{u})\rangle = 0,$$

then we have

$$\int_0^\infty \int_{\mathbb{S}^2} f(r\mathbf{u})\overline{R_k^l(r)\, Y_l^m(\mathbf{u})}r^2 \,\mathrm{d}\mathbf{u}\mathrm{d}r = 0.$$

But

$$\begin{aligned}
0 &= \int_0^\infty \int_{\mathbb{S}^2} f(r\mathbf{u}) R_k^l(r)\, \overline{Y_l^m(\mathbf{u})}r^2 \,\mathrm{d}\mathbf{u}\mathrm{d}r \\
&= \int_{\mathbb{S}^2} \left(\int_0^\infty f(r\mathbf{u}) R_k^l(r) r^2 \mathrm{d}r\,\mathrm{d}r\right) \overline{Y_l^m(\mathbf{u})}\,\mathrm{d}\mathbf{u},
\end{aligned}$$

and since spherical harmonics are an orthogonal basis for $L^2(\mathbb{S}^2)$, hence the coefficients are zero, i.e.

$$\left(\int_0^\infty f(r\mathbf{u}) R_k^l(r) r^2 \,\mathrm{d}r\right) = 0.$$

Also we know radial basis functions are weighted version of associated Laguerre polynomials and since associated Laguerre polynomials form a basis for $L^2(\mathbb{R}^+)$, hence we have $f = 0$. □

Definition 2.3.5 *We call the set*

$$\left\{ R_k^l(r)\, Y_l^m(\mathbf{u});\ k,\ l,\ |m| \in \mathbb{N}_0,\ k > l \geq |m| \geq 0 \right\},$$

GTO spherical polar radial basis functions.

These functions constitute an orthogonal basis for square integrable functions on $\mathbb{R}^3$, therefore each function f on $L^2(\mathbb{R}^3)$ can be written uniquely as

$$f(\mathbf{x}) = f(r\mathbf{u}) = \sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{f}_{klm} R_k^l(r) Y_l^m(\mathbf{u}), \tag{2.41}$$

where

$$\hat{f}_{klm} = \int_0^{\infty} \int_{\mathbb{S}^2} f(r\mathbf{u}) \overline{R_k^l(r) Y_l^m(\mathbf{u})} r^2 \, \mathrm{d}\mathbf{u} \mathrm{d}r, \tag{2.42}$$

are called GTO spherical polar radial Fourier coefficients. Since $R_k^l\,(r)$s are real valued functions, therefore we have

$$\hat{f}_{klm} = \int_0^{\infty} \int_{\mathbb{S}^2} f(r\mathbf{u}) R_k^l(r) \overline{Y_l^m(\mathbf{u})} r^2 \, d\mathbf{u} \mathrm{d}r. \tag{2.43}$$

Now we introduce another orthonormal basis for $L^2(\mathbb{R}^3)$.

Definition 2.3.6 *We call the set*

$$\left\{ V_k^l(r)\, Y_l^m(\mathbf{u});\ k,\ l,\ m \in \mathbb{N}_0,\ k > l \geq |m| \geq 0 \right\},$$

ETO spherical polar radial functions where $V_k^l(r)$s are ETO radial basis functions and $Y_l^m(\mathbf{u})$s are spherical harmonics.

Now in the following lemma we show that ETO spherical polar radial functions are an orthonormal basis for $L^2(\mathbb{R}^3)$.

Lemma 2.3.11 *The set $\left\{ V_k^l(r)\, Y_l^m(\mathbf{u});\ k,\ l,\ m \in \mathbb{N}_0,\ k > l \geq |m| \geq 0 \right\}$ of ETO pherical polar radial functions constitute an orthonormal basis for $L^2(\mathbb{R}^3)$.*

Proof. At first we show ETO spherical polar radial functions are orthonormal. We have

$$\begin{aligned}
\langle V_k^l(r)\, Y_l^m(\mathbf{u}),\, V_{k'}^{l'}(r)\, Y_{l'}^{m'}(\mathbf{u}) \rangle &= \int_0^{\infty} \int_{\mathbb{S}^2} V_k^l(r)\, Y_l^m(\mathbf{u}) \cdot V_{k'}^{l'}(r) \overline{Y_{l'}^{m'}(\mathbf{u})} r^2 \, \mathrm{d}\mathbf{u} \mathrm{d}r \\
&= \int_0^{\infty} V_k^l(r)\, V_{k'}^{l'}(r) r^2 \left(\int_{\mathbb{S}^2} Y_l^m(\mathbf{u}) \overline{Y_{l'}^{m'}(\mathbf{u})} \, \mathrm{d}\mathbf{u} \right) \mathrm{d}r \\
&= \int_0^{\infty} V_k^l(r)\, V_{k'}^{l'}(r) r^2 \delta_{l,l'} \delta_{m,m'} \, \mathrm{d}r \\
&= \delta_{k,k'} \delta_{l,l'} \delta_{m,m'}.
\end{aligned}$$

Therefore the ETO spherical polar radial function constitute an orthonormal set in the Hilbert space $L^2(\mathbb{R}^3)$ and by the 1sh part of Proposition 2.3.1, we prove this set is an orthonormal basis for $L^2(\mathbb{R}^3)$. If we assume for all integers k, l and m where $k > l \geq |m| \geq 0$,

$$\langle f(r\mathbf{u}),\, V_k^l(r)\, Y_l^m(\mathbf{u})\rangle = 0,$$

then we have

$$\int_0^\infty \int_{\mathbb{S}^2} f(r\mathbf{u})\, \overline{V_k^l(r)\, Y_l^m(\mathbf{u})} r^2 \,\mathrm{d}\mathbf{u}\mathrm{d}r = 0,$$

but since

$$\begin{aligned} 0 &= \int_0^\infty \int_{\mathbb{S}^2} f(r\mathbf{u})\, V_k^l(r)\, \overline{Y_l^m(\mathbf{u})} r^2 \,\mathrm{d}\mathbf{u}\mathrm{d}r \\ &= \int_{\mathbb{S}^2} \left(\int_0^\infty f(r\mathbf{u})\, V_k^l(r) r^2 \,\mathrm{d}r \right) \overline{Y_l^m(\mathbf{u})}\,\mathrm{d}\mathbf{u}, \end{aligned}$$

and spherical harmonics are an orthogonal basis for $L^2(\mathbb{S}^2)$, hence the coefficients should be zero, i.e.

$$\left(\int_0^\infty f(r\mathbf{u})\, V_k^l(r) r^2 \,\mathrm{d}r \right) = 0.$$

Also we know radial basis functions are weighted version of the associated Laguerre polynomials and since associated Laguerre polynomials form a basis for $L^2(\mathbb{R}^+)$, hence the function $f = 0$. $\square$

Here we illustrate an interpretation of the GTO and ETO spherical polar radial basis functions. From physical point of view, an atomic orbital is a mathematical function that can be applied to compute the probability of finding any electron of an atom in any specific region around the atom's nucleus. The simplest case is considering an atom with one electron which is called hydrogen like orbital. So atomic orbitals can be the hydrogen like orbitals which are the exact solutions to the Schrödinger equation. The Schrödinger equation for the hydrogen atom is written as

$$\mathcal{S}_{klm}(r\mathbf{u}) = N_{kl}\mathrm{e}^{-\rho/2}\rho^l L_{k-l-1}^{(2l+1)}(\rho), \tag{2.44}$$

where N_{kl} are the normalization factor and ρ is a scaled distance, cf. Ritchie [78, p. 25, Equation 2.102]. Alternatively, atomic orbitals refer to functions that depend on the coordinates of one electron (hydrogen like orbitals), are also used as the starting point to approximate radial functions, for example here $R_k^l(r)$ and $V_k^l(r)$, that depend on the simultaneous coordinates of all the electrons in an atom or molecule. The coordinate systems for atomic orbitals are usually chosen spherical coordinates (r, θ, ϕ). The advantage of spherical coordinates is that an orbital wave function is a product of radial functions (here $R_k^l(r)$ or $V_k^l(r)$) by spherical harmonics $Y_l^m(\theta, \phi)$ for each $k,\ l$ and $m \in \mathbb{N}_0$ with the condition $k > l \geq |m| \geq 0$ where the integers $k,\ l$ and m are called the quantum numbers.

There are typically three mathematical forms for the radial basis functions which can be chosen as a starting point for the computation of the properties of atoms and hence molecules with many electrons. According to the mentioned three types of radial basis function, we have three types of orbitals, i.e.

1. Gaussian Type Orbital (GTO): The form of the Gaussian type orbital has no radial nodes and decays as $\mathrm{e}^{-(\text{distance})^2}$, see Definition 2.3.5 and Lemma 2.3.10.

2. Exponential Type Orbital (ETO): The hydrogen like atomic orbitals are derived from the exact solution of the Schrödinger Equation for one electron and a nucleus. The part of the function that depends on the distance from the nucleus has radial nodes and decays as $\mathrm{e}^{-(\text{constant}\cdot\text{distance})}$, see Definition 2.3.6.

3. The Slater type Orbital (STO): STO is a form without radial nodes but decays from the nucleus as does the hydrogen like orbital. In this work we are not going to describe about this group of orbitals and only for more information we remind the STO.

For more details refer to the Subsection 2.3.6 and also [70]. In modern computational chemistry and quantum mechanics, computations are typically performed within a finite set of GTO or ETO spherical polar radial basis functions to create the atomic orbitals. In most literatures, the GTO or the ETO spherical polar radial basis functions and atomic orbital are used interchangeably although it should be noted that these basis functions are not actually the exact atomic orbitals due to approximation and simplifications of their analytic formulas, for further information see R. M. Balabin [9].

2.3.8. Bessel Functions

The function

$$J_v(w) = (w/2)^v \sum_{k=0}^{\infty} \frac{(-1)^k (w/2)^{2k}}{k!\,(v+k+1)}, \tag{2.45}$$

is called the *general Bessel function of degree v and complex argument w*. Also

$$j_l(w) = \sqrt{\frac{\pi}{2w}}\, J_{l+1/2}(w), \tag{2.46}$$

is called *spherical Bessel function of integer degree l*. For more details see [78, p. 25-27]. Spherical Bessel functions satisfy the orthogonality condition

$$\int_0^{\infty} j_l\,(\beta r)\, j_l(\beta r')\beta^2 \,\mathrm{d}\beta = \frac{\pi}{2r}\delta_{rr'}, \tag{2.47}$$

cf. Gottfried [38] or Ritchie [78, p. 27, Equation 2.112]. The *spherical Bessel transform* of a function $f(r)$ is defined as

$$\hat{f}_l(\beta) = \sqrt{\frac{2}{\pi}} \int_0^{\infty} f(r) j_l(\beta r) r^2 \,\mathrm{d}r, \tag{2.48}$$

where by (2.47),

$$f(r) = \sqrt{\frac{2}{\pi}} \int_0^{\infty} \hat{f}_l(\beta) j_l(\beta r) \beta^2 \,\mathrm{d}\beta \tag{2.49}$$

and is called the *inverse spherical Bessel transform.*

2.3.9. Wigner D-Functions

We consider the Hilbert space $L^2(SO(3))$ with the following inner product

$$\langle f_1, f_2 \rangle = \int_{SO(3)} f_1(\mathbf{R})\overline{f_2(\mathbf{R})}\, \mathrm{d}\mathbf{R} = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} f_1\left(\mathbf{R}\left(\alpha,\beta,\gamma\right)\right)\overline{f_2\left(\mathbf{R}\left(\alpha,\beta,\gamma\right)\right)} \times \sin\beta\, \mathrm{d}\alpha\, \mathrm{d}\beta\, \mathrm{d}\gamma, \tag{2.50}$$

where f_1 and $f_2 \in L^2(SO(3))$. We are going to define an orthogonal system in $L^2(SO(3))$, related to the above inner product.

Definition 2.3.7 (Wigner D-function) *Let $l \in \mathbb{N}_0$ and $m,\ m' = -l, \ldots,\ l$. We define*

$$D_l^{mm'}\left(\mathbf{R}\left(\alpha,\beta,\gamma\right)\right) = \mathrm{e}^{-\mathrm{i}m\alpha}\mathrm{e}^{-\mathrm{i}m'\gamma} d_l^{mm'}\left(\cos\beta\right),$$

where

$$d_l^{mm'}(x) = \frac{(-1)^{l-m}}{2^l}\sqrt{\frac{(l+m)!\,(1-x)^{m'-m}}{(l-m)!\,(l-m')!\,(l+m')!}}\frac{\mathrm{d}^{\mathrm{l-m}}}{\mathrm{d}x^{l-m}}\left(\frac{(1+x)^{m'+l}}{(1-x)^{m'-l}}\right),$$

respectively as Wigner D-functions and Wigner d-functions of degree l, and m, m'.

Note that in some literature, Wigner D-functions are called generalized spherical harmonics and also Wigner d-functions are called generalized associated Legendre functions, see Hielscher et al. [47]. According to our requirement we utilize the above definition, but in general Wigner D-functions are defined as the representative function of the irreducible unitary representation of the rotation group $SO(3)$, for more details see Vollrath [96]. Wigner D-functions satisfy the following property

$$D_l^{mm'}\left(\mathbf{R}\mathbf{R}'\right) = \sum_{n=-l}^{l} D_l^{mn}\left(\mathbf{R}\right) D_l^{nm'}\left(\mathbf{R}'\right). \tag{2.51}$$

Also Wigner D-functions satisfy the following orthogonality condition

$$\int_{SO(3)} D_l^{mm'}\left(\mathbf{R}\right)\overline{D_{l'}^{nn'}\left(\mathbf{R}\right)}\,\mathrm{d}\mathbf{R} = \frac{8\pi^2}{2l+1}\delta_{ll'}\delta_{mm'}\delta_{nn'}. \tag{2.52}$$

2.3.10. Wigner 3-j Symbols

In literature, there are different ways to define the 3-j symbols $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$. Here we modify the 3−j symbols which are also called Wigner 3-j or 3-jm symbols.

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} := (-1)^{j_1-j_2-m_3}\sqrt{\Delta\left(j_1,j_2,j_3\right)} \times \sum_{t=t_{min}}^{t_{max}} \frac{(-1)^t}{z} \times \sqrt{(j_1+m_1)!\,(j_1-m_1)!\,(j_2+m_2)!\,(j_2-m_2)!\,(j_3+m_3)!\,(j_3-m_3)!}, \tag{2.53}$$

where

$$\Delta\left(j_1, j_2, j_3\right) = \frac{\left(j_1 + j_2 - j_3\right)!\left(j_1 - j_2 + j_3\right)!\left(-j_1 + j_2 + j_3\right)!}{\left(j_1 + j_2 + j_3 + 1\right)!}, \tag{2.54}$$

is called triangle coefficients and

$$\begin{aligned} z = t!\left(j_3 - j_2 + t + m_1\right)!\left(j_3 + j_1 + t - m_2\right)!\left(j_1 + j_2 - j_3 - t\right)!\left(j_1 - t - m_1\right)! \\ \times\left(j_2 - t + m_2\right)!. \end{aligned} \tag{2.55}$$

The sum is over all integers t for which $t_{min} = \max\left(0, j_2 - j_3 - m_2, j_1 + m_2 - j_3\right)$ and $t_{max} = \min\left(j_1 + j_2 - j_3, j_1 - m_1, j_2 + m_2\right)$.

The Wigner 3-j symbols are zero unless the following conditions are satiefied:

1. $m_1 + m_2 + m_3 = 0$.
2. $j_1 + j_2 + j_3$ is an integer number but if $m_1 = m_2 = m_3 = 0$, then $j_1 + j_2 + j_3$ is an odd integer number.
3. $0 \leq |m_i| \leq j_i$, for $i = 1,\ 2,\ 3$.
4. $|j_1 - j_2| \leq j_3 \leq j_1 + j_2$ (triangle inequality).

In the following equation which is called Gaunt's integral, we can see the relation between the 3-j symbols and spherical harmonics, i.e.

$$\begin{aligned} \int_{\mathbb{S}^2} Y_{l_1}^{m_1}(\theta, \phi)\, Y_{l_2}^{m_2}(\theta, \phi)\, Y_{l_3}^{m_3}(\theta, \phi) \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)}{4\pi}} \\ \times \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \end{aligned} \tag{2.56}$$

where l_1, l_2 and $l_3 \in \mathbb{Z}$.

CHAPTER 3

FTM ALGORITHM ON SHAPE & ELECTROSTATIC COMPLEMENTARITY

3.1. FTM Algorithm On Shape Complementarity

3.1.1. Introduction

We know proteins as special molecules are building blocks of our body cells. We know the problem of determining a relative motion $(\mathbf{R}, \mathbf{t})$ in $SE(3)$ for a pair of proteins or more and their compounds that form a stable complex, reproducible in nature is known as protein-protein docking, Bajaj [7]. In this section we present an overview on fast translational matching (FTM) on surface complementarity (SC), discussed by Bajaj, see e.g. [7] & [8] and Vollrath [96]. Here affinity functions are modeled in terms of Grant-Pickup's idea, cf. [41], to facilitate using FFT to efficiently solve the docking problem. For docking based shape complementarity, we maximize the overlap of the surface of molecule B with the complementarity space of molecule A.

3.1.2. Modeling for Molecular Shape

A protein is made up of a long chain of amino acids that each of them links to its neighbor via covalent bonds, see Figure 3.1. Generally in chemistry to each molecule that consists of amino $(-NH_2)$ and carboxylic acid $(-COOH)$ functional groups, along with a $(-R)$ groups which determine the type of amino acid, is said amino acid. The letter "R" is used as a sort of chemical variable. The stable balance of attractive and repulsive forces between atoms when they share electrons is known as covalent bonding, see Campbel et al. [18]. The Figure 3.2 shows a schematic picture of the structure of amino acid. There are twenty different types of amino acids found in proteins. Each has a different R-group. Protein size is usually measured in terms of the number of amino acids that comprise it. Proteins can range from fewer than 20 to more than 5000 amino acids in lengh, although an average protein is about 350 amino acid in length, cf. Tompa [91]. An average protein's molecule typically consists of hundreds of amino acids, thousands

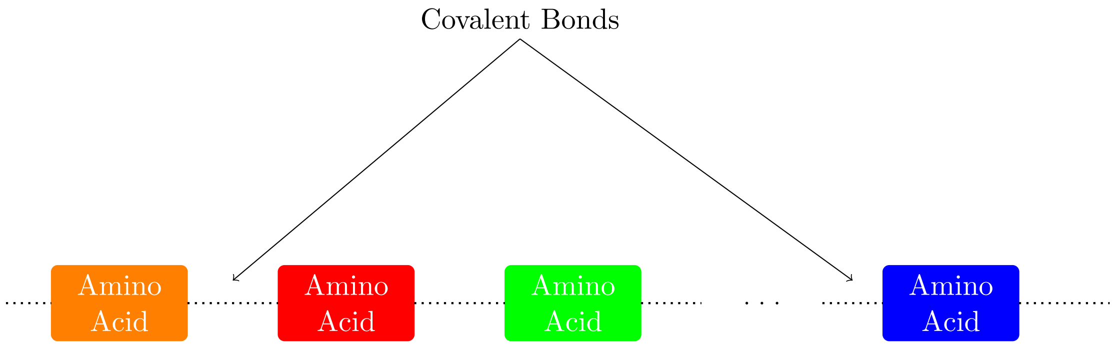


Figure 3.1.: The structure of protein can be considered as a chain of amino acids that each amino acid links to its neighbors through covalent bonds.

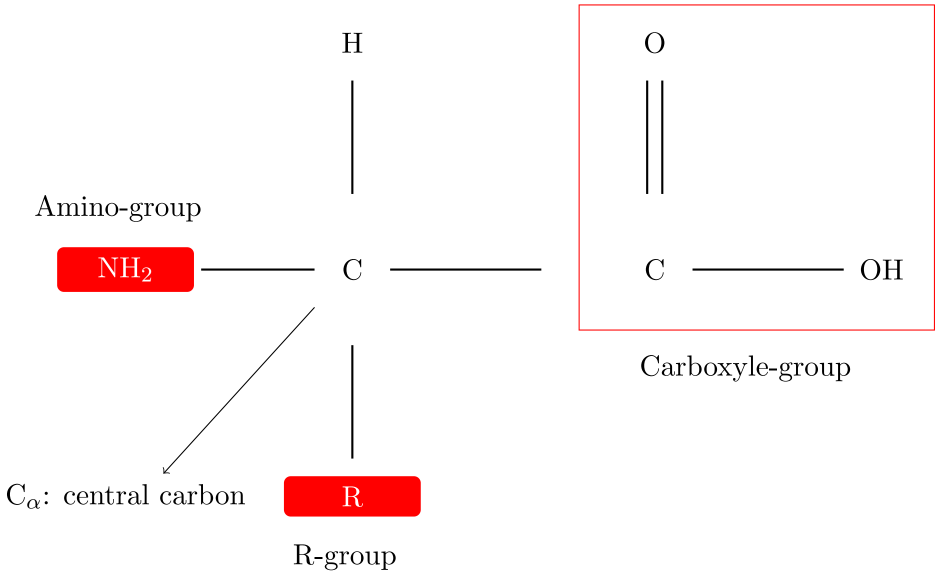


Figure 3.2.: The Structure of Amino Acid. To each molecule that consists of amino ($-NH_2$) and carboxylic acid ($-COOH$) functional groups along with a ($-R$) group which determine the type of amino acid is said amino acid.

of atoms and tens of thousands of electrons.

Now we have an imagination of protein as a molecule with special properties, so we should be able to define a mathematical model for a molecule and hence for a protein. In quantum mechanics, atoms are often treated as fixed arrangement of atomic nuclei surrounded by clouds of electrons, see Figure 3.3. Mathematically this may be represented as a superposition of electronic wave functions centred on the nuclear coordinates which together define a probabilistic model of how electrons are distributed through space. Therefore in a protein with at least hundreds of electrons to more than thousands of electrons, it is very expensive or even impossible to represent and compute the properties of protein using electronic wave functions, cf. Ritchie [78].

A common and straightforward way to display the structures of proteins and in general case molecules is simply to draw each atom of a molecule as a sphere of a given

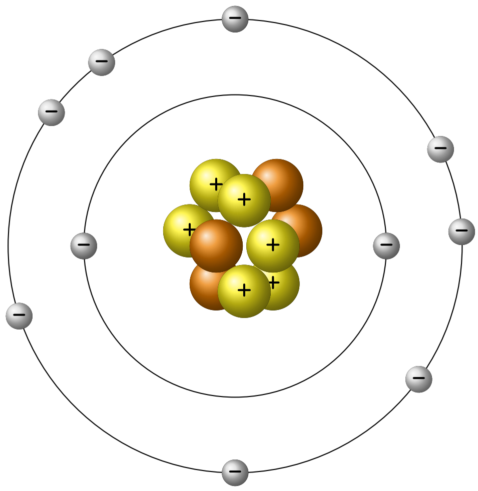


Figure 3.3.: Molecules are collection of atoms and atoms are often assumed as fixed arrangement of atomic nuclei surrounded by clouds of electrons.

radius which is called the van der Waals (VDW) radius, see Ritchie [78]. When the sphere of two atoms just touch, the interatomic distance is equal with the summation of the VDW radii of them. The boundary of the union of these spheres for a molecule is called the van der Waals surface (VDWS) of that molecule. A solvent molecule usually water that rolls over the VDWS of a molecule is called probe molecule. If this probe molecule is rolled over the VDWS without any penetration then the trace of the probe's centroid is called the solvent accessible surface (SAS). The volume bounded by the van der Waals surface and SAS was called by Ritchie the skin volume and plays a key role in docking calculations.

Grant and Pickup [41], in 1995 have shown an effective way to describe a molecule in terms of Gaussian density function. The overall matter of molecule M of N_{M} atoms can be represented by the sum of atomic densities

$$\rho(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{M}}} \alpha \mathrm{e}^{-\beta\left(\frac{\|\mathbf{x}\|_2^2}{r_j^2}\right)}, \tag{3.1}$$

where r_j is the van der Waals radius of the j-th atom and α and β are adjustable parameters, cf. Ritchie [78].

3.1.3. Affinity Functions in General

With inspiration of the Grant-Pickup's idea, see (3.1), for a representation of three-dimensional shape density of molecules, we define affinity functions for different properties of the two molecules that should be docked. The idea for affinity functions is the same for almost every property. Therefore we consider M as a molecule with N_{M} atoms and a desired property. The general affinity function is defined by

$$Q_{\mathrm{M}}^{\mathrm{Property}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{M}}} \gamma^{\mathrm{Property}}(\mathbf{x}_j)\kappa_{\mathcal{G}}^{j}\left(\mathbf{x} - \mathbf{x}_j\right), \tag{3.2}$$

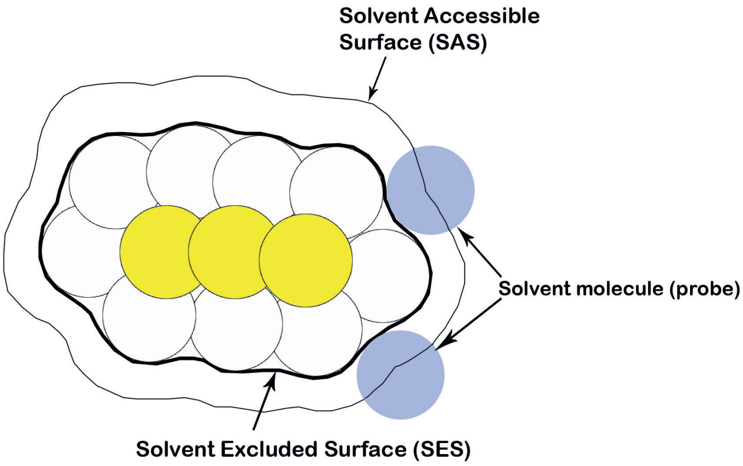


Figure 3.4.: Molecular Surfaces. The van der Waals surface (VDWS) of a molecule is the boundary of the union of spheres of the atoms in the molecule. The solvent molecule (probe) rolls over the molecule's van der Waals surface. The trace of the probe's centroid is called the solvent accessible surface (SAS) and the boundary of the volume which the probe can not penetrate is called solvent excluded surface (SES) or sometimes Connolly surface.

where $\mathbf{x}_j$ is the centre of the j-th atom, the function $\gamma^{\text{Property}}(\mathbf{x}_j)$ assigns weights to the j-th atom and

$$\kappa_{\mathcal{G}}^{j}(\mathbf{x}) = \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{x}\|_2^2}{r_j^2}\right)}, \tag{3.3}$$

is the Gaussian density function where r_j is the van der Waals radius of the j-th atom and β controls the sharpness of the Gaussian density function.

3.1.4. Shape Complementarity Score

For the shape based docking we always maximize the overlap of the surface of one molecule with the complementary space of the other molecule, therefore we define two skin regions and two core regions for the two supposed molecules A and B, i.e.

1. The surface skin of molecule B which is the VDWS of the molecule B.
2. The surface skin of molecule A defined by introducing a one-layer of pseudo-atoms on the VDWS of molecule A, for further information about pseudo atom see [64].
3. The atoms of molecule A and inner atoms of molecule B form the core regions, see Figure 3.5.

According to (3.2), we define our affinity functions for molecules A and B respectively by

$$Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{A}}} \gamma^{\mathrm{SC,A}}(\mathbf{x}_j)\kappa_{\mathcal{G}}^{j}(\mathbf{x}-\mathbf{x}_j), \tag{3.4}$$

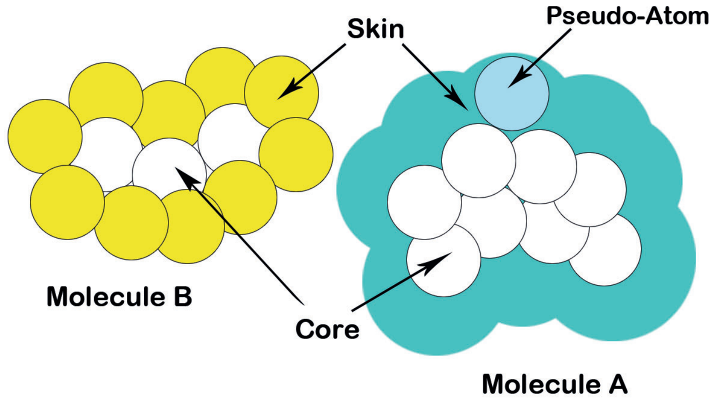


Figure 3.5.: This pictures shows skin and core regions in shape complementarity. For more details read the text.

and

$$Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{B}}} \gamma^{\mathrm{SC,B}}(\mathbf{x}_j)\kappa_{\mathcal{G}}^{j}(\mathbf{x}-\mathbf{x}_j). \tag{3.5}$$

Here we consider the shape as a property where the function $\gamma^{\mathrm{SC,A}}(\mathbf{x})$ assigns different values to the defined regions skin and core of the molecule A by

$$\gamma^{\mathrm{SC,A}}(\mathbf{x}) = \begin{cases} 1 & \text{if } \mathbf{x} \in \text{skin A} \\ \varrho \mathrm{i} & \text{if } \mathbf{x} \in \text{core A} \\ 0 & \text{otherwise,} \end{cases} \tag{3.6}$$

and $\varrho \gg 1$. Analogously we can define $\gamma^{\mathrm{SC,B}}(\mathbf{x})$.

Now we define the overlap of these two functions by

$$\mathcal{C}^{\mathrm{SC}}((\mathbf{R},\mathbf{t})) = \mathrm{Re}\int_{\mathbb{R}^3} Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) \cdot \mathcal{T}^{\mathbf{t}}\Lambda_{\mathbf{R}}\left(Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x})\right)\,\mathrm{d}\mathbf{x}. \tag{3.7}$$

For the next step, we need to find a fast algorithm to maximize the scoring function (3.7). Protein docking algorithms typically produce a set of candidate solutions and the scoring function is used to assess the goodness of the candidate solutions.

3.1.5. Fast Translational Matching Algorithm on Shape Complementarity

Here our goal is introducing an efficient algorithm to solve the docking problem, hence we need to compute the scoring function for certain number of different motions $(\mathbf{R},\mathbf{t}) \in SE(3)$. From (2.7) and (2.8), we have

- $\forall\,(\mathbf{R},\mathbf{t}) \in SE(3); \qquad (\mathbf{R},\mathbf{t}) = (\mathbb{I},\mathbf{t}) \circ (\mathbf{R},\mathbf{0}) = \mathcal{T}^{\mathbf{t}}\Lambda_{\mathbf{R}},$
- $\forall\,(\mathbf{R},\mathbf{t}) \in SE(3)$ and $\forall \mathbf{x} \in \mathbb{R}^3; \qquad (\mathbf{R},\mathbf{t}) \cdot \mathbf{x} = \mathbf{R}\mathbf{x} - \mathbf{t},$

Figure 3.6.: This is a picture of a particular affinity function $Q_{\mathrm{M}}^{\mathrm{SC}}(\mathbf{x})$ with $N_{\mathrm{M}} = 8$ and $\mathbf{x}_1 = (4.060, 7.307, 5.186)$, $\mathbf{x}_2 = (4.042, 7.776, 6.533)$, $\mathbf{x}_3 = (2.668, 8.426, 6.664)$, $\mathbf{x}_4 = (1.987, 8.438, 5.606)$, $\mathbf{x}_5 = (5.090, 8.827, 6.797)$, $\mathbf{x}_6 = (6.338, 8.761, 5.929)$, $\mathbf{x}_7 = (6.576, 9.758, 5.241)$, $\mathbf{x}_8 = (7.065, 7.759, 5.948)$ and $\gamma^{\mathrm{SC,M}}(\mathbf{x}_1) = \gamma^{\mathrm{SC,M}}(\mathbf{x}_2) = \ldots = \gamma^{\mathrm{SC,M}}(\mathbf{x}_8) = 1$.

therefore the scoring function (3.7) can be written as

$$\mathcal{C}^{\mathrm{SC}}\left((\mathbf{R}, \mathbf{t})\right) = \mathrm{Re} \int_{\mathbb{R}^3} Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) \cdot Q_{\mathrm{B}}^{\mathrm{SC}}\left(\mathbf{R}\mathbf{x} - \mathbf{t}\right) \, \mathrm{d}\mathbf{x}. \tag{3.8}$$

As a rigid body motion $(\mathbf{R}, \mathbf{t}) \in SE(3)$ has six degrees of freedom, the search space for the docking problem is six-dimensional. For each fixed rotation $\mathbf{R} \in SO(3)$, the scoring function $\mathcal{C}^{\mathrm{SC}}\left((\mathbf{R}, \mathbf{t})\right)$ is a correlation of affinity functions $Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x})$ and $Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x})$, and can be computed by NFFT and its adjoint, see e.g. [74], and also Lemma 2.3.2. Since for all favorable rotations $\mathbf{R} \in SO(3)$, we have to compute $\mathcal{C}^{\mathrm{SC}}\left((\mathbf{R}, \mathbf{t})\right)$, therefore different translations will be computed by NFFT, hence this approach in protein docking is called “Fast taranslational matching (FTM)” approach.

In the following we describe the needed modifications on the defined affinity functions in the fast translational matching approach.

First of all, we need to consider molecules A and B in the unit cube $[-\frac{1}{2}, \frac{1}{2}]^3$, thefore we compute the diameters

$$d_{\mathrm{A}} = \max \|\mathbf{x}_j - \mathbf{x}_k\|_2 \quad \text{where} \quad j, k \in \{1,\ 2,\ \ldots,\ N_{\mathrm{A}}\} \tag{3.9}$$

and

$$d_{\mathrm{B}} = \max \|\mathbf{x}_j - \mathbf{x}_k\|_2 \quad \text{where} \quad j, k \in \{1,\ 2,\ \ldots,\ \mathrm{N_B}\}, \tag{3.10}$$

for molecules A and B and also the centres of them by

$$\mathbf{c}_{\mathrm{A}} = \frac{1}{N_{\mathrm{A}}} \sum_{k=1}^{N_{\mathrm{A}}} \mathbf{x}_k \tag{3.11}$$

and

$$\mathbf{c}_{\mathrm{B}} = \frac{1}{N_{\mathrm{B}}} \sum_{k=1}^{N_{\mathrm{B}}} \mathbf{x}_k. \tag{3.12}$$

With having the molecules diameters and molecule centres, we can compute the modified atomic centres of the molecules A and B by

$$\mathbf{z}_j = \frac{\mathbf{x}_j - \mathbf{c}_{\mathrm{A}}}{2D}, \quad j = 1,\ 2,\ \ldots,\ N_{\mathrm{A}} \tag{3.13}$$

and

$$\mathbf{z}_j = \frac{\mathbf{x}_j - \mathbf{c}_{\mathrm{B}}}{2D}, \quad j = 1,\ 2,\ \cdots,\ N_{\mathrm{B}}, \tag{3.14}$$

where $D = \max\{d_{\mathrm{A}}, d_{\mathrm{B}}\} + \omega$. Adding ω to the maximum diameters ensures the outermost atoms are inside the unite cube, see Vollrath [96, 6.4, p. 103]. Now we have the relocated and scaled atomic centres and we have to scale the van der Waals radii of atoms by the factor $\frac{1}{2D}$ to adjust the atoms in the unit cube $[-\frac{1}{2}, \frac{1}{2}]^3$, i.e.

$$\kappa_{\mathcal{G}}^{j}(\mathbf{x}) = \mathrm{e}^{\beta\left(1 - \frac{\|\mathbf{x}\|_2^2}{r_j^2}\right)} \longmapsto \hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{x}) = \begin{cases} \kappa_{\mathcal{G}}^{j}(\frac{\mathbf{x}}{2D}) & \text{if} - D \le \|\mathbf{x}\|_\infty \le D \\ 0 & \text{otherwise.} \end{cases} \tag{3.15}$$

Now we approximate the Gaussian function in the unite cube as in the following:

$$\hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{x}) \approx \tilde{\kappa}_{\mathcal{G}}^{j}(\mathbf{x}) = \sum_{\mathbf{k} \in \mathcal{I}_n} \hat{h}_{\mathbf{k}} \mathrm{e}^{2\pi \mathrm{i} \mathbf{x} \cdot \mathbf{k}}, \tag{3.16}$$

where

$$\mathcal{I}_n = \left\{ \mathbf{k} \in \mathbb{Z}^3; \quad k \in \left[-\frac{n}{2}, \frac{n}{2}\right)^3,\ n \in 2\mathbb{N} \right\} \tag{3.17}$$

and

$$\hat{h}_{\mathbf{k}} = \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{x}) \mathrm{e}^{-2\pi \mathrm{i} \mathbf{x} \cdot \mathbf{k}} \, \mathrm{d}\mathbf{x} \tag{3.18}$$

are the Fourier coefficients. Now we have the following approximation of $\mathrm{Q}_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x})$ in the assumed unit cube by using (3.16). We have

$$\begin{aligned} \mathrm{Q}_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) \approx \tilde{\mathrm{Q}}_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) &= \sum_{j=1}^{N_{\mathrm{A}}} \gamma^{\mathrm{SC,A}}(\mathbf{z}_j) \tilde{\kappa}_{\mathcal{G}}^{j}(\mathbf{x} - \mathbf{z}_j) \\ &= \sum_{j=1}^{N_{\mathrm{A}}} \gamma^{\mathrm{SC,A}}(\mathbf{z}_j) \left(\sum_{\mathbf{k} \in \mathcal{I}_n} \hat{h}_{\mathbf{k}} \mathrm{e}^{2\pi \mathrm{i} (\mathbf{x} - \mathbf{z}_j) \cdot \mathbf{k}} \right) \\ &= \sum_{\mathbf{k} \in \mathcal{I}_n} \hat{h}_{\mathbf{k}} \alpha_{\mathbf{k}} e^{2\pi \mathrm{i} \mathbf{x} \cdot \mathbf{k}}, \end{aligned} \tag{3.19}$$

where

$$\alpha_{\mathbf{k}} = \sum_{j=1}^{N_{\mathrm{A}}} \gamma^{\mathrm{SC,A}}(\mathbf{z}_j)\mathrm{e}^{-2\pi\mathrm{i}\mathbf{z}_j\cdot\mathbf{k}}. \tag{3.20}$$

In this approximated affinity function, the fuction has been separated into a molecule independent part and molecule dependent part $\alpha_{\mathbf{k}}$. We will see the advantage of this separation. Also we have

$$Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{Rx}-\mathbf{t}) = \sum_{j=1}^{N_{\mathrm{B}}} \gamma^{\mathrm{SC,B}}(\mathbf{z}_j)\hat{\kappa}_{\mathcal{G}}^{j}\left((\mathbf{Rx}-\mathbf{t})-\mathbf{z}_j\right). \tag{3.21}$$

So for approximation of the affinity function $Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{Rx}-\mathbf{t})$, first of all we need to know the effect of a rotation $\mathbf{R} \in SO(3)$ on the Gaussian function $\hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{x}-\mathbf{z}_j)$. Since

$$\hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{Rx}-\mathbf{z}_j) = \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{R}^{\mathrm{t}}\mathbf{x}-\mathbf{z}_j\|_2^2}{r_j^2}\right)}, \tag{3.22}$$

and also from the Lemma 2.1.1, we know

$$\|\mathbf{R}^{\mathrm{t}}\mathbf{x}-\mathbf{z}_j\|_2^2 = \|\mathbf{R}\left(\mathbf{R}^{\mathrm{t}}\mathbf{x}-\mathbf{z}_j\right)\|_2^2. \tag{3.23}$$

Now by substituting (3.23) in (3.22), we have

$$\begin{aligned}\hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{Rx}-\mathbf{z}_j) &= \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{R}\left(\mathbf{R}^{\mathrm{t}}\mathbf{x}-\mathbf{z}_j\right)\|_2^2}{r_j^2}\right)}\\ &= \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{x}-\mathbf{Rz}_j\|_2^2}{r_j^2}\right)}\\ &= \hat{\kappa}_{\mathcal{G}}^{j}(\mathbf{x}-\mathbf{Rz}_j).\end{aligned} \tag{3.24}$$

Using the formulas (3.24) and (3.16), we can approximate the rotated and translated Gaussian functions by

$$\begin{aligned}\tilde{\kappa}_{\mathcal{G}}^{j}\left((\mathbf{Rx}-\mathbf{t})-\mathbf{z}_j\right) &= \tilde{\kappa}_{\mathcal{G}}^{j}\left((\mathbf{x}-\mathbf{t})-\mathbf{Rz}_j\right)\\ &= \sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}}\mathrm{e}^{2\pi\mathrm{i}((\mathbf{x}-\mathbf{t})-\mathbf{Rz}_j)\cdot\mathbf{k}}\\ &= \sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}}\mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}}\mathrm{e}^{-2\pi\mathrm{i}\mathbf{Rz}_j\cdot\mathbf{k}}.\end{aligned} \tag{3.25}$$

Now we are ready to approximate $Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{Rx}-\mathbf{t})$. So

$$\begin{aligned}\tilde{Q}_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{Rx}-\mathbf{t}) &= \sum_{j=1}^{N_{\mathrm{B}}} \gamma^{\mathrm{SC,B}}(\mathbf{z}_j)\tilde{\kappa}_{\mathcal{G}}^{j}\left((\mathbf{Rx}-\mathbf{t})-\mathbf{z}_j\right)\\ &= \sum_{j=1}^{N_{\mathrm{B}}} \gamma^{\mathrm{SC,B}}(\mathbf{z}_j)\left(\sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}}\mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}}\mathrm{e}^{-2\pi\mathrm{i}\mathbf{Rz}_j\cdot\mathbf{k}}\right)\\ &= \sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}}\beta_{\mathbf{k}}^{\mathbf{R}}\mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}},\end{aligned} \tag{3.26}$$

where

$$\beta_{\mathbf{k}}^{\mathbf{R}} = \sum_{j=1}^{N_{\mathrm{B}}} \gamma^{\mathrm{SC,B}}(\mathbf{z}_j) \mathrm{e}^{-2\pi \mathrm{i} \mathbf{R} \mathbf{z}_j \cdot \mathbf{k}}. \tag{3.27}$$

Similar to (3.19), this affinity function was separated into molecule independent part and also molecule dependent part $\beta_{\mathbf{k}}^{\mathbf{R}}$, which is also dependent on the rotations $\mathbf{R} \in SO(3)$.

Now we can approximate the scoring function (3.8) by

$$\begin{aligned}
\mathcal{C}^{\mathrm{SC}}\left((\mathbf{R},\mathbf{t})\right) &= \mathrm{Re} \int_{\mathbb{R}^3} Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) \cdot Q_{\mathrm{B}}^{\mathrm{SC}}\left(\mathbf{R}\mathbf{x} - \mathbf{t}\right) \, \mathrm{d}\mathbf{x} \\
&\approx \mathrm{Re} \int_{[-\frac{1}{2},\frac{1}{2}]^3} \tilde{\mathrm{Q}}_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x}) \cdot \tilde{\mathrm{Q}}_{\mathrm{B}}^{\mathrm{SC}}\left(\mathbf{R}^{\mathrm{t}}\mathbf{x} - \mathbf{t}\right) \, \mathrm{d}\mathbf{x} \\
&= \mathrm{Re} \int_{[-\frac{1}{2},\frac{1}{2}]^3} \sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}} \alpha_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}} \sum_{\mathbf{k}'\in\mathcal{I}_n} \hat{h}_{\mathbf{k}'} \beta_{\mathbf{k}'}^{\mathbf{R}} \mathbf{x} \mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}'} \, \mathrm{d}\mathbf{x} \\
&= \mathrm{Re} \left(\sum_{\mathbf{k}\in\mathcal{I}_n} \sum_{\mathbf{k}'\in\mathcal{I}_n} \hat{h}_{\mathbf{k}} \hat{h}_{\mathbf{k}'} \alpha_{\mathbf{k}} \beta_{\mathbf{k}'}^{\mathbf{R}} \mathrm{e}^{-2\pi\mathrm{i}\mathbf{t}\cdot\mathbf{k}'} \left(\int_{[-\frac{1}{2},\frac{1}{2}]^3} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}'} \, \mathrm{d}\mathbf{x} \right) \right).
\end{aligned} \tag{3.28}$$

We have $\int_{[-\frac{1}{2},\frac{1}{2}]^3} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}'} \, \mathrm{d}\mathbf{x} = \delta_{\mathbf{k}',-\mathbf{k}}$, so $\mathbf{k}' = -\mathbf{k}$, also since $\kappa_{\mathcal{G}}^{j}(\mathbf{x}) = \kappa_{\mathcal{G}}^{j}(-\mathbf{x})$, hence by (3.18) we get $\hat{h}_{\mathbf{k}} = \hat{h}_{-\mathbf{k}}$, therefore

$$\begin{aligned}
\mathcal{C}^{\mathrm{SC}}\left((\mathbf{R},\mathbf{t})\right) &\approx \mathrm{Re} \left(\sum_{\mathbf{k}\in\mathcal{I}_n} \sum_{\mathbf{k}'\in\mathcal{I}_n} \hat{h}_{\mathbf{k}} \hat{h}_{\mathbf{k}'} \alpha_{\mathbf{k}} \beta_{\mathbf{k}'}^{\mathbf{R}} \mathrm{e}^{-2\pi\mathrm{i}\mathbf{t}\cdot\mathbf{k}'} \delta_{\mathbf{k},\mathbf{k}'} \right) \\
&= \mathrm{Re} \left(\sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}}^2 \alpha_{\mathbf{k}} \beta_{-\mathbf{k}}^{\mathbf{R}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{t}\cdot\mathbf{k}} \right).
\end{aligned} \tag{3.29}$$

Finally we have an algorithm which is called fast translational matching (FTM) algorithm for our docking problem. For precomputed coefficients $\hat{h}_{\mathbf{k}}$, $\alpha_{\mathbf{k}}$ and $\beta_{-\mathbf{k}}^{\mathbf{R}}$, where $\alpha_{\mathbf{k}}$ and $\beta_{-\mathbf{k}}^{\mathbf{R}}$, are computed by NFFT and the computational complexity of them respectively are $\mathcal{O}\left(N_{\mathrm{A}} + n^3 \log n\right)$ and $\mathcal{O}\left(N_{\mathrm{B}} + n^3 \log n\right) N_{\mathbf{R}}^3$, this algorithm can be computed by NFFT, and the computational complexity of that is $\mathcal{O}\left(\left(N_{\mathbf{R}}^3 + n^3 \log n\right) N_{\mathbf{t}}^3\right)$, where $N_{\mathbf{R}}$ and $N_{\mathbf{t}}$ respectively denote the number of rotations and translations in one dimension.

If we compute the docking problem (3.8), directly without using the fast translational matching algorithm, the computational complexity in comparison, is very expensive, because the computational complexity for all required motions $(\mathbf{R},\mathbf{t}) \in SE(3)$, for $Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x})$, is N_{A} and similarly the computational complexity of $Q_{\mathrm{B}}^{\mathrm{SC}}\left(\mathbf{R}\mathbf{x} - \mathbf{t}\right)$, only for one motion $(\mathbf{R},\mathbf{t}) \in SE(3)$, is N_{B}, and hence the computational complexity for all required motions, i.e. $N_{\mathbf{R}}^3$ rotations and $N_{\mathbf{t}}^3$ translations is $N_{\mathrm{B}} N_{\mathbf{R}}^3 N_{\mathbf{t}}^3$, therefore the computational complexity of the straightforward docking approch is $N_{\mathrm{A}} N_{\mathrm{B}} N_{\mathbf{R}}^3 N_{\mathbf{t}}^3$.

Algorithm 1: FTM Algorithm on Shape Complementarity

Input:
n: The degree of Fourier approximation
N_{A} & N_{B}: The number of atomic coordinates of molecules A and B
A set of motions $(\mathbf{R}, \mathbf{t}) \in SE(3)$

foreach $\mathbf{x}_j$ *with* $j \in N_{\mathrm{A/B}}$ **do**
  Compute the modified atomic centers $\mathbf{z}_j^{\mathrm{A}}$ and $\mathbf{z}_j^{\mathrm{B}}$, respectively of (3.13) and (3.14).
end
foreach $\mathbf{k} \in \mathcal{I}_n$ **do**
  Compute coefficients $\hat{h}_{\mathbf{k}}$ of (3.18).
  Compute $\alpha_{\mathbf{k}}$ of (3.20) by NFFT.
  foreach *Rotation* $\mathbf{R} \in SO(3)$ **do**
    Compute $\beta_{-\mathbf{k}}^{\mathbf{R}}$ of (3.27) by NFFT.
  end
end
foreach *motion* $(\mathbf{R}, \mathbf{t}) \in SE(3)$ **do**
  Compute $\mathrm{Re}\left(\sum_{\mathbf{k} \in \mathcal{I}_n} \hat{h}_{\mathbf{k}}^2 \alpha_{\mathbf{k}} \beta_{-\mathbf{k}}^{\mathbf{R}} \mathrm{e}^{2\pi \mathrm{i} \mathbf{t} \cdot \mathbf{k}}\right)$ in (3.29) by NFFT.
end
Output: The solution of the docking problem.

Complexity: $\mathcal{O}\left(\left(N_{\mathbf{R}}^3 + n^3 \log n\right) N_{\mathbf{t}}^3\right)$ operations.

3.2. FTM Algorithm on a Simplified Model for Electrostatic Complementarity

3.2.1. Introduction

We know molecular docking is the study of how two or more molecular structures fit together best to make a complex, but from the physical point of view, the most precise way for studying the structure of matter is to apply quantum mechanics to the situations, therefore the interaction between two macromolecules could be realized by solving the combined Schrödinger equation of both systems. It is impossible to find an explicit solution for this difficult problem, although it is possible to find a numerical solution which is computationally too expensive to produce truly applied results, cf. Kaapro et al. [50]. Although there is no escape of some quantum phenomena, like covalent bonds between atoms and also Pauli exclusion principle (PEP) which states if the distance between two particles is very small, then they experience a strong repulsive force, we need to study the quality and quantity of forces between the interactive particles. Often forces are divided into five categories, for more details see A. Kaapro and J. Ojanen [50].

1. Forces with Electrostatic Origin

Forces with electrostatic origin are due to charges residing in the matter. The solid or liquid phases of matter for a molecule or atom are due to attractive forces between the molecules or atoms. If no attractive forces exist, then a collection of molecules or atoms would remain in the gas phases. The most common interactions are charge-charge, charge-dipole and dipole-dipole. These forces can be calculated by basic law of Coulomb. Coulombs's law states that the force acting between two point charges q_1 and q_2 separated by a distance r in a vacuum is

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}. \tag{3.30}$$

If the two charges have the same sign, either both positive or both negative, then $F > 0$ and the force is repulsive, see Figure 3.7. If the two charges are of opposing sign, then $F < 0$ and the force is attractive, see Figure 3.8. Note that, if the two charges are not in a vacuum but are instead separated by another medium then the force acting between them is reduced. Coulomb's law must be modified with the vacuum permittivity ϵ_0 replaced by the permittivity of the medium $\epsilon = \epsilon_0 \epsilon_R$ and hence

$$F = \frac{q_1 q_2}{4\pi\epsilon r^2}. \tag{3.31}$$

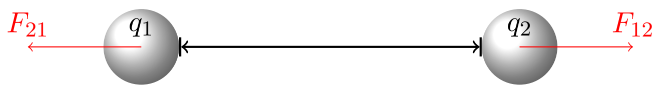


Figure 3.7.: Coulomb's Law: Repulsion. The vector F_{21} is the electrostatic force exprienced by q_1 and the vector F_{12} is the force exprienced by q_2. Here $q_1 q_2 > 0$, so the forces are repulsive and $|F_{12}| = |F_{21}|$.

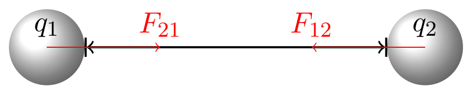


Figure 3.8.: Coulomb's Law: Attraction. Here $q_1 q_2 < 0$, so the kind of forces are attraction and $|F_{12}| = |F_{21}| = k\frac{|q_1 q_2|}{r^2}$ where r is the distance between the two charges q_1 and q_2.

The potential energy resulting from the electrostatic interaction between two charges q_1 and q_2 is

$$\Phi = k\frac{q_1 q_2}{r}, \tag{3.32}$$

where $k = 1/(4\pi\epsilon_0)$ and Φ is equivalent to the work that must be done to bring the two charges together from an infinite separation.

Dependencies on the distance of these interactions with electrostatic origin are as the following:

- Charge-Charge (ion-ion) $\propto 1/r$
- Charge-Dipole (ion-dipole) $\propto 1/r^2$

- Dipole-Dipole (hydrogen bonds) $\propto 1/r^3$

2. Forces with Electrodynamic Origin

In addition to electrostatic forces, there exist forces with electrodynamic background. Atoms, those are normally electrically neutral may develop an induced dipole moment when an external electric field is applied. The most common interactions are dispersion forces and induced dipole-induced dipole. Dispersion forces are attractive forces that arise as a result of temporary dipoles induced in atoms and can be categorized in two groups, chare-induced dipole and dipole-induced dipole. Note that van der Waals interaction is the force between the two induced dipoles and it has a very short range. Range dependencies are as the following:

- Charge-Induced Dipole (ion-induced dipole) $\propto 1/r^4$
- Dipole-Induced Dipole (ion-induced dipole) $\propto 1/r^5$
- Induced Dipole-Induced Dipole (van der Waals) $\propto 1/r^6$

3. Forces with Electromagnetic Origin

Electromagnetic force is a special force that effects anything in the nature like gravity. Since materials in solid and liquid forms are made of charges having a unique order, they also may be manipulated by this force. It is also responsible for giving things strength, shape and hardness. The electromagnetic force can be generated by three types of fields known as electrostatic field, magnetostatic field and the electromagnetic field , for further information see `http://emandpplabs.nscee.edu`.

4. Steric Forces

Steric effects arise from the fact that each atom within a molecule occupies a certain amount of space. If atoms are brought too close together, the overlapping of electron clouds between them spent more energy due to repulsive forces, and this may affect the molecule's shape.

To understand about steric forces is an important subject in chemistry and pharmacology. In chemistry steric effects affect energies and the rates of most chemical reactions. In pharmacology, steric effects determine how and at what rate a drug interact with the disease causing. The most common types of steric forces are steric hinderance, steric shielding, steric attraction, steric repulsion and chain crossing. The structure, properties, and reactivity of a molecule is dependent on bonding. This bonding supplies a basic molecular skeleton that is modified by repulsive forces. These repulsive forces include the steric interactions, for more details see Newman [66].

5. Solvent-Related Forces

Solvent-related forces are due to the structural changes of the solvent. These structural changes are generated when ions, proteins, etc. are added into the structure of solvent.

For example, when water is acting as a solvent, one must take the polaric nature of water molecule into account.

It is very hard to determine the solvent-related interactions because their modeling depends very much on the way that the actual solvent is modeled. Examples are hydrophilic interactions and hydrophobic interactions.

3.2.2. A Simplified Model for Electrostatic Complementarity

Gabb et al., cf. [36], have described a simplified model for electrostatics and also Bajaj et al. in [8] and [7] have used FTM algorithm on this simplified model. In the previous section, we modeled our affinity functions using Gaussian function and in this section we will follow Gabb and Bajaj with a little change in the affinity functions used in electrostatic complementarity. At first we try to explain simply the notions of charge density, electrostatic potential and electrostatic potential energy in a system.

We know matter is made of molecules and molecules are a collection of atoms. Atoms consist of a dense central nucleus contains a mix of positively charged protons and electrically neutral neutrons, surrounded by a cloud of negatively charged electrons, see Figure 3.3. Atoms typically have equal numbers of protons and electrons in which case their charges cancel out, yielding a net charge of zero thus making the atom neutral. Hence the electric charge is the fundamental property of forms of matter that exhibit electrostatic attraction or repulsion and Coulomb's law (3.30) and (3.31) computes the electrostatic force between charges. A point like charge is an idealized model of a particle that has an electric charge. So the charge in a region consists of N discrete point like charge carriers (volume charge density) is expressed via the Dirac delta function, i.e.

$$\rho_q(\mathbf{x}) = \sum_{i=1}^{N} q_i \delta\left(\mathbf{x} - \mathbf{x}_i\right), \tag{3.33}$$

where $\mathbf{x}_i$ is the position of point like charge carrier q_i. Also the electrostatic potential generated by these N discrete point like charge carriers is computed by

$$\Phi(\mathbf{x}) = \sum_{i=1}^{N} \frac{q_i}{\epsilon\left(\mathbf{x} - \mathbf{x}_i\right) \|\mathbf{x} - \mathbf{x}_i\|_2}, \tag{3.34}$$

where

$$\epsilon\left(\mathbf{x}\right) = \begin{cases} 4 & \text{if} \quad \|\mathbf{x}\|_2 \leq 6 \\ 80 & \text{if} \quad \|\mathbf{x}\|_2 \geq 8 \\ 38\|\mathbf{x}\|_2 - 224 & \text{otherwise,} \end{cases} \tag{3.35}$$

for more details see Gabb et al. [36]. The electrostatic potential energy $E\left(\mathbf{x}\right)$, stored in a system with volume charge density $\rho_q(\mathbf{x})$ and electrostatics potential $\Phi(\mathbf{x})$ is computed by

$$E\left(\mathbf{x}\right) = \int_{\mathbb{R}^3} \rho_q(\mathbf{x}) \Phi(\mathbf{x}) \, \mathrm{d}\mathbf{x}. \tag{3.36}$$

Now we define our affinity functions. We are given two molecules A and B. These two molecules are considered as two volumes with N_{A} and N_{B} point like charge carriers. Hence we define our affinity functions by

$$Q_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{A}}} \frac{q_j}{\epsilon\left(\mathbf{x}-\mathbf{x}_j\right)\left\|\mathbf{x}-\mathbf{x}_j\right\|_2} \kappa_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{x}_j\right) \tag{3.37}$$

and

$$Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{B}}} q_j \kappa_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{x}_j\right), \tag{3.38}$$

where q_j is the point charge at position $\mathbf{x}_j$, $\epsilon\left(\mathbf{x}\right)$ has been defined in (3.35), and

$$\kappa_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{x}_j\right) = \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{x}-\mathbf{x}_j\|_2^2}{r_j^2}\right)}.$$

We fix molecule A and we rotate and translate molecule B, hence we define the scoring function by

$$\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{t}\right) = \mathrm{Re}\int_{\mathbb{R}^3} Q_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) \cdot \Lambda_{\mathbf{R}}\mathcal{T}^{\mathbf{t}} Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{x})\,\mathrm{d}\mathbf{x}. \tag{3.39}$$

3.2.3. Fast Translational Matching on Electrostatic Complementarity

Here we will apply the fast translational matching algorithm to efficiently compute the scoring function (3.39). Similar to the shape complementarity approach, we describe all the essential modifications in the fast translational matching approach. Here also we relocate and scale the molecules such that they can be inside the unit cube $[-\frac{1}{2},\frac{1}{2}]^3$. In the previous section from (3.9) to (3.18), we described all the details. To avoid of repetition, we consider all the steps from (3.9) to (3.18), but we do not rewrite these steps again.

Now we suppose molecules A and B are inside the unit cube $[\frac{-1}{2},\frac{1}{2}]^3$, so we can approximate the affinity function $\mathrm{Q}_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x})$ using (3.16). We have

$$Q_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{A}}} q_j \widehat{\kappa'}_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{z}_j\right), \tag{3.40}$$

where

$$\widehat{\kappa'}_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{z}_j\right) = \frac{q_j}{\epsilon\left(\mathbf{x}-\mathbf{z}_j\right)\left\|\mathbf{x}-\mathbf{z}_j\right\|_2} \hat{\kappa}_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{z}_j\right). \tag{3.41}$$

Similar to (3.16), we have

$$\widehat{\kappa'}_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{z}_j\right) \approx \widetilde{\kappa'}_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{z}_j\right) = \sum_{k\in\mathcal{I}_n} \widehat{h'}_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{z}_j)\cdot\mathbf{k}} \tag{3.42}$$

and

$$\widehat{h'}_{\mathbf{k}} = \int_{[\frac{-1}{2},\frac{1}{2}]^3} \widehat{\kappa'}_{\mathcal{G}}^{j}\left(\mathbf{x}-\mathbf{z}_j\right) \mathrm{e}^{-2\pi\mathrm{i}\left(\mathbf{x}-\mathbf{z}_{\mathrm{j}}\right)\cdot\mathbf{k}}\,\mathrm{d}\mathbf{x}. \tag{3.43}$$

Hence we have

$$\begin{aligned}
\mathrm{Q}_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) \approx \tilde{\mathrm{Q}}_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) &= \sum_{j=1}^{N_{\mathrm{A}}} q_j \widetilde{\kappa'}^{j}_{\mathcal{G}}\left(\mathbf{x}-\mathbf{z}_j\right) \\
&= \sum_{j=1}^{N_{\mathrm{A}}} q_j \left(\sum_{\mathbf{k}\in\mathcal{I}_n} \widehat{h'}_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{z}_j)\cdot\mathbf{k}} \right) \\
&= \sum_{\mathbf{k}\in\mathcal{I}_n} \widehat{h'}_{\mathbf{k}} \alpha_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}},
\end{aligned} \tag{3.44}$$

where

$$\alpha_{\mathbf{k}} = \sum_{j=1}^{N_{\mathrm{A}}} q_j \mathrm{e}^{-2\pi\mathrm{i}\mathbf{z}_j\cdot\mathbf{k}}. \tag{3.45}$$

In analogy to the last section, here also we could divide the affinity function into molecule independent part and molecule dependent part $\alpha_{\mathbf{k}}$.

Now with the aid of (3.21) and (3.24), we can approximate $Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{Rx}-\mathbf{t})$, so

$$\begin{aligned}
\tilde{Q}_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{Rx}-\mathbf{t}) &= \sum_{j=1}^{N_{\mathrm{B}}} q_j \tilde{\kappa}^{j}_{\mathcal{G}}\left((\mathbf{Rx}-\mathbf{t})-\mathbf{z}_j\right) \\
&= \sum_{j=1}^{N_{\mathrm{B}}} q_j \left(\sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}} \mathrm{e}^{-2\pi\mathrm{i}\mathbf{R}\mathbf{z}_j\cdot\mathbf{k}} \right) \\
&= \sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}_{\mathbf{k}} \beta_{\mathbf{k}}^{\mathbf{R}} \mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}},
\end{aligned} \tag{3.46}$$

where

$$\beta_{\mathbf{k}}^{\mathbf{R}} = \sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{-2\pi\mathrm{i}\mathbf{R}\mathbf{z}_j\cdot\mathbf{k}}. \tag{3.47}$$

Here also the affinity function was divided into molecule independent part and molecule dependent part $\beta_{\mathbf{k}}^{\mathbf{R}}$ which also depends on the rotations $\mathbf{R} \in SO(3)$.

Now we can approximate the scoring function (3.39), namely

$$\begin{aligned}
\mathcal{C}^{\mathrm{EC}}\left((\mathbf{R},\mathbf{t})\right) &= \mathrm{Re} \int_{\mathbb{R}^3} Q_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) \cdot Q_{\mathrm{B}}^{\mathrm{EC}}\left(\mathbf{Rx}-\mathbf{t}\right) \,\mathrm{d}\mathbf{x} \\
&\approx \mathrm{Re} \int_{[-\frac{1}{2},\frac{1}{2}]^3} \tilde{Q}_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x}) \cdot \tilde{Q}_{\mathrm{B}}^{\mathrm{EC}}\left(\mathbf{R}^{\mathrm{t}}\mathbf{x}-\mathbf{t}\right) \,\mathrm{d}\mathbf{x} \\
&= \mathrm{Re} \left(\int_{[-\frac{1}{2},\frac{1}{2}]^3} \sum_{\mathbf{k}\in\mathcal{I}_n} \hat{h}'_{\mathbf{k}} \alpha_{\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}} \sum_{\mathbf{k}'\in\mathcal{I}_n} \hat{h}_{\mathbf{k}'} \beta_{\mathbf{k}'}^{\mathbf{R}} \mathrm{e}^{2\pi\mathrm{i}(\mathbf{x}-\mathbf{t})\cdot\mathbf{k}'} \right) \mathrm{d}\mathbf{x} \\
&= \mathrm{Re} \left(\sum_{\mathbf{k}\in\mathcal{I}_n} \sum_{\mathbf{k}'\in\mathcal{I}_n} \widehat{h'}_{\mathbf{k}} \hat{h}_{\mathbf{k}'} \alpha_{\mathbf{k}} \beta_{\mathbf{k}'}^{\mathbf{R}} \mathrm{e}^{-2\pi\mathrm{i}\mathbf{t}\cdot\mathbf{k}'} \left(\int_{[-\frac{1}{2},\frac{1}{2}]^3} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}'} \,\mathrm{d}\mathbf{x} \right) \right).
\end{aligned} \tag{3.48}$$

Since $\int_{[-\frac{1}{2},\frac{1}{2}]^3} \mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}}\mathrm{e}^{2\pi\mathrm{i}\mathbf{x}\cdot\mathbf{k}'}\,\mathrm{d}\mathbf{x} = \delta_{\mathbf{k}',-\mathbf{k}}$, so $\mathbf{k}' = -\mathbf{k}$ and hence we have

$$\begin{aligned}\mathcal{C}^{\mathrm{EC}}\left((\mathbf{R},\mathbf{t})\right) &\approx \mathrm{Re}\left(\sum_{\mathbf{k}\in\mathcal{I}_n}\sum_{\mathbf{k}'\in\mathcal{I}_n} \widehat{h'}_{\mathbf{k}}\hat{h}_{\mathbf{k}'}\alpha_{\mathbf{k}}\beta^{\mathbf{R}}_{\mathbf{k}'}\mathrm{e}^{-2\pi\mathrm{i}\mathbf{t}\cdot\mathbf{k}'}\delta_{\mathbf{k},\mathbf{k}'}\right) \\ &= \mathrm{Re}\left(\sum_{\mathbf{k}\in\mathcal{I}_n} \widehat{h'}_{\mathbf{k}}\hat{h}_{-\mathbf{k}}\alpha_{\mathbf{k}}\beta^{\mathbf{R}}_{-\mathbf{k}}\mathrm{e}^{2\pi\mathrm{i}\mathbf{t}\cdot\mathbf{k}}\right).\end{aligned} \tag{3.49}$$

The summation represents a three-dimensional Fourier sum that can be computed by NFFT with the computational complexity $\mathcal{O}\left(n^3\log n + N^3_{\mathbf{R}}\right)$ operations. The sum to compute $\alpha_{\mathbf{k}}$ is a three-dimensional Fourier sum and can be computed by NFFT algorithm and its computational complexity is $\mathcal{O}\left(N_{\mathrm{A}} + n^3\log n\right)$ operations. Also the sum to compute $\beta^{\mathbf{R}}_{-\mathbf{k}}$ is a three-dimensional Fourier sum and is computed by NFFT with the computational complexity $\mathcal{O}\left(\left(N_{\mathrm{B}} + n^3\log n\right)N^3_{\mathbf{R}}\right)$ operations.

In straightforward way, for computation of the scoring function $\mathcal{C}^{\mathrm{EC}}\left((\mathbf{R},\mathbf{t})\right)$, for all given motions $(\mathbf{R},\mathbf{t})$ of $SE(3)$, we have to compute the affinity functions $Q^{\mathrm{EC}}_{\mathrm{A}}(\mathbf{x})$ which takes $\mathcal{O}(N_{\mathrm{A}})$ operations and the affinity functions $Q^{\mathrm{EC}}_{\mathrm{B}}(\mathbf{R}^{\mathrm{t}}\mathbf{x}-\mathbf{t})$ which takes $\mathcal{O}\left(N_{\mathrm{B}}N^3_{\mathbf{R}}N^3_{\mathbf{t}}\right)$ operations and hence the overall computational complexity is $\mathcal{O}\left(N_{\mathrm{A}}N_{\mathrm{B}}N^3_{\mathbf{R}}N^3_{\mathbf{t}}\right)$ operations. Therefore we see the advantage of FTM approach in comparison to the straightforward way, for improvement the computational complexity.

Algorithm 2: FTM Algorithm on Electrostatic Complementarity

Input:
n: The degree of Fourier approximation
N_{A} & N_{B}: The number of atomic coordinates of molecules A and B
A set of motions $(\mathbf{R}, \mathbf{t}) \in SE(3)$

foreach $\mathbf{x}_j$ *with* $j \in N_{\mathrm{A/B}}$ **do**
    Compute the modified atomic centers $\mathbf{z}_j^{\mathrm{A}}$ and $\mathbf{z}_j^{\mathrm{B}}$, respectively of (3.13) and (3.14).
end
foreach $\mathbf{k} \in \mathcal{I}_n$ **do**
    Compute coefficients $\widehat{h'}_{\mathbf{k}}$ of (3.43).
    Compute coefficients $\hat{h}_{-\mathbf{k}}$ of (3.18).
    Compute $\alpha_{\mathbf{k}}$ of (3.45) by NFFT.
    foreach *Rotation* $\mathbf{R} \in SO(3)$ **do**
        Compute $\beta_{-\mathbf{k}}^{\mathbf{R}}$ of (3.47) by NFFT.
    end
end
foreach $(\mathbf{R}, \mathbf{t}) \in SE(3)$ **do**
    Compute $\mathrm{Re}\left(\sum_{\mathbf{k} \in \mathcal{I}_n} \widehat{h'}_{\mathbf{k}} \hat{h}_{-\mathbf{k}} \alpha_{\mathbf{k}} \beta_{-\mathbf{k}}^{\mathbf{R}} \mathrm{e}^{2\pi \mathrm{i} \mathbf{t} \cdot \mathbf{k}}\right)$ in (3.49) by NFFT.
end
Output: The solution of the docking problem.

Complexity: $\mathcal{O}\left(\left(N_{\mathbf{R}}^3 + n^3 \log n\right) N_{\mathbf{t}}^3\right)$ operations.

CHAPTER 4

FRM ALGORITHM ON SURFACE & ELECTROSTATICS COMPLEMENTARITY

4.1. FRM on Surface Complementarity

4.1.1. Introduction

So far, we have obtained fast translational matching (FTM) algorithm to search for the maximum of the scoring function (3.8) with respect to the different translations. In this algorithm we could improve the computational complexity of the docking problem by accelerating the computation of the scoring function (3.8) for the three translational degrees of freedom in each motion $(\mathbf{R}, \mathbf{t}) \in SE(3)$.

Analogously, it is possible to repeat the computation of the correlation for different rotations and this procedure is called fast rotational matching (FRM). A novel method developed by Kovacs and Wriggers [58] that the fast Fourier transform (FFT) accelerates all three rotational degrees of freedom. Also Vollrath in [96] has presented a method that uses the computation of correlation for different rotations. Also she has discussed how to compute correlation of functions in $L^2(\mathbb{S}^2)$ by FFT on the rotation group $SO(3)$, therefore in this method we are able to accelerate the computation of the scoring function for the rotational degrees of freedom, cf. [96, 6.5].

Here, we present another method that considers the correlation as a function of two rotations and one displacement parameter t. In this method we handle more degrees of freedom and hence it speeds up the computation of the scoring function. In the rest of this section, we use the Kovacs-Wriggers' idea in [57] by recasting the docking problem into a formulation involving five angles and only one translational parameter. It is possible to accelerate, five of the six degrees of freedom of the docking problem by NFFT.

4.1.2. General Affinity Function in Spherical Coordinate System

In the Section 3.1.3, we have seen the general form of an affinity function $Q_{\mathrm{M}}^{\mathrm{Property}}(\mathbf{x})$, see (3.2), for a molecule M with specific property that in general we have denoted by "Property", i.e.

$$Q_{\mathrm{M}}^{\mathrm{Property}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{M}}} \gamma^{\mathrm{Property}}(\mathbf{x}_j) \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{x}-\mathbf{x}_j\|_2^2}{\varsigma_j^2}\right)},$$

where ς_j is the van der Waals radius of the j-th atom and β controls the sharpness of the Gaussian density function. Now we represent the general affinity function in a spherical coordinate system.

Lemma 4.1.1 *The general affinity function* $Q_{\mathrm{M}}^{\mathrm{Property}}(\mathbf{x})$ *in* (3.2) *has the following form in the spherical coordinate system*

$$Q_{\mathrm{M}}^{\mathrm{Property}}(r\mathbf{u}) = \sum_{j=1}^{N_{\mathrm{M}}} \gamma^{\mathrm{Property}}(\mathbf{x}_j) \mathrm{e}^{\beta\left(1-\frac{r^2+r_j^2-2rr_j\left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j+\cos\theta\cos\theta_j\right)}{\varsigma_j^2}\right)},$$

where $\mathbf{x} = r\mathbf{u}$*,* $r = \|\mathbf{x}\|_2$*, and* $\mathbf{u} = (\theta, \phi) \in [0, \pi] \times [0, 2\pi)$ *and similarly* $\mathbf{x}_j = r_j\mathbf{u}_j$*,* $r_j = \|\mathbf{x}_j\|_2$*,* $\mathbf{u}_j = (\theta_j, \phi_j) \in [0, \pi] \times [0, 2\pi)$*.*

Proof. We know each vector $\mathbf{x} = (x,\ y,\ z) \in \mathbb{R}^3$ in Cartesian coordinate system has the form

$$\mathbf{x} = (r\cos\phi\sin\theta,\ r\sin\phi\sin\theta,\ r\cos\theta)\,, \tag{4.1}$$

in the spherical coordinate system that we represent it by

$$\mathbf{x} = r\mathbf{u}, \quad r = \|\mathbf{x}\|_2 \quad \text{and } \mathbf{u} = (\cos\phi\sin\theta,\ \sin\phi\sin\theta,\ \cos\theta)\,, \tag{4.2}$$

and briefly we denote it by

$$\mathbf{u} := (\theta,\ \phi) \in [0, \pi] \times [0, 2\pi). \tag{4.3}$$

Hence we have

$$\begin{aligned}
&\|\mathbf{x}-\mathbf{x}_j\|_2^2 \\
&= \|\,(r\cos\phi\sin\theta - r_j\cos\phi_j\sin\theta_j, r\sin\phi\sin\theta - r_j\sin\phi_j\sin\theta_j, r\cos\theta - r_j\cos\theta_j)\,\|_2^2 \\
&= (r\cos\phi\sin\theta - r_j\cos\phi_j\sin\theta_j)^2 + (r\sin\phi\sin\theta - r_j\sin\phi_j\sin\theta_j)^2 + (r\cos\theta - r_j\cos\theta_j)^2 \\
&= r^2 + r_j^2 - 2rr_j\left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j + \cos\theta\cos\theta_j\right).
\end{aligned} \tag{4.4}$$

Substituting (4.4) in the general affinity function (4.1.2), proves the lemma. □

4.1.3. GTO Spherical Polar Radial Fourier Coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$

In order to catch the detailed shapes of molecules sufficiently well, we apply the GTO spherical polar radial basis functions $\{\mathrm{R}^l_k(r)\,Y^m_l(\mathbf{u})\}_{klm}$. This essentially causes to use the mass density model instead of using the notion of defined surfaces for molecules, cf. Ritchie [78]. Therefore for each property of interest we represent our affinity functions according to Lemma 4.1.1. For shape complementarity (SC), our affinity functions are defined as

$$Q^{\mathrm{SC}}(r\mathbf{u}) = \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r^2+r_j^2-2rr_j\left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j+\cos\theta\cos\theta_j\right)}{\varsigma_j^2}\right)} \tag{4.5}$$

and hence this function can be written uniquely in terms of GTO spherical polar radial basis functions, see Lemma 2.3.10, i.e.

$$Q^{\mathrm{SC}}(r\mathbf{u}) = \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \hat{Q}^{\mathrm{SC}}_{klm} R^l_k(r)\,Y^m_l(\mathbf{u}), \tag{4.6}$$

where k, l and m are integer numbers with the condition $k > l \geq |m| \geq 0$ and so

$$\hat{Q}^{\mathrm{SC}}_{klm} = \int_0^{\infty}\int_{\mathbb{S}^2} \mathrm{Q}^{\mathrm{SC}}(r\mathbf{u}) R^l_k(r)\,\overline{Y^m_l(\mathbf{u})} r^2\,\mathrm{d}\mathbf{u}\,\mathrm{d}r \tag{4.7}$$

are called the GTO spherical polar radial Fourier coefficients.

If we cut off the Fourier series $Q^{\mathrm{SC}}(r\mathbf{u})$ in (4.6) to order N, then it remains $N(N+1)(2N+1)/6$, GTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$. For example, an expression to order $N = 13$ involves $N(N+1)(2N+1)/6$= 819 of these coefficients.

Remark 4.1.1 *If the affinity function $Q^{\mathrm{SC}}(r\mathbf{u})$ in* (4.6) *is rotated by a rotation $\mathbf{R} \in SO(3)$, then the GTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$ are multiplied by the Wigner-D functions, i.e.*

$$\begin{aligned}
\Lambda_{\mathbf{R}} Q^{\mathrm{SC}}(r\mathbf{u}) = Q'^{\mathrm{SC}}(r\mathbf{u}) &= \Lambda_{\mathbf{R}}\left(\sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \hat{Q}^{\mathrm{SC}}_{klm} R^l_k(r)\,Y^m_l(\mathbf{u})\right) \\
&= \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \hat{Q}^{\mathrm{SC}}_{klm} R^l_k(r)\,(\Lambda_{\mathbf{R}}\,Y^m_l(\mathbf{u})) \\
&= \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \hat{Q}^{\mathrm{SC}}_{klm} R^l_k(r)\left(\sum_{n=-l}^{l} \mathrm{D}^{nm}_l \Lambda_{\mathbf{R}}\,Y^n_l(\mathbf{u})\right) \\
&= \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \left(\sum_{n=-l}^{l} \hat{Q}^{\mathrm{SC}}_{klm} \mathrm{D}^{nm}_l(\mathbf{R})\right) R^l_k(r)\,Y^n_l(\mathbf{u}).
\end{aligned}$$

Hence, the rotated coefficients $\widehat{Q'}^{\mathrm{SC}}_{klm}$ are related to the unrotated coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$ by

$$\widehat{Q'}^{\mathrm{SC}}_{klm} = \sum_{n=-l}^{l} \hat{Q}^{\mathrm{SC}}_{klm} \mathrm{D}^{nm}_l(\mathbf{R}).$$

Now our goal is to find an efficient way to compute the GTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}(r\mathbf{u})$.

Lemma 4.1.2 *The GTO spherical polar radial Fourier coefficients* (4.7) *are computed by*

$$\begin{aligned}
\hat{Q}^{\mathrm{SC}}_{klm} = \sum_{j=0}^{N_{\mathrm{M}}} \sum_{\substack{n=0 \\ n+l \text{ even}}}^{\infty} & \left(2^{-2l} \mathrm{i}^m \sqrt{\frac{(k-l-1)!}{\Gamma(k+1/2)} \times \frac{\pi}{2} \times \frac{(2l+1)(l-m)!}{(l+m)!}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \right. \\
& \times \mathrm{e}^{-\mathrm{i}m\phi_j} \left(\frac{\beta r_j}{\varsigma_j^2}\right)^n / n! \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-1/2}{k-l-1-j'} \left(\frac{1}{2}+\frac{\beta}{\varsigma_j^2}\right)^{-\frac{(3+l+n+2j')}{2}} \\
& \times \Gamma\left(\frac{3+l+n+2j'}{2}\right) \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(2l-2t)! 2^{2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \\
& \times \sum_{t'=0}^{m+1} \binom{m+1}{t'} \sum_{q=m}^{m+2n} \binom{n}{q} \left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q (\cos\theta_j)^{n-q} \binom{q}{\frac{q-m}{2}} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \\
& \left. \times \sum_{v=0}^{n-q} \binom{n-q}{v} \frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''} \right).
\end{aligned} \tag{4.8}$$

Proof. By (4.7), we have

$$\begin{aligned}
\hat{Q}^{\mathrm{SC}}_{klm} = & \int_0^\infty \int_0^{2\pi} \int_0^\pi \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r^2+r_j^2-2rr_j\left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j+\cos\theta\cos\theta_j\right)}{\varsigma_j^2}\right)} \\
& \times R_k^l(r) \overline{Y_l^m(\phi,\theta)} r^2 \sin\theta \, d\theta \, \mathrm{d}\phi \, \mathrm{d}r.
\end{aligned}$$

For more simplification, we denote

$$b_j := 2\beta \frac{r_j}{\varsigma_j^2} \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j + \cos\theta\cos\theta_j\right). \tag{4.9}$$

Hence,

$$\begin{aligned}
\hat{Q}^{\mathrm{SC}}_{klm} &= \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \int_0^\infty \int_0^{2\pi} \int_0^\pi \mathrm{e}^{-\frac{\beta}{\varsigma_j^2} r^2} \mathrm{e}^{b_j r} R_k^l(r) \overline{Y_l^m(\theta,\phi)} r^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \, \mathrm{d}r \\
&= \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \int_0^{2\pi} \int_0^\pi \overline{Y_l^m(\theta,\phi)} \sin\theta \left(\int_0^\infty \mathrm{e}^{-\frac{\beta}{\varsigma_j^2} r^2} \mathrm{e}^{b_j r} R_k^l(r) r^2 \, \mathrm{d}r \right) \mathrm{d}\theta \, \mathrm{d}\phi.
\end{aligned} \tag{4.10}$$

Substituting $R_k^l(r)$ by (2.37) gives

$$\begin{aligned}\hat{Q}_{klm}^{\mathrm{SC}} &= \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \int_0^{2\pi}\int_0^{\pi} \overline{Y_l^m(\theta,\phi)} \sin\theta \Bigg(\int_0^{\infty} \mathrm{e}^{-\frac{\beta}{\varsigma_j^2}r^2} \mathrm{e}^{b_j r} \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})}} \\ &\quad \times \mathrm{e}^{-\frac{r^2}{2}} r^l \sum_{j'=0}^{k-l-1} \frac{1}{j'!} \binom{k-\frac{1}{2}}{k-l-1-j'} (-r^2)^{j'} r^2 \,\mathrm{d}r\Bigg) \mathrm{d}\theta\,\mathrm{d}\phi \\ &= \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})}} \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-\frac{1}{2}}{k-l-1-j'} \\ &\quad \times \int_0^{2\pi}\int_0^{\pi} \overline{Y_l^m(\theta,\phi)} \sin\theta \left(\int_0^{\infty} \mathrm{e}^{-\left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)r^2} \mathrm{e}^{b_j r} r^{l+2j'+2}\,\mathrm{d}r\right) \mathrm{d}\theta\,\mathrm{d}\phi.\end{aligned} \tag{4.11}$$

For computing the coefficients in (4.11), at first we need to compute the inner integral

$$\int_0^{\infty} \mathrm{e}^{-\left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)r^2} \mathrm{e}^{b_j r} r^{l+2j'+2}\,\mathrm{d}r.$$

Since

$$\mathrm{e}^{b_j r} = \sum_{n=0}^{\infty} \frac{(b_j r)^n}{n!}, \tag{4.12}$$

we have

$$\begin{aligned}\int_0^{\infty} \mathrm{e}^{-\left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)r^2} \mathrm{e}^{b_j r} r^{l+2j'+2}\,\mathrm{d}r &= \int_0^{\infty} \mathrm{e}^{-\left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)r^2} \sum_{n=0}^{\infty} \frac{(b_j r)^n}{n!} r^{l+2j'+2}\,\mathrm{d}r \\ &= \sum_{n=0}^{\infty} \frac{b_j^n}{n!} \int_0^{\infty} \mathrm{e}^{-\left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)r^2} r^{l+2j'+n+2}\,\mathrm{d}r \\ &= \sum_{n=0}^{\infty} \frac{(b_j)^n}{n!} \times \frac{1}{2} \left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)^{-\frac{1}{2}(3+l+n+2j')} \Gamma\left(\frac{3+l+n+2j'}{2}\right).\end{aligned} \tag{4.13}$$

Replacing (4.13) in (4.11) gives

$$\begin{aligned}\hat{Q}_{klm}^{\mathrm{SC}} &= \sum_{j=1}^{N_{\mathrm{M}}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \sqrt{\frac{2(k-l-1)!}{\Gamma\left(k+\frac{1}{2}\right)}} \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-\frac{1}{2}}{k-l-1-j'} \sum_{n=0}^{\infty} \frac{1}{n!} \times \frac{1}{2} \\ &\quad \times \left(\frac{\beta}{\varsigma_j^2}+\frac{1}{2}\right)^{-\frac{1}{2}(3+l+n+2j')} \Gamma\left(\frac{3+l+n+2j'}{2}\right) \int_0^{2\pi}\int_0^{\pi} b_j^n \overline{Y_l^m(\theta,\phi)} \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi.\end{aligned} \tag{4.14}$$

In this step of computation of $\hat{Q}^{\mathrm{SC}}_{klm}$, we need to handle the following double integral on $\mathbb{S}^2$ by the aid of spherical harmonics according to the Lemma 2.3.4, i.e.

$$\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi} b_j^n \overline{Y_l^m(\theta,\phi)}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \int_0^{2\pi}\int_0^{\pi} b_j^n \left(\frac{1}{2}\right)^l \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \\
&\times \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!} (\sin\theta)^m (\cos\theta)^{l-m-2t}\,\mathrm{e}^{-\mathrm{i}m\phi}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \left(\frac{1}{2}\right)^l \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \times \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!} \\
&\times \int_0^{2\pi}\int_0^{\pi} b_j^n (\sin\theta)^{m+1} (\cos\theta)^{l-m-2t}\,\mathrm{e}^{-\mathrm{i}m\phi}\,\mathrm{d}\theta\,\mathrm{d}\phi.
\end{aligned} \tag{4.15}$$

Now, again we need to compute the following double integral

$$\int_0^{2\pi}\int_0^{\pi} b_j^n (\sin\phi)^{m+1} (\cos\phi)^{l-m-2t}\,\mathrm{e}^{-\mathrm{i}m\theta}\,\mathrm{d}\phi\,\mathrm{d}\theta, \tag{4.16}$$

and in order to compute this double integral, we do the following steps:

1. We have

$$\begin{aligned}
b_j^n &= \left(2\frac{\beta}{\varsigma_j^2} r_j \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j + \cos\theta\cos\theta_j\right)\right)^n \\
&= \left(2\frac{\beta}{\varsigma_j^2} r_j\right)^n \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j + \cos\theta\cos\theta_j\right)^n \\
&= \left(2\frac{\beta}{\varsigma_j^2} r_j\right)^n \sum_{q=0}^{n} \binom{n}{q} \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j\right)^q \left(\cos\theta\cos\theta_j\right)^{n-q} \\
&= \left(2\frac{\beta}{\varsigma_j^2} r_j\right)^n \sum_{q=0}^{n} \binom{n}{q} \left(\frac{\mathrm{e}^{\mathrm{i}(\phi-\phi_j)} + \mathrm{e}^{-\mathrm{i}(\phi-\phi_j)}}{2}\right)^q \left(\frac{\mathrm{e}^{\mathrm{i}\theta} - \mathrm{e}^{-\mathrm{i}\theta}}{2\mathrm{i}}\right)^q \\
&\times (\sin\theta_j)^q \left(\frac{\mathrm{e}^{\mathrm{i}\theta} + \mathrm{e}^{-\mathrm{i}\theta}}{2}\right)^{n-q} (\cos\theta_j)^{n-q}.
\end{aligned}$$

Using the binomial theorem, gives

$$\begin{aligned}
b_j^n &= \left(\frac{\beta}{\varsigma_j^2} r_j\right)^n \sum_{q=0}^{n} \binom{n}{q} \left(-\frac{\mathrm{i}}{2}\right)^q (\sin\theta_j)^q (\cos\theta_j)^{n-q} \sum_{s=0}^{q} \binom{q}{s} \mathrm{e}^{-\mathrm{i}(\phi-\phi_j)s} \\
&\times \mathrm{e}^{\mathrm{i}(\phi-\phi_j)(q-s)} \sum_{u=0}^{q} (-1)^u \binom{q}{u} \mathrm{e}^{-\mathrm{i}\theta u}\mathrm{e}^{\mathrm{i}\theta(q-u)} \sum_{v=0}^{n-q} \binom{n-q}{v} \mathrm{e}^{-\mathrm{i}\theta v}\mathrm{e}^{\mathrm{i}\theta(n-q-v)} \\
&= \left(\frac{\beta}{\varsigma_j^2} r_j\right)^n \sum_{q=0}^{n} \binom{n}{q} \left(-\frac{\mathrm{i}}{2}\right)^q (\sin\theta_j)^q (\cos\theta_j)^{n-q} \sum_{s=0}^{q} \binom{q}{s} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \\
&\times \sum_{v=0}^{n-q} \binom{n-q}{v} \mathrm{e}^{\mathrm{i}(\phi-\phi_j)(q-2s)}\mathrm{e}^{\mathrm{i}(n-2u-2v)\theta}.
\end{aligned} \tag{4.17}$$

2. Also we need to rewrite

$$
\begin{aligned}
(\sin\theta)^{m+1} &= \left(\frac{\mathrm{e}^{\mathrm{i}\theta}-\mathrm{e}^{-\mathrm{i}\theta}}{2\mathrm{i}}\right)^{m+1} = \left(-\frac{\mathrm{i}}{2}\right)^{m+1}\sum_{t'=0}^{m+1}\binom{m+1}{t'}(-\mathrm{e}^{-\mathrm{i}\theta})^{t'}(\mathrm{e}^{\mathrm{i}\theta})^{m+1-t'} \\
&= \left(-\frac{\mathrm{i}}{2}\right)^{m+1}\sum_{t'=0}^{m+1}\binom{m+1}{t'}(-1)^{t'}\mathrm{e}^{\mathrm{i}(m+1-2t')\theta}.
\end{aligned}
\tag{4.18}
$$

3. Finally, it remains to rewrite the following by

$$
\begin{aligned}
(\cos\theta)^{l-m-2t} &= \left(\frac{\mathrm{e}^{\mathrm{i}\theta}+\mathrm{e}^{-\mathrm{i}\theta}}{2}\right)^{l-m-2t} = \left(\frac{1}{2}\right)^{l-m-2t}\sum_{t''=0}^{l-2t-m}\binom{l-m-2t}{t''}\left(\mathrm{e}^{-\mathrm{i}\theta}\right)^{t''} \\
&\times\left(\mathrm{e}^{\mathrm{i}\theta}\right)^{l-m-2t-t''} \\
&= \left(\frac{1}{2}\right)^{l-2t-m}\sum_{t''=0}^{l-2t-m}\binom{l-m-2t}{t''}\mathrm{e}^{\mathrm{i}(l-m-2t-2t'')\theta}.
\end{aligned}
\tag{4.19}
$$

Now, we replace (4.17), (4.18) and (4.19) into the double integral (4.16), hence

$$
\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi} b_j^n(\sin\theta)^{m+1}(\cos\theta)^{l-m-2t}\,\mathrm{e}^{-\mathrm{i}m\phi}\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \left(\frac{\beta}{\varsigma_j^2}r_j\right)^n\sum_{q=0}^{n}\binom{n}{q}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\sum_{s=0}^{q}\binom{q}{s}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\sum_{v=0}^{n-q}\binom{n-q}{v} \\
&\times\left(-\frac{\mathrm{i}}{2}\right)^{m+1}\sum_{t'=0}^{m+1}(-1)^{t'}\binom{m+1}{t'}\left(\frac{1}{2}\right)^{l-m-2t}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''} \\
&\times\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{\mathrm{i}(n-2u-2v)\theta}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\mathrm{e}^{\mathrm{i}(m+1-2t')\theta}\mathrm{e}^{\mathrm{i}(l-m-2t-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\,\mathrm{d}\theta\,\mathrm{d}\phi.
\end{aligned}
$$

We simplify the above expression and hence we have

$$
\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi} b_j^n(\sin\theta)^{m+1}(\cos\theta)^{l-m-2t}\,\mathrm{e}^{-\mathrm{i}m\phi}\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \left(\frac{\beta}{\varsigma_j^2}r_j\right)^n\left(-\frac{\mathrm{i}}{2}\right)^{m+1}\left(\frac{1}{2}\right)^{l-m-2t}\sum_{q=0}^{n}\binom{n}{q}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\sum_{s=0}^{q}\binom{q}{s} \\
&\times\sum_{u=0}^{q}\binom{q}{u}(-1)^u\sum_{v=0}^{n-q}\binom{n-q}{v}\sum_{t'=0}^{m+1}\binom{m+1}{t'}(-1)^{t'}\sum_{t''=0}^{l-2t-m}\binom{l-m-2t}{t''} \\
&\times\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{\mathrm{i}(n+l+1-2u-2v-2t-2t'-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\,\mathrm{d}\theta\,\mathrm{d}\phi.
\end{aligned}
\tag{4.20}
$$

Now we need to compute the double integral (4.20), so

$$
\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{\mathrm{i}(n+l+1-2u-2v-2t-2t'-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\left(\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(q-2s-m)\phi}\left(\int_0^{\pi}\mathrm{e}^{\mathrm{i}(n+l+1-2u-2v-2t-2t'-2t'')\theta}\,\mathrm{d}\theta\right)\,\mathrm{d}\phi\right).
\end{aligned}
\tag{4.21}
$$

We have

$$\int_0^{2\pi} \mathrm{e}^{\mathrm{i}(q-2s-m)\phi}\, d\phi = 2\pi\delta_{m,q-2s} \tag{4.22}$$

and also

$$\int_0^{\pi} \mathrm{e}^{\mathrm{i}(n+l+1-2u-2v-2t-2t'-2t'')\theta}\, \mathrm{d}\theta := \lambda_{n,l,u,v,t,t',t''}, \tag{4.23}$$

where

$$\lambda_{n,l,u,v,t,t',t''} = \begin{cases} \pi & \text{if } n+l+1-2u-2v-2t-2t'-2t''=0 \\ \frac{2\mathrm{i}}{n+l+1-2u-2v-2t-2t'-2t''} & \text{if } (n+l+1-2u-2v-2t-2t'-2t'') \text{ odd} \\ 0 & \text{otherwise,} \end{cases}$$

or equivalently

$$\lambda_{n,l,u,v,t,t',t''} = \begin{cases} \pi & \text{if } n+l=2u+2v+2t+2t'+2t''-1 \\ \frac{2\mathrm{i}}{n+l+1-2u-2v-2t-2t'-2t''} & \text{if } (n+l) \text{ even} \\ 0 & \text{otherwise.} \end{cases} \tag{4.24}$$

Therefore

$$\begin{aligned} &\int_0^{2\pi}\int_0^{\pi} \mathrm{e}^{\mathrm{i}(n+l+1-2u-2v-2t-2t'-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\,\mathrm{d}\theta\,\mathrm{d}\phi \\ &= \mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\left(\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(q-2s-m)\phi}\left(\int_0^{\pi}\mathrm{e}^{\mathrm{i}(n+l+1-2u-2v-2t-2t'-2t'')\theta}\,\mathrm{d}\theta\right)\mathrm{d}\phi\right) \\ &= \mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\times 2\pi\delta_{m,q-2s}\times\lambda_{n,l,u,v,t,t',t''}. \end{aligned} \tag{4.25}$$

Thus we could compute the double integral (4.21) and consequently the double integral (4.20). Therefore having (4.15) gives

$$\begin{aligned} \hat{Q}^{\mathrm{SC}}_{klm} &= \sum_{j=1}^{N_{\mathrm{M}}}\gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)}\sqrt{\frac{2(k-l-1)!}{\Gamma\left(k+\frac{1}{2}\right)}}\sum_{j'=0}^{k-l-1}\frac{(-1)^{j'}}{j'!}\binom{k-\frac{1}{2}}{k-l-1-j'} \\ &\times\left(\frac{1}{2}\right)^{l+1}\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{2}+\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+2j')}\Gamma\left(\frac{3+l+n+2j'}{2}\right) \\ &\times\sqrt{\frac{(2l+1)\,(l-m)!}{4\pi(l+m)!}}\sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor}\frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!}(\beta r_j)^n \\ &\times\sum_{q=0}^{n}\binom{n}{q}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\sum_{s=0}^{q}\binom{q}{s}\sum_{u=0}^{q}(-1)^u\binom{q}{u} \\ &\times\sum_{v=0}^{n-q}\binom{n-q}{v}\left(-\frac{\mathrm{i}}{2}\right)^{m+1}\sum_{t'=0}^{m+1}\binom{m+1}{t'}(-1)^{t'}\left(\frac{1}{2}\right)^{l-m-2t} \\ &\times\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''}\mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\times 2\pi\delta_{m,q-2s}\times\lambda_{n,l,u,v,t,t',t''}. \end{aligned} \tag{4.26}$$

Now considering the Kronecker delta function $\delta_{m,q-2s}$ implies $q = m + 2s$, and since $s = s(q) = \frac{q-m}{2}$ is an integer-valued function and $q = 0,\ 1,\ \ldots,\ n$, hence we have

$$\begin{aligned}
\hat{Q}^{\mathrm{SC}}_{klm} = \sum_{j=1}^{N_{\mathrm{M}}} \sum_{\substack{n=0 \\ n+l \text{ even}}}^{\infty} & \left(\left(\frac{1}{2}\right)^{2l} \pi\ \mathrm{i}^m \sqrt{\frac{(k-l-1)!}{\Gamma\left(k+\frac{1}{2}\right)} \times \frac{(2l+1)(l-m)!}{2\pi(l+m)!}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \right. \\
& \times \mathrm{e}^{-\mathrm{i}m\phi_j} (\frac{\beta}{\varsigma_j^2} r_j)^n / n! \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-\frac{1}{2}}{k-l-1-j'} \left(\frac{1}{2} + \frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+2j')} \\
& \times \Gamma\left(\frac{3+l+n+2j'}{2}\right) \sum_{q=m}^{m+2n} \binom{n}{q} \left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^q (\cos\theta_j)^{n-q} \binom{q}{\frac{q-m}{2}} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \\
& \times \sum_{v=0}^{n-q} \binom{n-q}{v} \sum_{t'=0}^{m+1} \binom{m+1}{t'} \times \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \\
& \left. \times \frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''} \right) + \mathcal{A},
\end{aligned} \tag{4.27}$$

where

$$\begin{aligned}
\mathcal{A} = \sum_{j=1}^{N_{\mathrm{M}}} \sum_{\substack{n=0 \\ n+l=2u+2v+2t+2t'+2t''-1}}^{\infty} & \left(\left(\frac{1}{2}\right)^{2l} \pi\ \mathrm{i}^m \sqrt{\frac{(k-l-1)!}{\Gamma\left(k+\frac{1}{2}\right)} \times \frac{(2l+1)(l-m)!}{2\pi(l+m)!}} \right. \\
& \times \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \mathrm{e}^{-\mathrm{i}m\phi_j} (\frac{\beta}{\varsigma_j^2} r_j)^n / n! \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-\frac{1}{2}}{k-l-1-j'} \left(\frac{1}{2} + \frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+2j')} \\
& \times \Gamma\left(\frac{3+l+n+2j'}{2}\right) \sum_{q=m}^{m+2n} \binom{n}{q} \left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^q (\cos\theta_j)^{n-q} \binom{q}{\frac{q-m}{2}} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \\
& \left. \times \sum_{v=0}^{n-q} \binom{n-q}{v} \sum_{t'=0}^{m+1} \binom{m+1}{t'} \times \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \pi \right),
\end{aligned}$$

but since when $n+l$ is the odd number $2u+2v+2t+2t'+2t''-1$, the following expression is zero, i.e.

$$\begin{aligned}
& \sum_{q=m}^{m+2n} \binom{n}{q} \left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^q (\cos\theta_j)^{n-q} \binom{q}{\frac{q-m}{2}} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \sum_{v=0}^{n-q} \binom{n-q}{v} \\
& \times \sum_{t'=0}^{m+1} \binom{m+1}{t'} \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \pi = 0
\end{aligned}$$

and therefore $\mathcal{A}=0$, so we have

$$\hat{Q}^{\mathrm{SC}}_{klm}=\sum_{j=1}^{N_{\mathrm{M}}}\sum_{\substack{n=0\\ n+l\ \text{even}}}^{\infty}\left(\left(\frac{1}{2}\right)^{2l}\pi\ \mathrm{i}^m\sqrt{\frac{(k-l-1)!}{\Gamma\left(k+\frac{1}{2}\right)}\times\frac{(2l+1)(l-m)!}{2\pi(l+m)!}}\gamma_j\mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)}\right.$$
$$\times\,\mathrm{e}^{-\mathrm{i}m\phi_j}\left(\frac{\beta}{\varsigma_j^2}r_j\right)^n/n!\sum_{j'=0}^{k-l-1}\frac{(-1)^{j'}}{j'!}\binom{k-\frac{1}{2}}{k-l-1-j'}\left(\frac{1}{2}+\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+2j')}$$
$$\times\,\Gamma\left(\frac{3+l+n+2j'}{2}\right)\sum_{q=m}^{m+2n}\binom{n}{q}\left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^q(\cos\theta_j)^{n-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u$$
$$\times\sum_{v=0}^{n-q}\binom{n-q}{v}\sum_{t'=0}^{m+1}\binom{m+1}{t'}\times\sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor}\frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''}$$
$$\left.\times\,\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}\right).\ \square$$

Remark 4.1.2 *Note that during the proof in* (4.17), (4.18) *and* (4.19), *we have used the binomial theorem which describes the algebraic expansion of nonnegative integer powers of a binomial. Therefore m should be a nonnegative integer. On the other hand we have, $m=-l,\ldots,0,\ldots,l$. Therefore for the negative integers m, we will use the Remark* 2.21. *In other words, for negative integers m, we apply the same procedure for the nonnegative integers m, just we multiply the GTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$ with the factors $\frac{(-1)^m(l-m)!}{(l+m)!}$ where l and m are integers and $l\geq m\geq 0$.*

Corollary 4.1.1 *The GTO spherical polar radial Fourier coefficients* (4.7) *are computed by*

$$\hat{Q}^{\mathrm{SC}}_{klm}=\sum_{j=1}^{N_{\mathrm{M}}}\sum_{\substack{n=l\\ n+l\ \text{even}}}^{\infty}\left(2^{-2l}\mathrm{i}^m\sqrt{\frac{(k-l-1)!}{\Gamma(k+1/2)}\times\frac{\pi}{2}\times\frac{(2l+1)(l-m)!}{(l+m)!}}\gamma_j\mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)}\right.$$
$$\times\,\mathrm{e}^{-\mathrm{i}m\phi_j}\left(\frac{\beta r_j}{\varsigma_j^2}\right)^n/n!\sum_{j'=0}^{k-l-1}\frac{(-1)^{j'}}{j'!}\binom{k-1/2}{k-l-1-j'}\left(\frac{1}{2}+\frac{\beta}{\varsigma_j^2}\right)^{-\frac{(3+l+n+2j')}{2}}$$
$$\times\,\Gamma\left(\frac{3+l+n+2j'}{2}\right)\sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor}\frac{(2l-2t)!2^{2t}}{(l-m-2t)!(l-t)!t!}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''}$$
$$\times\sum_{t'=0}^{m+1}\binom{m+1}{t'}\sum_{q=m}^{m+2n}\binom{n}{q}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u$$
$$\left.\times\sum_{v=0}^{n-q}\binom{n-q}{v}\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}\right).$$

Now, In the following lemma we rewrite a part of the Corollary 4.1.1 to find a better representation for the GTO spherical polar radial Fourier coefficients.

Lemma 4.1.3 *According to the condition of the above corollary we have*

$$\begin{aligned}
&\sum_{q=m}^{m+2n}\binom{n}{q}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\\
&\times\sum_{v=0}^{n-q}\binom{n-q}{v}\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}\\
&=n!\left(-\frac{\mathrm{i}}{2}\tan\theta_j\right)^m(\cos\theta_j)^n\sum_{p=0}^{n}\binom{2p+m}{p}\left(-\tan^2\theta_j/4\right)^p\\
&\times\sum_{u=0}^{2p+m}\frac{(-1)^u}{u!(2p+m-u)!}\sum_{v=0}^{n-m-2p}\frac{1}{v!(n-m-2p-v)!}\\
&\times\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}.
\end{aligned}$$

Proof. We have

$$\begin{aligned}
&\sum_{q=m}^{m+2n}\binom{n}{q}\left(\frac{-\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\\
&\times\sum_{v=0}^{n-q}\binom{n-q}{v}\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}\\
&=\sum_{q=m}^{m+2n}\frac{n!q!}{\left(\frac{q-m}{2}\right)!\left(\frac{q+m}{2}\right)!}\left(\frac{-\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{n-q}\sum_{u=0}^{q}\frac{(-1)^u}{u!(q-u)!}\\
&\times\sum_{v=0}^{n-q}\frac{1}{v!\,(n-q-v)!}\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}.
\end{aligned}$$

Since $q=m,\ m+2,\ \ldots,\ m+2n$, so setting $p=\frac{q-m}{2}$ implies that $p=0,\ 1,\ \ldots,\ n$, and also $q=m+2p$. Changing the variable in (4.1.3), gives

$$\begin{aligned}
&\sum_{p=0}^{n}\frac{n!(2p+m)!}{p!(p+m)!}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^{m+2p}(\cos\theta_j)^{n-m-2p}\sum_{u=0}^{2p+m}\frac{(-1)^u}{u!\,(2p+m-u)!}\\
&\times\sum_{v=0}^{n-m-2p}\frac{1}{v!\,(n-m-2p-v)!}\left(\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}\right)\\
&=n!\left(-\frac{\mathrm{i}}{2}\right)^m(\sin\theta_j)^m(\cos\theta_j)^{n-m}\sum_{p=0}^{n}\binom{2p+m}{p}\left(-\frac{\mathrm{i}}{2}\right)^{2p}(\tan\theta_j)^{2p}\\
&\times\sum_{u=0}^{2p+m}\frac{(-1)^u}{u!\,(m+2p-u)!}\sum_{v=0}^{n-m-2p}\frac{1}{v!\,(n-m-2p-v)!}\\
&\times\frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}.
\end{aligned}$$

With some simplifications like $\left(-\frac{\mathrm{i}}{2}\right)^{2p}=\left(-\frac{1}{4}\right)$, we obtain the final result. $\square$

Now with the aid of this lemma, we can find another representation for the spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$ that the $\hat{Q}^{\mathrm{SC}}_{klm}$s can be written as the multiplication of the angular dependent part $\mathbf{u} = (\theta, \phi)$ by the part $(r, \gamma, \varsigma, \beta)$, where (r, θ, ϕ), γ, ς and β are respectively the spherical coordinates of an atom positioned at $\mathbf{x} \in \mathbb{R}^3$, assigned weights to the atom, van der Waals radius of the atom and sharpness of the Gaussian density function. We summarize it in the following theorem.

Theorem 4.1.1 *The GTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$, for given integers k, l and m where $k > l \geq m \geq 0$ can be computed by*

$$Q^{\mathrm{SC}}_{klm} = C_{klm} \sum_{j=1}^{N_{\mathrm{M}}} \left(\sum_{\substack{n=0 \\ n+l \text{ even}}}^{\infty} A^j_{kln}\left(r_j, \gamma_j, \varsigma_j, \beta\right) B^j_{lmn}\left(\theta_j, \phi_j\right) \right),$$

where

$$\begin{aligned} A^j_{kln}\left(r_j, \gamma_j, \varsigma_j, \beta\right) &:= \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \left(\frac{\beta r_j}{\varsigma_j^2}\right)^n \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-1/2}{k-l-1-j'} \\ &\times \left(\frac{1}{2} + \frac{\beta}{\varsigma_j^2}\right)^{-\frac{(3+l+n+2j')}{2}} \Gamma\left(\frac{3+l+n+2j'}{2}\right), \end{aligned}$$

$$\begin{aligned} B^j_{lmn}\left(\theta_j, \phi_j\right) &:= \mathrm{e}^{-\mathrm{i}m\phi_j} \left(\tan\theta_j\right)^m \left(\cos\theta_j\right)^n \sum_{t=0}^{\lfloor \frac{l-m}{2} \rfloor} \frac{(2l-2t)! 2^{2t}}{(l-m-2t)!(l-t)!t!} \\ &\times \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \sum_{t'=0}^{m+1} \binom{m+1}{t'} \sum_{p=0}^{n} \binom{2p+m}{p} \left(-\tan^2\theta_j/4\right)^p \\ &\times \sum_{u=0}^{2p+m} \frac{(-1)^u}{u!(2p+m-u)!} \sum_{v=0}^{n-m-2p} \frac{1}{v!(n-m-2p-v)!} \\ &\times \frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''} \end{aligned}$$

and

$$C_{klm} = 2^{-(2l+m)} \sqrt{\frac{(k-l-1)!}{\Gamma(k+1/2)} \times \frac{\pi}{2} \times \frac{(2l+1)(l-m)!}{(l+m)!}}.$$

Proof. Replacing Lemma 4.1.3 into the Corollary 4.1.1, gives

$$\hat{Q}^{\mathrm{SC}}_{klm} = \sum_{j=1}^{N_{\mathrm{M}}} \sum_{\substack{n=l\\ n+l \text{ even}}}^{\infty} \left(2^{-2l} \mathrm{i}^m \sqrt{\frac{(k-l-1)!}{\Gamma(k+1/2)} \times \frac{\pi}{2} \times \frac{(2l+1)(l-m)!}{(l+m)!}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \right.$$
$$\times \mathrm{e}^{-\mathrm{i}m\phi_j} \left(\frac{\beta r_j}{\varsigma_j^2}\right)^n /n! \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-1/2}{k-l-1-j'} \left(\frac{1}{2}+\frac{\beta}{\varsigma_j^2}\right)^{-\frac{(3+l+n+2j')}{2}}$$
$$\times \Gamma\left(\frac{3+l+n+2j'}{2}\right) \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(2l-2t)!2^{2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''}$$
$$\times \sum_{t'=0}^{m+1} \binom{m+1}{t'} n! \left(-\frac{\mathrm{i}}{2}\tan\theta_j\right)^m (\cos\theta_j)^n \sum_{p=0}^{n} \binom{2p+m}{p} \left(-\tan^2\theta_j/4\right)^p$$
$$\times \sum_{u=0}^{2p+m} \frac{(-1)^u}{u!(2p+m-u)!} \sum_{v=0}^{n-m-2p} \frac{1}{v!(n-m-2p-v)!}$$
$$\left. \times \frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''} \right).$$

We simplify the above expression therefore we obtain

$$\hat{Q}^{\mathrm{SC}}_{klm} = \sum_{j=1}^{N_{\mathrm{M}}} \sum_{\substack{n=l\\ n+l \text{ even}}}^{\infty} 2^{-(2l+m)} \sqrt{\frac{(k-l-1)!}{\Gamma(k+1/2)} \times \frac{\pi}{2} \times \frac{(2l+1)(l-m)!}{(l+m)!}} \gamma_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)}$$
$$\times \mathrm{e}^{-\mathrm{i}m\phi_j} \left(\frac{\beta r_j}{\varsigma_j^2}\right)^n \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k-1/2}{k-l-1-j'} \left(\frac{1}{2}+\frac{\beta}{\varsigma_j^2}\right)^{-\frac{(3+l+n+2j')}{2}}$$
$$\times \Gamma\left(\frac{3+l+n+2j'}{2}\right) \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(2l-2t)!2^{2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''}$$
$$\times \sum_{t'=0}^{m+1} \binom{m+1}{t'} \left(-\frac{\mathrm{i}}{2}\tan\theta_j\right)^m (\cos\theta_j)^n \sum_{p=0}^{n} \binom{2p+m}{p} \left(-\tan^2\theta_j/4\right)^p$$
$$\times \sum_{u=0}^{2p+m} \frac{(-1)^u}{u!(2p+m-u)!} \sum_{v=0}^{n-m-2p} \frac{1}{v!(n-m-2p-v)!}$$
$$\times \frac{(-1)^{t+t'}}{n+l+1-2u-2v-2t-2t'-2t''}.$$

With some replacements, we get the final results. □

This theorem describes an algorithm to compute the GTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{SC}}_{klm}$. The advantage of this theorem is that we could figure out that the GTO spherical polar radial Fourier coefficients consist of two different parts, i.e.

$$\hat{Q}^{\mathrm{SC}}_{klm} = \sum_{n=0}^{\infty} \hat{Q}_{lmn}(\theta,\phi)\,\hat{Q}_{kln}(r,\gamma,\varsigma,\beta)\,, \tag{4.28}$$

so, the affinity function can be written as

$$
\begin{aligned}
Q_{klm}^{\mathrm{SC}} &= \sum_{klm} \hat{Q}_{klm}^{\mathrm{SC}} R_k^l(r) \mathrm{Y}_l^m(\theta,\phi) \\
&= \sum_{klm} \left(\sum_{n=0}^{\infty} \hat{Q}_{lmn}(\theta,\phi)\, \hat{Q}_{kln}(r,\gamma,\varsigma,\beta) \right) R_k^l(r) \mathrm{Y}_l^m(\theta,\phi) \\
&= \sum_{klmn} \left(\hat{Q}_{lmn}(\theta,\phi)\, \mathrm{Y}_l^m(\theta,\phi) \right) \left(\hat{Q}_{kln}(r,\gamma,\varsigma,\beta)\, R_k^l(r) \right).
\end{aligned}
\tag{4.29}
$$

In comparison to the FTM algorithms in the last chapter, the affinity functions could be written as the product of molecule dependent terms and molecule independet terms, here we can say an affinity function can be written as the product of the spherical part and the radial part. The overall computational complexity is $\mathcal{O}\left(N_{\mathrm{M}} N^4\right)$ operations, where N_{M} refers to the number of atoms in each molecule M and N is the cut off degree.

Algorithm 3: GTO spherical polar radial Fourier coefficients $\hat{Q}_{klm}^{\mathrm{SC}}$

Input:
N: Cut off degree
N_{M}: The number of the atomic coordinates of the molecule
β: Decay constant

foreach *atomic coordinate* $\mathbf{x}_j = (x_j, y_j, z_j)$ *with* $j \in N_{\mathrm{M}}$ **do**
  Compute the centre of molecule M.
  Compute the relocate atomic centres.
end
foreach *atomic coordinate* $\mathbf{x}_j = (x_j, y_j, z_j)$ *with* $j \in N_{\mathrm{M}}$ **do**
  Convert the Cartesian coordinate $\mathbf{x}_j$ to spherical coordinates (r_j, θ_j, ϕ_j) and also take the van der Waals radius ς_j of the PDB.
end
foreach (k, l, m, n, j) *with* $k > l \geq |m| \geq 0,\ n = l \ldots N$ *and* $j \in N_{\mathrm{M}}$ **do**
  Compute $A_{kln}^j(r_j, \gamma_j, \varsigma_j, \beta)$.
  Compute $B_{lmn}^j(\theta_j, \phi_j)$.
  Compute C_{klm}.
end
foreach (k, l, m) *with* $k > l \geq |m| \geq 0$ **do**
  Compute $C_{klm} \sum_{j=1}^{N_{\mathrm{M}}} \left(\sum_{\substack{n=0 \\ n+l \text{ even}}}^{N} A_{kln}^j(r_j, \gamma_j, \varsigma_j, \beta)\, B_{lmn}^j(\theta_j, \phi_j) \right)$.
end
Output: GTO spherical polar radial Fourier coefficients $\hat{Q}_{klm}^{\mathrm{SC}}$.

Complexity: $\mathcal{O}(MN^4)$ operations.

4.1.4. The GTO Translational Coefficients $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$

We still seek to evaluate the scoring function (3.8) to find the best arrangement of the two molecules. Here, in order to describe the relative positions and orientations of both molecules A and B, we follow Ritchi and Kemp [82] and also Wriggers et al. [57], rotating both molecules and translating molecule B along the positive z-axis by $\mathbf{t} = (0, 0, t)$. Hence our scoring function is defined by

$$\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R}, \left(\mathbf{R}', \mathbf{t}\right)\right) = \mathrm{Re} \int_{\mathbb{R}^3} \Lambda_{\mathbf{R}} Q^{\mathrm{SC}}_{\mathrm{A}}(\mathbf{x}) \cdot \Lambda_{\mathbf{R}'} \mathcal{T}^{\mathbf{t}} Q^{\mathrm{SC}}_{\mathrm{B}}(\mathbf{x})\, \mathrm{d}\mathbf{x}. \tag{4.30}$$

We are given two affinity functions $Q^{\mathrm{SC}}_{\mathrm{A}}$ and $Q^{\mathrm{SC}}_{\mathrm{B}}$ in $\mathbb{R}^3$. Since the GTO spherical polar radial functions constitute a basis for $L^2(\mathbb{R}^3)$, therefore the affinity functions can be written uniquely as

$$Q^{\mathrm{SC}}_{\mathrm{A}}(r\mathbf{u}) = \sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} R^{l}_{k}(r)\, Y^{m}_{l}(\mathbf{u}) \tag{4.31}$$

and

$$Q^{\mathrm{SC}}_{\mathrm{B}}(r\mathbf{u}) = \sum_{k'=1}^{\infty} \sum_{l'=0}^{k'-1} \sum_{m'=-l'}^{l'} \hat{Q}^{\mathrm{B}}_{k'l'm'} R^{l'}_{k'}(r)\, Y^{m'}_{l'}(\mathbf{u}). \tag{4.32}$$

Note that, the reference point on each molecule is in principle arbitrary but it is convenient to adopt the centre of mass (COM). Here we assume that the molecule A is at the origin of the coordinate system, r is the distance of a generic point $\mathbf{x}$ from the reference point of molecule A and ϕ is its colatitude (polar angle). The reference point of the molecule B is located at $\mathbf{t} = (0,\ 0,\ t)$ and r' and ϕ' be analogous quantities relative to this reference point. We have the following relation between the quantities of these two molecules, namely

$$z = r\cos\theta, \qquad z' = r'\cos\theta' \quad \text{and} \qquad z - z' = t, \tag{4.33}$$

where $t = \|\mathbf{t}\|_2$. Also we have

$$\mathbf{x} - \mathbf{t} = \mathbf{x}' = r'\mathbf{u}' \quad \text{where} \quad \mathbf{x} = r\mathbf{u}, \tag{4.34}$$

and $r = \|\mathbf{x}\|_2$ and $\mathbf{u} = (\theta, \phi) \in [0, \pi] \times [0, 2\pi]$. The spherical coordinates of point $\mathbf{x} \in \mathbb{R}^3$ are $(r\cos\phi\sin\theta, r\sin\phi\sin\theta, r\cos\theta)$, therefore

$$\begin{aligned} r' = \|\mathbf{x}'\|_2 &= \sqrt{(r\cos\phi\sin\theta - 0)^2 + (r\sin\phi\sin\theta - 0)^2 + (r\cos\theta - t)^2} \\ &= \sqrt{r^2 - 2tr\cos\theta + t^2}. \end{aligned} \tag{4.35}$$

Corresponding to $\mathbf{u} = (\theta,\ \phi) \in \mathbb{S}^2$, we have $\mathbf{u}' = (\theta',\ \phi') \in \mathbb{S}'^2$ where

$$(\theta',\ \phi') = \left(\arccos\frac{z - t}{\sqrt{r^2 - 2rt\cos\phi + t^2}},\ \phi\right). \tag{4.36}$$

According to these assumptions, we present the following triple integral that plays a fundamental role in this section.

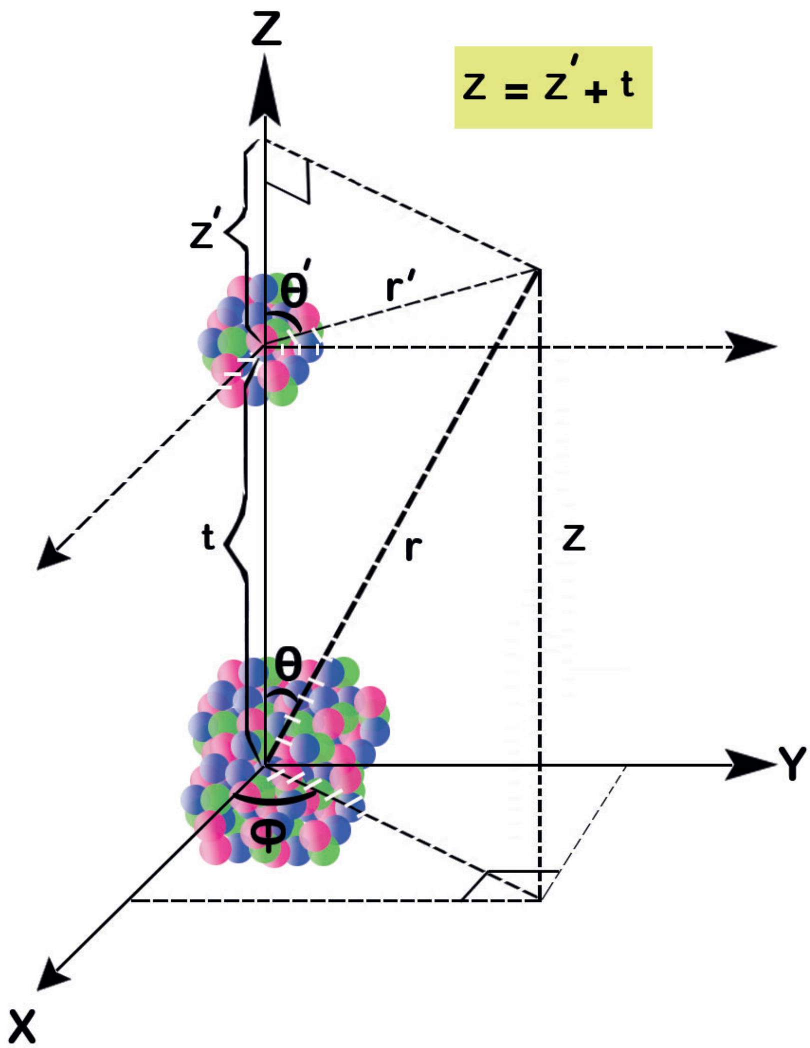


Figure 4.1.: This figure shows a schematic picture of our molecular docking. We consider the molecule A at the origin of the coordinate system and molecule B at $(0, 0, t)$. We rotate molecule A and also we rotate and translate molecule B. Here (r, θ, ϕ) and (r', θ', ϕ) are the spherical coordinates of generic point $\mathbf{x} \in \mathbb{R}^3$ from molecule A and molecule B, respectively. For more details see the text.

Definition 4.1.1 *For given integers k, k', l, l', n, and n' where $k > l \geq |n| \geq 0$, $k' > l' \geq |n'| \geq 0$ and $n' = -n$, we define*

$$\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = \int_0^\infty \int_0^\pi \int_0^{2\pi} R_k^l(r)\, Y_l^n\,(\theta, \phi)\, R_{k'}^{l'}(r)\, Y_{l'}^{n'}\left(\theta', \phi\right) r^2 \sin\theta \,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r,$$

which are called GTO translational coefficients.

In the following lemma, we present a method for the computation of the GTO translational coefficients. It is very important to find an efficient method to compute these coefficients fast.

Lemma 4.1.4 *The GTO translational coefficients $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$ can be computed by*

$$
\begin{aligned}
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = {} & \frac{\sqrt{(2l+1)(2l'+1)}}{2^{l+l'+1}}\sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma(k+\frac{1}{2})\Gamma(k'+\frac{1}{2})}} \\
& \times \mathrm{e}^{-\frac{t^2}{2}} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!}\binom{k-\frac{1}{2}}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!}\binom{k'-\frac{1}{2}}{k'-l'-1-j'} \\
& \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!(l'-q')!q!q'!} \\
& \times \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \sum_{n_2=0}^{j'+q'} \binom{j'+q'}{n_2} \sum_{n_4=0}^{n_2}\binom{n_2}{n_4} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3}(-1)^{n_3} \\
& \times t^{j'+q'+n_1-n_2+n_3+2n_4}\Gamma\left(\frac{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+3}{2}\right) \\
& \times \frac{(-1)^{l+l'+j'-q'+n_1-n_2-n_3}+1}{l+l'+j'-2q-q'+n_1-n_2-n_3+1}.
\end{aligned}
$$

Proof. Using the Definition 4.1.1 and the spherical harmonics in (2.20) gives

$$
\begin{aligned}
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = {} & \int_0^\infty \int_0^\pi R^l_k(r)R^{l'}_{k'}(r')\bigg(\int_0^{2\pi}\sqrt{\frac{(2l+1)(l-n)!}{4\pi(l+n)!}}\mathrm{P}^n_l(\cos\theta)\mathrm{e}^{\mathrm{i}n\phi} \\
& \times \sqrt{\frac{(2l'+1)(l'-n')!}{4\pi(l'+n')!}}\mathrm{P}^{n'}_{l'}(\cos\theta')\mathrm{e}^{\mathrm{i}n'\phi}\,\mathrm{d}\phi\bigg)\, r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
$$

We simplify the expression, hence

$$
\begin{aligned}
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = {} & \frac{\sqrt{(2l+1)(2l'+1)}}{4\pi}\sqrt{\frac{(l-n)!(l'-n')!}{(l+n)!(l'+n')!}} \\
& \times \int_0^\infty \int_0^\pi R^l_k(r)R^{l'}_{k'}(r')\mathrm{P}^n_l(\cos\theta)\mathrm{P}^{n'}_{l'}(\cos\theta')\,2\pi\delta_{n',-n}\, r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
$$

We apply the GTO spherical polar radial basis fuctions, see Definition 2.37, hence we have

$$
\begin{aligned}
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = {} & \frac{\sqrt{(2l+1)(2l'+1)}}{2}\sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\int_0^\infty\int_0^\pi \sqrt{\frac{2(k-l-1)!}{\Gamma(k+\frac{1}{2})}}\mathrm{e}^{-\frac{r^2}{2}}r^l \\
& \times L^{(l+\frac{1}{2})}_{k-l-1}(r^2)\sqrt{\frac{2(k'-l'-1)!}{\Gamma(k'+\frac{1}{2})}}\mathrm{e}^{-\frac{r'^2}{2}}r'^{l'}L^{(l'+\frac{1}{2})}_{k'-l'-1}(r'^2)\mathrm{P}^n_l(\cos\theta)\mathrm{P}^{-n}_{l'}(\cos\theta') \\
& \times r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}r \\
= {} & \sqrt{\frac{(2l+1)(2l'+1)(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma(k+\frac{1}{2})\Gamma(k'+\frac{1}{2})}}\times\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t),
\end{aligned}
\tag{4.37}
$$

where

$$\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t) := \int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{1}{2}(r^2+r'^2)} r^l r'^{l'} L^{l+\frac{1}{2}}_{k-l-1}(r^2) L^{l'+\frac{1}{2}}_{k'-l'-1}(r'^2) \mathrm{P}^n_l(\cos\theta) \mathrm{P}^{-n}_{l'}(\cos\theta') \times r^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}r. \tag{4.38}$$

For computing $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$, we need to compute $\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t)$. Using the definitions of associated Laguerre polynomials, associated Legendre polynomials and also r', see (4.35), necessitates to have

$$\begin{aligned}\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t) = &\int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{1}{2}(r^2+r^2-2rt\cos\theta+t^2)} r^l \left(\sqrt{r^2-2rt\cos\theta+t^2}\right)^{l'} \sum_{j=0}^{k-l-1} \frac{1}{j!} \\ &\times \binom{k-\frac{1}{2}}{k-l-1-j} (-r^2)^j \sum_{j'=0}^{k'-l'-1} \frac{1}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \left(-r^2+2rt\cos\theta-t^2\right)^{j'} \\ &\times \left(\frac{1}{2}\right)^l \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \frac{(-1)^{q+n}(2l-2q)!}{(l-n-2q)!(l-q)!q!} \left(\sin^2\theta\right)^{\frac{n}{2}} (\cos\theta)^{l-n-2q} \left(\frac{1}{2}\right)^{l'} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \\ &\times \frac{(-1)^{q'-n}(2l'-2q')!}{(l'+n-2q')!\;(l'-q')!\;q'!} \left(\sin^2\theta'\right)^{-\frac{n}{2}} \left(\cos\theta'\right)^{l'+n-2q'} r^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}r.\end{aligned}$$

We simplify the expression so we have

$$\begin{aligned}\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t) = &\int_0^\infty \int_0^\pi \mathrm{e}^{-\left(r^2-rt\cos\theta+\frac{t^2}{2}\right)} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} r^{l+2j+2} \\ &\times \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \left(r^2-2rt\cos\theta+t^2\right)^{\frac{l'}{2}+j'} \left(\frac{1}{2}\right)^l \\ &\times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \frac{(-1)^{q+n}(2l-2q)!}{(l-n-2q)!(l-q)!q!} (\sin\theta)^n (\cos\theta)^{l-n-2q} \left(\frac{1}{2}\right)^{l'} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \\ &\times \frac{(-1)^{q'-n}(2l'-2q')!}{(l'+n-2q')!(l'-q')!q'!} \left(\sin\theta'\right)^{-n} \left(\cos\theta'\right)^{l'+n-2q'} \sin\theta \, \mathrm{d}\theta \, \mathrm{d}r.\end{aligned} \tag{4.39}$$

Using trigonometric identities gives us the following equations for the relation between the angles θ and θ'.

$$\cos\theta' = \cos\left(\arccos\left(\frac{z-t}{\sqrt{r^2-2rt\cos\theta+t^2}}\right)\right) = \frac{r\cos\theta-t}{\sqrt{r^2-2rt\cos\theta+t^2}} \tag{4.40}$$

and

$$\begin{aligned}\sin\theta' &= \sin\left(\arccos\left(\frac{z-t}{\sqrt{r^2-2rt\cos\theta+t^2}}\right)\right) = \sqrt{1-\frac{(z-t)^2}{r^2-2rt\cos\theta+t^2}} \\ &= \sqrt{\frac{r^2-r^2\cos^2\theta}{r^2-2rt\cos\theta+t^2}} = \frac{r\sin\theta}{\sqrt{r^2-2rt\cos\theta+t^2}}\ .\end{aligned} \tag{4.41}$$

Therefore we have

$$\begin{aligned}\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t) = & \int_0^\infty \int_0^\pi \mathrm{e}^{-\left(r^2 - rt\cos\theta + \frac{t^2}{2}\right)} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} r^{l+2j+2} \\ & \times \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \left(r^2 - 2rt\cos\theta + t^2\right)^{\frac{l'}{2}+j'} \left(\frac{1}{2}\right)^l \\ & \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \frac{(-1)^{q+n}(2l-2q)!}{(l-n-2q)!(l-q)!q!} (\sin\theta)^n (\cos\phi)^{l-n-2q} \left(\frac{1}{2}\right)^{l'} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \\ & \times \frac{(-1)^{q'-n}(2l'-2q')!}{(l'+n-2q')!(l'-q')!q'!} \left(\frac{r\sin\theta}{\sqrt{r^2-2rt\cos\theta+t^2}}\right)^{-n} \sin\theta \\ & \times \left(\frac{r\cos\theta - t}{\sqrt{r^2-2rt\cos\theta+t^2}}\right)^{l'+n-2q'} \mathrm{d}\theta\,\mathrm{d}r.\end{aligned}$$

Again by more simplification we get

$$\begin{aligned}\mathcal{J}^{\mathrm{SC}}_{kk',ll',n}(t) = & \left(\frac{1}{2}\right)^{l+l'} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \\ & \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \left(\frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!\,(l'-q')!q!q'!}\right) \times \mathcal{T}^{\mathrm{SC}}_{kk',ll',n}(t),\end{aligned} \tag{4.42}$$

where

$$\begin{aligned}\mathcal{T}^{\mathrm{SC}}_{kk',ll',n}(t) = & \int_0^\infty \int_0^\pi \mathrm{e}^{-(r^2 - rt\cos\theta + \frac{t^2}{2})} r^{l+2j-n+2} \left(r^2 - 2rt\cos\theta + t^2\right)^{j'+q'} \\ & \times (r\cos\theta - t)^{l'+n-2q'} \sin\theta\,(\cos\theta)^{l-n-2q}\,\mathrm{d}\theta\,\mathrm{d}r.\end{aligned} \tag{4.43}$$

For computing $\mathcal{T}^{\mathrm{SC}}_{kk',ll',n}(t)$, we use the binomial theorem and exponential function in terms of power series, hence

$$\begin{aligned}\mathcal{T}^{\mathrm{SC}}_{kk',ll',n}(t) = & \int_0^\infty \int_0^\pi \mathrm{e}^{-(r^2+\frac{t^2}{2})} \sum_{n_1=0}^{\infty} \frac{(rt\cos\theta)^{n_1}}{n_1!} r^{l+2j-n+2} \sum_{n_2=0}^{j'+q'} \binom{j'+q'}{n_2} \\ & \times \left(r^2+t^2\right)^{n_2} (-2rt\cos\theta)^{j'+q'-n_2} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} (-t)^{n_3} \\ & \times (r\cos\theta)^{l'+n-2q'-n_3} \sin\theta\,(\cos\theta)^{l-n-2q}\,\mathrm{d}\theta\,\mathrm{d}r.\end{aligned} \tag{4.44}$$

Again by using binomial theorem for $\left(r^2+t^2\right)^{n_2}=\sum_{n_4=0}^{n_2}\binom{n_2}{n_4}t^{2n_4}r^{2n_2-2n_4}$ in (4.44), we have

$$\begin{aligned}\mathcal{T}^{\mathrm{SC}}_{kk',ll',n}(t)&=\mathrm{e}^{-\frac{t^2}{2}}\sum_{n_1=0}^{\infty}\frac{t^{n_1}}{n_1!}\sum_{n_2=0}^{j'+q'}\binom{j'+q'}{n_2}\sum_{n_4=0}^{n_2}\binom{n_2}{n_4}(-2)^{j'+q'-n_2}\,t^{j'+q'-n_2+2n_4}\\&\times\sum_{n_3=0}^{l'+n-2q'}\binom{l'+n-2q'}{n_3}(-t)^{n_3}\int_0^\infty\int_0^\pi\mathrm{e}^{-r^2}r^{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+2}\\&\times\sin\theta\,(\cos\theta)^{l+l'-2q+j'-q'+n_1-n_2-n_3}\;\mathrm{d}\theta\,\mathrm{d}r.\end{aligned}\tag{4.45}$$

So

$$\begin{aligned}&\int_0^\infty\int_0^\pi\mathrm{e}^{-r^2}r^{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+2}\sin\theta\,(\cos\theta)^{l+l'-2q+j'-q'+n_1-n_2-n_3}\;\mathrm{d}\theta\,\mathrm{d}r\\&=\int_0^\infty\mathrm{e}^{-r^2}r^{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+2}\left(\int_0^\pi\sin\theta\,(\cos\theta)^{l+l'-2q+j'-q'+n_1-n_2-n_3}\;\mathrm{d}\theta\right)\mathrm{d}r.\end{aligned}\tag{4.46}$$

For computing (4.46), we need to compute the following inner integral, namely

$$\begin{aligned}&\int_0^\pi\sin\theta\,(\cos\theta)^{l+l'+j'-2q-q'+n_1-n_2-n_3}\;\mathrm{d}\theta=\left[\frac{-\left(\cos\theta\right)^{l+l'-2q+j'-q'+n_1-n_2-n_3+1}}{l+l'-2q+j'-q'+n_1-n_2-n_3+1}\right]_0^\pi\\&=\begin{cases}\frac{-(-1)^{l+l'-2q+j'-q'+n_1-n_2-n_3+1}-1}{l+l'-2q+j'-q'+n_1-n_2-n_3+1} & \text{if }\ (l+l'-2q+j'-q'+n_1-n_2-n_3+1)\ \text{ odd}\\ 0 & \text{if }\ (l+l'-2q+j'-q'+n_1-n_2-n_3+1)\ \text{ even}\end{cases}\end{aligned}$$

and hence we get

$$\begin{aligned}&\int_0^\pi\sin\theta\,(\cos\theta)^{l+l'+j'-2q-q'+n_1-n_2-n_3}\;\mathrm{d}\theta=\\&=\begin{cases}\frac{(-1)^{l+l'-2q+j'-q'+n_1-n_2-n_3}+1}{l+l'-2q+j'-q'+n_1-n_2-n_3+1} & \text{if }\ (l+l'-2q+j'-q'+n_1-n_2-n_3)\ \text{ even}\\ 0 & \text{if }\ (l+l'-2q+j'-q'+n_1-n_2-n_3)\ \text{ odd.}\end{cases}\end{aligned}\tag{4.47}$$

Also

$$\begin{aligned}&\int_0^\infty\mathrm{e}^{-r^2}r^{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+2}\,\mathrm{d}r\\&\qquad=\frac{1}{2}\Gamma\left(\frac{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+3}{2}\right)\end{aligned}\tag{4.48}$$

and with some replacements, we get the final result. □

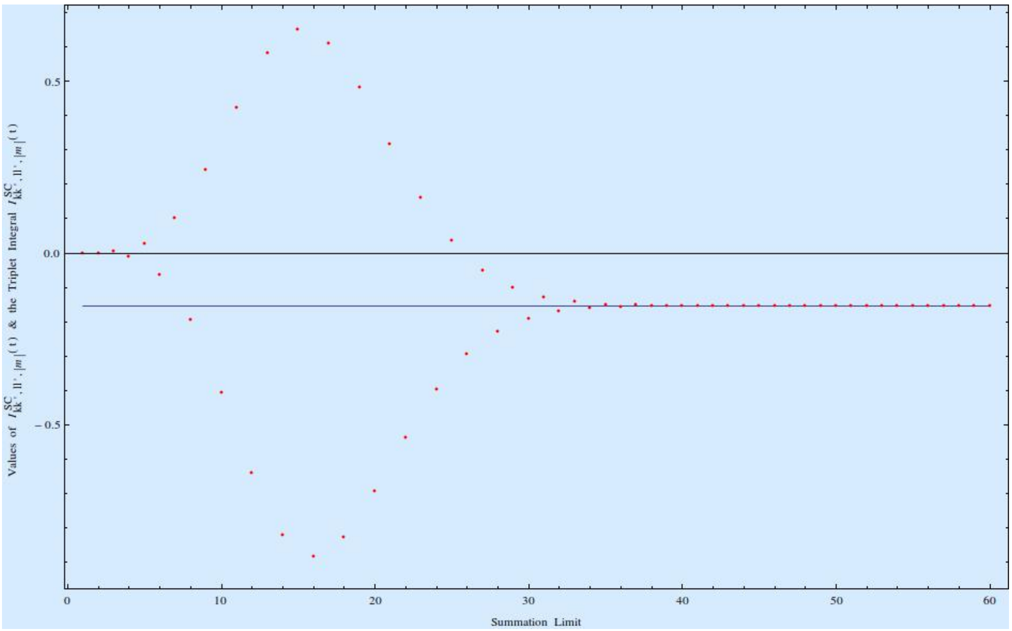


Figure 4.2.: Comparison of the exact value and the approximated value according to the Lemma 4.1.4 of the GTO translational coefficients. Here we considered $k = 5$, $k' = 4$, $l = 3$, $l' = 2$, $t = 5$ and the cut off degree $n_1 = 60$. As you see for $n_1 \geq 34$, the exact value and the approximated value are almost the same.

So far we have presented a method, see Lemma 4.1.4, that can compute the GTO translational coefficients $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$. Now in the following theorem we show that the GTO translational coefficients are the multiplication of a Gaussian function by a polynomial of degree $2(k+k')-(l+l')-6$. This is a very promising result because then the computation of the GTO translational coefficients can be accelerated by estimating the polynomials.

Theorem 4.1.2 *The GTO translational coefficients $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$ are the multiplication of the polynomial $\mathcal{P}(t)$ of degree $d = 2(k+k')-(l+l')-6$ by the Gaussian function $\mathrm{e}^{-\frac{t^2}{4}}$, i.e.*

$$\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = \mathcal{P}(t) \cdot \mathrm{e}^{-\frac{t^2}{4}},$$

where

$$\mathcal{P}(t) = \sum_{w=0}^{d} a_w^{(kk',ll',n)} t^w$$

and

$$
\begin{aligned}
a_w^{(kk',ll',n)} &= \frac{\sqrt{(2l+1)(2l'+1)}}{2^{(l+l'+1)}}\sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\sqrt{\frac{(k-l-1)!\;(k'-l'-1)!}{\Gamma(k+\frac{1}{2})\Gamma(k'+\frac{1}{2})}}\\
&\times\sum_{j=0}^{k-l-1}\frac{(-1)^j}{j!}\binom{k-\frac{1}{2}}{k-l-1-j}\sum_{j'=0}^{k'-l'-1}\frac{(-1)^{j'}}{j'!}\binom{k'-\frac{1}{2}}{k'-l'-1-j'}\\
&\times\sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor}\sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor}\frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!(l'+n-2q')!(l-q)!(l'-q')!\;q!\;q'!}\\
&\times\sum_{n_2=0}^{j'+q'}\binom{j'+q'}{n_2}\sum_{n_4=0}^{n_2}\binom{n_2}{n_4}\sum_{n_3=0}^{l'+n-2q'}\binom{l'+n-2q'}{n_3}(-1)^{n_3}\\
&\times\sum_{s_1=0}^{w-\frac{j'+q'-n_2+n_3+2n_4}{2}}\frac{(-1)^{s_1}}{s_1!\,(w-j'-q'+n_2-n_3-2n_4-2s_1)!}\\
&\times\Gamma\left(\frac{l+l'+2j-2q'+w+2n_2-2n_3-4n_4-2s_1+3}{2}\right)\\
&\times\frac{\left((-1)^{l+l'+w}+1\right)(-2)^{(j'+q'-n_2-2s_1)}}{l+l'-2q-2q'+w-2n_3-2n_4-2s_1+1}.
\end{aligned}
$$

Proof. In the Lemma 4.1.4, we replace $\mathrm{e}^{-\frac{t^2}{2}}$ by $\mathrm{e}^{-\frac{t^2}{4}}\cdot\sum_{s_1=0}^{\infty}\left(\frac{-t^2}{4}\right)^{s_1}/s_1!$, hence we have

$$
\begin{aligned}
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) &= \frac{\sqrt{(2l+1)(2l'+1)}}{2^{l+l'+1}}\sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma\left(k+\frac{1}{2}\right)\Gamma\left(k'+\frac{1}{2}\right)}}\\
&\times\mathrm{e}^{-\frac{t^2}{4}}\sum_{j=0}^{k-l-1}\frac{(-1)^j}{j!}\binom{k-\frac{1}{2}}{k-l-1-j}\sum_{j'=0}^{k'-l'-1}\frac{(-1)^{j'}}{j'!}\binom{k'-\frac{1}{2}}{k'-l'-1-j'}\\
&\times\sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor}\sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor}\frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!(l'-q')!q!q'!}\\
&\times\sum_{n_2=0}^{j'+q'}\binom{j'+q'}{n_2}\sum_{n_4=0}^{n_2}\binom{n_2}{n_4}\sum_{n_3=0}^{l'+n-2q'}\binom{l'+n-2q'}{n_3}(-1)^{n_3}\\
&\times\sum_{n_1=0}^{\infty}\frac{1}{n_1!}\sum_{s_1=0}^{\infty}\frac{\left(\frac{-1}{4}\right)^{s_1}}{s_1!}t^{j'+q'+n_1-n_2+n_3+2n_4+2s_1}\\
&\times\Gamma\left(\frac{l+l'+2j+j'-q'+n_1+n_2-n_3-2n_4+3}{2}\right)\\
&\times\frac{(-1)^{l+l'+j'-q'+n_1-n_2-n_3+1}+1}{l+l'+j'-2q-q'+n_1-n_2-n_3+1}\times(-2)^{(j'+q'-n_2)}.
\end{aligned}
$$

Setting $w = j' + q' + n_1 - n_2 + n_3 + 2n_4 + 2s_1$, gives $n_1 = w - j' - q' + n_2 - n_3 - 2n_4 - 2s_1$ and therefore

$$
\begin{aligned}
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = {}& \frac{\sqrt{(2l+1)(2l'+1)}}{2^{l+l'+1}} \sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}} \sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma\left(k+\frac{1}{2}\right)\Gamma\left(k'+\frac{1}{2}\right)}} \\
& \times \mathrm{e}^{-\frac{t^2}{4}} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \\
& \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!(l'-q')!q!q'!} \\
& \times \sum_{n_2=0}^{j'+q'} \binom{j'+q'}{n_2} \sum_{n_4=0}^{n_2} \binom{n_2}{n_4} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} (-1)^{n_3} \\
& \times \sum_{s_1=0}^{\infty} \frac{\left(\frac{-1}{4}\right)^{s_1}}{s_1!} \sum_{w=j'+q'+n_1-n_2+n_3+2n_4+2s_1}^{\infty} \frac{t^w}{(w-j'-q'+n_2-n_3-2n_4-2s_1)!} \\
& \times \Gamma\left(\frac{l+l'+2j-2q'+w+2n_2-2n_3-4n_4-2s_1+3}{2}\right) \\
& \times \frac{(-1)^{l+l'+w}+1}{l+l'-2q-2q'+w-2n_3-2n_4-2s_1+1} \times (-2)^{(j'+q'-n_2)}.
\end{aligned}
$$

With further simplifications, we get the following expression

$$
\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) = \sum_{w=0}^{\infty} a_w^{(kk',ll',n)} t^w \cdot \mathrm{e}^{-\frac{t^2}{4}},
$$

where

$$
\begin{aligned}
a_w^{(kk',ll',n)} = {}& \frac{\sqrt{(2l+1)(2l'+1)}}{2^{l+l'+1}} \sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}} \sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma\left(k+\frac{1}{2}\right)\Gamma\left(k'+\frac{1}{2}\right)}} \\
& \times \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \\
& \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \frac{(-1)^{q+q'}(2l-2q)!\,(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!\,(l'-q')!q!q'!} \\
& \times \sum_{n_2=0}^{j'+q'} \binom{j'+q'}{n_2} \sum_{n_4=0}^{n_2} \binom{n_2}{n_4} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} (-1)^{n_3} \\
& \times \sum_{s_1=0}^{\infty} \frac{\left(\frac{-1}{4}\right)^{s_1}}{s_1!} \times \frac{1}{(w-j'-q'+n_2-n_3-2n_4-2s_1)!} \\
& \times \Gamma\left(\frac{l+l'+2j-2q'+w+2n_2-2n_3-4n_4-2s_1+3}{2}\right) \\
& \times \frac{(-1)^{l+l'+w}+1}{l+l'-2q-2q'+w-2n_3-2n_4-2s_1+1} \times (-2)^{(j'+q'-n_2)},
\end{aligned}
$$

and $w \geq j' + q' - n_2 + n_3 + 2n_4 + 2s_1$. According to this condition, we rewrite s_1 in terms of w, in other words, $s_1 = s_1(w) \leq \frac{w-(j'+q'-n_2+n_3+2n_4)}{2}$, so

$$
\begin{aligned}
a_w^{(kk',ll',n)} &= \frac{\sqrt{(2l+1)(2l'+1)}}{2^{l+l'+1}} \sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}} \sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma\left(k+\frac{1}{2}\right)\Gamma\left(k'+\frac{1}{2}\right)}} \\
&\times \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \\
&\times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \frac{(-1)^{q+q'}(2l-2q)!\,(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!\,(l'-q')!q!q'!} \\
&\times \sum_{n_2=0}^{j'+q'} \binom{j'+q'}{n_2} \sum_{n_4=0}^{n_2} \binom{n_2}{n_4} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} (-1)^{n_3} \\
&\times \sum_{s_1=0}^{\frac{w-(j'+q'-n_2+n_3+2n_4)}{2}} \frac{(-1)^{s_1}}{s_1!\,(w-j'-q'+n_2-n_3-2n_4-2s_1)!} \\
&\times \Gamma\left(\frac{l+l'+2j-2q'+w+2n_2-2n_3-4n_4-2s_1+3}{2}\right) \\
&\times \frac{\left((-1)^{l+l'+w}+1\right)(-2)^{(j'+q'-n_2-2s_1)}}{l+l'-2q-2q'+w-2n_3-2n_4-2s_1+1}.
\end{aligned}
\tag{4.49}
$$

Now we show the series $\sum_{w=0}^{\infty} a_w^{(kk',ll',n)} t^w$ is a finite sum. If we simplify (4.49), then we obtain

$$
\begin{aligned}
a_w^{(kk',ll',n)} &= \frac{\sqrt{(2l+1)(2l'+1)}}{2^{l+l'+1}} \sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}} \sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma\left(k+\frac{1}{2}\right)\Gamma\left(k'+\frac{1}{2}\right)}} \\
&\times \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k-\frac{1}{2}}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'-\frac{1}{2}}{k'-l'-1-j'} \\
&\times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \frac{(-1)^{q+q'}(2l-2q)!\,(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!\,(l'-q')!q!q'!} \\
&\times \sum_{n_2=0}^{j'+q'} \binom{j'+q'}{n_2} \sum_{n_4=0}^{n_2} \binom{n_2}{n_4} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} (-1)^{n_3} \\
&\times \frac{{}_3F_2\left[\{a_1,a_2,a_3\},\{b_1,b_2\};1\right]}{(w-j'-q'+n_2-n_3-2n_4)!} \\
&\times \Gamma\left(\frac{l+l'+2j-2q'+w+2n_2-2n_3-4n_4+3}{2}\right) \\
&\times \frac{\left((-1)^{l+l'+w}+1\right)(-2)^{(j'+q'-n_2)}}{l+l'+w-2q-2q'-2n_3-2n_4+1},
\end{aligned}
\tag{4.50}
$$

where

$$
\begin{aligned}
a_1 &= \frac{j' + q' - n_2 + n_3 + 2n_4 - w}{2}, \\
a_2 &= \frac{j' + q' - n_2 + n_3 + 2n_4 - w}{2} + \frac{1}{2}, \\
a_3 &= \frac{-\left(l + l' + w + 1\right)}{2} + n_3 + n_4 + q + q', \\
b_1 &= -j - \frac{l + l' + w + 1}{2} - n_2 + n_3 + 2_4 + q', \\
b_2 &= \frac{-\left(l + l' + w\right)}{2} + n_3 + n_4 + q + q'.
\end{aligned}
\tag{4.51}
$$

Therefore we get

$$a_1 = a_2 + \frac{1}{2} \quad \text{and} \quad b_2 = a_3 + 1, \tag{4.52}$$

hence one of the a_1 or a_2 is a negative integer, but according to our assumption a_1 is a negative integer. We say $a_1 = -N$ where $N = 0, 1, 2, \ldots$. Since

$${}_3F_2\left[\{a_1, a_2, a_3\}, \{b_1, b_2\}; 1\right] = \sum_{p=0}^{\infty} \frac{(a_1)_p (a_2)_p (a_3)_p}{(b_1)_p (b_2)_p} \frac{1}{p!} \tag{4.53}$$

and by the assumption

$$(a_1)_n = (-N)_n = 0, \tag{4.54}$$

therefore the hypergeometric function ${}_3F_2\left[\{a_1, a_2, a_3\}, \{b_1, b_2\}; 1\right]$ is finite, in other words, there exist a positive integer N, such that for $p > N$, the hypergeometric function is zero. Also since we assumed

$$a_1 = \frac{j' + q' - n_2 + n_3 + 2n_4 - w}{2} = N, \tag{4.55}$$

so w is finite and since according to our assumption always $w + (l + l')$ should be an even number therefore the maximum w can be $d = 2(k + k') - (l + l') - 6$. $\square$

Corollary 4.1.2 *The GTO translational coefficients have the following properties:*

1. $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|m|}(t) = \mathcal{I}^{\mathrm{SC}}_{k'k,l'l,|m|}(-t) = (-1)^{(l'-l)} \mathcal{I}^{\mathrm{SC}}_{k'k,l'l,|m|}(t)$.
2. $\displaystyle\sum_{k=0}^{\infty} \sum_{l=0}^{k-1} \mathcal{I}^{\mathrm{SC}}_{kk',ll',|m|}(t) \mathcal{I}^{\mathrm{SC}}_{kk'',ll'',|m|}(t) = \delta_{k'k''} \delta_{l'l''}$.

4.1.5. GTO Translational Coefficients & Ritchie's Matrix Elements of the Translation Operator

In Theorem 4.1.2, we obtained an expression for computing the GTO translational coefficients $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|m|}(t)$. Ritchie in [80, equation 10, p. 810] has described the translation matrix elements for the GTO spherical polar radial basis function. We recall Ritchie's theorem here, because then we have two different possibilities to compute the molecular docking.

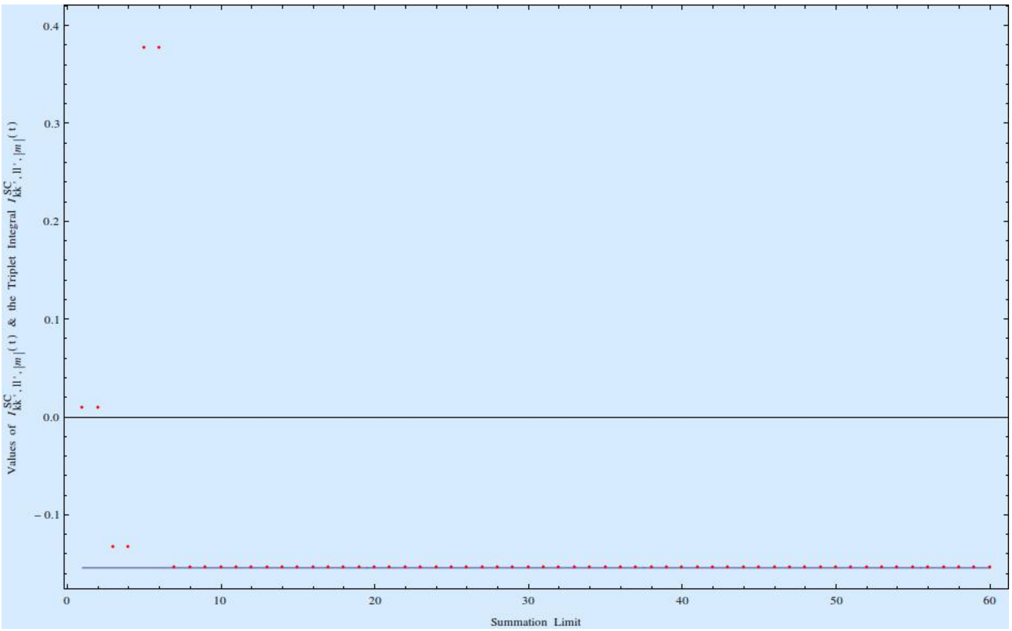


Figure 4.3.: Comparison of the exact value and the approximated value, according to the Theorem 4.1.2, for the GTO translational coefficients. We considered $k = 5$, $k' = 4$, $l = 3$, $l' = 2$, $t = 5$ and the cut off degree $n_1 = 60$. Here we can say precisely, from the degree "$2(k + k') - (l + l') - 6 = 7$" on, the GTO translational coefficients obtained from the Theorem 4.1.2 are exact.

Algorithm 4: GTO Translational Coefficient Algorithm

Input:
Integers $k,\ k',\ l,\ l'$ & m where $k > l \geq |m| \geq 0$ and $k' > l' \geq |m| \geq 0$

foreach (k, l, m) *and* (k', l', m) **do**
  Compute $d = 2(k + k') - (l + l') - 6$.
  Compute $a_w^{(kk',ll',m)}$ of Theorem 4.1.2.
  foreach *Rotation* d **do**
    Compute $\mathcal{P}(t) = \sum_{w=0}^{d} a_w^{(kk',ll',m)} t^w$.
  end
end
foreach *polynomial* $\mathcal{P}(t)$ **do**
  Multiply $\mathcal{P}(t)$ by $e^{t^2/4}$.
end
Output: The GTO translational Coefficients $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|m|}(t)$.

Definition 4.1.2 *For integers k, k', l, l and m where $k > l \geq |m| > 0$ and $k' > l' \geq$*

$|m| > 0$, the

$$\mathcal{T}^{(|m|)}_{k'l',kl}(t) = \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|} \int_0^\infty \tilde{R}^{l'}_{k'}(\beta)\tilde{R}^{l}_{k}(\beta) j_p(\beta t)\, \beta^2 \,\mathrm{d}\beta,$$

where $j_p(\beta t)$ are Bessel functions, see (2.46), and $A_p^{ll'|m|}$ are given by

$$A_p^{ll'|m|} = (-1)^{\frac{p+u-l}{2}+m}(2p+1)\sqrt{(2l'+1)(2l+1)} \begin{pmatrix} l & l' & p \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & p \\ m & -m & 0 \end{pmatrix},$$

are called the translational matrix elements for GTO spherical polar radial basis functions.

Lemma 4.1.5 *For integer numbers k, k', l, l' and m where $k > l \geq |m| \geq 0$ and $k' > l' \geq |m| \geq 0$, one has*

$$\mathcal{T}^{(|m|)}_{k'l',kl}(t) = \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|} \sum_{i=0}^{(k+k')-(l+l')-2} \mathcal{C}_i^{(kl,k'l')} \mathcal{M}! \mathrm{e}^{-\frac{t^2}{4}} \left(\frac{t^2}{4}\right)^{p/2} L_{\mathcal{M}}^{(p+\frac{1}{2})}\left(\frac{t^2}{4}\right),$$

where

$$A_p^{ll'|m|} = (-1)^{\frac{p+u-l}{2}+m}(2p+1)\sqrt{(2l'+1)(2l+1)} \begin{pmatrix} l & l' & p \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & p \\ m & -m & 0 \end{pmatrix},$$

$$\mathcal{C}_i^{(kl,k'l')} = \sum_{j=0}^{k-l-1} \sum_{j'=0}^{k'-l'-1} \delta_{i,j+j'} \mathcal{X}_{klj} \mathcal{X}_{k'l'j'},$$

$$\mathcal{X}_{klj} = \sqrt{\frac{(k-l-1)!\,(1/2)_k}{2}} \frac{(-1)^{k-l-1-j}}{j!\,(k-l-1-j)!\,(1/2)_{l+j+1}},$$

$$\mathcal{M} = i + \frac{l+l'+p}{2},$$

also $(1/2)_k$ and $(1/2)_{l+j+1}$ are Pochhammer symbols and $\delta_{i,j+j'}$, is the Kronecker delta function.

Proof. By assumption two coordinate systems $\mathbf{x} = (r, \theta, \phi)$ and $\mathbf{x}' = (r', \theta', \phi)$ may be related functionally by multiplying the vector equation $\mathbf{x}' = \mathbf{x} - \mathbf{t}$ by an arbitray complex vector $\mathrm{i}\mathbf{s}$ where $\mathbf{s} = (s, \theta_s, \phi_s)$ and $\mathbf{t} = (t, \theta_t, \phi_t)$ gives

$$\mathrm{e}^{\mathrm{i}\mathbf{s}\cdot\mathbf{x}} = \mathrm{e}^{\mathrm{i}\mathbf{s}\cdot(\mathbf{t}+\mathbf{x}')} = \mathrm{e}^{\mathrm{i}\mathbf{s}\cdot\mathbf{t}}\mathrm{e}^{\mathrm{i}\mathbf{s}\cdot\mathbf{x}'}. \tag{4.56}$$

By Raleigh's plane wave equation of [16], we have

$$\mathrm{e}^{\mathrm{i}\mathbf{s}\cdot\mathbf{x}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{i}^l j_l(sr) \overline{Y_l^m(\theta_s, \phi_s)}\, Y_l^m(\theta, \phi). \tag{4.57}$$

Now substituting the Raleigh's plane wave equatin (4.57) in (4.56), gives

$$4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{i}^l j_l(sr) \overline{Y_l^m(\theta_s, \phi_s)}\, Y_l^m(\theta, \phi) = 4\pi \sum_{p=0}^{\infty} \sum_{q=-p}^{p} \mathrm{i}^p j_p(st) \overline{Y_p^q(\theta_s, \phi_s)}\, Y_p^q(\theta_t, \phi_t)$$
$$\times 4\pi \sum_{u=0}^{\infty} \sum_{v=-u}^{u} \mathrm{i}^u j_u(sr') \overline{Y_u^v(\theta_s, \phi_s)}\, Y_u^v(\theta', \phi).$$

We simplify this equation, therefore

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} j_l(sr)\,\overline{Y_l^m(\theta_s,\phi_s)}\,Y_l^m(\theta,\phi) = 4\pi\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sum_{u=0}^{\infty}\sum_{v=-u}^{u} \mathrm{i}^{p+u-l} j_p(st) j_u(sr') \times \overline{Y_p^q(\theta_s,\phi_s)}\,Y_p^q(\theta_t,\phi_t)\,\overline{Y_u^v(\theta_s,\phi_s)}\,Y_u^v(\theta',\phi)\,. \tag{4.58}$$

Multiplying both sides of the equation (4.58) by $Y_l^m(\theta_s,\phi_s)$ and integrating on (θ_s,ϕ_s) gives

$$j_l(sr)\,Y_l^m(\theta,\phi) = 4\pi\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sum_{u=0}^{\infty}\sum_{v=-u}^{u} \mathrm{i}^{p+u-l} j_p(st) j_u(sr')\,Y_p^q(\theta_t,\phi_t)\,Y_u^v(\theta',\phi) \times \int_0^{\pi}\int_0^{2\pi} \overline{Y_p^q(\theta_s,\phi_s)}\,\overline{Y_u^v(\theta_s,\phi_s)}\,Y_l^m(\theta_s,\phi_s)\sin\theta_s\,\mathrm{d}\phi_s\,\mathrm{d}\theta_s. \tag{4.59}$$

We have generally, $\overline{Y_l^m(\theta,\phi)} = (-1)^m\,Y_l^{-m}(\theta,\phi)$, consequently

$$j_l(sr)\,Y_l^m(\theta,\phi) = 4\pi\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sum_{u=0}^{\infty}\sum_{v=-u}^{u} \mathrm{i}^{p+u-l} j_p(st) j_u(sr')\,Y_p^q(\theta_t,\phi_t)\,Y_u^v(\theta',\phi) \times (-1)^{q+v}\int_0^{\pi}\int_0^{2\pi} Y_p^{-q}(\theta_s,\phi_s)\,Y_u^{-v}(\theta_s,\phi_s)\,Y_l^m(\theta_s,\phi_s)\sin\theta_s\,\mathrm{d}\phi_s\,\mathrm{d}\theta_s. \tag{4.60}$$

Then by using the Gaunt's integral in (2.56), we have

$$j_l(sr)\,Y_l^m(\theta,\phi) = 4\pi\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sum_{u=0}^{\infty}\sum_{v=-u}^{u} \mathrm{i}^{p+u-l} j_p(st) j_u(sr')\,Y_p^q(\theta_t,\phi_t)\,Y_u^v(\theta',\phi) \times (-1)^{q+v}\sqrt{\frac{(2p+1)(2u+1)(2l+1)}{4\pi}}\begin{pmatrix} l & u & p\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & u & p\\ m & -v & -q\end{pmatrix}. \tag{4.61}$$

Now, in (4.61), the first 3-j symbols vanishes when $l+u+p$, is an odd integer. Furthermore the second 3-j symbol vanishes unless $m-v-q=0$, therefore $m-v=q$ and hence by substituting $q=m-v$ the expression (4.61) reduces to the following triple sum

$$j_l(sr)\,Y_l^m(\theta,\phi) = 4\pi\sum_{p=0}^{\infty}\sum_{u=0}^{\infty}\sum_{v=-u}^{u} \mathrm{i}^{p+u-l} j_p(st) j_u(sr')\,Y_p^{m-v}(\theta_t,\phi_t)\,Y_u^v(\theta',\phi) \times (-1)^{m}\sqrt{\frac{(2p+1)(2u+1)(2l+1)}{4\pi}}\begin{pmatrix} l & u & p\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & u & p\\ m & -v & v-m\end{pmatrix}. \tag{4.62}$$

By assumption $\mathbf{t}=(t,0,0)$ is a translation along the positive z-axis which entails $m-v=0$, this means $m=v$ and allows the summation over v be eliminated, i.e.

$$j_l(sr)\,Y_l^m(\theta,\phi) = 4\pi\sum_{p=0}^{\infty}\sum_{u=0}^{\infty}\sum_{v=-u}^{u} \mathrm{i}^{p+u-l} j_p(st) j_u(sr')\,Y_p^{0}(0,0)\,Y_u^m(\theta',\phi) \times (-1)^{m}\sqrt{\frac{(2p+1)(2u+1)(2l+1)}{4\pi}}\begin{pmatrix} l & u & p\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & u & p\\ m & -m & 0\end{pmatrix}. \tag{4.63}$$

We have $Y_p^0(0,0) = \sqrt{\frac{(2p+1)}{4\pi}}$, $\mathrm{i}^{p+u-l} = (-1)^{(p+l-u)/2}$ and also using the triangular inequality for 3-j symbols gives

$$j_l(sr)\, Y_l^m(\theta,\phi) = \sum_{u=0}^{\infty} \sum_{p=|l-u|}^{l+u} A_p^{lu|m|} j_p(st) j_u(sr')\, Y_u^m(\theta',\phi), \tag{4.64}$$

where

$$A_p^{lu|m|} = (-1)^{(p+l-u)/2}(2p+1)\sqrt{(2u+1)(2l+1)} \begin{pmatrix} l & u & p \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & u & p \\ m & -m & 0 \end{pmatrix}. \tag{4.65}$$

Relabelling u by l', therefore we have

$$j_l(sr)\, Y_l^m(\theta,\phi) = \sum_{l'=0}^{\infty} \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|} j_p(st) j_{l'}(sr')\, Y_{l'}^m(\theta',\phi), \tag{4.66}$$

where

$$A_p^{ll'|m|} = (-1)^{(p+l-l')/2}(2p+1)\sqrt{(2l'+1)(2l+1)} \begin{pmatrix} l & l' & p \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & p \\ m & -m & 0 \end{pmatrix}. \tag{4.67}$$

Applying the inverse Bessel transform on (4.66) or equivalently multiplying each side of (4.66) by $\sqrt{\frac{2}{\pi}}\hat{R}_k^l(s)$ and integrating over s gives

$$\sqrt{\frac{2}{\pi}} \int_0^\infty j_l(sr)\, Y_l^m(\theta,\phi)\, \hat{R}_k^l(s) s^2 \,\mathrm{d}s = \sum_{l'=0}^{\infty} \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|}$$
$$\times \sqrt{\frac{2}{\pi}} \int_0^\infty j_p(st) j_{l'}(sr')\, Y_{l'}^m(\theta',\phi)\, \hat{R}_k^l(s) s^2 \,\mathrm{d}s.$$

We simplify the above expression, hence we obtain

$$R_k^l(r)\, Y_l^m(\theta,\phi) = \sum_{l'=0}^{\infty} \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|} \times \sqrt{\frac{2}{\pi}} \int_0^\infty j_p(st) j_{l'}(sr')\, Y_{l'}^m(\theta',\phi)\, \hat{R}_k^l(s) s^2 \,\mathrm{d}s. \tag{4.68}$$

Now, we multiply each side of the equation (4.68) by $R_{k'}^{l''}(r')\, Y_{l''}^{m'}(\theta',\phi)$ and integrating over all space in the corresponding variables gives

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} R_k^l(r)\, Y_l^m(\theta,\phi)\, R_{k'}^{l''}(r')\, Y_{l''}^{m'}(\theta',\phi)\, r'^2 \sin\theta' \,\mathrm{d}\phi\,\mathrm{d}\theta'\,\mathrm{d}r' = \int_0^\infty \int_0^\pi \int_0^{2\pi}$$
$$\left(\sum_{l'=0}^{\infty} \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|} \sqrt{\frac{2}{\pi}} \int_0^\infty j_p(st) j_{l'}(sr')\, Y_{l'}^m(\theta',\phi)\, \hat{R}_k^l(s) s^2 \,\mathrm{d}s \right)$$
$$\times R_{k'}^{l''}(r')\, Y_{l''}^{m'}(\theta',\phi)\, r'^2 \sin\theta' \,\mathrm{d}\phi\,\mathrm{d}\theta'\,\mathrm{d}r'.$$

We simplify the above equation, hence we obtain

$$\mathcal{T}_{k'l',kl}^{|m|}(t) = \sum_{l'=0}^{\infty} \sum_{p=|l-l'|}^{l+l'} A_p^{ll'|m|} \int_0^\infty j_p(st)\hat{R}_k^l(s) s^2$$
$$\left(\sqrt{\frac{2}{\pi}} \int_0^\infty j_{l'}(sr') \left(\int_0^\pi \int_0^{2\pi} Y_{l'}^m(\theta',\phi)\; Y_{l''}^{m'}(\theta',\phi) \sin\theta' \,\mathrm{d}\phi\,\mathrm{d}\theta' \right) R_{k'}^{l''}(r') r'^2 \,\mathrm{d}r' \right) \mathrm{d}s. \tag{4.69}$$

Computing the inner integral gives

$$\begin{aligned}\mathcal{T}^{|m|}_{k'l',kl}(t) &= \sum_{p=|l-l'|}^{l+l'} A^{ll'|m|}_p \int_0^\infty j_p(st)\hat{R}^l_k(s)s^2 \left(\sqrt{\frac{2}{\pi}}\int_0^\infty j_{l'}(sr')R^{l'}_{k'}(r')r'^2\,\mathrm{d}r'\right)\mathrm{d}s \\ &= \sum_{p=|l-l'|}^{l+l'} A^{ll'|m|}_p \int_0^\infty j_p(st)\hat{R}^l_k(s)\hat{R}^{l'}_{k'}(s)s^2\,\mathrm{d}s.\end{aligned} \tag{4.70}$$

Now we apply three identities about the associated Laguerre polynomials defined in (2.34), as

$$(k+1)\,L^{(\alpha)}_{k+1}(x) = (2k+\alpha+1-x)\,L^{(\alpha)}_k(x) - (k+\alpha)\,L^{(\alpha)}_{k-1}(x), \tag{4.71}$$

$$L^{(\alpha)}_0(x) = 1, \tag{4.72}$$

and

$$L^{(\alpha)}_1(x) = \alpha + 1 - x. \tag{4.73}$$

From Erdelyi et al. [31, p. 42, equation 3] and also Ritchie [80, equation 17], we know the GTO spherical polar radial basis functions are eigenfunctions of the spherical Bessel transform, so

$$\hat{R}^l_k(s) = (-1)^{k-l-1}\sqrt{\frac{2\,(k-l-1)!}{\sqrt{\pi}\,(1/2)_k}}\mathrm{e}^{\frac{-x^2}{2}}x^l\,L^{(l+1/2)}_{k-l-1}(x^2), \tag{4.74}$$

where $x^2 = s$. Now we can write

$$\hat{R}^l_k(s) = \sqrt{\frac{4}{\sqrt{\pi}}}\sum_{j=0}^{k-l-1}\mathcal{X}_{klj}\mathrm{e}^{\frac{-x^2}{2}}x^{2j+l}, \tag{4.75}$$

where

$$\mathcal{X}_{klj} = \sqrt{\frac{(k-l-1)!\,(1/2)_k}{2}}\frac{(-1)^{k-l-1-j}}{j!\,(k-l-1-j)!\,(1/2)_{l+j+1}}. \tag{4.76}$$

We substitute twice (4.74) into (4.70), hence we have

$$\begin{aligned}\mathcal{T}^{|m|}_{k'l',kl}(t) = \sum_{p=|l-l'|}^{l+l'} A^{ll'|m|}_p \int_0^\infty j_p(xt)&\left(\sqrt{\frac{4}{\sqrt{\pi}}}\sum_{j=0}^{k-l-1}\mathcal{X}_{klj}\mathrm{e}^{-\frac{x^2}{2}}x^{2j+l}\right) \\ &\left(\sqrt{\frac{4}{\sqrt{\pi}}}\sum_{j'=0}^{k'-l'-1}\mathcal{X}_{k'l'j'}\mathrm{e}^{\frac{-x^2}{2}}x^{2j'+l'}\right)x^2\,\mathrm{d}x.\end{aligned} \tag{4.77}$$

Collecting the coefficient of x^{2i}, using

$$\mathcal{C}^{(kl,k'l')}_i = \sum_{j=0}^{k-l-1}\sum_{j'=0}^{k'-l'-1}\delta_{i,j+j'}\mathcal{X}_{klj}\mathcal{X}_{k'l'j'}, \tag{4.78}$$

gives the following GTO translation matrix element

$$\mathcal{T}^{|m|}_{k'l',kl}(t) = \sum_{p=|l-l'|}^{l+l'} A^{ll'|m|}_p \sum_{i=0}^{(k-l-1)+(k'-l'-1)}\mathcal{C}^{(kl,k'l')}_i\frac{4}{\sqrt{\pi}}\int_0^\infty j_p(xt)x^{2i+l+l'}x^2\,\mathrm{d}x. \tag{4.79}$$

For computing the integral, we apply the following relation of Erdelyi et al. [31, p. 30, equation 13], see Ritchie [80, equation 22].

$$\frac{4}{\sqrt{\pi}}\int_0^\infty \mathrm{e}^{-x^2}x^{2m+p}j_p(xy)x^2\,\mathrm{d}x = m!\mathrm{e}^{\frac{-y^2}{4}}\left(\frac{y^2}{4}\right)^{p/2}L_m^{(p+1/2)}\left(\frac{y^2}{4}\right). \tag{4.80}$$

This gives the final result. □

4.1.6. Fast Rotational Matching on Shape Complementarity

The correlation of two affinity functions $Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x})$ and $Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x})$ is a new function of rotations $\mathbf{R}$, $\mathbf{R}'$ and distance parameter t along the positive z-axis, see (4.30)

$$\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\left(\mathbf{R}',\mathbf{t}\right)\right)=\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right):=\int_{\mathbb{R}^3}\Lambda_{\mathbf{R}}Q_{\mathrm{A}}^{\mathrm{SC}}(\mathbf{x})\cdot\mathcal{T}^{\mathbf{t}}\Lambda_{\mathbf{R}'}Q_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x})\,\mathrm{d}\mathbf{x}.$$

For given integers l and m with the condition $l\geq|m|\geq 0$ and a rotation $\mathbf{R}\in SO(3)$, we have

$$\Lambda_{\mathbf{R}}\,Y_l^m(\mathbf{u})=\sum_{n=-l}^{l}D_l^{nm}(\mathbf{R})\,Y_l^n(\mathbf{u}). \tag{4.81}$$

Considering (4.81), gives

$$\begin{aligned}\Lambda_{\mathbf{R}}\mathrm{Q}_{\mathrm{A}}^{SC}(r\mathbf{u})&=\sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l}\hat{Q}_{klm}^{\mathrm{A}}R_k^l(r)\Lambda_{\mathbf{R}}\left(Y_l^m(\mathbf{u})\right)\\&=\sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m,n=-l}^{l}\hat{Q}_{klm}^{\mathrm{A}}D_l^{nm}(\mathbf{R})R_k^l(r)\,Y_l^n(\mathbf{u}),\end{aligned} \tag{4.82}$$

and the effect of a rotation $\mathbf{R}'\in SO(3)$ together with a translation $\mathbf{t}$ along an axis on the $\mathrm{Q}_{\mathrm{B}}^{\mathrm{SC}}(r\mathbf{u})$ is written as

$$\begin{aligned}&\Lambda_{\mathbf{R}'}\mathcal{T}^{\mathbf{t}}\mathrm{Q}_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x})=\Lambda_{\mathbf{R}'}\mathrm{Q}_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x}-\mathbf{t})=\Lambda_{\mathbf{R}'}\mathrm{Q}_{\mathrm{B}}^{\mathrm{SC}}(\mathbf{x}')=\Lambda_{\mathbf{R}'}\mathrm{Q}_{\mathrm{B}}^{\mathrm{SC}}(r'\mathbf{u}')\\&=\sum_{k'=1}^{\infty}\sum_{l'=0}^{k'-1}\sum_{m',n'=-l'}^{l'}\hat{Q}_{k'l'm'}^{\mathrm{B}}D_{l'}^{n'm'}(\mathbf{R}')R_{k'}^{l'}(r')\,Y_{l'}^{n'}(\mathbf{u}').\end{aligned} \tag{4.83}$$

We present the general form of the correlation of two affinity functions in $L^2\left(\mathbb{R}^3\right)$ in the following result.

Theorem 4.1.3 *The scoring function* (4.30) *can be computed by*

$$\begin{aligned}\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right)=\sum_{k=1}^{\infty}\sum_{k'=1}^{\infty}\sum_{l=0}^{k-1}\sum_{l'=0}^{k'-1}\sum_{m=-l}^{l}\sum_{m'=-l'}^{l'}\sum_{n=-l}^{l}\hat{Q}_{klm}^{\mathrm{A}}\hat{Q}_{k'l'm'}^{\mathrm{B}}D_l^{nm}(\mathbf{R})D_{l'}^{-nm'}(\mathbf{R}')\\ \times\mathcal{I}_{kk',ll',|n|}^{\mathrm{SC}}(t).\end{aligned}$$

Proof. By the relation between $\mathbf{u}$ and $\mathbf{u}'$ in (4.36), we have

$$\begin{aligned}\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right) &= \int_0^\infty \int_{\mathbb{S}^2} \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l}\sum_{n=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} D_l^{nm}(\mathbf{R}) R_k^l(r)\, Y_l^n(\mathbf{u}) \\ &\times \sum_{k'=1}^{\infty}\sum_{l'=0}^{k'-1}\sum_{m=-l'}^{l'}\sum_{n'=-l'}^{l'} \hat{Q}^{\mathrm{B}}_{k'l'm'} D_{l'}^{n'm'}(\mathbf{R}') R_{k'}^{l'}(r')\, Y_{l'}^{n'}(\mathbf{u}') r^2 \,\mathrm{d}\mathbf{u}\,\mathrm{d}r \\ &= \sum_{kk',ll',mm',nn'} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} D_l^{nm}(\mathbf{R}) D_{l'}^{n'm'}(\mathbf{R}') \\ &\times \int_0^\infty\int_0^\pi\int_0^{2\pi} R_k^l(r) R_{k'}^{l'}(r')\, Y_l^n(\mathbf{u})\, Y_{l'}^{n'}(\mathbf{u}') r^2 \sin\theta \,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r.\end{aligned}$$

According to Definition 4.2.1, we have

$$\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right) = \sum_{kk',ll',mm',n} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} D_l^{nm}(\mathbf{R}) D_{l'}^{-nm'}(\mathbf{R}') \times \mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t). \;\square$$

The above theorem describes an algorithm to compute the scoring function (4.30). In modern computational chemistry and quantum mechanics which are related to our algorithms, computations are typically performed within a finite set, so suppose that we cut off k and k' to degree $N \in \mathbb{N}$ and we are given the precomputed coefficients $\hat{Q}^{\mathrm{A}}_{klm}$, $\hat{Q}^{\mathrm{B}}_{k'l'm'}$ and $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$, the scoring function $\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right)$ can be computed in the following four steps:

1. We compute

$$\hat{a}_{kln,l'm'}(t) = \sum_{k'=1}^{N} \hat{Q}^{\mathrm{B}}_{k'l'm'} \mathcal{I}_{kk',ll',|n|}(t), \tag{4.84}$$

which takes $\mathcal{O}(N^6 N_t)$ operations and N_t shows the number of one-dimensional translations.

2. In the second step we have

$$\hat{b}^{\mathbf{R}'}_{kln}(t) = \sum_{l'=0}^{k'-1}\sum_{m'=-l'}^{l'} \hat{a}_{kln,l'm'}(t) \mathrm{D}_{l'}^{-nm'}(\mathbf{R}'), \tag{4.85}$$

which is computed by NFSOFT in $\mathcal{O}\left(\left(N^3\left(N^2\log N + \widetilde{N_{\mathbf{R}'}}\right) + N^6\right) N_t\right)$ operations and $\widetilde{N_{\mathbf{R}'}}$ denotes the overall rotations for $\mathbf{R}'$.

3. In the third step we compute

$$\hat{c}^{\mathbf{R}'}_{lmn}(t) = \sum_{k=1}^{N} \hat{b}^{\mathbf{R}'}_{kln}(t) \hat{Q}^{\mathrm{A}}_{klm}, \tag{4.86}$$

and it takes $\mathcal{O}\left(\left(N^4 \widetilde{N_{\mathbf{R}'}} + \left(N^3\left(N^2\log N + \widetilde{N_{\mathbf{R}'}}\right) + N^6\right)\right) N_t\right)$ operations.

4. Finally in the last step we compute $\mathcal{C}^{\mathrm{SC}}(\mathbf{R}, \mathbf{R}'; t)$ by NFSOFT, hence

$$\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R}, \mathbf{R}'; t\right) = \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \sum_{n=-l}^{l} \hat{c}_{lmn}^{\mathbf{R}'}(t) \mathrm{D}_l^{nm}(\mathbf{R}), \tag{4.87}$$

with the computational complexity

$$\mathcal{O}\left(\left(\widetilde{N_{\mathbf{R}'}}\left(N^3 \log N + N_{\mathbf{R}}\right) + \left(N^4 \widetilde{N_{\mathbf{R}'}} + \left(N^3\left(N^2 \log N + \widetilde{N_{\mathbf{R}'}}\right) + N^6\right)\right)\right) N_t\right),$$

therefore the whole computational complexity is $\mathcal{O}\left(\left(N^6 + N^4 \widetilde{N_{\mathbf{R}'}} + N_{\mathbf{R}} \widetilde{N_{\mathbf{R}'}}\right) N_t\right)$ operations.

Algorithm 5: FRM on Shape Complementarity by NFSOFT

Input:
N: Cut off degree
N_{A} and N_{B}: The number of atomic coordinates of molecules A and B
A set of motions $(\mathbf{R}, \mathbf{t})$ in $SE(3)$ and rotations $\mathbf{R}' \in SO(3)$

foreach $\mathbf{x}_j$ *with* $j \in N_{\mathrm{A}} \cup N_{\mathrm{B}}$ **do**
  Compute the centeres $\mathbf{c}_{\mathrm{A}}$ and $\mathbf{c}_{\mathrm{B}}$ of both molecules A and B.
  Compute the relocate atomic centeres $\mathbf{z}_j^{\mathrm{A/B}} = \mathbf{x}_j - \mathbf{c}_{\mathrm{A/B}}$.
end
foreach $\left(k, l, m\right)$ *and* $\left(k', l', m'\right)$ *with* $k > l \geq |m| \geq 0$ *and* $k' > l' \geq |m'| \geq 0$ **do**
  Compute $\hat{Q}_{klm}^{\mathrm{A}}$ and $\hat{Q}_{k'l'm'}^{\mathrm{B}}$ of Theorem 4.1.1.
end
foreach *translation* $\mathbf{t} \in \mathbb{R}^3$ *with* $t = \|\mathbf{t}\|_2$, $\left(k, k', l, l', n\right)$ *with* $k > l \geq |n| \geq 0$ *and* $k' > l' \geq |n| \geq 0$ **do**
  Compute $\mathcal{I}_{kk',ll',|n|}^{\mathrm{SC}}(t)$ of Theorem 4.1.2.
end
foreach $\left(k, l, n, l', m'\right)$ *with* $k > l \geq |n| \geq 0$ *and* $l' \geq |m'| \geq 0$ **do**
  Compute $\hat{a}_{kln,l'm'}$ of (4.84).
end
foreach *rotation* $\mathbf{R}' \in SO(3)$ *and* $\left(k, l, n\right)$ *with* $k > l \geq |n| \geq 0$ **do**
  Compute $\hat{b}_{kln}^{\mathbf{R}'}$ by NFSOFT of (4.85).
end
foreach $\left(l, m, n\right)$ *with* $l \geq |n|, |m| \geq 0$ **do**
  Compute $\hat{c}_{lmn}^{\mathbf{R}'}$ of (4.86).
end
foreach *rotation* $\mathbf{R} \in SO(3)$ **do**
  Compute $\mathcal{C}^{\mathrm{SC}}(\mathbf{R}, \mathbf{R}'; t)$ by NFSOFT of (4.87).
end
Output: The solution of the docking problem.

Complexity: $\mathcal{O}\left(\left(N^6 + N^4 \widetilde{N_{\mathbf{R}'}} + N_{\mathbf{R}} \widetilde{N_{\mathbf{R}'}}\right) N_t\right)$ operations.

Now we use Wriggers' approach to show a more useful representation of the correlation by factorizing the rotations $\mathbf{R}$ and $\mathbf{R}' \in SO(3)$ in term of Euler angles, see [58].

Corollary 4.1.3 *The scoring function in Theorem 4.1.3 is a function of five Euler angles and one displacement translation parameter and can be computed by*

$$\begin{aligned}&\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right)=\mathcal{C}^{\mathrm{SC}}\left(\sigma,\eta,\omega,\eta',\omega',t\right)\\&=\sum_{kk',ll',mm',n,ss'}\hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'}\,d_l^{ns}\,d_l^{sm}\,d_{l'}^{-ns'}\,d_{l'}^{s'm'}\,\mathrm{e}^{\mathrm{i}(n\sigma+s\eta+m\omega+s'\eta'+m'\omega')}\times\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t).\end{aligned}$$

Proof. If $\mathbf{R}=\mathbf{R}\left(\alpha,\beta,\gamma\right)$ and $\mathbf{R}'=\mathbf{R}'\left(\alpha',\beta',\gamma'\right)$ then $\mathbf{R}=\mathbf{R}_1\cdot\mathbf{R}_2$ and $\mathbf{R}'=\mathbf{R}'_1\cdot\mathbf{R}'_2$ where

$$\mathbf{R}_1=\mathbf{R}_1\left(\zeta,\frac{\pi}{2},0\right),\ \mathbf{R}_2=\mathbf{R}_2\left(\eta,\frac{\pi}{2},\omega\right)$$

and

$$\mathbf{R}'_1=\mathbf{R}'_1\left(\zeta',\frac{\pi}{2},0\right),\ \mathbf{R}'_2=\mathbf{R}'_2\left(\eta',\frac{\pi}{2},\omega'\right)$$

together with the following relations

$$\zeta=\alpha-\frac{\pi}{2},\quad \eta=\pi-\beta,\quad \omega=\gamma-\frac{\pi}{2}$$

and

$$\zeta'=\alpha'-\frac{\pi}{2},\quad \eta'=\pi-\beta',\quad \omega'=\gamma'-\frac{\pi}{2}.$$

Using the definition of Wigner-D function, i.e.

$$D_l^{nm}\left(\mathbf{R}\left(\alpha,\beta,\gamma\right)\right)=\mathrm{e}^{-\mathrm{i}n\alpha}\mathrm{e}^{-\mathrm{i}m\gamma}\,d_l^{nm}(\beta),$$

and the identity (2.51),

$$D_l^{nm}\left(\mathbf{R}_1\cdot\mathbf{R}_2\right)=\sum_{s=-l}^{l}D_l^{ns}(\mathbf{R}_1)D_l^{sm}(\mathbf{R}_2),$$

implies that

$$\begin{aligned}&D_l^{nm}(\mathbf{R})=D_l^{nm}\left(\mathbf{R}_1\cdot\mathbf{R}_2\right)=D_l^{nm}\left(\mathbf{R}_1\left(\zeta,\frac{\pi}{2},0\right)\cdot\mathbf{R}_2\left(\eta,\frac{\pi}{2},\omega\right)\right)\\&=\sum_{s=-l}^{l}D_l^{ns}\big(\zeta,\frac{\pi}{2},0\big)D_l^{sm}\big(\eta,\frac{\pi}{2},\omega\big)=\sum_{s=-l}^{l}\mathrm{e}^{-\mathrm{i}n\zeta}d_l^{ns}(\frac{\pi}{2})\mathrm{e}^{-\mathrm{i}s\eta}\mathrm{e}^{-\mathrm{i}m\omega}d_l^{sm}(\frac{\pi}{2})\\&=\sum_{s=-l}^{l}d_l^{ns}(\frac{\pi}{2})d_l^{sm}(\frac{\pi}{2})\mathrm{e}^{-\mathrm{i}(n\zeta+s\eta+m\omega)}=\sum_{s=-l}^{l}d_l^{ns}\,d_l^{sm}\mathrm{e}^{-\mathrm{i}(n\zeta+s\eta+m\omega)}.\end{aligned}$$

Similarly

$$D_{l'}^{n'm'}(\mathbf{R}')=\sum_{s'=-l'}^{l'}d_{l'}^{n's'}\,d_{l'}^{s'm'}\,\mathrm{e}^{-\mathrm{i}(n'\zeta'+s'\eta'+m'\omega')}.$$

Note that, for brevity, we denote each $d_l^{rs}(\frac{\pi}{2}) = d_l^{rs}$. Now by replacing these assumptions into the Theorem 4.1.3, we have

$$\begin{aligned}
\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right) &= \sum_{kk',ll',mm',n} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} D_l^{nm}(\mathbf{R}) D_{l'}^{-nm'}(\mathbf{R}') \times \mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) \\
&= \sum_{kk',ll',mm',n} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} \sum_{s=-l}^{l} d_l^{ns} d_l^{sm} \mathrm{e}^{-\mathrm{i}(n\zeta+s\eta+m\omega)} \sum_{s'=-l'}^{l'} d_{l'}^{-ns'} d_{l'}^{s'm'} \mathrm{e}^{-\mathrm{i}(-n\zeta'+s'\eta'+m'\omega')} \\
&\times \mathcal{I}^{\mathrm{SC}}_{kk',ll',n}(t) \\
&= \sum_{kk',ll',mm',n,ss'} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} d_l^{ns} d_l^{sm} d_{l'}^{-ns'} d_{l'}^{s'm'} \mathrm{e}^{\mathrm{i}(n\zeta+s\eta+m\omega-n\zeta'+s'\eta'+m'\omega')} \times \mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t) \\
&= \sum_{kk',ll',mm',n,ss'} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} d_l^{ns} d_l^{sm} d_{l'}^{-ns'} d_{l'}^{s'm'} \mathrm{e}^{\mathrm{i}(n(\zeta-\zeta')+s\eta+m\omega+s'\eta'+m'\omega')} \times \mathcal{I}_{kk',ll',|n|}(t).
\end{aligned}$$

Letting $\delta = \zeta - \zeta'$, we have

$$\begin{aligned}
\mathcal{C}^{\mathrm{SC}}\left(\mathbf{R},\mathbf{R}';t\right) = \sum_{kk',ll',mm',n,ss'} & \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} d_l^{ns} d_l^{sm} d_{l'}^{-ns'} d_{l'}^{s'm'} \mathrm{e}^{\mathrm{i}(n\sigma+s\eta+m\omega+s'\eta'+m'\omega')} \\
& \times \mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t). \square
\end{aligned}$$

From the above corollary we infer that the scoring function is a function of the five angles $\sigma, \eta, \omega, \eta', \omega'$ and the distance parameter t, and the Fourier coefficients of the scoring function are

$$\hat{\mathcal{C}}^{\mathrm{SC}}\left(n,s,m,s',m'\right) = \sum_{kk',ll'} \hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'} d_l^{ns} d_l^{sm} d_{l'}^{-ns'} d_{l'}^{s'm'} \mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t).$$

The above corollary provides an algorithm. For each t, a five-dimensional FT yields the correlation on a grid in $(\sigma, \eta, \omega, \eta', \omega')$ space. As we need to compute the scoring function $\mathcal{C}^{\mathrm{SC}}(\mathbf{R},\mathbf{R}';t)$ for five rotational degrees of freedom for different Euler angles, we cut off k and k' to degree $N \in \mathbb{N}$ and supposing we are given the precomputed coefficients $\hat{Q}^{\mathrm{A}}_{klm}$, $\hat{Q}^{\mathrm{B}}_{k'l'm'}$ and $\mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t)$, the scoring function $\mathcal{C}^{\mathrm{SC}}(\mathbf{R},\mathbf{R}';t)$ can be computed in the following three steps:

1. At first, we compute

$$\hat{a}_{klnm'}(t) = \sum_{k'=1}^{N}\sum_{l'=0}^{k'-1} \hat{Q}^{\mathrm{B}}_{k'l'm'} \mathcal{I}^{\mathrm{SC}}_{kk',ll',|n|}(t), \tag{4.88}$$

which takes $\mathcal{O}(N^6 N_t)$ operations, and N_t denotes the number of one-dimensional translations.

2. In the second step, we compute

$$\hat{b}_{mm'n}(t) = \sum_{k=1}^{N}\sum_{l=0}^{k-1} \hat{a}_{klnm'}(t)\hat{Q}^{\mathrm{A}}_{klm}, \tag{4.89}$$

and its computational complexity is $\mathcal{O}\left(\left(N^5 + N^6\right) N_t\right)$ operations

3. Finally we compute the following expression by FFT, namely

$$\mathcal{C}^{\mathrm{SC}}\left(\sigma,\eta,\omega,\eta',\omega';t\right) = \sum_{m=-l}^{l}\sum_{m'=-l}^{l}\sum_{n=-l}^{l}\sum_{s=-l}^{l}\sum_{s'=-l}^{l} \hat{b}_{mm'n}(t)\, d_l^{ns}\, d_l^{sm}\, d_{l'}^{-ns'}\, d_{l'}^{s'm'} \times \mathrm{e}^{\mathrm{i}(n\sigma+s\eta+m\omega+s'\eta'+m'\omega')} \tag{4.90}$$

with the computational complexity $\mathcal{O}\left(\left(N^5\log N + N_{\mathbf{R}}^5 + N^5 + N^6\right)N_t\right)$ operations and $N_{\mathbf{R}}$ denotes the maximum number of the Euler angles σ, η, η', ω and ω'.

Therefore the overall computational complexity yields $\mathcal{O}\left(\left(N^6 + N_{\mathbf{R}}^5\right)N_t\right)$ operations.

Algorithm 6: FRM on Shape Complementarity by FFT

Input:
N: Cut off degree
N_{A} and N_{B}: The number of atomic coordinates of molecules A and B
A set of motions $(\mathbf{R},\mathbf{t})$ in $SE(3)$ and rotations $\mathbf{R}$ of $SO(3)$, with the conditions $\mathbf{R} = \mathbf{R}(\alpha,\beta,\gamma)$ and $\mathbf{R}' = \mathbf{R}'(\alpha',\beta',\gamma')$ where $\mathbf{R} = \mathbf{R}_1\left(\zeta,\frac{\pi}{2},0\right)\mathbf{R}_2\left(\eta,\frac{\pi}{2},\omega\right)$ and $\mathbf{R}' = \mathbf{R}'_1\left(\zeta',\frac{\pi}{2},0\right)\mathbf{R}'_2\left(\eta',\frac{\pi}{2},\omega'\right)$ where $\zeta = \alpha - \frac{\pi}{2},\ \eta = \pi - \beta,\ \omega = \gamma - \frac{\pi}{2}$, $\zeta' = \alpha' - \frac{\pi}{2},\ \eta' = \pi - \beta',\ \omega' = \gamma' - \frac{\pi}{2}$ and $\delta = \zeta - \zeta'$

foreach $\mathbf{x}_j$ *with* $j \in N_{\mathrm{A}} \cup N_{\mathrm{B}}$ **do**
  Compute the centeres of both molecules A and B.
  Compute the relocate atomic centeres of both molecules A and B.
end
foreach $\left(k,l,m\right)$ *and* $\left(k',l',m'\right)$ *with* $k > l \geq |m| \geq 0$ *and* $k' > l' \geq |m'| \geq 0$ **do**
  Compute $\hat{Q}_{klm}^{\mathrm{A}}$ and $\hat{Q}_{k'l'm'}^{\mathrm{B}}$ of Theorem 4.1.1.
end
foreach *translation* $\mathbf{t} \in \mathbb{R}^3$ *with* $t = \|\mathbf{t}\|_2$, $\left(k,k',l,l',n\right)$ *with* $k > l \geq |n| \geq 0$ *and* $k' > l' \geq |n| \geq 0$ **do**
  Compute $\mathcal{I}_{kk',ll',|n|}^{SC}(t)$ of Theorem 4.1.2.
end
foreach $\left(k,l,n,m'\right)$ *with* $k > l \geq |n| \geq 0$ *and* $l' \geq |m'| \geq 0$ **do**
  Compute $\hat{a}_{klnm'} of (4.88)$.
end
foreach $\left(m,m',n\right)$ *with* $m,n = -l,\ldots,l$ *and* $m' = -l',\ldots,l'$ **do**
  Compute $\hat{b}_{mm'n}$ of (4.89).
end
foreach $(\sigma,\eta,\omega,\eta',\omega')$ *of Euler angles* **do**
  Compute $\mathcal{C}^{\mathrm{SC}}(\sigma,\eta,\omega,\eta',\omega';t)$ by FFT of (4.90).
end
Output: The solution of the docking problem.

Complexity: $\mathcal{O}\left(\left(N^6 + N_{\mathbf{R}}{}^5\right)N_t\right)$ operations.

4.2. FRM on Electrostatic Complementarity

4.2.1. Introduction

In analogy to the previous chapter, FTM on shape complementarity, we present new computational methods for FRM on electrostatic complementarity. In this section with the aid of the ETO spherical polar radial basis functions, see Definition 2.3.6 and Lemma 2.3.11, the affinity functions are defined. Also we describe two methods for the computation of the ETO spherical polar radial Fourier coefficients Q^{EC}_{klm}. Also we define the ETO translational coefficients I^{EC} and we present a method to compute the I^{EC} coefficients. Finally we bring forward our algorithm that computes the scoring function by applying the ETO spherical polar radial Fourier coefficients, the ETO translational coefficients and the Wigner D-functions.

4.2.2. Affinity Functions & Electrostatic Complementarity Score

Shape complementarity together with electrostatic complementarity are typically used as the initial steps to obtain possible docking sites. Electrostatic complementarity is another important aspect in evaluating the fitness of the possible docking results. We have described the notions of charge density and electrostatic potential in (3.33) and (3.34). In molecular docking in terms of electrostatics, the molecules A and B are considered as two volumes with N_{A} and N_{B} point like charge carriers. Hence we have two affinity functions introduced in (3.37) and (3.38), i.e.

$$Q^{\mathrm{EC}}_{\mathrm{A}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{A}}} \frac{q_j}{\epsilon\left(\mathbf{x}-\mathbf{x}_j\right)\left\|\mathbf{x}-\mathbf{x}_j\right\|_2} \kappa^j_{\mathcal{G}}\left(\mathbf{x}-\mathbf{x}_j\right)$$

and

$$Q^{\mathrm{EC}}_{\mathrm{B}}(\mathbf{x}) = \sum_{j=1}^{N_{\mathrm{B}}} q_j \kappa^j_{\mathcal{G}}\left(\mathbf{x}-\mathbf{x}_j\right),$$

where q_j is the point-like charge on the j-th atom, $\epsilon\left(\mathbf{x}\right)$ has been defined in (3.35) and

$$\kappa^j_{\mathcal{G}}\left(\mathbf{x}-\mathbf{x}_j\right) = \mathrm{e}^{\beta\left(1-\frac{\|\mathbf{x}-\mathbf{x}_j\|_2^2}{r_j^2}\right)}.$$

Here we rotate molecule A by $\mathbf{R} \in SO(3)$ and also we rotate and translate molecule B by $(\mathbf{R}', \mathbf{t}) \in SE(3)$ where $\mathbf{t} = (0, 0, t)$, see Figure 4.1. Hence we define the scoring function by

$$\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R}, \left(\mathbf{R}', \mathbf{t}\right)\right) = \mathrm{Re}\int_{\mathbb{R}^3} \Lambda_{\mathbf{R}} Q^{\mathrm{EC}}_{\mathrm{A}}(\mathbf{x}) \cdot \Lambda_{\mathbf{R}'} \mathcal{T}^{\mathbf{t}} Q^{\mathrm{EC}}_{\mathrm{B}}(\mathbf{x})\, \mathrm{d}\mathbf{x}. \tag{4.91}$$

Since the ETO spherical polar radial functions are basis for $L^2(\mathbb{R}^3)$, the affinity function $Q^{\mathrm{EC}}_{\mathrm{A}}(\mathbf{x})$ can be written uniquely in terms of ETO spherical polar radial basis functions, i.e.

$$Q^{\mathrm{EC}}_{\mathrm{B}}(\mathbf{x}) = \sum_{i=0}^{N_{\mathrm{B}}} q_i \kappa_{\mathcal{G}}\left(\mathbf{x}-\mathbf{x}_i\right) = \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \hat{Q}^{\mathrm{B}}_{klm}\, V^l_k(r)\, Y^m_l\left(\mathbf{u}\right), \tag{4.92}$$

where $\mathbf{x}_i \in \mathbb{R}^3$, $\mathbf{x}-\mathbf{x}_i = r_i\mathbf{u}_i$, $r_i = \|\mathbf{x}-\mathbf{x}_i\|_2$ & $\mathbf{u}_i = (\theta_i, \phi_i) \in \mathbb{S}^2$ and

$$\hat{Q}^{\mathrm{B}}_{klm} = \sum_{i=0}^{N_{\mathrm{B}}} q_i \int_0^{\infty} \int_{\mathbb{S}^2} \kappa_{\mathcal{G}}(r_i\mathbf{u}_i)\, V_k^l(r)\, \overline{Y_l^m\left(\mathbf{u}\right)} r^2 \,\mathrm{d}\mathbf{u}\mathrm{d}r. \tag{4.93}$$

Analogously, the affinity function $Q^{\mathrm{EC}}_{\mathrm{A}}(\mathbf{x})$ can be written uniquely in terms of ETO spherical polar radial Fourier series, namely

$$Q^{\mathrm{EC}}_{\mathrm{A}}\left(\mathbf{x}\right) = Q^{\mathrm{EC}}_{\mathrm{A}}\left(r\mathbf{u}\right) = \sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm}\, V_k^l(r)\, Y_l^m\left(\mathbf{u}\right), \tag{4.94}$$

where the ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{A}}_{klm}$ are computed by the ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{B}}_{klm}$ in (4.92) by solving Poisson's equation

$$\bigtriangledown^2 Q^{\mathrm{EC}}_{\mathrm{A}}\left(r\mathbf{u}\right) = -4\pi Q^{\mathrm{EC}}_{\mathrm{B}}\left(r\mathbf{u}\right), \tag{4.95}$$

cf. Ritchie [78]. Now, in the next step, at first we need to compute the FTO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{B}}_{klm}$ and then by solving Poisson's equation (4.95), we are able to compute $\hat{Q}^{\mathrm{A}}_{klm}$.

4.2.3. ETO Spherical Polar Radial Fourier Coefficients $\hat{Q}^{\mathrm{EC}}_{klm}$

Now in the following lemma, we present a method for computing the ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{B}}_{klm}$, in (4.93).

Lemma 4.2.1 *For given integers k, l and m where $k > l \geq |m| \geq 0$, the ETO spherical polar radial Fourier coefficients* (4.93) *are computed by*

$$\begin{aligned}
\hat{Q}^{\mathrm{B}}_{klm} = \sum_{j=0}^{N_{\mathrm{B}}}\sum_{n=0}^{\infty}\sum_{\substack{p=0\\ p+l \text{ even}}}^{n} \Bigg(& 2^{-(2l+n-p-m)}\mathrm{i}^m \sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)} \times \frac{\pi(2l+1)(l-m)!}{(l+m)!}} \\
& \times q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \mathrm{e}^{-\mathrm{i}m\phi_j}/n! \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!}\binom{k+l+1}{k-l-1-j'}\left(\frac{\beta}{\varsigma_j^2}\right)^{-\frac{(3+l+n+j')}{2}} \\
& \times \Gamma\left(\frac{3+l+n+j'}{2}\right) \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(2l-2t)!2^{2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''} \\
& \times \sum_{t'=0}^{m+1}\binom{m+1}{t'} \sum_{q=m}^{m+2p}\left(\frac{\beta r_j}{\varsigma_j^2}\right)^p \binom{p}{q}\left(\frac{-\mathrm{i}}{2}\sin\theta_j\right)^q (\cos\theta_j)^{p-q}\binom{q}{\frac{q-m}{2}} \\
& \times \sum_{u=0}^{q}\binom{q}{u}(-1)^u \sum_{v=0}^{p-q}\binom{p-q}{v}\frac{(-1)^{t+t'}}{p+l+1-2u-2v-2t-2t'-2t''}\Bigg).
\end{aligned}$$

Proof. By (4.92), we have

$$\begin{aligned}
\hat{Q}^{\mathrm{B}}_{klm} = & \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{\beta\left(1-\frac{r^2+r_j^2-2rr_j\left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j+\cos\theta\cos\theta_j\right)}{\varsigma_j^2}\right)} \\
& \times V_k^l(r)\,\overline{Y_l^m\left(\phi,\theta\right)} r^2 \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r.
\end{aligned}$$

We denote

$$b_j := 2\beta \frac{r_j}{\varsigma_j^2} \left(\cos\left(\phi - \phi_j\right) \sin\theta \sin\theta_j + \cos\theta \cos\theta_j\right) \tag{4.96}$$

and hence

$$\begin{aligned}
\hat{Q}^{\mathrm{B}}_{klm} &= \sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \int_0^\infty \int_0^{2\pi} \int_0^\pi \mathrm{e}^{-\frac{\beta}{\varsigma_j^2} r^2} \mathrm{e}^{b_j r}\, V_k^l(r) \overline{Y_l^m\left(\theta,\phi\right)} r^2 \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi \,\mathrm{d}r \\
&= \sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \int_0^{2\pi} \int_0^\pi \overline{Y_l^m\left(\theta,\phi\right)} \sin\theta \left(\int_0^\infty \mathrm{e}^{-\frac{\beta}{\varsigma_j^2} r^2} \mathrm{e}^{b_j r}\, V_k^l(r) r^2 \, dr \right) \mathrm{d}\theta \ \mathrm{d}\phi.
\end{aligned}$$

Substituting the ETO radial basis functions V_k^l by (2.38), gives

$$\begin{aligned}
\hat{Q}^{\mathrm{B}}_{klm} &= \sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \int_0^{2\pi} \int_0^\pi \overline{Y_l^m\left(\theta,\phi\right)} \sin\theta \Bigg(\int_0^\infty \mathrm{e}^{-\frac{\beta}{\varsigma_j^2} r^2} \mathrm{e}^{b_j r} \\
&\quad \times \sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)}} \mathrm{e}^{-\frac{r}{2}} r^l \sum_{j'=0}^{k-l-1} \frac{1}{j'!} \binom{k+l+1}{k-l-1-j'} (-r)^{j'} r^2 \,\mathrm{d}r \Bigg) \mathrm{d}\theta \,\mathrm{d}\phi \\
&= \sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \sqrt{\frac{(k-l-1)!}{\Gamma\left(k+l+2\right)}} \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k+l+1}{k-l-1-j'} \\
&\quad \times \int_0^{2\pi} \int_0^\pi \overline{Y_l^m\left(\theta,\phi\right)} \sin\theta \left(\int_0^\infty \mathrm{e}^{-\frac{\beta r^2}{\varsigma_j^2}} \mathrm{e}^{\left(b_j - \frac{1}{2}\right) r} r^{l+j'+2} \,\mathrm{d}r \right) \mathrm{d}\theta \,\mathrm{d}\phi.
\end{aligned} \tag{4.97}$$

For computing the coefficients (4.97), at first we need to compute the inner integral

$$\int_0^\infty \mathrm{e}^{-\frac{\beta r^2}{\varsigma_j^2}} \mathrm{e}^{\left(b_j - \frac{1}{2}\right) r} r^{l+j'+2} \,\mathrm{d}r.$$

Since

$$\mathrm{e}^{\left(b_j - \frac{1}{2}\right) r} = \sum_{n=0}^\infty \frac{\left(b_j - \frac{1}{2}\right)^n r^n}{n!}, \tag{4.98}$$

we have

$$\begin{aligned}
\int_0^\infty \mathrm{e}^{-\frac{\beta r^2}{\varsigma_j^2}} \mathrm{e}^{\left(b_j - \frac{1}{2}\right) r} r^{l+j'+2} \,\mathrm{d}r &= \int_0^\infty \mathrm{e}^{-\frac{\beta r^2}{\varsigma_j^2}} \sum_{n=0}^\infty \frac{\left(b_j - \frac{1}{2}\right)^n r^n}{n!} r^{l+j'+2} \,\mathrm{d}r \\
&= \sum_{n=0}^\infty \frac{\left(b_j - \frac{1}{2}\right)^n}{n!} \int_0^\infty \mathrm{e}^{-\frac{\beta r^2}{\varsigma_j^2}} r^{l+j'+n+2} \,\mathrm{d}r \\
&= \sum_{n=0}^\infty \frac{\left(b_j - \frac{1}{2}\right)^n}{n!} \times \frac{1}{2} \left(\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+j')} \Gamma\left(\frac{3+l+n+j'}{2}\right).
\end{aligned} \tag{4.99}$$

Replacing (4.99) by (4.97), gives

$$\hat{Q}^{\mathrm{B}}_{klm} = \sum_{j=1}^{N_{\mathrm{A}}} q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)}} \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k+l+2}{k-l-1-j'} \sum_{n=0}^{\infty} \frac{1}{n!} \times \frac{1}{2}$$
$$\times \left(\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+j')} \Gamma\left(\frac{3+l+n+j'}{2}\right) \int_0^{2\pi}\int_0^{\pi} \left(b_j - \frac{1}{2}\right)^n \overline{Y_l^m(\theta,\phi)} \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\phi. \tag{4.100}$$

Now our task is handling the above double integral on $\mathbb{S}^2$ by applying the spherical harmonics, see Lemma (2.3.4), i.e.

$$\begin{aligned}\int_0^{2\pi}\int_0^{\pi} \left(b_j - \frac{1}{2}\right)^n \overline{Y_l^m(\theta,\phi)} \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\phi &= \int_0^{2\pi}\int_0^{\pi} \left(b_j - \frac{1}{2}\right)^n \left(\frac{1}{2}\right)^l \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \\ &\times \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!} (\sin\theta)^m (\cos\theta)^{l-m-2t} \mathrm{e}^{-\mathrm{i}m\phi} \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\ &= \left(\frac{1}{2}\right)^l \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \times \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!} \\ &\times \int_0^{2\pi}\int_0^{\pi} \left(b_j - \frac{1}{2}\right)^n (\sin\theta)^{m+1} (\cos\theta)^{l-m-2t} \mathrm{e}^{-\mathrm{i}m\phi} \,\mathrm{d}\theta\,\mathrm{d}\phi.\end{aligned} \tag{4.101}$$

Now, again we need to compute the following double integral

$$\int_0^{2\pi}\int_0^{\pi} \left(b_j - \frac{1}{2}\right)^n (\sin\phi)^{m+1} (\cos\phi)^{l-m-2t} \mathrm{e}^{-\mathrm{i}m\theta} \,\mathrm{d}\phi\,\mathrm{d}\theta, \tag{4.102}$$

and in order to do this, we do the following steps:

1. We compute

$$\left(b_j - \frac{1}{2}\right)^n = \sum_{p=0}^{n} \binom{n}{p} b_j^p \left(\frac{-1}{2}\right)^{n-p}, \tag{4.103}$$

where

$$\begin{aligned} b_j^p &= \left(2\frac{\beta}{\varsigma_j^2} r_j \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j + \cos\theta\cos\theta_j\right)\right)^p \\ &= \left(2\frac{\beta}{\varsigma_j^2} r_j\right)^p \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j + \cos\theta\cos\theta_j\right)^p \\ &= \left(2\frac{\beta}{\varsigma_j^2} r_j\right)^p \sum_{q=0}^{p} \binom{p}{q} \left(\cos(\phi-\phi_j)\sin\theta\sin\theta_j\right)^q \left(\cos\theta\cos\theta_j\right)^{p-q} \\ &= \left(2\frac{\beta}{\varsigma_j^2} r_j\right)^p \sum_{q=0}^{p} \binom{p}{q} \left(\frac{\mathrm{e}^{\mathrm{i}(\phi-\phi_j)} + \mathrm{e}^{-\mathrm{i}(\phi-\phi_j)}}{2}\right)^q \left(\frac{\mathrm{e}^{\mathrm{i}\theta} - \mathrm{e}^{-\mathrm{i}\theta}}{2\mathrm{i}}\right)^q \\ &\times (\sin\theta_j)^q \left(\frac{\mathrm{e}^{\mathrm{i}\theta} + \mathrm{e}^{-\mathrm{i}\theta}}{2}\right)^{p-q} (\cos\theta_j)^{p-q}. \end{aligned}$$

Using the binomial theorem, necessitates to have

$$\begin{aligned}
b_j^p &= (\frac{\beta}{\varsigma_j^2} r_j)^p \sum_{q=0}^{p} \binom{p}{q} \left(\frac{-\mathrm{i}}{2}\right)^q (\sin\theta_j)^q (\cos\theta_j)^{p-q} \sum_{s=0}^{q} \binom{q}{s} \mathrm{e}^{-\mathrm{i}(\phi-\phi_j)s} \\
&\times \mathrm{e}^{\mathrm{i}(\phi-\phi_j)(q-s)} \sum_{u=0}^{q} (-1)^u \binom{q}{u} \mathrm{e}^{-\mathrm{i}\theta u} \mathrm{e}^{\mathrm{i}\theta(q-u)} \sum_{v=0}^{p-q} \binom{p-q}{v} \mathrm{e}^{-\mathrm{i}\theta v} \mathrm{e}^{\mathrm{i}\theta(p-q-v)} \\
&= \left(\frac{\beta}{\varsigma_j^2} r_j\right)^p \sum_{q=0}^{p} \binom{p}{q} \left(-\frac{\mathrm{i}}{2}\right)^q (\sin\theta_j)^q (\cos\theta_j)^{p-q} \sum_{s=0}^{q} \binom{q}{s} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \\
&\times \sum_{v=0}^{p-q} \binom{p-q}{v} \mathrm{e}^{\mathrm{i}(\phi-\phi_j)(q-2s)} \mathrm{e}^{\mathrm{i}(p-2u-2v)\theta}.
\end{aligned} \tag{4.104}$$

2. Also we need to rewrite

$$\begin{aligned}
(\sin\theta)^{m+1} &= \left(\frac{\mathrm{e}^{\mathrm{i}\theta} - \mathrm{e}^{-\mathrm{i}\theta}}{2\mathrm{i}}\right)^{m+1} = \left(-\frac{\mathrm{i}}{2}\right)^{m+1} \sum_{t'=0}^{m+1} \binom{m+1}{t'} (-\mathrm{e}^{-\mathrm{i}\theta})^{t'} (\mathrm{e}^{\mathrm{i}\theta})^{m+1-t'} \\
&= \left(-\frac{\mathrm{i}}{2}\right)^{m+1} \sum_{t'=0}^{m+1} \binom{m+1}{t'} (-1)^{t'} \mathrm{e}^{\mathrm{i}(m+1-2t')\theta}.
\end{aligned} \tag{4.105}$$

3. Finally we have

$$\begin{aligned}
(\cos\theta)^{l-m-2t} &= \left(\frac{\mathrm{e}^{\mathrm{i}\theta} + \mathrm{e}^{-\mathrm{i}\theta}}{2}\right)^{l-m-2t} \\
&= \left(\frac{1}{2}\right)^{l-m-2t} \sum_{t''=0}^{l-2t-m} \binom{l-m-2t}{t''} \left(\mathrm{e}^{-\mathrm{i}\theta}\right)^{t''} \left(\mathrm{e}^{\mathrm{i}\theta}\right)^{l-m-2t-t''} \\
&= \left(\frac{1}{2}\right)^{l-m-2t} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \mathrm{e}^{\mathrm{i}(l-m-2t-2t'')\theta}.
\end{aligned} \tag{4.106}$$

Now, replacing (4.104), (4.105) and (4.106), into the double integral (4.102), gives

$$\begin{aligned}
&\int_0^{2\pi} \int_0^{\pi} \left(b_j - \frac{1}{2}\right)^n (\sin\theta)^{m+1} (\cos\theta)^{l-m-2t} \mathrm{e}^{-\mathrm{i}m\phi} \, \mathrm{d}\theta \, \mathrm{d}\phi \\
&= \sum_{p=0}^{n} \binom{n}{p} \left(\frac{-1}{2}\right)^{n-p} \left(\frac{\beta}{\varsigma_j^2} r_j\right)^p \sum_{q=0}^{p} \binom{p}{q} \left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q (\cos\theta_j)^{p-q} \sum_{s=0}^{q} \binom{q}{s} \sum_{u=0}^{q} \binom{q}{u} \\
&\times (-1)^u \sum_{v=0}^{p-q} \binom{p-q}{v} \left(-\frac{\mathrm{i}}{2}\right)^{m+1} \sum_{t'=0}^{m+1} (-1)^{t'} \binom{m+1}{t'} \left(\frac{1}{2}\right)^{l-m-2t} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \\
&\times \int_0^{2\pi} \int_0^{\pi} \mathrm{e}^{\mathrm{i}(p-2u-2v)\theta} \mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)} \mathrm{e}^{\mathrm{i}(m+1-2t')\theta} \mathrm{e}^{\mathrm{i}(l-m-2t-2t'')\theta} \mathrm{e}^{-\mathrm{i}m\phi} \, \mathrm{d}\theta \, \mathrm{d}\phi,
\end{aligned} \tag{4.107}$$

and hence we have

$$
\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi}\left(b_j-\frac{1}{2}\right)^n(\sin\theta)^{m+1}(\cos\theta)^{l-m-2t}\,\mathrm{e}^{-\mathrm{i}m\phi}\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&=\sum_{p=0}^{n}\binom{n}{p}\left(\frac{-1}{2}\right)^{n-p}\left(\frac{\beta}{\varsigma_j^2}r_j\right)^p\left(-\frac{\mathrm{i}}{2}\right)^{m+1}\left(\frac{1}{2}\right)^{l-m-2t}\sum_{q=0}^{p}\binom{p}{q}\left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^q(\cos\theta_j)^{p-q} \\
&\times\sum_{s=0}^{q}\binom{q}{s}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\sum_{v=0}^{p-q}\binom{p-q}{v}\sum_{t'=0}^{m+1}\binom{m+1}{t'}(-1)^{t'}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''} \\
&\times\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{\mathrm{i}(p+l+1-2u-2v-2t-2t'-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\,\mathrm{d}\theta\,\mathrm{d}\phi.
\end{aligned}
\tag{4.108}
$$

Again, we compute the double integral in (4.108), so

$$
\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{\mathrm{i}(p+l+1-2u-2v-2t-2t'-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&=\mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\left(\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(q-2s-m)\phi}\left(\int_0^{\pi}\mathrm{e}^{\mathrm{i}(p+l+1-2u-2v-2t-2t'-2t'')\theta}\,\mathrm{d}\theta\right)\mathrm{d}\phi\right).
\end{aligned}
\tag{4.109}
$$

Since we have

$$
\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(q-2s-m)\phi}\,d\phi=2\pi\delta_{m,q-2s}
\tag{4.110}
$$

and

$$
\int_0^{\pi}\mathrm{e}^{\mathrm{i}(p+l+1-2u-2v-2t-2t'-2t'')\theta}\,\mathrm{d}\theta:=\lambda_{p,l,u,v,t,t',t''},
$$

where

$$
\lambda_{p,l,u,v,t,t',t''}=\begin{cases}\pi & \text{if }\ (p+l+1-2u-2v-2t-2t'-2t'')=0\\ \frac{2\mathrm{i}}{p+l+1-2u-2v-2t-2t'-2t''} & \text{if }\ (p+l+1-2u-2v-2t-2t'-2t'')\ \text{odd}\\ 0 & \text{otherwise,}\end{cases}
$$

or equivalently

$$
\lambda_{n,l,u,v,t,t',t''}=\begin{cases}\pi & \text{if }\ (p+l)=2u+2v+2t+2t'+2t''-1\\ \frac{2\mathrm{i}}{p+l+1-2u-2v-2t-2t'-2t''} & \text{if }\ (p+l)\ \text{even}\\ 0 & \text{otherwise,}\end{cases}
\tag{4.111}
$$

therefore we have

$$
\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{\mathrm{i}(p+l+1-2u-2v-2t-2t'-2t'')\theta}\mathrm{e}^{-\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}(q-2s)(\phi-\phi_j)}\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&=\mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\left(\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(q-2s-m)\phi}\left(\int_0^{\pi}\mathrm{e}^{\mathrm{i}(p+l+1-2u-2v-2t-2t'-2t'')\theta}\,\mathrm{d}\theta\right)\mathrm{d}\phi\right) \\
&=\mathrm{e}^{-\mathrm{i}(q-2s)\phi_j}\times 2\pi\delta_{m,q-2s}\times\lambda_{p,l,u,v,t,t',t''}.
\end{aligned}
\tag{4.112}
$$

Thus, we could compute the double integral (4.109) and consequently double integral (4.108), so by (4.101) we obtain

$$
\begin{aligned}
\hat{Q}^{\mathrm{B}}_{klm} = & \sum_{j=1}^{N_{\mathrm{B}}} q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \sqrt{\frac{(k-l-1)!}{\Gamma\left(k+l+2\right)}} \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k+l+1}{k-l-1-j'} \left(\frac{1}{2}\right)^{l+1} \\
& \times \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{\beta}{\varsigma_j^2}\right)^{\frac{-1}{2}(3+l+n+j')} \Gamma\left(\frac{3+l+n+j'}{2}\right) \sqrt{\frac{(2l+1)\,(l-m)!}{4\pi(l+m)!}} \\
& \times \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(-1)^{t+m}(2l-2t)!}{(l-m-2t)!(l-t)!t!} \sum_{p=0}^{n} \binom{n}{p} \left(\frac{-1}{2}\right)^{n-p} \left(\frac{\beta}{\varsigma_j^2} r_j\right)^{p} \sum_{q=0}^{p} \binom{p}{q} \\
& \times \left(-\frac{\mathrm{i}}{2}\sin\theta_j\right)^{q} (\cos\theta_j)^{p-q} \sum_{s=0}^{q} \binom{q}{s} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \sum_{v=0}^{p-q} \binom{p-q}{v} \\
& \times \left(-\frac{\mathrm{i}}{2}\right)^{m+1} \sum_{t'=0}^{m+1} (-1)^{t'} \binom{m+1}{t'} \left(\frac{1}{2}\right)^{l-m-2t} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \\
& \times \mathrm{e}^{-\mathrm{i}(q-2s)\phi_j} \times 2\pi\delta_{m,q-2s} \times \lambda_{p,l,u,v,t,t',t''}.
\end{aligned}
\tag{4.113}
$$

Now, considering the Kronecker delta functions $\delta_{m,q-2s}$, implies $q = m + 2s$ and since $s = s(q) = \frac{q-m}{2}$ is an integer valued function and since $q = 0,\ 1,\ \ldots,\ p$, hence

$$
\begin{aligned}
\hat{Q}^{\mathrm{B}}_{klm} = & \sum_{j=1}^{N_{\mathrm{B}}} \sum_{n=0}^{\infty} \sum_{\substack{p=0 \\ p+l \text{ even}}}^{n} \left(\left(\frac{1}{2}\right)^{2l+1} \pi\ \mathrm{i}^m \sqrt{\frac{(k-l-1)!}{\Gamma\left(k+l+2\right)} \times \frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \right. \\
& \times q_j \mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)} \mathrm{e}^{-\mathrm{i}m\phi_j} 1/n! \sum_{j'=0}^{k-l-1} \frac{(-1)^{j'}}{j'!} \binom{k+l+1}{k-l-1-j'} \left(\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+j')} \\
& \times \Gamma\left(\frac{3+l+n+j'}{2}\right) \sum_{p=0}^{n} \binom{n}{p} \left(\frac{-1}{2}\right)^{n-p} \left(\frac{\beta}{\varsigma_j^2} r_j\right)^{p} \sum_{q=m}^{m+2p} \binom{p}{q} \left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^{q} \\
& \times (\cos\theta_j)^{p-q} \binom{q}{\frac{q-m}{2}} \sum_{u=0}^{q} \binom{q}{u} (-1)^u \sum_{v=0}^{p-q} \binom{p-q}{v} \sum_{t'=0}^{m+1} \binom{m+1}{t'} \\
& \times \sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor} \frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!} \sum_{t''=0}^{l-m-2t} \binom{l-m-2t}{t''} \\
& \left. \times \frac{(-1)^{t+t'}}{p+l+1-2u-2v-2t-2t'-2t''} \right) + \mathcal{B},
\end{aligned}
$$

where

$$\mathcal{B}=\sum_{j=1}^{N_{\rm B}}\sum_{n=0}^{\infty}\sum_{\substack{p=0\\p+l=2u+2v+2t+2t'+2t''-1}}^{n}\left(\left(\frac{1}{2}\right)^{2l+1}\pi\ \mathrm{i}^m\sqrt{\frac{(k-l-1)!}{\Gamma\left(k+l+2\right)}\times\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}\right.$$
$$\times\, q_j\mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)}\mathrm{e}^{-\mathrm{i}m\phi_j}1/n!\sum_{j'=0}^{k-l-1}\frac{(-1)^{j'}}{j'!}\binom{k+l+1}{k-l-1-j'}\left(\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+j')}$$
$$\times\,\Gamma\left(\frac{3+l+n+j'}{2}\right)\sum_{p=0}^{n}\binom{n}{p}\left(\frac{-1}{2}\right)^{n-p}\left(\frac{\beta}{\varsigma_j^2}r_j\right)^{p}\sum_{q=m}^{m+2p}\binom{p}{q}\left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^{q}$$
$$\times\,(\cos\theta_j)^{p-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\sum_{v=0}^{p-q}\binom{p-q}{v}\sum_{t'=0}^{m+1}\binom{m+1}{t'}$$
$$\left.\times\sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor}\frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''}\pi\right)$$

and since, when $p+l$ is the odd integer "$2u+2v+2t+2t'+2t''-1$", the following expression is zero, i.e.

$$\sum_{q=0}^{p}\binom{p}{q}\left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^{q}(\cos\theta_j)^{p-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\sum_{v=0}^{p-q}\binom{p-q}{v}$$
$$\times\sum_{t'=0}^{m+1}\binom{m+1}{t'}\sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor}\frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''}\pi=0, \tag{4.114}$$

therefore $\mathcal{B}=0$ and hence we have

$$\hat{Q}^{\rm B}_{klm}=\sum_{j=1}^{N_{\rm B}}\sum_{n=0}^{\infty}\sum_{\substack{p=0\\p+l\ \text{even}}}^{n}\left(\left(\frac{1}{2}\right)^{2l+1}\pi\ \mathrm{i}^m\sqrt{\frac{(k-l-1)!}{\Gamma\left(k+l+2\right)}\times\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}\right.$$
$$\times\, q_j\mathrm{e}^{\beta\left(1-\frac{r_j^2}{\varsigma_j^2}\right)}\mathrm{e}^{-\mathrm{i}m\phi_j}1/n!\sum_{j'=0}^{k-l-1}\frac{(-1)^{j'}}{j'!}\binom{k+l+1}{k-l-1-j'}\left(\frac{\beta}{\varsigma_j^2}\right)^{-\frac{1}{2}(3+l+n+j')}$$
$$\times\,\Gamma\left(\frac{3+l+n+j'}{2}\right)\sum_{p=0}^{n}\binom{n}{p}\left(\frac{-1}{2}\right)^{n-p}\left(\frac{\beta}{\varsigma_j^2}r_j\right)^{p}\sum_{q=m}^{m+2p}\binom{p}{q}\left(-\frac{\mathrm{i}\sin\theta_j}{2}\right)^{q}$$
$$\times\,(\cos\theta_j)^{p-q}\binom{q}{\frac{q-m}{2}}\sum_{u=0}^{q}\binom{q}{u}(-1)^u\sum_{v=0}^{p-q}\binom{p-q}{v}\sum_{t'=0}^{m+1}\binom{m+1}{t'}$$
$$\times\sum_{t=0}^{\lfloor\frac{l-m}{2}\rfloor}\frac{(2l-2t)!(\frac{1}{2})^{-2t}}{(l-m-2t)!(l-t)!t!}\sum_{t''=0}^{l-m-2t}\binom{l-m-2t}{t''}$$
$$\left.\times\,\frac{(-1)^{t+t'}}{p+l+1-2u-2v-2t-2t'-2t''}\right). \tag{4.115}$$

In this proof, we have applied the binomial theorem which describes the algebraic expansion of nonnegative integer powers of a binomial in (4.104), (4.105) and (4.106), therefore m should be a nonnegative integer. On the other hand we have, $m = -l, \dots, 0, \dots, l$. Therefore for the negative integers m, we will use the Remark 2.21. In other words, for negative integers m, we apply the same procedure as for the nonnegative integers m, just we multiply the ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{B}}_{klm}$ with the factors $\frac{(-1)^m (l-m)!}{(l+m)!}$ where l and m are integers and $l \geq m \geq 0$. □

Now in the following lemma we present the Ritchie's procedure to compute the ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{A}}_{klm}$, see [78], or [82]

Lemma 4.2.2 *For the integers k, k', l and m where k', $k' \geq 1 \geq m \geq 0$, the ETO spherical polar radial Fourier coefficients $\hat{Q}^{\mathrm{A}}_{klm}$ can be computed from the following equation*

$$\sum_{k=1}^{\infty} \hat{Q}^{\mathrm{A}}_{klm} \mathrm{G}^{(l)}_{kk'} = -4\pi \hat{Q}^{\mathrm{B}}_{k'lm},$$

where

$$\mathrm{G}^{(l)}_{kk'} = \frac{1}{4} \sum_{j=0}^{k-l-1} \sum_{j'=0}^{k'-l-1} \mathrm{D}_{klj} \mathrm{D}_{k'lj'} \left(k + k' + 2l\right)! \left(\left(k - k'\right)^2 - \left(k - k'\right) - 2\left(2l+1\right)\left(l+1\right) \right),$$

and

$$\mathrm{D}_{klj} = \sqrt{\frac{(k-l-1)!}{\Gamma\left(k+l+2\right)}} \frac{(-1)^j}{j!} \binom{k+l+1}{k-l-1-j}.$$

Proof. Substituting the series expansion of the ETO spherical polar radial basis functions in Poisson's equation (4.95), gives

$$\bigtriangledown^2 \left(\sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} V^l_k(r) \, Y^m_l\left(\mathbf{u}\right) \right) = -4\pi \sum_{k'=1}^{\infty} \sum_{l'=0}^{k'-1} \sum_{m'=-l'}^{l'} \hat{Q}^{\mathrm{B}}_{k'l'm'} V^{l'}_{k'}(r) \, Y^{m'}_{l'}\left(\mathbf{u}\right).$$

Applying the Laplace operator $\bigtriangledown^2$ on the ETO spherical polar radial basis functions, gives

$$\begin{aligned}
&\bigtriangledown \left(\sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} V^l_k(r) \, Y^m_l\left(\mathbf{u}\right) \right) \\
&= \sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} \left(\frac{1}{r} \left(\frac{\partial^2}{\partial r^2} \right) r + \frac{1}{r^2} \Lambda^2 \right) V^l_k(r) \, Y^m_l\left(\mathbf{u}\right) \\
&= \sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} \left(\frac{Y^m_l\left(\mathbf{u}\right)}{r} \frac{\partial^2}{\partial r^2} \left(r \, V^l_k(r) \right) + \frac{V^l_k(r)}{r^2} \Lambda^2 \, Y^m_l\left(\mathbf{u}\right) \right) \\
&= \sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} \left(V''^l_k(r) + \frac{2}{r} V'^l_k(r) - \frac{l(l+1)}{r^2} V^l_k(r) \right) Y^m_l(\mathbf{u}),
\end{aligned} \tag{4.116}$$

where ${V'}^{l}_{k}(r)$ and ${V''}^{l}_{k}(r)$ are the first and second derivatives of $V^l_k(r)$. Now with having (4.116), we come back to the equation (4.2.3), hence we have

$$\begin{aligned}\int_0^\infty \int_{\mathbb{S}^2} \nabla^2 \left(\sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm}\, V^l_k(r)\, Y^m_l\,(\mathbf{u}) \right) V^{l'}_{k'}(r)\, \overline{Y^{m'}_{l'}\,(\mathbf{u})} r^2 \,\mathrm{d}\mathbf{u}\,\mathrm{d}r \\ = -4\pi \hat{Q}^{\mathrm{B}}_{k'l'm'}.\end{aligned} \tag{4.117}$$

We simplify both sides of the equation (4.117), hence we have

$$\begin{aligned}\sum_{k=1}^{\infty} \sum_{l=0}^{k-1} \sum_{m=-l}^{l} \hat{Q}^{\mathrm{A}}_{klm} \int_0^\infty \int_{\mathbb{S}^2} \left({V''}^{l}_{k}(r) + \frac{2}{r}\, {V'}^{l}_{k}(r) - \frac{l(l+1)}{r^2}\, V^l_k(r) \right) Y^m_l\,(\mathbf{u})\, V^{l'}_{k'}(r)\, \overline{Y^{m'}_{l'}\,(\mathbf{u})} \\ r^2 \mathrm{d}\mathbf{u}\,\mathrm{d}r = -4\pi \hat{Q}^{\mathrm{B}}_{k'l'm'},\end{aligned} \tag{4.118}$$

and more simplifications on (4.118), gives

$$\sum_{k=l}^{\infty} \hat{Q}^{\mathrm{A}}_{klm} \int_0^\infty \left({V''}^{l}_{k}(r) + \frac{2}{r}\, {V'}^{l}_{k}(r) - \frac{l(l+1)}{r^2}\, V^l_k(r) \right) V^l_{k'}(r) r^2 \,\mathrm{d}r = -4\pi \hat{Q}^{\mathrm{B}}_{k'lm}. \tag{4.119}$$

We set

$$\mathrm{G}^{(l)}_{kk'} = \int_0^\infty \left({V''}^{l}_{k}(r)\, V^l_{k'}(r) + \frac{2}{r}\, {V'}^{l}_{k}(r)\, V^l_{k'}(r) - \frac{l(l+1)}{r^2}\, V^l_k(r)\, V^l_{k'}(r) \right) r^2 \,\mathrm{d}r, \tag{4.120}$$

and since each element of $\mathrm{G}^{(l)}$ has the symmetric form

$$\mathrm{G}^{(l)}_{kk'} = -\int_0^\infty \left({V'}^{l}_{k}(r)\, {V'}^{l}_{k'}(r) r^2 + l(l+1)\, V^l_k(r)\, V^l_{k'}(r) \right) \mathrm{d}r. \tag{4.121}$$

It can be seen that for each l and m, the equation (4.119) represents a set of simultaneous equations in the coefficients $\hat{Q}^{\mathrm{A}}_{klm}$ which can be determind by inverting each $\mathrm{G}^{(l)}$ matrix. The elements of $\mathrm{G}^{(l)}$ may be calculated by the ETO spherical polar radial basis functions (2.38). After some computation on (4.121), we obtain

$$\begin{aligned}\mathrm{G}^{(l)}_{kk'} = \frac{1}{4} \sum_{j=0}^{k-l-1} \sum_{j'=0}^{k'-l-1} \sqrt{\frac{(k-l-1)!\,(k'-l-1)!}{\Gamma\,(k+l+2)\,\Gamma\,(k'+l+2)}}\, \frac{(-1)^{j+j'}}{j!j'!} \binom{k+l+1}{k-l-1-j} \\ \times \binom{k'+l+1}{k'-l-1-j'} \left(k+k'+2l\right)! \left(\left(k-k'\right)^2 - \left(k-k'\right) - 2\,(2l+1)\,(l+1) \right). \ \square\end{aligned}$$

4.2.4. The ETO Translational Coefficients $\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t)$

Definition 4.2.1 *For given integers k, k', l, l' and n where $k > l \geq |n| \geq 0$, $k' > l' \geq |n'| \geq 0$ and $n' = -n$, we define*

$$\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t) = \int_0^\infty \int_0^\pi \int_0^{2\pi} V^l_k(r)\, Y^n_l\,(\theta,\phi)\; V^{l'}_{k'}(r)\, Y^{n'}_{l'}\,\left(\theta',\phi\right) r^2 \sin\theta \,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r,$$

which are called ETO translational coefficients.

Lemma 4.2.3 *The ETO translational coefficients* $\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t)$ *are computed by*

$$\begin{aligned}
\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t) &= \sqrt{\frac{(2l+1)(2l'+1)(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma(k+l+2)\Gamma\,(k'+l'+2)}}\\
&\times \sum_{j=0}^{k-l-1}\frac{(-1)^j}{j!}\binom{k+l+1}{k-l-1-j}\sum_{j'=0}^{k'-l'-1}\frac{(-1)^{j'}}{j'!}\binom{k'+l'+1}{k'-l'-1-j'}\\
&\times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor}\sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor}\frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!(l'-q')!q!q'!}\\
&\times \sum_{n_1=0}^{\infty}\frac{(-1/2)^{n_1}}{n_1!}\sum_{n_4=0}^{n_1}\binom{n_1}{n_4}\sum_{n_2=0}^{\infty}\binom{j'/2+q'}{n_2}\sum_{n_3=0}^{l'+n-2q'}\binom{l'+n-2q'}{n_3}\\
&\times \sum_{n_5=0}^{n_4+n_2}\binom{n_4+n_2}{n_5}(-1)^{j'/2+q'+n_1-n_2+n_3-n_4}2^{j+j'-2q+2q'+l+l'+2n_1-n_3-2n_5+3}\\
&\times \Gamma\left(l+l'+j+j'/2-2q+q'+n_1+n_2-n_3+n_4-2n_5+3\right)\\
&\times \frac{(-1)^{l+l'+j'/2+q'+n_1-n_2-n_3-n_4}+1}{l+l'+j'/2-4q+q'+n_1-n_2-n_3-n_4+1}t^{j'/2+q'+n_1+n_2+n_3-n_4}.
\end{aligned}$$

Proof. Using the Definition 4.2.1 and the spherical harmonics, see (2.20), gives

$$\begin{aligned}
\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t) &= \int_0^\infty\int_0^\pi V^l_k(r)\,V^{l'}_{k'}(r')\bigg(\int_0^{2\pi}\sqrt{\frac{(2l+1)(l-n)!}{4\pi(l+n)!}}\mathrm{P}^n_l(\cos\theta)\mathrm{e}^{in\phi}\\
&\times\sqrt{\frac{(2l'+1)(l'-n')!}{4\pi(l'+n')!}}\mathrm{P}^{n'}_{l'}(\cos\theta')\mathrm{e}^{in'\phi}\,\mathrm{d}\phi\bigg)\,r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}$$

We simplify the above expression, so we obtain

$$\begin{aligned}
\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t) &= \frac{\sqrt{(2l+1)(2l'+1)}}{4\pi}\sqrt{\frac{(l-n)!(l'-n')!}{(l+n)!(l'+n')!}}\\
&\times\int_0^\infty\int_0^\pi V^l_k(r)\,V^{l'}_{k'}(r')\mathrm{P}^n_l(\cos\theta)\mathrm{P}^{n'}_{l'}(\cos\theta')\,2\pi\delta_{n',-n}\,r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}\tag{4.122}$$

We apply the the ETO spherical polar radial basis fuctions, hence we have

$$\begin{aligned}
\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t) &= \frac{\sqrt{(2l+1)(2l'+1)}}{2}\sqrt{\frac{(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\int_0^\infty\int_0^\pi\sqrt{\frac{(k-l-1)!}{\Gamma(k+l+2)}}\mathrm{e}^{-\frac{r}{2}}r^l\\
&\times L^{(2l+2)}_{k-l-1}(r)\sqrt{\frac{(k'-l'-1)!}{\Gamma(k'+l'+2)}}\mathrm{e}^{-\frac{r'}{2}}r'^{l'}L^{(2l'+2)}_{k'-l'-1}(r')\mathrm{P}^n_l(\cos\theta)\mathrm{P}^{-n}_{l'}(\cos\theta')r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}r\\
&= 1/2\sqrt{\frac{(2l+1)(2l'+1)(l-n)!(l'+n)!}{(l+n)!(l'-n)!}}\sqrt{\frac{(k-l-1)!\,(k'-l'-1)!}{\Gamma(k+l+2)\Gamma(k'+l'+2)}}\times\mathcal{J}^{\mathrm{EC}}_{kk',ll',n}(t),
\end{aligned}\tag{4.123}$$

where

$$\mathcal{J}^{\mathrm{EC}}_{kk',ll',n}(t) = \int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{1}{2}(r+r')} r^l r'^{l'} L^{(2l+2)}_{k-l-1}(r) L^{(2l'+2)}_{k'-l'-1}(r') \mathrm{P}^n_l(\cos\theta) \mathrm{P}^{-n}_{l'}(\cos\theta') \\ \times r^2 \sin\theta \, \mathrm{d}\theta \mathrm{d}r. \tag{4.124}$$

For computing $\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t)$, we need to compute $\mathcal{J}^{\mathrm{EC}}_{kk',ll',n}(t)$. Using the associated Laguerre polynomials, associated Legendre polynomials and also r', see (4.35), gives

$$\mathcal{J}^{\mathrm{EC}}_{kk',ll',n}(t) = \int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{r}{2}} \mathrm{e}^{\left(r^2-2rt\cos\theta+t^2\right)^{1/2}} r^l \left(\sqrt{r^2-2rt\cos\theta+t^2}\right)^{l'} \sum_{j=0}^{k-l-1} \frac{1}{j!}$$
$$\times \binom{k+l+1}{k-l-1-j} (-r)^j \sum_{j'=0}^{k'-l'-1} \frac{1}{j'!} \binom{k'+l'+1}{k'-l'-1-j'} \left(-\sqrt{r^2-2rt\cos\theta+t^2}\right)^{j'}$$
$$\times \left(\frac{1}{2}\right)^l \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \frac{(-1)^{q+n}(2l-2q)!}{(l-n-2q)!(l-q)!q!} \left(\sin^2\theta\right)^{\frac{n}{2}} \left(\cos\theta\right)^{l-n-2q} \left(\frac{1}{2}\right)^{l'} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor}$$
$$\times \frac{(-1)^{q'-n}(2l'-2q')!}{(l'+n-2q')!\,(l'-q')!\,q'!} \left(\sin^2\theta'\right)^{-\frac{n}{2}} \left(\cos\theta'\right)^{l'+n-2q'} r^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}r.$$

Simplification the above expression, gives

$$\begin{aligned} \mathcal{J}^{\mathrm{EC}}_{kk',ll',n}(t) = \int_0^\infty \int_0^\pi & \mathrm{e}^{\frac{-r}{2}} \mathrm{e}^{\left(r^2-2rt\cos\theta+t^2\right)^{1/2}} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k+l+1}{k-l-1-j} r^{l+j+2} \\ & \times \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'+l'+1}{k'-l'-1-j'} \left(r^2-2rt\cos\theta+t^2\right)^{\frac{l'+j'}{2}} \left(\frac{1}{2}\right)^l \\ & \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \frac{(-1)^{q+n}(2l-2q)!}{(l-n-2q)!(l-q)!q!} \left(\sin\theta\right)^n \left(\cos\theta\right)^{l-n-2q} \left(\frac{1}{2}\right)^{l'} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \\ & \times \frac{(-1)^{q'-n}(2l'-2q')!}{(l'+n-2q')!(l'-q')!q'!} \left(\sin\theta'\right)^{-n} \left(\cos\theta'\right)^{l'+n-2q'} \sin\theta \, \mathrm{d}\theta \, \mathrm{d}r. \end{aligned} \tag{4.125}$$

Using the following assumptions (4.40) and (4.41), namely

$$\cos\theta' = \frac{r\cos\theta - t}{\sqrt{r^2-2rt\cos\theta+t^2}}$$

and

$$\sin\theta' = \frac{r\sin\theta}{\sqrt{r^2-2rt\cos\theta+t^2}},$$

gives

$$
\begin{aligned}
\mathcal{J}^{\mathrm{CE}}_{kk',ll',n}(t) = & \int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{r}{2}} \mathrm{e}^{\left(r^2-2rt\cos\theta+t^2\right)^{1/2}} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k+l+1}{k-l-1-j} r^{l+j+2} \\
& \times \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'+l'+1}{k'-l'-1-j'} \left(r^2-2rt\cos\theta+t^2\right)^{\frac{l'+j'}{2}} \left(\frac{1}{2}\right)^{l} \\
& \times \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \frac{(-1)^{q+n}(2l-2q)!}{(l-n-2q)!(l-q)!q!} (\sin\theta)^n (\cos\phi)^{l-n-2q} \left(\frac{1}{2}\right)^{l'} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \\
& \times \frac{(-1)^{q'-n}(2l'-2q')!}{(l'+n-2q')!\;(l'-q')!\;q'!} \left(\frac{r\sin\theta}{\sqrt{r^2-2rt\cos\theta+t^2}}\right)^{-n} \sin\theta \\
& \times \left(\frac{r\cos\theta-t}{\sqrt{r^2-2rt\cos\theta+t^2}}\right)^{l'+n-2q'} \mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
\tag{4.126}
$$

Again by simplifying the above equation, we obtain

$$
\begin{aligned}
\mathcal{J}^{\mathrm{EC}}_{kk',ll',n}(t) = & \left(\frac{1}{2}\right)^{l+l'} \sum_{j=0}^{k-l-1} \frac{(-1)^j}{j!} \binom{k+l+1}{k-l-1-j} \sum_{j'=0}^{k'-l'-1} \frac{(-1)^{j'}}{j'!} \binom{k'+l'+1}{k'-l'-1-j'} \\
\times & \sum_{q=0}^{\lfloor\frac{l-n}{2}\rfloor} \sum_{q'=0}^{\lfloor\frac{l'+n}{2}\rfloor} \left(\frac{(-1)^{q+q'}(2l-2q)!(2l'-2q')!}{(l-n-2q)!\,(l'+n-2q')!(l-q)!(l'-q')!q!q'!}\right) \times \mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t),
\end{aligned}
\tag{4.127}
$$

where

$$
\begin{aligned}
\mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t) = & \int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{r}{2}} \mathrm{e}^{\left(r^2-2rt\cos\theta+t^2\right)^{1/2}} r^{l+j-n+2} \left(r^2-2rt\cos\theta+t^2\right)^{\frac{j'}{2}+q'} \\
& \times (r\cos\theta-t)^{l'+n-2q'} \sin\theta\,(\cos\theta)^{l-n-2q}\; \mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
\tag{4.128}
$$

For computing $\mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t)$, we apply the generalized binomial theorem and the exponential function in term of power series, hence

$$
\begin{aligned}
\mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t) = & \int_0^\infty \int_0^\pi \mathrm{e}^{-\frac{r}{2}} \sum_{n_1=0}^{\infty} \frac{\left(-1/2\left(r^2-2rt\cos\theta+t^2\right)\right)^{n_1}}{n_1!} r^{l+j-n+2} \sum_{n_2=0}^{\infty} \binom{j'/2+q'}{n_2} \\
& \times \left(r^2+t^2\right)^{n_2} (-2rt\cos\theta)^{\frac{j'}{2}+q'-n_2} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} \\
& \times (r\cos\theta)^{l'+n-2q'-n_3} (-t)^{n_3} \sin\theta\,(\cos\theta)^{l-n-2q}\; \mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
\tag{4.129}
$$

Using the binomial theorem for the expression

$$
\left(r^2+t^2-2rt\cos\theta\right)^{n_1} = \sum_{n_4=0}^{n_1} \binom{n_1}{n_4} \left(r^2+t^2\right)^{n_4} (-2rt\cos\theta)^{n_1-n_4},
$$

in equation (4.129), gives

$$
\begin{aligned}
\mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t) = & \int_0^{\infty}\int_0^{\pi} \mathrm{e}^{-\frac{r}{2}} \sum_{n_1=0}^{\infty} \frac{(-1/2)^{n_1}}{n_1!} \sum_{n_4=0}^{n_1} \binom{n_1}{n_4} \left(r^2+t^2\right)^{n_4} (-2rt\cos\theta)^{n_1-n_4} \\
& \times r^{l+j-n+2} \sum_{n_2=0}^{\infty} \binom{\frac{j'}{2}+q'}{n_2} \left(r^2+t^2\right)^{n_2} (-2rt\cos\theta)^{\frac{j'}{2}+q'-n_2} \\
& \times \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} (-t)^{n_3} (r\cos\theta)^{l'+n-2q-n_3} \sin\theta \\
& \times (\cos\theta)^{l-n-2q} \,\mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
\tag{4.130}
$$

We simplify the above expression, so

$$
\begin{aligned}
\mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t) = & \sum_{n_1=0}^{\infty} \frac{(-1/2)^{n_1}}{n_1!} \sum_{n_4=0}^{n_1} \binom{n_1}{n_4} \sum_{n_2=0}^{\infty} \binom{\frac{j'}{2}+q'}{n_2} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} \\
& \times (-t)^{n_3} \int_0^{\infty}\int_0^{\pi} \mathrm{e}^{-\frac{r}{2}} \left(r^2+t^2\right)^{n_2+n_4} (-2rt\cos\theta)^{\frac{j'}{2}+q'+n_1-n_2-n_4} \\
& \times r^{l+j-n+2} (r\cos\theta)^{l'+n-2q-n_3} \sin\theta\,(\cos\theta)^{l-n-2q} \,\mathrm{d}\theta\,\mathrm{d}r.
\end{aligned}
\tag{4.131}
$$

Again we apply the binomial theorem for $\left(r^2+t^2\right)^{n_2+n_4}$ and also we simplify the expression (4.131), hence we have

$$
\begin{aligned}
\mathcal{T}^{\mathrm{EC}}_{kk',ll',n}(t) = & \sum_{n_1=0}^{\infty} \frac{(-1/2)^{n_1}}{n_1!} \sum_{n_4=0}^{n_1} \binom{n_1}{n_4} \sum_{n_2=0}^{\infty} \binom{\frac{j'}{2}+q'}{n_2} \sum_{n_3=0}^{l'+n-2q'} \binom{l'+n-2q'}{n_3} \\
& \times \sum_{n_5=0}^{n_4+n_2} (-1)^{n_3} (-2)^{\frac{j'}{2}+q'+n_1-n_2-n_4} t^{2n_5+j'/2+q'+n_1-n_2-n_4+n_3} \\
& \times \left(\int_0^{\infty} \mathrm{e}^{-\frac{r}{2}} r^{j+\frac{j'}{2}-2q+q'+l+l'+n_1+n_2-n_3+n_4-2n_5+2} \right. \\
& \times \left. \left(\int_0^{\pi} \sin\theta\,(\cos\theta)^{\frac{j'}{2}-4q+q'+l+l'+n_1-n_2-n_3-n_4} \,\mathrm{d}\theta \right) \mathrm{d}r \right).
\end{aligned}
\tag{4.132}
$$

For computing (4.132), we need to compute the following integrals

$$
\begin{aligned}
& \int_0^{\pi} \sin\theta\,(\cos\theta)^{\frac{j'}{2}-4q+q'+l+l'+n_1-n_2-n_3-n_4} \,\mathrm{d}\theta \\
& = \frac{1-(-1)^{\frac{j'}{2}+q'+l+l'+n_1-n_2-n_3-n_4+1}}{\frac{j'}{2}-4q+q'+l+l'+n_1-n_2-n_3-n_4+1}
\end{aligned}
\tag{4.133}
$$

and

$$
\begin{aligned}
\int_0^{\infty} \mathrm{e}^{\frac{-r}{2}} r^{j+\frac{j'}{2}-2q+q'+l+l'+n_1+n_2-n_3+n_4-2n_5+2} \,\mathrm{d}r = & \, 2^{j+\frac{j'}{2}-2q+q'+l+l'+n_1+n_2-n_3+n_4-2n_5+1} \\
& \times \Gamma\left(j+\frac{j'}{2}-2q+q'+l+l'+n_1+n_2-n_3+n_4-2n_5+1\right).
\end{aligned}
\tag{4.134}
$$

With some simplifications, we obtain the final result. □

4.2.5. Fast Rotational Matching on Electrostatic Complementarity

We defined the scoring function in (4.91) by

$$\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\left(\mathbf{R}',\mathbf{t}\right)\right)=\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{R}';t\right):=\int_{\mathbb{R}^3}\Lambda_{\mathbf{R}}Q_{\mathrm{A}}^{\mathrm{EC}}(\mathbf{x})\cdot\mathcal{T}^{\mathbf{t}}\Lambda_{\mathbf{R}'}Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{x})\,\mathrm{d}\mathbf{x}.$$

We know from (4.81), for given integers l and m with the condition $l\geq|m|\geq 0$ and a rotation $\mathbf{R}\in SO(3)$,

$$\Lambda_{\mathbf{R}}\,Y_l^m(\mathbf{u})=\sum_{n=-l}^{l}D_l^{nm}(\mathbf{R})\,Y_l^n(\mathbf{u})$$

and hence, we have

$$\begin{aligned}\Lambda_{\mathbf{R}}Q_{\mathrm{A}}^{\mathrm{EC}}(r\mathbf{u})&=\sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m=-l}^{l}\hat{Q}_{klm}^{\mathrm{A}}\,V_k^l(r)\Lambda_{\mathbf{R}}\left(\,Y_l^m(\mathbf{u})\right)\\&=\sum_{k=1}^{\infty}\sum_{l=0}^{k-1}\sum_{m,n=-l}^{l}\hat{Q}_{klm}^{\mathrm{A}}D_l^{nm}(\mathbf{R})\,V_k^l(r)\,Y_l^n(\mathbf{u})\end{aligned}\tag{4.135}$$

and the effect of a rotation $\mathbf{R}'\in SO(3)$ together with a translation $\mathbf{t}\in\mathbb{R}^3$ along an axis on the $Q_{\mathrm{B}}^{\mathrm{EC}}(r\mathbf{u})$ is

$$\begin{aligned}&\Lambda_{\mathbf{R}'}\mathcal{T}^{\mathbf{t}}Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{x})=\Lambda_{\mathbf{R}'}Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{x}-\mathbf{t})=\Lambda_{\mathbf{R}'}Q_{\mathrm{B}}^{\mathrm{EC}}(\mathbf{x}')=\Lambda_{\mathbf{R}'}Q_{\mathrm{B}}^{\mathrm{EC}}(r'\mathbf{u}')\\&=\sum_{k'=1}^{\infty}\sum_{l'=0}^{k'-1}\sum_{m',n'=-l'}^{l'}\hat{Q}_{k'l'm'}^{\mathrm{B}}D_{l'}^{n'm'}(\mathbf{R}')\,V_{k'}^{l'}(r')\,Y_{l'}^{n'}(\mathbf{u}').\end{aligned}\tag{4.136}$$

In the following theorem, we present the general form of the scoring function (4.91).

Theorem 4.2.1 *The scoring function defined in* (4.91)*, can be computed by*

$$\begin{aligned}\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{R}';t\right)=\sum_{k=1}^{\infty}\sum_{k'=1}^{\infty}\sum_{l=0}^{k-1}\sum_{l'=0}^{k'-1}\sum_{m=-l}^{l}\sum_{m'=-l'}^{l'}\sum_{n=-l}^{l}\hat{Q}_{klm}^{\mathrm{A}}\hat{Q}_{k'l'm'}^{\mathrm{B}}D_l^{nm}(\mathbf{R})D_{l'}^{-nm'}(\mathbf{R}')\\\times\mathcal{I}_{kk',ll',|n|}^{\mathrm{EC}}(t).\end{aligned}$$

Proof. By the relation between $\mathbf{u}$ and $\mathbf{u}'$ in (4.36), we have

$$\begin{aligned}\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{R}';t\right)&=\int_0^{\infty}\int_{\mathbb{S}^2}\sum_{k,l,m,n}\hat{Q}_{klm}^{\mathrm{A}}D_l^{nm}(\mathbf{R})\,V_k^l(r)\,Y_l^n(\mathbf{u})\\&\quad\times\sum_{k',l',m',n'}\hat{Q}_{k'l'm'}^{\mathrm{B}}D_{l'}^{n'm'}(\mathbf{R}')\,V_{k'}^{l'}(r')\,Y_{l'}^{n'}(\mathbf{u}')r^2\,\mathrm{d}\mathbf{u}\,\mathrm{d}r\\&=\sum_{kk',ll',mm',nn'}\hat{Q}_{klm}^{\mathrm{A}}\hat{Q}_{k'l'm'}^{\mathrm{B}}D_l^{nm}(\mathbf{R})D_{l'}^{n'm'}(\mathbf{R}')\\&\quad\times\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}V_k^l(r)\,V_{k'}^{l'}(r')\,Y_l^n(\mathbf{u})\,Y_{l'}^{n'}(\mathbf{u}')r^2\sin\theta\,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r.\end{aligned}$$

According to the Definition 4.2.1, the triple integral is the ETO translational coefficients $\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t)$ and hence

$$\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{R}';t\right)=\sum_{kk',ll',mm',n}\hat{Q}^{\mathrm{A}}_{klm}\hat{Q}^{\mathrm{B}}_{k'l'm'}D^{nm}_{l}(\mathbf{R})D^{-nm'}_{l'}(\mathbf{R}')\times\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t).\ \square$$

Now according to the above theorem, it is easy to explain an algorithm to compute the scoring function (4.91). Suppose k and k' cut off to degree $N\in\mathbb{N}$ and we are given the precomputed vectors $\hat{Q}^{\mathrm{A}}_{klm}$, $\hat{Q}^{\mathrm{B}}_{k'l'm'}$ and $\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t)$, then the scoring function $\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{R}';t\right)$ can be computed in the following four steps:

1. At first, we compute

$$\hat{a}_{kln,l'm'}(t)=\sum_{k'=1}^{N}\hat{Q}^{\mathrm{B}}_{k'l'm'}\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t), \tag{4.137}$$

where its computational complexity is $\mathcal{O}(N^6N_t)$ operations and N_t denotes the number of one-dimensional translations.

2. In the second step, by NFSOFT we compute

$$\hat{b}^{\mathbf{R}'}_{kln}(t)=\sum_{l'=0}^{k'-1}\sum_{m'=-l'}^{l'}\hat{a}_{kln,l'm'}(t)\mathrm{D}^{-nm'}_{l'}(\mathbf{R}'), \tag{4.138}$$

which takes $\mathcal{O}\left(\left(N^3\left(N^2\log N+\widetilde{N_{\mathbf{R}'}}\right)+N^6\right)N_t\right)$ operations and $\widetilde{N_{\mathbf{R}'}}$ denotes the number of overall rotations for $\mathbf{R}'$.

3. We have

$$\hat{c}^{\mathbf{R}'}_{lmn}(t)=\sum_{k=1}^{N}\hat{b}^{\mathbf{R}'}_{kln}(t)\hat{Q}^{\mathrm{A}}_{klm}, \tag{4.139}$$

which is computed in $\mathcal{O}\left(\left(N^4\widetilde{N_{\mathbf{R}'}}+\left(N^3\left(N^2\log N+\widetilde{N_{\mathbf{R}'}}\right)+N^6\right)\right)N_t\right)$ operations.

4. Finally, in the last step we compute

$$\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R},\mathbf{R}';t\right)=\sum_{l=0}^{k-1}\sum_{m=-l}^{l}\sum_{n=-l}^{l}\hat{c}^{\mathbf{R}'}_{lmn}(t)\mathrm{D}^{nm}_{l}(\mathbf{R}), \tag{4.140}$$

by NFSOFT with the computational complexity

$$\mathcal{O}\left(\left(\widetilde{N_{\mathbf{R}'}}\left(N^3\log N+N_{\mathbf{R}}\right)+\left(N^4\widetilde{N_{\mathbf{R}'}}+\left(N^3\left(N^2\log N+\widetilde{N_{\mathbf{R}'}}\right)+N^6\right)\right)\right)N_t\right).$$

Therefore the overall computational complexity is $\mathcal{O}\left(\left(N^6+N^4\widetilde{N_{\mathbf{R}'}}+N_{\mathbf{R}}\widetilde{N_{\mathbf{R}'}}\right)N_t\right)$. operations. Here we presented our FRM algorithm on electrostatic complementarity. The advantage of the FRM in comparison to the straightforward way is the improvement of the computational complexity. In straightforward way, we have to compute the rotated affinity functions $\Lambda_{\mathbf{R}}Q^{\mathrm{EC}}_{\mathrm{A}}(\mathbf{x})$ which takes $\mathcal{O}\left(N_{\mathrm{A}}N_{\mathbf{R}}\right)$ operations and the computation of the rotated translated affinity function $Q^{EC}_{\mathrm{B}}\left(\mathbf{R}'^{t}\mathbf{x}-\mathbf{t}\right)$ takes $\mathcal{O}\left(N_{\mathrm{B}}N_{\mathbf{R}'}N_{\mathbf{t}}\right)$ operations, therefore the whole computational complexity is $\mathcal{O}\left(N_{\mathrm{A}}N_{\mathrm{B}}N_{\mathbf{R}}N_{\mathbf{R}'}N_{\mathbf{t}}\right)$ operations.

Algorithm 7: FRM on Electrostatic Complementarity by NFSOFT

Input:
N: Cut off degree
N_{A} and N_{B}: The number of atomic coordinates of molecules A and B
A set of motions $(\mathbf{R}, \mathbf{t})$ in $SE(3)$ and $\mathbf{R}' \in SO(3)$

foreach $\mathbf{x}_j$ *with* $j \in N_{\mathrm{A}} \cup N_{\mathrm{B}}$ **do**
  Compute the centeres of both molecules A and B.
  Compute the relocate atomic centeres of both molecules A and B.
end
foreach $\big(k, l, m\big)$ *and* $\big(k', l', m'\big)$ *with* $k > l \geq |m| \geq 0$ *and* $k' > l' \geq |m'| \geq 0$ **do**
  Compute $\hat{Q}^{\mathrm{A}}_{klm}$ of Lemma 4.2.2 and $\hat{Q}^{\mathrm{B}}_{k'l'm'}$ of Lemma 4.2.1.
end
foreach *translation* $\mathbf{t} \in \mathbb{R}^3$ *with* $t = \|\mathbf{t}\|_2$, $\big(k, k', l, l', n\big)$ *with* $k > l \geq |n| \geq 0$ *and* $k' > l' \geq |n| \geq 0$ **do**
  Compute $\mathcal{I}^{\mathrm{EC}}_{kk',ll',|n|}(t)$ of Lemma 4.2.3.
end
foreach $\big(k, l, n, l', m'\big)$ *with* $k > l \geq |n| \geq 0$ *and* $l' \geq |m'| \geq 0$ **do**
  Compute $\hat{a}_{kln,l'm'}$ of (4.137).
end
foreach *rotation* $\mathbf{R}' \in SO(3)$ *and* $\big(k, l, n\big)$ *with* $k > l \geq |n| \geq 0$ **do**
  Compute $\hat{b}^{\mathbf{R}'}_{kln}$ by NFSOFT of (4.138).
end
foreach $\big(l, m, n\big)$ *with* $l \geq |n|, |m| \geq 0$ **do**
  Compute $\hat{c}^{\mathbf{R}'}_{lmn}$ of (4.139).
end
foreach *rotation* $\mathbf{R} \in SO(3)$ **do**
  Compute $\mathcal{C}^{\mathrm{EC}}\left(\mathbf{R}, \mathbf{R}'; t\right)$ by NFSOFT of (4.140).
end
Output: The solution of the docking problem.

Complexity: $\mathcal{O}\left(\left(N^6 + N^4 \widetilde{N_{\mathbf{R}'}} + N_{\mathbf{R}} \widetilde{N_{\mathbf{R}'}}\right) N_t\right)$ operations.

Appendices

APPENDIX A

FOURIER SERIES

In this work, we need to know how to expand a function into a trigonometric series. Here we will survey of such series. Since each term of the trigonometric series is periodic, it is clear that if we are to expand functions in such series, the functions should be periodic.

Definition A.0.2 *A function $f(x)$ is said to be periodic with period T if for all x, $f(x+T) = f(x)$ where T is a positive constant. The least positive value of T is called the period of $f(x)$.*

As an example, we know the functions $\sin x$ and $\cos x$ have periods 2π, $4\pi \ldots$, because

$$\sin(x + 2k\pi) = \sin x \quad \text{and} \quad \cos(x + 2k\pi) = \cos x \text{ where } k \in \mathbb{Z},$$

and since 2π is the the smallest number that $\sin(x + 2\pi) = \sin x$ and $\cos(x + 2\pi) = \cos x$, so 2π is the period of $\sin x$ and $\cos x$.

Definition A.0.3 *Let $f(x)$ be defined in an interval $[-T, T]$ and determined outside of this interval by $f(x + 2\pi) = f(x)$. The Fourier series corresponding to $f(x)$ is defined by*

$$\frac{a_0}{2} + \sum_{n=1}^{\infty} \left(a_n \cos \frac{n\pi x}{T} + b_n \sin \frac{n\pi x}{T} \right), \tag{A.1}$$

where the Fourier coefficients a_n and b_n for $n = 0,\ 1,\ 2,\ \ldots$ are

$$a_n = \frac{1}{T} \int_{-T}^{T} f(x) \cos \frac{n\pi x}{T} \, \mathrm{d}x \tag{A.2}$$

and

$$b_n = \frac{1}{T} \int_{-T}^{T} f(x) \sin \frac{n\pi x}{T} \, \mathrm{d}x. \tag{A.3}$$

If $T = \pi$ then function in this case has the period 2π and the Fourier series (A.1) and the Fourier coefficiens a_n (A.2) and b_n (A.3) are simple to compute.

Definition A.0.4 *A function $f(x)$ is piecewise continuous if*

1. *the interval can be divided into a finite number of subintervals such that $f(x)$ is continuous on each subinterval and*

2. *on each subinterval, the limits of $f(x)$ as x approaches to the endpoints of this subinterval have to be finite.*

Definition A.0.5 *A function $f(x)$ is called piecewise smooth on an interval, if $f(x)$ and $f'(x)$ are both piecewise continuous on the interval.*

We do not know whether the Fourier series (A.1) converges or not, and if it converges whether it converges to $f(x)$. In the following lemma we know about this problem.

Lemma A.0.4 (Dirichlet Conditions) *If $f(x)$ is piecewise smooth and periodic in $(-T,T)$ then the Fourier series* (A.1) *with the Fourier coefficients defined in* (A.2) *and* (A.3) *converges to*

1. *$f(x)$, if x is a point of continuity.*

2. *$\frac{f(x+0)+f(x-0)}{2}$, if x is a point of discontinuity.*

So according to the Dirichlet conditions, if x is a point of continuity we can write

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos\frac{n\pi x}{T} + b_n \sin\frac{n\pi x}{T}\right), \tag{A.4}$$

and if x is a point of discontinuity, then

$$\frac{f(x+0)+f(x-0)}{2} = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos\frac{n\pi x}{T} + b_n \sin\frac{n\pi x}{T}\right). \tag{A.5}$$

The Dirichlet conditions are sufficient conditions imposed on $f(x)$ not necessary. In other words, if the imposed conditions of $f(x)$ hold, then the convergence is guaranteed otherwise the Fourier series may or may not converge.

Using Euler's identity $\mathrm{e}^{\mathrm{i}\theta} = \cos\theta + \mathrm{i}\sin\theta$ where $\mathrm{i}^2 = -1$ enables us to write the Fourier series for $f(x)$ as

$$f(x) = \sum_{n=-\infty}^{\infty} \hat{f}_n \mathrm{e}^{\frac{\mathrm{i}n\pi x}{\mathrm{T}}}, \tag{A.6}$$

where

$$\hat{f}_n = \frac{1}{T}\int_{-T}^{T} f(x)\mathrm{e}^{\frac{-\mathrm{i}n\pi x}{T}}\,\mathrm{d}x. \tag{A.7}$$

Here we are supposing that the Dirichlet conditions are satisfied and further that $f(x)$ is continuous at x. If $f(x)$ is discontinuous at x, then

$$\frac{f(x+0)+f(x-0)}{2} = \sum_{n=-\infty}^{\infty} \hat{f}_n \mathrm{e}^{\frac{\mathrm{i}n\pi x}{T}}, \tag{A.8}$$

Lemma A.0.5 (Parseval's Identity) *Suppose $f(x)$ satisfies the Dirichlet's conditions and a_n and b_n are the Fourier coefficients corresponding to $f(x)$, then*

$$\frac{1}{T}\int_{-T}^{T} |f(x)|^2 \,\mathrm{d}x = \frac{a_0^2}{2} + \sum_{n=1}^{\infty} \left(a_n^2 + b_n^2\right).$$

Again we recall some basic definitions and lemmas without proof of mathematical.

Suppose we have an infinite series $\{f_n(x)\}_{n\in\mathbb{N}}$. We define the N-th partial sum of this sequence by

$$S_N(x) = \sum_{n=1}^{N} f_n(x).$$

We say the infinite series $\sum_{n=1}^{\infty} f_n(x)$ converges to $f(x)$ in the interval (a, b), if for each $\epsilon > 0$ there exist for each $x \in (a, b)$, a positive N such that for all $n > N$, we have

$$|S_n(x) - f(x)| < \epsilon, \tag{A.9}$$

where here the positive number N depends on ϵ and x. But the important case occurs when the positive number N depends on ϵ and not on $x \in (a, b)$. In this case we say the infinite series is uniformly convergent to $f(x)$. We demonstrate the most important properties of the uniformly convergent series in the frame of two lemmas.

Lemma A.0.6 *Suppose we have an infinite series $\sum_{n=1}^{\infty} f_n(x)$. If each term $f_n(x)$ where $n \in \mathbb{N}$ is continuous in an interval (a, b) and also the infinite series is uniformly convergent to $f(x)$ in this interval, then*

1. *$f(x)$ is also continuous in the interval (a, b).*
2. $\displaystyle\int_a^b \sum_{n=1}^{\infty} f_n(x)\,\mathrm{d}x = \sum_{n=1}^{\infty} \int_a^b f_n(x)\,\mathrm{d}x.$

Lemma A.0.7 *Suppose we have an infinite series $\sum_{n=1}^{\infty} f_n(x)$. If each term $f_n(x)$ where $n \in \mathbb{N}$ is differentiable in an interval (a, b) and also the infinite series of derivatives is uniformly convergent, then*

$$\frac{\mathrm{d}}{\mathrm{d}x}\sum_{n=1}^{\infty} f_n(x) = \sum_{n=1}^{\infty} \frac{\mathrm{d}}{\mathrm{d}x} f_n(x).$$

Integration and differentiation of Fourier series can be justified by using Lemma A.0.6 and Lemma A.0.7 that hold for infinite series generally but note that these lemmas provide sufficient conditions which are not necessary. The following lemma for integration is very useful.

Lemma A.0.8 *The Fourier series corresponding to $f(x)$ may be integrated term by term from a to x and the resulting series will converges uniformly to $\int_a^x f(u)\,\mathrm{d}u$ provided that $f(x)$ is piecewise continuous in $[-T, T]$ and both a and x are in this interval.*

For more details, see Spiegel [87].

BIBLIOGRAPHY

[1] Abramowitz, M., and Stegun, I. A. *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, ninth Dover printing, tenth GPO printing ed. Dover, New York, 1964.

[2] Aloy, P., and Russell, R. B. Ten thousand interactions for the molecular biologist. *Nature Biotechnology*, 22 (2004), 1317–1321.

[3] Alpert, B. K., and Rokhlin, V. A fast algorithm for the evaluation of Legendre expansions. *SIAM J. Sci. Stat. Comput.*, 12 (1990), 158–179.

[4] Askey, R. *Orthogonal Polynomials and Special Functions.* SIAM, 1975.

[5] Atkins, P., and de Paula, J. *Physical Chemistry for the Life Sciences.* Oxford University Press, 1973.

[6] Bailey, R. About.com.biology. Tech. rep. Also available as http://biology.about.com/od/molecularbiology/a/aa101904a.htm.

[7] Bajaj, C., Chowdhury, R., Keidel, D., Moussalem, M., Olson, A., Rasheed, M., and Sanner, M. F2 Dock 2.0 and GB-rerank. Submitted 2011.

[8] Bajaj, C., Chowdhury, R., and Siddahanavalli, V. F2 Dock: Fast Fourier protein-protein docking. *IEEE/ACM Trans. Comput. Biol. Bioinf. 1*, 8 (2009).

[9] Balabin, R. M. Intermolecular basis set superposition error as a measure of basis set incompeleteness: Can one reach the basis set limit without extrapolation? *J. Chem. Phys. 21*, 132 (2010).

[10] Baszenski, G., and Tasche, M. Fast polynomial multiplication and convolution related to the discrete cosine transform. *Linear Algebra Appl.*, 252 (1997), 1–5.

[11] Becker, T. Protein-protein docking mit fast rotational matching. Master's thesis, Institute of Mathematics of the University of Luebeck, 2008.

[12] Beylkin, G. On the fast Fourier transform of functions with singularities. *Appl. Comput. Harmon. Anal.*, 2 (1995), 363–381.

[13] Biedenharn, L. C., and Louck, J. C. *Angular Momentum in Quantum Physics.* Addison-Wesley, 1981.

[14] Biedenharn, L. C., and Louck, J. C. *The Racah-Wigner Algebra in Quantum Theory.* Addison-Wesley, 1981.

[15] Bondi, A. van der Waals volumes and radii. *J. Phys. Chem.*, 68 (1964), 441–451.

[16] Bransden, B. H., and Joachain, C. J. *Introduction to Quantum Mechanics.* Addison Wesley Longman, Harlow, UK, 1997.

[17] Campasso, V. *Mathematical Structures of Epidemic Systems.* Springer-Verlag, Berlin Heidelberg, 2008.

[18] Campbell, A. N., Williamson, B., and Heyden, R. J. *Biology: Exploring Life.* Pearson Prentice Hall, 2006.

[19] Castrillon-Candas, J. E., Bajaj, C., and Siddavanahalli, V. An adaptive irregularly spaced Fourier method for protein-protein docking. *J. Mol. Biol. 1*, 272 (1997), 106–120.

[20] Castrillon-Candas, J. E., Siddavanahalli, V., and Bajaj, C. Nonequispaced Fourier transform for protein-protein docking. *ICES Report*.

[21] Chirikjian, G. S., and Kyatkin, A. B. *Engineering Application of Noncommutative Harmonic Analysis: With Emphasis on Rotation and Motion Groups.* CRC Press, New York, 2001.

[22] Connolly, M. L. Analytical molecular surface calculation. *J. Appl. Cryst.*, 16 (1983), 548–558.

[23] Cooly, J. W., and Tukey, J. W. An algorithm for machine calculation of complex Fourier series. *Math. Comput.*, 19 (1965), 297–301.

[24] Corey, R. B., and Pauling, L. Molecular models of amino acids, peptides and proteins. *Review of Scientific Instruments* (1997), 621–627.

[25] Creighton, T. E. *Protein Structures and Molecular Properties.* New York, 1965.

[26] Driscoll, J. R., and Healy, D. Computing Fourier transform and convolution on the 2-sphere. *Adv. Appl. Math.*, 15 (1994), 202–250.

[27] Driscoll, J. R., Healy, D., and Rockmore, D. Fast discrete polynomial transforms with applications to data analysis for distance transitive graphs. *SIAM J. Comput.*, 26 (1996), 1066–1099.

[28] Duncan, B. S., and Olson, A. J. Shape analysis of molecular surface. *Biopolymers*, 33 (1993), 231–238.

[29] Dutt, A., and Rokhlin, V. Fast transform for nonequispaced data. *SIAM J. Sci. Stat. Comput.*, 14 (1993), 1368–1393.

[30] Eisenstein, M., and Katchalski-Katzir, E. On proteins, grids, correlations and docking. *CR Biol.*, 327 (2004), 409–420.

[31] Erdelyi, A., Magnus, W., Oberhettinger, F., and Tricomi, F. G. *Table of Integral Transforms.* McGraw, New York, 1953.

[32] Filbir, F., and Schmidt, D. Stability results for approximation by positive definite functions on SO(3). *J. Approx. Theory*, 153 (2008), 170–183.

[33] Floudas, C. A., and Pardalos, P. M. *Optimization in Computational Chemistry and Molecular Biology.* Kluwer Academic Publishers, London, 2000.

[34] Freeden, W., Gervens, T., and Schreiner, M. *Constructive Approximation on the Sphere.* Oxford University Press, Oxford, 1998.

[35] Fulton, W., and Harris, J. *A Representation Theory.* Springer Science + Bussiness Media, LLC, 2004.

[36] Gabb, H. A., Jackson, R. M., and Stenberg, M. J. E. Modelling protein docking using shape complementarity, electrostatic and biochemistry information. *J. Mol. Biol.*, 272 (1997), 106–120.

[37] Garzon, J. I., Lopez-Blanco, J. R., Pons, C., Kovacs, J., Abagyan, R., Fernandez-Ricio, J., and Chacon, P. FRODOCK: A new approach for fast rotational protein-protein docking. *Struct. Bioinf. 25*, 19 (2009), 2544–2551.

[38] Gottfried, K. *Quantum Mechanics.* Benjamin, New York, 1960.

[39] Graef, M., and Kunis, S. Stability results for scattered data interpolation on the rotation group. *Electron. Trans. Numer. Anal.*, 31 (2008), 30–39.

[40] Graef, M., and Potts, D. Sampling set and quadrature formula on the rotation group. *Numer. Func. Anal. Optim.*, 30 (2009), 655–688.

[41] Grant, J. A., and Pickup, B. T. A gaussian description of molecular shape. *J. Phys. Chem.*, 99 (1995), 3503–3510.

[42] Gray, J. J., Moughon, S., Wang, C., Schueler-Furman, O., Kulman, B., Rohl, C. A., and Baker, D. Protein-protein docking with simultaneous optimization of rigid-body displacement and side-chain conformations. *J. Mol. Biol.*, 331 (2003), 281–299.

[43] Gutzmer, T. Interpolation by positive definite functions on locally compact groups with application to SO(3). *Results Math.*, 29 (1996), 69–77.

[44] Halperin, I., Ma, B., Wolfson, H., and Nussinov, R. Principles of docking: An overview of search algorithms and guide to scoring functions. *PROTEINS: Struct. Funct. Genet.*, 47 (2002), 409–443.

[45] Heifetz, A., Katchalski-Katzir, E., and Eisenstein, M. Electrostatics in protein-protein docking. *Protein Sciences*, 11 (2002), 571–587.

[46] Helgason, S. *Groups and Geometric Analysis.* Academic Press Inc., New York, 1984.

[47] Hielscher, R., Prestin, J., and Vollrath, A. Fast summation of function on SO(3). *Geosci.*, 42 (2010), 773–794.

[48] Huang, J. S. *Lecture on Representation Theory.* World Scientific Publishing Inc., Singapore, 1999.

[49] Jackson, J. D. *Classical Electrodynamics.* Wiley., New York, 1975.

[50] Kaapro, A., and Ojanen, J. Protein docking. Tech. rep.

[51] Katchalski-Katzir, E., Shariv, I., Eisenstein, M., Friesen, A. A., Aflalo, C., and Vakser, I. A. Molecular surface recognition: Determination of geometric fit between protein and their ligands by correlating tachniques. *Proc. Nat. Acad. Sci. USA*, 89 (1992), 2195–2199.

[52] Keiner, J., Kunis, S., and Potts, D. Fast summation of radial functions on the sphere. *Computing*, 78 (2006), 1–15.

[53] Keiner, J., Kunis, S., and Potts, D. Fast evaluation of quadrature on the sphere. *Math. Comput.*, 77 (2008), 397–419.

[54] Kevin, W., Peterson, M. W., Pierce, B., Mintseris, J., and z. Weng. protein-protein docking: Overview and performance analysis methods. *Mol. Biol.*, 413 (2008), 283–314.

[55] Koerner, T. W. *A Companion to Analysis, A second First and First Second Course in Analysis.* AMS, 2004.

[56] Kostelec, P. J., and Rockmore, D. N. FFTs on the rotation group. *J. Fourier Anal. Appl.*, 14 (2008), 145–179.

[57] Kovacs, J. A., Chacon, P., Cong, Y., Metwally, E., and Wriggers, W. Fast rotational matching of rigid bodies by fast Fourier transform acceleration of five degrees of freedom. *Acta Crystallographica Section D*, 59 (2003), 1371–1376.

[58] Kovacs, J. A., and Wriggers, W. Fast rotational matching. *Acta Crystallographica Section D*, 58 (2002), 1371–1376.

[59] Kunis, S. A., and Potts, D. Fast spherical Fourier algorithms. *J. Comput. Appl. Math.*, 161 (2003), 75–98.

[60] Lee, K. Computational study for protein-protein docking using global optimization and emprical potentials. *Int. J. Mol. Sci.*, 9 (2008), 65–77.

[61] Maslen, D. K., and Rockmore, D. N. Generalized FFTs - A survey of some recent results. *DIMACS Workshop in Groups and Computation 28* (1995), 183–238.

[62] Miller, W. *Lie Theory and Spherical Functions.* Academic Press Inc., New York, 1968.

[63] Mohlenkamp, M. J. A fast transform on spherical harmonics. *J. Fourier Anal. Appl.*, 5 (1999), 159–184.

[64] MOSHINSKY, M., NOVARO, O., and CALLES, A. The pseudo-atom: A soluble many body problem. *DE PHYSIQUE*, 31 (1970), C4–125.

[65] Mueller, C. *Analysis of Spherical Symmetries in Euclidean Space.* Springer-Verlag, New York, 1998.

[66] Newman, M. S. *Steric Effects in Organic Chemistry.* John Wiely, New York, 1956.

[67] Norel, R., Petrey, D., Wolfson, H. J., and Nussinov, R. Examination of shape complementarity in docking of unbound proteins. *Proteins.*, 39 (1999), 178–194.

[68] Norel, R., Sheinerman, F., Petery, D., and Honig, B. Electrostatic contribution to protein-protein interaction: Fast energetic filters for docking and their physical basis. *Protein Sciences*, 10 (2001), 2147–2167.

[69] Olver, P. J. *Application of Lie Groups to Differential Equations.* Springer-Verlag, New York, 1993.

[70] Orchin, M., Macomber, R. S., Pinhas, A., and Wilson, R. M. *The Vocabulary and Concepts of Organic Chemistry*, second ed. John Wiley & Sons, Inc., 2005.

[71] Palma, P. N., Krippahl, L., Wampler, J. E., and Moura, J. J. G. Bigger: A new (soft) docking algorithm for predicting protein interactions. *PROTEINS: Struct. Funct. Genet.*, 39 (2000), 75–98.

[72] Potts, D., Prestin, J., and Vollrath, A. A fast algorithm for nonequispaced Fourier transform on the rotation group. *Numer. Algorithms*, 52 (2009), 355–384.

[73] Potts, D., and Steidl, G. Fast summation at nonequispaced knots by NFFTs. *SIAM J. Sci. Comput.*, 24 (2003), 2013–2037.

[74] Potts, D., Steidl, G., and Tasche, M. Fast fourier transform for nonequispaced data: A tutorial.

[75] Potts, D., Steidl, G., and Tasche, M. Fast algorithms for discrete polynomial transforms. *Math. Comput.*, 67 (1998), 1577–1590.

[76] Potts, D., Steidl, G., and Tasche, M. Numerical stability of fast trigonometric transforms-a new worst case study. *J. Concrete Appl. Math.*, 1 (2003), 1–36.

[77] Risbo, T. Fourier transform summation of Legendre series and D-functions. *J. Geod.*, 70 (1996), 383–396.

[78] Ritchie, D. W. High performance algorithms for molecular shape recognition. Authorisation to Manage Research from Universite Henri Poincare.

[79] Ritchie, D. W. Evaluation of protein docking prediction using Hex 3.1 in CAPRI rounds 1 and 2. *PROTEINS: Struct. Funct. and Genet.*, 52 (2003), 98–106.

[80] Ritchie, D. W. High order analytic translation matrix elements for real six-dimensional polar Fourier correlations. *J. Appl. Cryst.*, 38 (2005), 808–818.

[81] Ritchie, D. W. Recent progress and future directions in protein-protein docking. *Curr. Prot. Pep. Sci.*, 9 (2008), 1–15.

[82] Ritchie, D. W., and Kemp, G. J. L. Protein docking using spherical polar Fourier correlations. *PROTEINS: Struct. Funct. and Genet.*, 39 (2000).

[83] Ritchie, D. W., Kozako, D., and Vajda, S. Accelerating and focusing protein-protein docking correlation using multi-dimensional rotational FFT generating functions. *Structural Bioinformatics 24*, 17 (2008), 1865–1873.

[84] Robinson, J. *Applied Analysis Lecture Notes.* University of Warwick, 2006.

[85] Rokhlin, V., and Tygert, M. Fast algorithms for spherical harmonic expansions. *SIAM J. Sci. Comput.*, 27 (2006), 1903–1928.

[86] Sheng, G. *Harmonic Analysis on Classical Groups.* Springer-Verlag, Berlin, 1991.

[87] Spiegel, M. R. *Theory and Problems of Fourier Analysis.* McGraw-Hill, 1979.

[88] Sumikoshi, K., Terada, T., Nakamura, S., and Shimizu, K. A fast protein-protein docking using series expansions in terms of spherical basis functions. *Genome Informatics*, 16 (2005).

[89] Szego, G. *Orthogonal Polynomials.* Amer. Math. Soci., Providence, 1975.

[90] Tilma, T., and Sudarshan, E. C. G. Generalized Euler angle parametrization for SU(n). *J. Phys. A: Math. Gene.*, 35 (2002), 10467–10501.

[91] Tompa, M. Lecture notes on biological sequence analysis. Tech. rep., Washington University, 2000.

[92] Varshalovichi, D. A., Moskalev, A. N., and Kherosanski, V. K. *Quantum Theory of Angular Momentum.* World Scientific Publishing Inc., Singapore, 1988.

[93] Vilenkin, N. J. *Special Functions and the Theory of Group Representations.* Amer. Math. Soci., Providence, 1968.

[94] Vilenkin, N. J., and Klimyk, A. U. *Representation of Lie Groups and Special Functions.* Kluwer Academic Publishers, Dordrecht, 1991.

[95] Virchenko, N. O., and Fedotova, I. *Generalized Associated Legendre Functions and their Applications.* Singapore, 2001.

[96] Vollrath, A. *The Nonequispaced Fast SO(3) Fourier Transform, Generalisations and Applications.* PhD thesis, Institute of Mathematics of the University of Luebeck, 2010.

[97] Weyl, H. *The Theory of Groups and Quantum Mechanics.* Dover Publications, New York, 1931.

[98] Wigner, E. P. *Group Theory and It's Application to the Quantum Mechanics of Atomic Spectra.* Academic Press Inc., New York, 1959.

[99] Wodak, S. J., and Janin, J. Computer analysis of protein-protein interaction. *J. Mol. Biol.*, 124 (1978), 323–342.

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