Harmonic Analysis on Isometry Groups of Objective Structures and its Applications to Objective Density Functional Theory

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Dedicated to the memory of my uncle
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Abstract

Objective structures (defined in James [2006]) generalize the notion of crystals and are atomic/molecular structures in which all the constituent atoms/molecules of the structure "see" the same environment up to orthogonal transformations and translations. It has been conjectured [James, 2006] that the high degree of symmetry associated with these structures can lead to interesting material properties such as ferromagnetism, ferroelectricity and superconductivity. This provides a motivation to systematically study the electronic properties of these structures and to formulate Density Functional Theory methods specifically designed for objective structures. We term density functional methods/algorithms designed for studying Objective Structures as Objective Density Functional Theory.

The purpose of this work is to serve as the first important step toward the formulation and implementation of objective density functional theory. Keeping in mind, that density functional theory methods designed for studying crystals obtain leverage out of the translational symmetry of the underlying periodic system, the primary theoretical issue in formulating objective density functional theory methods, becomes quantifying the effects of (non-translational) symmetry on electronic structure computation. In this work, we borrow ideas from abstract harmonic analysis/group representation theory, in order to understand how the symmetry of objective structures generated by finite groups of isometries interacts with the boundary value problems of Kohn-Sham density functional theory. To achieve our goal, we first work through the formulation of a suitable group representation theory. We then apply this representation theory to simplified versions of the boundary value problems associated with electronic structure calculation and we demonstrate how this results in simplifications of those problems. Finally, we formulate symmetry adapted finite difference and spectral schemes for numerical solution of the boundary value problems.

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Chapter 1

Introduction

Prediction of new materials with properties of engineering and scientific interest is the central goal of theoretical materials science. Methods used by the theoretical materials scientist often include sophisticated mathematical tools for modeling and analysis of the physical phenomena associated with materials, as well as the numerical simulation of these phenomena. Most of these phenomena involve multiple temporal and spatial scales and so, the physical theories employed range from continuum to quantum mechanics [Tadmor and Miller, 2011].

Physical symmetry usually plays a very important role in the theories used for the modeling and simulation of materials. Presence of symmetry is usually associated with interesting material properties, or sometimes, symmetry provides an explanation for the lack of such properties. On the continuum scale for instance, one can employ symmetry related ideas to conclude that an isotropic elastic material can have only two independent elastic constants [Gurtin, 1981]. At the molecular level, symmetry related ideas can be used to draw conclusions about the vibrational spectra and optical properties of molecules [Hammermesh, 1989]. In fact, the most widely studied molecular structures in materials science and solid state physics are crystals, whose wide variety of interesting material properties are usually directly related to their underlying space group symmetries [Lax, 2001; Hammermesh, 1989].

The usual manner by which one searches for materials with interesting properties, is what can be called a constitution based search. In this approach, different atomic and molecular constitutions are envisioned and one tries to systematically verify if any interesting material properties are present. Underlying symmetries of the molecular arrangement are often

used to simplify necessary computations. However, given the important role that symmetry seems to play in the occurrence of interesting material properties, one can adopt a slightly different viewpoint in which the search would be based on possible symmetry classes. The idea of objective structures seems to provide a unifying frame-work for carrying out this program.

As defined in James [2006], an *objective atomic structure* is a collection of atoms, represented by mass points or ions, for which every atom sees precisely the same atomic environment up to orthogonal transformation and translation. An *objective molecular structure* is a collection of molecules in which corresponding atoms in each molecule see the same environment up to orthogonal transformation and translation. It is clear from these definitions that objective structures are intrinsically associated with symmetry and therefore, one might hope to search for interesting materials by looking at all possible objective structures.

Some of the most widely studied atomic/molecular structures in materials science and nanotechnology fall into the category of objective structures [James, 2006]. Indeed, all perfect crystals are objective structures, as are nanotubes of arbitrary chirality. The list of objective structures also includes (but is not limited to) buckyballs, tail sheaths and capsids of viruses, graphene sheets and molecular bilayers. Figure 1.1 shows a collection of some non-crystalline objective structures.

The objective structures framework has already been linked to a variety of applications. Dumitrica and James [2007] have developed *objective molecular dynamics*, a natural extension of the classical technique of periodic molecular dynamics [Allen and Tildesley, 1987; Parrinello and Rahman, 1980], to objective structures. Dumitrica and James [2007] have used their method to study instability modes of nanotubes using empirical potentials. There have been extensions of this work to tightbinding calculations as well [Zhang et al., 2009, 2008]. The objective structures framework has also been used, in conjunction with multiscale ideas, for the study of viscometric flows and the design of viscometers [Dayal and James, 2010, 2011]. With the objective structures framework already being used for molecular level simulations, it is perhaps natural to extend the framework to the electronic structure level and this work can be seen as an important step towards that goal.

To use the objective structures framework for searching new materials, a key step is to identify all possible objective structures. It turns out that this question is intimately related to the derivation of all possible discrete groups of isometries in three dimensions [Dayal et al., 2010]. The derivation of these groups is a classical topic [Opechowski, 1986] and some of the groups are summarized in the International Tables of Crystallography [Hahn, 2003]. Of

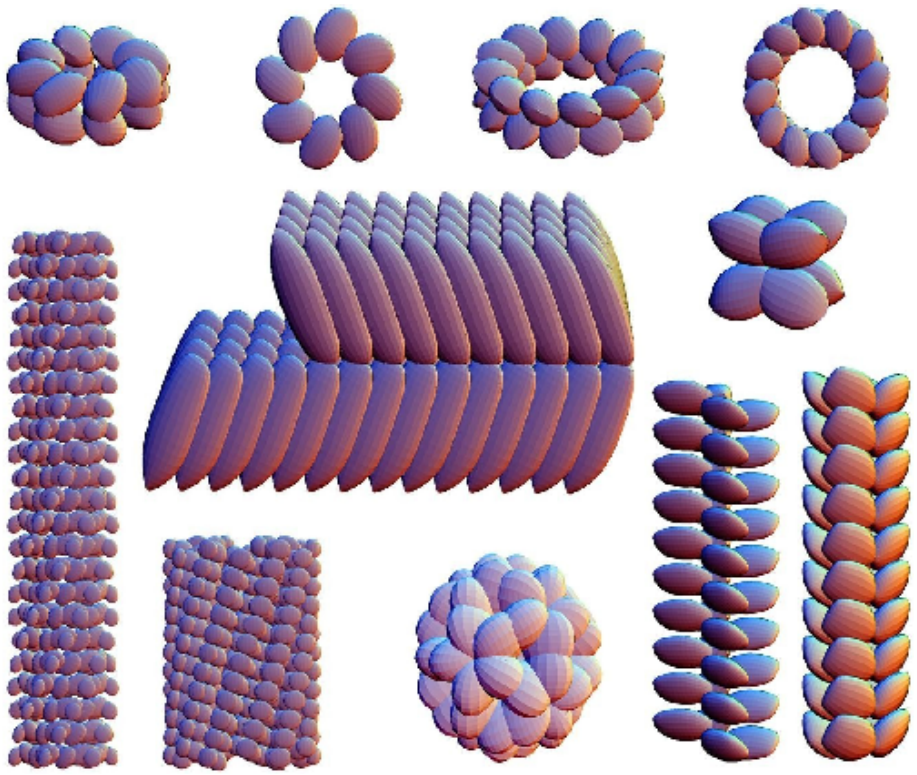

Figure 1.1: A zoology of objective structures. (Image courtesy of Prof. R.D. James)

special interest for objective structures are the subperiodic groups, that is, the ones that do not contain three linearly independent translations. Volume E of the International Tables contains an incomplete listing of the subperiodic groups. Another problem with the listings of these groups is that only the abstract groups are listed, whereas for using the objective structures framework, the explicit isometries, and particularly the allowed parameter dependence of these isometries, is needed. Dayal et al. [2010] have calculated from the basic definition, the explicit forms of all subperiodic, discrete groups of isometries and therefore, we now have an exhaustive list of all possible objective structures.

The effects of physical symmetry on electronic structure have been well studied in many cases. The work of F. Bloch on the single electron theory of a crystalline solid [Bloch, 1929], is perhaps one of the earliest works in this direction. In Bouckaert et al. [1936], an explicit connection of the Bloch theory with space group symmetries was made. These works have subsequently led to the formulation of symmetry adapted quadrature and Brillouin zone sampling techniques [te Velde and Baerends, 1992; Evarestov and Smirnov, 1983; Defranceschi and Le Bris, 2000], as well as simplifications in Linear Combination of Atomic Orbital (LCAO) based methods [Slater and Koster, 1954; Roothaan, 1960;

Zicovich-Wilson and Dovesi, 1998a,b]. While the above mentioned works are primarily concerned with systems that have periodic and/or point group symmetries, there have been extensions of these works to helical and other quasi one-dimensional systems [Milosević et al., 2006; Dakić et al., 2009; White et al., 1993]. Many popular electronic structure computation codes now have various degrees of symmetry exploitation routines built into them: examples would include the packages CRYSTAL [Noel et al., 2010], turbomole [Ahlrichs et al., 1989], fhi96md [Bockstedte et al., 1997], Gulp [Gale, 1997] and PARSEC [Kronik et al., 2006].

Our point of view is that the literature on symmetry adapted techniques seems to be missing the unifying theme that the objective structures framework provides. It is also not clear to us, how the symmetry principles that have been employed in some of the aforementioned literature, can be rigorously justified from first principles. For instance, while dealing with point group symmetries, theorems from group representation, in the context of finite dimensional vector spaces, are often cited (see for instance Noel et al. [2010]). The connection between this finite dimensional representation theory, and the solutions of the equations of density functional theory (which represent a nonlinear infinite dimensional problem) are not made clear however. In particular, these works do not demonstrate that there is a natural "cell problem" associated with the electronic structure computation problem of atomic/molecular structures that are associated with point group symmetries.

It is our hope, that this work will take an important step towards addressing some of the above issues, in a mathematically rigorous way. The scope of this work will be limited to objective structures generated by finite groups of isometries. For the purpose of analyzing how the equations of density functional theory interact with underlying symmetry, we have formulated an appropriate representation theory on a general class of Hilbert spaces. This has helped us in establishing clear connections between electronic structure calculation of objective structures and the harmonic analysis of finite groups of isometries. We have witnessed a good interplay of ideas from the theory of elliptic partial differential equations, functional analysis and abstract harmonic analysis during the formulation of many of these connections. In spirit, this work extends the canonical analysis of periodic systems that is carried out using the Fourier transform, to systems with point group symmetries. A similar extension, for the case of objective structures generated by (infinite) helical groups of isometries, will be the focus of future work.

The rest of this work is outlined as follows. Chapter 2 provides some of the basic background material on objective structures and density functional theory. In Chapter 3 we de-

velop the necessary tools of group representation theory. We apply these tools to simplified versions of the electronic structure computation problem (with appropriate justifications) in Chapter 4. We formulate symmetry adapted numerical schemes in Chapter 5. Chapter 6 concludes the thesis.

Chapter 2

Background Material

We use this chapter to provide a background on the theory of objective structures as well as electronic structure calculation theories. This also provides us with a chance to introduce some notations that are employed throughout this work.

2.1 Isometry Groups of Objective Structures

Following the developments in James [2006] and Dayal et al. [2010] we adopt a mathematical definition of objective structures in terms of discrete groups of isometries. This requires that we introduce a few related ideas first. Let $\mathrm{Lin}(3)$ denote the set of linear transformations on $\mathbb{R}^3$ and let $\mathbf{O}(3)$ denote the orthogonal group in three dimensions, that is, $\mathbf{O}(3) = \{\mathbf{R} \in \mathrm{Lin}(3) : \mathbf{R}^T\mathbf{R} = \mathbf{I}\}$. We recall that an isometry is an affine map $\Upsilon : \mathbb{R}^3 \to \mathbb{R}^3$ of the form $\Upsilon = (\mathbf{R}|\mathbf{c})$ with $\mathbf{R} \in \mathbf{O}(3), \mathbf{c} \in \mathbb{R}^3$ such that the point $\mathbf{x} \in \mathbb{R}^3$ is mapped to the point $\mathbf{R}\mathbf{x} + \mathbf{c}$. As the name implies, isometries preserve distances (and hence angles), that is $\forall \mathbf{x}, \mathbf{y} \in \mathbb{R}^3,\ |\Upsilon(\mathbf{x}) - \Upsilon(\mathbf{y})| = |\mathbf{x} - \mathbf{y}|$. The product of two isometries $\Upsilon_1 = (\mathbf{R}_1|\mathbf{c}_1)$ and $\Upsilon_2 = (\mathbf{R}_2|\mathbf{c}_2)$ is defined as a composition of their maps, that is, $(\Upsilon_1 \circ \Upsilon_2)(\mathbf{x}) = \Upsilon_1(\Upsilon_2(\mathbf{x}))$. This implies that $\Upsilon_1 \circ \Upsilon_2$ admits the representation $(\mathbf{R}_1\mathbf{R}_2|\mathbf{R}_1\mathbf{c}_2 + \mathbf{c}_1)$. The identity isometry maps every $\mathbf{x} \in \mathbb{R}^3$ to itself and is represented by $(\mathbf{I}|\mathbf{0})$. It follows that the inverse of the isometry $\Upsilon = (\mathbf{R}|\mathbf{c})$ is the isometry $(\mathbf{R}^T| - \mathbf{R}^T\mathbf{c})$ and this is denoted as Υ^{-1}. A group of isometries is a set of isometries which includes the identity isometry and which forms a group with the product and inverse operations described above.

If $\mathcal{G}$ is a group of isometries, then the orbit of a point $\mathbf{x} \in \mathbb{R}^3$ is the set $\{\Upsilon(\mathbf{x}) : \Upsilon \in \mathcal{G}\}$ and we denote this as $\mathrm{Orb}(\mathcal{G}, \mathbf{x})$. The set $\mathrm{Stab}(\mathcal{G}, \mathbf{x})$ is the set of isometries whose action

on $\mathbf{x}$ leave it invariant, that is $\text{Stab}(\mathcal{G}, \mathbf{x}) = \{\Upsilon \in \mathcal{G} : \Upsilon(\mathbf{x}) = \mathbf{x}\}$. One can easily verify that $\text{Stab}(\mathcal{G}, \mathbf{x})$ is in fact always a subgroup of $\mathcal{G}$ for any $\mathbf{x} \in \mathbb{R}^3$. A group of isometries is termed discrete if for every $\epsilon > 0$ and every $\mathbf{x}, \mathbf{y} \in \mathbb{R}^3$, the open ball of radius ϵ centered about $\mathbf{y}$ contains only finitely many points from the orbit of $\mathbf{x}$, that is:

$$\text{Orb}(\mathcal{G}, \mathbf{x}) \cap \mathcal{B}_\epsilon(\mathbf{y}) = \text{a finite set}, \ \forall \epsilon > 0 \text{ and } \forall \mathbf{x}, \mathbf{y} \in \mathbb{R}^3. \tag{2.1}$$

We are now in a position to define objective structures:

Definition 2.1.1. Let $M \subset \mathbb{R}^3$ be a finite collection of distinct points and let $\mathcal{G}$ be a discrete group of isometries such that $\text{Stab}(\mathcal{G}, \mathbf{x}) = \{(\mathbf{I}|\mathbf{0})\}$ or $\mathcal{G}$ for all $\mathbf{x} \in M$. Then

$$\mathcal{S} = \bigcup_{x \in M} \text{Orb}(\mathcal{G}, \mathbf{x}) \tag{2.2}$$

is called an objective structure with $\mathcal{G}$ as its underlying discrete group of isometries provided that there is at least one $\mathbf{x} \in M$ such that $\text{Stab}(\mathcal{G}, \mathbf{x}) = \{(\mathbf{I}|\mathbf{0})\}$. In particular, if $\text{Stab}(\mathcal{G}, \mathbf{x}) = \{(\mathbf{I}|\mathbf{0})\}$ for all $\mathbf{x} \in M$, then we say that the objective structure is fixed point free. If M consists of only one point then the we say that $\mathcal{S}$ is an Objective Atomic Structure and if M consists of more than one point, we say that $\mathcal{S}$ is an Objective Molecular Structure. □

We will only concern ourselves with objective structures which are fixed point free in this work. The extension to objective molecular structures which are not fixed point free (such as a molecule of methane with the position vectors of the carbon atom and any single hydrogen atom forming the set M) only provides algorithm implementation and coding challenges and does not pose any serious theoretical challenges. The need for having at least one point which has a nontrivial orbit (that is, a point for which $\text{Stab}(\mathcal{G}, \mathbf{x}) = \{(\mathbf{I}|\mathbf{0})\}$) arises so as to prevent one from associating unrelated groups and structures. Note however, that neither of the above definitions require an objective structure to be of finite extent and so, the group $\mathcal{G}$ can be infinite.[1]

Physically, given a discrete group of isometries, an objective structure generated from the group would have mass points or ions located at the points dictated by Definition 2.1.1. It is therefore meaningful to expect that there should be a nonzero minimum distance between these points. The following easy result shows that this physical requirement is met if the

[1] An objective structure which is of infinite extent, that is for which $\sup_{\mathbf{x},\mathbf{y} \in \mathcal{S}} |\mathbf{x} - \mathbf{y}| = \infty$ cannot be generated by a finite group of isometries unless M contains points which are an infinite distance apart.

objective structure is generated by a discrete group of isometries (as required by the above definitions):

Proposition 2.1.2. *Let $\mathcal{S}$ be a fixed point free objective molecular structure generated by the discrete group of isometries $\mathcal{G}$ acting on the distinct set of points M. Let*

$$\delta = \inf_{\mathbf{x}\neq\mathbf{y}} \{|\mathbf{x}-\mathbf{y}|, \mathbf{x}, \mathbf{y} \in \mathcal{S}\}. \tag{2.3}$$

Then it holds that $\delta > 0$.

Proof: Since we are considering the infimum among a set of non-negative real numbers, it can only be that $\delta \geq 0$. If the group $\mathcal{G}$ is finite, then we are considering the infimum among a finite set of positive numbers (this set being the pairwise distances between all points in $\mathcal{S}$) and so δ has to be positive. So the only possibility of having $\delta = 0$ is when $\mathcal{G}$ is an infinite group. We now assume for the sake of contradiction that $\delta = 0$. Since $\mathcal{S}$ is fixed point free, each $\mathbf{x} \in \mathcal{S}$ lies on the orbit of a unique $\mathbf{p} \in M$ and so, we may rewrite (2.3) as:

$$\delta = \inf_{\mathbf{p},\mathbf{q}\in M} \big\{ \inf_{\mathbf{x}\neq\mathbf{y}} \{|\mathbf{x}-\mathbf{y}|;\ \mathbf{x} \in \text{Orb}(\mathcal{G},\mathbf{p}), \mathbf{y} \in \text{Orb}(\mathcal{G},\mathbf{q})\}\big\}. \tag{2.4}$$

Since $\delta = 0$ and the outer minimization in (2.4) is over a finite set, it must be that at least one of the inner minimizations yield zero. Thus, there must exist $\mathbf{p}, \mathbf{q} \in M$ such that

$$\inf_{\mathbf{x}\neq\mathbf{y}} \{|\mathbf{x}-\mathbf{y}|;\ \mathbf{x} \in \text{Orb}(\mathcal{G},\mathbf{p}), \mathbf{y} \in \text{Orb}(\mathcal{G},\mathbf{q})\} = 0 \tag{2.5}$$

This implies that there exist $\{\mathbf{x}_k, \mathbf{y}_k\}, k \in \mathbb{N}$ such that $\mathbf{x}_k \in \text{Orb}(\mathcal{G},\mathbf{p}), \mathbf{y}_k \in \text{Orb}(\mathcal{G},\mathbf{q})$ and $|\mathbf{x}_k - \mathbf{y}_k| \to 0$ as $k \to \infty$. Let $\mathbf{x}_k = \Upsilon_k(\mathbf{p}), \mathbf{y}_k = \tilde{\Upsilon}_k(\mathbf{q})$. The isometries $\Upsilon_k, \tilde{\Upsilon}_k$ are uniquely determined because $\mathcal{S}$ is fixed point free. For each $k \in \mathbb{N}$,

$$\begin{aligned} |\mathbf{x}_k - \mathbf{y}_k| = |\Upsilon_k(\mathbf{p}) - \tilde{\Upsilon}_k(\mathbf{q})| &= |\Upsilon_k^{-1}(\Upsilon_k(\mathbf{p})) - \Upsilon_k^{-1}(\tilde{\Upsilon}_k(\mathbf{q}))| \\ &= |\mathbf{p} - \Upsilon_k^{-1} \circ \tilde{\Upsilon}_k(\mathbf{q})|. \end{aligned} \tag{2.6}$$

Since $|\mathbf{x}_k - \mathbf{y}_k| \to 0$ it follows that $\{\Upsilon_k^{-1} \circ \tilde{\Upsilon}_k(\mathbf{q})\}_{k\in\mathbb{N}} \to \mathbf{p}$. But this contradicts with the discreteness of $\mathcal{G}$ since $\{\Upsilon_k^{-1} \circ \tilde{\Upsilon}_k(\mathbf{q})\}_{k\in\mathbb{N}} \subset \text{Orb}(\mathcal{G},\mathbf{q})$ and a ball of any radius centered around $\mathbf{p}$ would contain infinitely many points from the convergent sequence $\{\Upsilon_k^{-1} \circ \tilde{\Upsilon}_k(\mathbf{q})\}_{k\in\mathbb{N}}$. Hence we can only have $\delta > 0$ in (2.3). ■

A consequence of defining objective structures through discrete groups of isometries (as in Definition 2.1.1 above) is that a study of these structures, in a large part, becomes a study of

the isometry groups that generate these structures.[2] We adopt this point of view and attempt to categorize the electronic structure calculation problem of objective structures through the different groups of isometries involved. The next question that arises, then, is what are all possible discrete groups of isometries in three spatial dimensions and if it is possible to write formulae for these groups of isometries in terms of parameters. The answer to these important questions is worked out in Dayal, Elliott, and James [2010] where the following important result is derived and we reproduce that result here without proof:

Theorem 2.1.3 (Dayal, Elliott and James)**.** *Every discrete group of isometries is either a space group, a net group, a helical group or a discrete group of rotations.*

Certain terms that appear in the above theorem need to be explained so that we are in a position to appreciate the limitations that this theorem places on the morphology of objective structures. A discrete group of isometries $\mathcal{G}$ is called a space group if it contains three translations $(\mathbf{I}|\mathbf{t}_1), (\mathbf{I}|\mathbf{t}_2), (\mathbf{I}|\mathbf{t}_3)$ with $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$ linearly independent and if every translation in $\mathcal{G}$ is in the group generated by these three translations. Thus, every translation in $\mathcal{G}$ is expressible in the form $(\mathbf{I}|\mu_1\mathbf{t}_1 + \mu_2\mathbf{t}_2 + \mu_3\mathbf{t}_3), \mu_1, \mu_2, \mu_3 \in \mathbb{Z}$. Similarly, a discrete group of isometries $\mathcal{G}$ is called a net group if it contains two translations $(\mathbf{I}|\mathbf{t}_1), (\mathbf{I}|\mathbf{t}_2)$ with $\mathbf{t}_1, \mathbf{t}_2$ linearly independent and every translation in $\mathcal{G}$ is expressible in the form $(\mathbf{I}|\mu_1\mathbf{t}_1 + \mu_2\mathbf{t}_2), \mu_1, \mu_2 \in \mathbb{Z}$. A discrete group of isometries $\mathcal{G}$ is called a rod group if it contains a translation $(\mathbf{I}|\mathbf{t})$ and every translation in $\mathcal{G}$ is expressible in the form $(\mathbf{I}|\mu\mathbf{t}), \mu \in \mathbb{Z}$. Finally, a helical group is a discrete group of isometries if it does not contain a translation and does not consist entirely of rotations. Dayal et al. [2010] also prove that a discrete group of rotations can only be a finite group and these consist of the symmetry groups of the Platonic solids as well as the cyclic and dihedral groups that fix an axis.

We may now try to interpret what bearing the above discussion has on the problem of electronic structure computation of objective structures. For objective structures that are generated by a space group, a net group or a rod group, one can exploit translational invariance since the isometry groups associated with these structures contain a group of translations as a normal subgroup. Hence, by proper choice of a periodic unit cell, one may hope to reduce the electronic structure problem posed on the entire objective structure to one posed only on the unit cell and augment this reduced problem with periodic boundary conditions. One should note however that this is not necessarily the most optimum method for performing electronic structure computations on these structures since only a subgroup

[2] In particular, Objective Atomic Structures and (fixed point free) Objective Molecular Structures need not be studied separately.

of the full symmetry group is being exploited.[3] Nevertheless, this is the canonical approach used by the computational materials science and solid state physics community to perform electronic structure computations on crystals [Martin, 2004; Kaxiras, 2003]. On the other hand, for the objective structures associated with helical groups or with discrete groups of rotations, there is no underlying periodicity and so we need to discover a procedure that is well suited for these symmetry groups. The way these groups are conventionally handled in the computational materials science/computational chemistry community is by use of the so called super-cell method [Martin, 2004]. The idea is to make the structure under study artificially periodic and then to study this periodic problem using methods designed for studying crystals. Thus, the supercell method does not really study the problem associated with the original structure, but only periodic approximations of the problem.The primary goal of this work, will be to formulate electronic structure calculation algorithms suited for discrete groups of rotations without resorting to any sort of artificial periodicity. The formulation of algorithms that are suited for helical groups is the scope of future work.

2.2 Electronic Structure Computation Theories

We begin with a discussion of the electronic structure computation problem as it applies to a system with a finite number of electrons at absolute zero temperature and we later extend our discussion to infinite periodic systems. These two types of systems serve as the ones that are most well studied conventionally [Martin, 2004]. We will try to outline only the general principles involved in this discussion - the numerous theoretical and implementation details involved will be brought up in later portions of this work as and when required. The primary focus of our discussion will be on Density Functional Theory. A more detailed discussion of electronic structure computation theories may be found in Parr and Yang [1994]; Szabo and Ostlund [1996] and Martin [2004]. Some of the rigorous mathematical foundations of these theories have been laid out in Kato [1957]; Lieb and Simon [1977a,b]; Lions [1987] and Lieb [1983] among others. Good overviews of the mathematical issues involved can be found in Le Bris [2005, 2003]; Defranceschi and Le Bris [2000] and references therein. Our presentation of the contents of this section, as well as our choice of notation are very much in the light of these more mathematical works. For the purpose of simplicity, we will omit the spin variable in this work with complete awareness however, of the great practical significance of spin in electronic structure calculations. The atomic unit system with $m_e = 1, e = 1, \hbar = 1, \frac{1}{4\pi\epsilon_0} = 1$, is chosen for the rest of the work.

[3] An example would be a body centered cubic lattice. A standard periodic unit cell would have 2 atoms per unit cell while a consideration of the complete symmetry group associated with the lattice would lead one to perform all computations on a (symmetry adapted) single atom cell.

2.2.1 Born-Oppenheimer Quantum Mechanics

In most quantum chemistry/computational materials science applications, it is legitimate to treat the nuclei of the system of interest as positively charged point masses which behave classically. So one assigns precise positions $(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_M)$ and charges $(z_1, z_2, \ldots, z_M)$ to the nuclei and treats the electrons as quantum mechanical particles. Under these assumptions,[4] determination of the ground state structure of a molecular system consisting of M nuclei and N electrons takes the following form:

$$\inf_{(\mathbf{x}_1,\ldots,\mathbf{x}_M)\in\mathbb{R}^{3M}} \left\{ W\big(\mathbf{x}_1,\ldots,\mathbf{x}_M\big) = U\big(\mathbf{x}_1,\ldots,\mathbf{x}_M\big) + \sum_{1\leq k\leq l\leq M} \frac{z_k z_l}{|\mathbf{x}_k - \mathbf{x}_l|} \right\}, \tag{2.7}$$

$$\text{where,} \quad U\big(\mathbf{x}_1,\ldots,\mathbf{x}_M\big) = \inf_{\psi_e\in\mathcal{H}_e} \left\{ \langle \psi_e, H_e^{(\mathbf{x}_1,\ldots,\mathbf{x}_M)}\psi_e\rangle_{L^2}, \|\psi_e\|_{L^2} = 1 \right\}, \tag{2.8}$$

with $H_e^{(\mathbf{x}_1,\ldots,\mathbf{x}_M)}$ denoting the (non-relativistic) electronic Hamiltonian and $\mathcal{H}_e$ denoting a suitable function space in which the minimization in (2.8) must be carried out. The minimization in (2.8) corresponds to determining the ground state electronic structure with the nuclei clamped at the positions $(\mathbf{x}_1, \ldots, \mathbf{x}_M)$. Our work will almost entirely focus on this electronic structure computation problem with the added constraint that $(\mathbf{x}_1, \ldots, \mathbf{x}_M)$ should be expressible in such a way that Definition 2.1.1 can be applied. The outer minimization in (2.7) is important while doing structural optimization computations and we should note that even this minimization problem is considerably simplified for the case of objective structures since one needs to optimize over a lower dimensional manifold of $\mathbb{R}^{3M}$.

The ground state electronic structure computation problem (2.8) consists of finding the lowest eigenvalue of the electronic Hamiltonian $H_e^{(\mathbf{x}_1,\ldots,\mathbf{x}_M)}$ parametrized by the positions of the nuclei. This Hamiltonian consists of a term accounting for the kinetic energy of the electrons, a term accounting for the electron-nuclei attraction and a term accounting for the electron-electron repulsion and can be written as:

$$H_e^{(\mathbf{x}_1,\ldots,\mathbf{x}_M)} = -\sum_{i=1}^{N} \frac{1}{2}\Delta_{\mathbf{y}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{y}_i - \mathbf{x}_k|} + \sum_{1\leq i\leq j\leq N} \frac{1}{|\mathbf{y}_i - \mathbf{y}_j|}. \tag{2.9}$$

The natural choice for the function space $\mathcal{H}_e$ turns out to be[5] the following subspace of

[4] Referred to as Born Oppenheimer approximation in literature.

[5] This follows from ensuring finiteness of the kinetic energy and fulfillment of the Pauli exclusion principle.

$\mathsf{L}^2(\mathbb{R}^{3N})$:

$$\mathcal{H}_e = \bigwedge_{i=1}^{N} \mathsf{H}^1(\mathbb{R}^3), \tag{2.10}$$

where, the wedge is used to denote the antisymmetrized tensor product and $\mathsf{H}^1(\mathbb{R}^3)$ denotes the Sobolev space of square integrable functions on $\mathbb{R}^3$ whose first order weak derivatives are also square integrable. The Euler-Lagrange equation of the minimization problem (2.8) is the eigenvalue problem:

$$H_e^{(\mathbf{x}_1,\ldots,\mathbf{x}_M)}\psi_e = E_e\psi_e, \tag{2.11}$$

with $E_e = U\big(\mathbf{x}_1,\ldots,\mathbf{x}_M\big)$ the lowest possible eigenvalue of the self-adjoint operator $H_e^{(\mathbf{x}_1,\ldots,\mathbf{x}_M)}$.

2.2.2 Density Functional Methods

Unfortunately however, for any practical problem, a direct numerical attack on the minimization problem (2.8) or the eigenvalue problem (2.11) is prohibitively expensive due to the large dimensionality involved. To overcome this difficulty, the generic philosophy is to trade the linearity of (2.11) for a reduction in dimensionality. Density functional methods are based on a reformulation of (2.8) in such a way that the unknown function is the electronic density:

$$\rho(\mathbf{y}) = N\int_{\mathbb{R}^{3(N-1)}} |\psi_e(\mathbf{y},\mathbf{y}_2,\ldots,\mathbf{y}_N)|^2\, d\mathbf{y}_2\ldots d\mathbf{y}_N, \tag{2.12}$$

which is a scalar field on $\mathbb{R}^3$ unlike the wavefunction ψ_e which is a scalar field on $\mathbb{R}^{3N}$. The justification behind this reformulation strategy comes from a seminal paper by Hohenberg and Kohn [Hohenberg and Kohn, 1964] who showed that electron-density as a basic variable is sufficient to describe the properties of a material system in its ground state. To see how (2.8) may be reformulated in terms of the density (2.12), we may follow Lieb [1983] and Le Bris [2005] to define:

$$E(\rho) = \inf_{\psi_e\in\mathcal{H}_e}\Bigg\{\langle\psi_e,\Big(-\sum_{i=1}^{N}\frac{1}{2}\Delta_{\mathbf{y}_i} + \sum_{1\le i\le j\le N}\frac{1}{|\mathbf{y}_i-\mathbf{y}_j|}\Big)\psi_e\rangle_{L^2}: \\ \|\psi_e\|_{L^2}=1, \psi_e \text{ has density } \rho\Bigg\} \tag{2.13}$$

$$\text{and}\quad \mathcal{I}_N = \Big\{\rho\ge 0 : \sqrt{\rho}\in\mathsf{H}^1(\mathbb{R}^3), \int_{\mathbb{R}^3}\rho = N\Big\}, \tag{2.14}$$

so that, problem (2.8) reduces to:

$$U\big(\mathbf{x}_1,\ldots,\mathbf{x}_M\big) = \inf_{\rho\in\mathcal{I}_N}\left\{E(\rho) - \int_{\mathbb{R}^3}\Big(\sum_{k=1}^{M}\frac{z_k}{|\mathbf{y}-\mathbf{x}_k|}\rho(\mathbf{y})\,d\mathbf{y}\Big)\right\} \tag{2.15}$$

The functional $E : \mathcal{I}_N \to \mathbb{R}^+$ is called a density functional and it is often described as being "universal" in literature (for example, Hohenberg and Kohn [1964]) since it does not depend on any particular molecular system. However, an explicit formula for this universal density functional $E(\rho)$ is not known and so, in practice one must construct approximations of this density functional by carefully studying reference systems that are in some sense "close" to the system being studied.

2.2.3 Kohn-Sham Density Functional Theory

A density functional model very widely used today is the one introduced by Kohn and Sham [Kohn and Sham, 1965] who considered a system of N non-interacting electrons as a reference. Under appropriate assumptions, the kinetic energy of such a system can be written as [Le Bris, 2005]:

$$T_{KS}(\rho) = \inf_{\phi_i\in\mathsf{H}^1(\mathbb{R}^3)}\left\{\frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|\nabla\phi_i|^2 : \langle\phi_i,\phi_j\rangle_{L^2} = \delta_{ij}, \sum_{i=1}^{N}|\phi_i|^2 = \rho\right\}. \tag{2.16}$$

The Kohn-Sham model first chooses this as an approximation for the kinetic energy for the system of interacting electrons that is being studied. It then adds electrostatic terms to account for the electron-electron repulsion and the electron nuclei attraction. It finally adds an exchange-correlation functional to the model, the purpose of this term being to account for the non-independence of the electrons. The Kohn-Sham model therefore reads as:

$$I_N^{KS} = \inf_{\phi_i\in\mathsf{H}^1(\mathbb{R}^3)}\left\{\frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}\rho V_{nu} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}\,d\mathbf{y} + E_{xc}(\rho) : \langle\phi_i,\phi_j\rangle_{L^2} = \delta_{ij}\right\} \tag{2.17}$$

The exact form of $E_{xc}(\rho)$ is of course, not known since a knowledge of it's exact form would amount to having the knowledge of the elusive density functional $E(\rho)$ that appears in (2.13) and (2.15). One of the common approximations for this term is the so called Local Density Approximation, in which $E_{xc}(\rho(\mathbf{y}))$ is expressed as $\int_{\mathbb{R}^3}F(\rho(\mathbf{y}))\,d\mathbf{y}$. The simplest form of the Local Density Approximation is obtained for the case of a uniform

non-interacting electron gas, in which case we have [Le Bris, 2005]:

$$E_{xc}(\rho) = -C_D \int_{\mathbb{R}^3} \rho^{4/3}(\mathbf{y})\, d\mathbf{y}, \text{ with } C_D = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}. \tag{2.18}$$

The Euler-Lagrange equations of (2.17) are the celebrated Kohn-Sham equations, which for a system with M nuclei are as follows:

$$K(\rho)\phi_i = \lambda_i \phi_i;\ \langle \phi_i, \phi_j \rangle_{L^2} = \delta_{ij} \quad . \tag{2.19}$$

$$K(\rho) = -\frac{1}{2}\Delta - \sum_{i=1}^{M} \frac{z_k}{|\mathbf{y} - \mathbf{x}_k|} + \left(\int_{\mathbb{R}^3} \frac{\rho(\mathbf{x})}{|\mathbf{y} - \mathbf{x}|}\, d\mathbf{x} \right) + V_{xc}(\rho) \quad . \tag{2.20}$$

with,

$$\rho(\mathbf{x}) = \sum_{i=1}^{N} |\phi_i(\mathbf{x})|^2, \text{ and } \quad V_{xc}(\rho) = \frac{\partial E_{xc}(\rho)}{\partial \rho} \quad . \tag{2.21}$$

The λ_i that appear in the (2.19) are the Lagrange multipliers of the orthonormality constraints. [6] They are taken to be the lowest N eigenvalues of the of the Kohn-Sham operator $K(\rho)$.

The usual method of solution of the Kohn-Sham equations is by a self-consistent approach [Kohn and Sham, 1965; Martin, 2004]. One starts from a guess of the density $\rho(\mathbf{x})$ and evaluates the electrostatic and exchange correlation terms. One then solves the linearized eigenvalue problem with these potentials and computes the lowest N states $\phi_i, i = 1, \ldots, N$. The expression for the density in (2.21) is used to compute the new electronic density from the ϕ_i. The potentials are then computed with this new density and the cycle repeats. It is not obvious however, that this iteration will converge and whether it will converge to the sought minimizer. In practice therefore, "mixing schemes" are employed [Martin, 2004], so that the newly computed density from the present iteration step is combined with densities from earlier iterations and this "mixed" density is used to evaluate the potentials in the current iteration step. The broad idea behind these mixing schemes of course is to create a contraction mapping from one iteration step to the next so that a fixed point of the iterations may be achieved.

We should mention in passing, that Kohn-Sham calculations for extended systems, such

[6] Owing to the fact that the Kohn-Sham energy functional (2.17) is invariant with respect to unitary transformations of the ϕ_i, the matrix of Lagrange multipliers may be diagonalized without loss of generality. This transformation also leaves the expression for the density in (2.21) unchanged.

as crystals, involve theoretical issues that are not originally present in Kohn-Sham Density Functional Theory. There exist several implementation level issues as well, and these need to be addressed before a computational strategy can be formulated for such systems.[7] In the context of the present work, this means that any future studies of the electronic structure of infinite objective structures (such as those generated by helical groups), should entail a program similar to the one employed for periodic systems, to address both the theoretical and implementation issues, that appear due to the infinite extent of the system.

[7]For instance, at the theoretical level, formal extension of the Kohn-Sham theory to such calculations, involves the introduction of a single electron band theory and ideas related to the density of states. At the implementation level, the computation of the electrostatic potentials and energies are done through so called Ewald sums. See Reed and Simon [1978]; Defranceschi and Le Bris [2000]; Le Bris [2003]; Martin [2004] and Pickett [1989] for more details.

Chapter 3

Results from Abstract Harmonic Analysis

The objective of this thesis is to investigate how density functional methods like the ones discussed in Chapter 2 can be adapted to study the electronic structure of objective structures. In the Kohn-Sham setting, this translates to investigating how the symmetry group of an objective structure interacts with the Kohn-Sham model (2.17) or the Kohn-Sham equations (2.19)-(2.21). However, the non-convexity of the functional appearing in (2.17) and the non-linearity of the system (2.19)-(2.21) make it somewhat difficult to answer these questions and in fact, loss of symmetry in self consistent solutions to the Kohn-Sham equations is quite well known [Prodan, 2005].

The concerns expressed above are somewhat generic with regard to the analysis of how symmetry interacts with non-linear problems associated with non-convex functionals. In these cases, a problem with a certain degree of symmetry may not exhibit solutions with the same degree of symmetry. Hence, the analysis of such problems is mainly focused on efficiently computing solutions which do have the right degree of symmetry should they exist [Healey, 1989], as well as on studying symmetry breaking bifurcating solutions [Healey, 1988; Healey and Kielhöfer, 1991].

On the other hand, the interaction of symmetry with linear problems is well understood and well characterized [1], the main mathematical tools for the study of such problems being provided by linear representation theory and abstract harmonic analysis. There seems to be a wealth of literature devoted to the analysis of such problems and their applications. A list

[1] The associated functional is quadratic and hence convex.

of references would include Hammermesh [1989] and McWeeny [2002] for applications to problems in physics and chemistry, Bossavit [1986, 1993] and Georg and Tausch [1994] for applications to linear boundary value problems and their solutions by Finite Element and Boundary Element techniques, Healey and Treacy [1991] and Fahmi and Potier-Ferry [1998] for applications to eigenvalue problems arising out of structural analysis, and Allgower et al. [1998]; Ahlander and Munthe-Kaas [2005, 2006]; Allgower and Georg [1999] for applications to numerical algorithms.

We will now focus on developing mathematical tools that will enable us to study the interaction of symmetry groups of objective structures with a broad class of linear problems. Our justification for studying linear problems comes from the fact that the self-consistent iteration scheme for computing solutions of the Kohn-Sham equations basically involves solution to linear problems at each stage of the iteration. Hence, a combination of the self-consistent scheme with the group theoretic methods, will give us a way of producing solutions to the Kohn-Sham equation associated with a given discrete group of isometries $\mathcal{G}$, or any of its subgroups.

In order to introduce the large number of ideas involved in representation theory in a coherent way, a fair bit of abstraction is needed at this point. The basic theme of the developments that follow is the formulation of a representation theory for a discrete group of isometries $\mathcal{G}$ on a Hilbert space of square integrable functions. The utility of this sort of abstraction is that it allow us to treat finite as well as infinite groups of isometries in a unified way later. Also, the development of these tools in terms of a rather generic Hilbert space has the distinct advantage of allowing us to study both linear partial differential equations as well as numerical discretizations of these equations (via finite differences, finite elements or spectral methods), with minor modifications. A linear problem may be viewed in terms of a linear operator posed on a suitable space of solutions. Therefore, the question of how the symmetry group $\mathcal{G}$ interacts with a particular linear problem may be formulated in terms of how representations of $\mathcal{G}$ on the space of solutions interact with the linear operator associated with the problem.

The material that we present in the following sections has been largely influenced by Folland [1994]; Barut and Raczka [1986] and Miller [1972]. However, we believe that our presentation is quite original in some respects. In many cases, we have had to adapt the more sophisticated general theory presented in the above references to our somewhat simplified needs. The main source of our simplification arises from the fact that the groups (of

isometries) associated with objective structures, are always discrete and hence countable.[2]

3.1 Group Actions

The notion of group actions was introduced in Section 2.1 in the context of groups of isometries acting on $\mathbb{R}^3$. We begin by generalizing this idea. Let G be a group with $\circ$ denoting the group operation and let S be an arbitrary set.

Definition 3.1.1. The Left Group Action[3] of G on S is a mapping $\bullet : G \times S \to S$ denoted as $g \bullet x$ for $g \in G, x \in S$ which satisfies:

1. $(g \circ h) \bullet x = g \bullet (h \bullet x), \forall g, h \in G, x \in S$.
2. If e denotes the identity element of G, then $e \bullet x = x, \forall x \in S$. □

As before, we denote $\text{Orb}(G, x) = \{g \bullet x : g \in G\}$ and $\text{Stab}(G, x) = \{g \in G : g \bullet x = x\}$. We extend the notation of actions and orbits to arbitrary subsets $A \subset S$ by denoting $g \bullet A = \{g \bullet x : x \in A\}$ and $\text{Orb}(G, A) = \{g \bullet A : g \in G\}$. In particular, we say that $A \subset S$ is a fundamental set for the action of G on S if $\text{Orb}(G, A) = S$. [4] Fundamental sets are of great importance to us since, broadly speaking, we are interested in reducing a problem posed over a set S with a symmetry group G, to a problem posed on a fundamental set for the action of G on S.

It is useful to note that our definition of group action automatically ensures that the map for the group action $\bullet : G \times S \to S$ is such that for each fixed first argument, it is a bijection in the second argument. [5] [6] The consequence of this is the following simple useful result:

Proposition 3.1.2. *There exists a fundamental set for the action of G on S.*

Proof: The bijection property guarantees that we may define an equivalence relation $\sim$ on $S \times S$ which is as follows: $\forall x, y \in S, x \sim y \Leftrightarrow \exists g \in G$ such that $y = g \bullet x$. By

[2] The result that discrete groups of isometries are always countable follows quite directly from Dayal et al. [2010, Lemma 5.1, Theorem 5.1].

[3] We may similarly define the right group action of G on S. However, every right group action may be re-interpreted as a left group action and so we only concern ourselves with left group actions here.

[4] In the context of Definition 2.1.1, it is easy to see that if $\mathcal{S}$ is an objective structure generated by a discrete group of isometries $\mathcal{G}$ acting on the set M, then M is in fact a fundamental set for the Objective Structure $\mathcal{S}$.

[5] The proof of this is as follows: The map is an injection because with $g \in G$ fixed, if $g \bullet x_1 = g \bullet x_2$ for any $x_1, x_2 \in S$, then $g^{-1} \bullet (g \bullet x_1) = g^{-1} \bullet (g \bullet x_2)$. Thus, by the laws of group action, we must have $x_1 = x_2$. Now, we assume for the sake of contradiction that the map is not a surjection. Thus there exists $g \in G$ such that $g \bullet S \subsetneq S$. Let $x \in S \backslash g \bullet S$. Now $g^{-1} \bullet x \in S$ and therefore, $g \bullet (g^{-1} \bullet x) \in g \bullet S$. By the laws of group action this implies a contradiction since we have $x \in g \bullet S$ as well as $x \in S \backslash g \bullet S$.

[6] The converse is not true in general since we may find $x \in S$ such that $\text{Stab}(G, x)$ is a non-trivial subgroup of G and so, for each fixed second argument, the group action is not a surjection in its first argument.

the fundamental property of equivalence relations [Naylor and Sell, 1971], the equivalence relation $\sim$ will partition S into the disjoint union of equivalence classes and in this case, the equivalence class of x will simply be $\text{Orb}(G, x)$. If we now define a set V such that it contains a member from each equivalence class, it is easy to check that $\text{Orb}(G, V) = S$ ensuring that V is a fundamental set. ■

We now consider how group actions on S can be used to define group actions on suitable function spaces on S. We will achieve this through a point-wise redefinition of the functions and so the technical issue of whether specifying a function point-wise actually specifies it uniquely, arises. To circumvent this, we assume that S is equipped with a topology such that for each fixed $g \in G$, the group action is a continuous map from S to S. If we confine our attention to the set of all maps $f : S \to \mathbb{C}$ which are continuous in this topology, we can prove the following result:

Proposition 3.1.3. *Let $\bullet : G \times S \to S$ denote the action of G on S and let $\mathsf{C}(S)$ denote the set of functions $f : S \to \mathbb{C}$ which are continuous (in the aforementioned topology). Then the map $\bullet : \mathcal{G} \times \mathsf{C}(S) \to \mathsf{C}(S) : f(x) \mapsto f(g^{-1} \bullet x)$ defines an action of G on $\mathsf{C}(S)$.*

Proof: First, we note that the pointwise definition of the group action makes sense since we are dealing with continuous functions. Next, we note that for any fixed $g \in G$, $f(g^{-1} \bullet x) \in \mathsf{C}(S)$ since it is the composition of two continuous maps. Now, for any $g, h \in G, x \in S$ and $f \in \mathsf{C}(S)$ we have:

$$\begin{aligned}(g \circ h) \bullet f(x) = f((g \circ h)^{-1} \bullet x) = f((h^{-1} \circ g^{-1}) \bullet x) = f(h^{-1} \bullet (g^{-1} \bullet x)) \\ = h \bullet f(g^{-1} \bullet x) = g \bullet (h \bullet f(x)),\end{aligned} \tag{3.1}$$

which verifies the first law. Also, $e \bullet f(x) = f(e^{-1} \bullet x) = f(x)$ which verifies the second law. This completes the proof. ■

The advantage of introducing group actions on continuous functions is that group actions can be defined on a large class of other function spaces by means of density theorems. A particular example would be the group action of a discrete group of isometries $\mathcal{G}$ on a suitable subset $\Omega \subset \mathbb{R}^3$ as discussed in Chapter 2. We may easily verify that the usual topology on $\mathbb{R}^3$ satisfies the hypotheses of Proposition 3.1.3. Hence, a group action on $\mathsf{C}(\Omega)$ may be defined. Next, by employing density theorems of continuous functions, this action can be extended to suitable function spaces on Ω that are relevant to the study of boundary value problems associated with electronic structure calculation. We carry out such a program in later sections of this work.

3.2 Representation Theory

3.2.1 Group Representations over Hilbert Spaces

Let $\mathsf{H}, \tilde{\mathsf{H}}$ denote nonzero Hilbert spaces. Let $\mathcal{L}(\mathsf{H}, \tilde{\mathsf{H}})$ denote the space of bounded linear operators from H to $\tilde{\mathsf{H}}$ that is:

$$\mathcal{L}(\mathsf{H}, \tilde{\mathsf{H}}) = \left\{T : \mathsf{H} \to \tilde{\mathsf{H}} : T \text{ is linear and } \exists\, C > 0 \text{ such that } \|Tf\|_{\tilde{\mathsf{H}}} < C\|f\|_{\mathsf{H}},\ \forall f \in \mathsf{H}\right\} \tag{3.2}$$

Further, let $\mathcal{U}(\mathsf{H}, \tilde{\mathsf{H}})$ denote the space of unitary operators from H to $\tilde{\mathsf{H}}$, that is,

$$\mathcal{U}(\mathsf{H}, \tilde{\mathsf{H}}) = \left\{T \in \mathcal{L}(\mathsf{H}, \tilde{\mathsf{H}}) : T \text{ is surjective and } \langle f_1, f_2\rangle_{\mathsf{H}} = \langle Tf_1, Tf_2\rangle_{\tilde{\mathsf{H}}},\ \ \forall f_1, f_2 \in \mathsf{H}\right\}. \tag{3.3}$$

We then introduce:

Definition 3.2.1. A map $\zeta : \mathcal{G} \to \mathcal{L}(\mathsf{H}, \mathsf{H})$ is a linear representation of the discrete group of isometries $\mathcal{G}$ on the carrier space H, provided that ζ is a homomorphism and it preserves the identity, i.e., $\forall g, h \in \mathcal{G}, \zeta(gh) = \zeta(g) \circ \zeta(h)$ and $\zeta(e) = I_{\mathsf{H}}$ (where e and I_{H} denote the identity element in $\mathcal{G}$ and the identity operator on H respectively). The dimension of the Hilbert space H is called the dimension of the representation. If, for a linear representation, the map ζ is a bijection onto it's range, then ζ is in fact an isomorphism and we call it a faithful linear representation of $\mathcal{G}$. If a linear representation is such that for each $g \in \mathcal{G}$, $\zeta(g) \in \mathcal{U}(\mathsf{H}, \mathsf{H})$, we call the map a unitary representation of $\mathcal{G}$. Finally, if all the elements of $\mathcal{G}$ are mapped to I_{H}, then we call the representation trivial. □

Thus, the image of $\mathcal{G}$ under the linear representation is a set of operators which form a group under the operation of composition of operators (denoted here as $\cdot$), and the identity element of this group is the identity operator on H. The condition that $\zeta(e) = I_{\mathsf{H}}$ guarantees that each linear operator in the image of the representation is an isomorphism on H. This observation follows from the fact that:

$$\forall g \in \mathcal{G}, \quad \zeta(g) \cdot \zeta(g^{-1}) = \zeta(g^{-1}) \cdot \zeta(g) = \zeta(g \circ g^{-1}) = \zeta(g^{-1} \circ g) = \zeta(e) = I_{\mathsf{H}}\,, \tag{3.4}$$

and so we must have $\zeta(g)^{-1} = \zeta(g^{-1}) \in \mathcal{L}(\mathsf{H}, \mathsf{H})$. Hence the inverse operator of each $\zeta(g)$ is well defined and bounded and so each $\zeta(g)$ is an isomorphism on H. In particular, for a unitary representation, we have $\zeta(g^{-1}) = \zeta(g)^{-1} = \zeta(g)^*$, where $*$ is used to denote the adjoint. [7] Henceforth, we will be interested in unitary representations for the most part

[7] For any $T \in \mathcal{L}(\mathsf{H}, \mathsf{H})$, the adjoint of T is the unique operator that satisfies $\langle Tf_1, f_2\rangle_{\mathsf{H}} = \langle f_1, T^* f_2\rangle_{\mathsf{H}},\ \forall f_1 \in \mathsf{H}, f_2 \in \mathsf{H}$. An operator $T \in \mathcal{U}(\mathsf{H}, \mathsf{H})$ if and only if T is invertible and $T^{-1} = T^*$.

because of the nicer properties of unitary operators. This may seem like a somewhat restrictive choice but as our next result demonstrates, unitary representations can be constructed quite routinely for most of our applications. In particular, this gives us a method of constructing unitary representations on some of the common function spaces associated with partial differential equations of interest to this work as well as finite dimensional spaces associated with discretized versions of those equations. While the theorem itself is quite intuitive and is a direct extension of Proposition 3.1.3, some minor technical details need to be sorted out. First we note that we call a Radon measure ν on a locally compact Hausdorff topological space S group invariant (from the left) if for any measurable subset $A \subseteq S$, $\nu(A) = \nu(g \circ A)$ for every group element g. Here, $g \circ A$ is a notation for $\bigcup_{p \in A} g \circ p$. Next, we have:

Lemma 3.2.2. *Let S be a locally compact Hausdorff topological space and let $\mathcal{G}$ be a discrete group of isometries such that the action of $\mathcal{G}$ on S is continuous for each fixed $g \in \mathcal{G}$. Let ν be a group invariant Radon measure on S and let $\mathsf{L}^2_\nu(S)$ denote the Hilbert space of complex valued square integrable functions. Then the following defines an action of $\mathcal{G}$ on any function $f \in \mathsf{L}^2_\nu(S)$:*

$$g \bullet f = \lim_{n \to \infty} f_n(g^{-1} \bullet x), \tag{3.5}$$

where $\{f_n\}_{n \in \mathbb{N}} \subset \mathsf{C_c}(S)$ is a sequence (of continuous functions with compact support in S) that converges to f in the $\|\cdot\|_{\mathsf{L}^2_\nu(S)}$ topology.

Proof: First, we ensure that the definition of the group action makes sense. If $f \in \mathsf{L}^2_\nu(S)$, then by density of $\mathsf{C_c}(S)$ in $\mathsf{L}^2_\nu(S)$ [Folland, 1999], there exists $\{f_n\}_{n \in \mathbb{N}} \subset \mathsf{C_c}(S)$ such that $\|f - f_n\|_{\mathsf{L}^2_\nu(S)} \to 0$ as $n \to \infty$. For each f_n, the function $f_n(g^{-1} \bullet x) \in \mathsf{C_c}(S)$ since the map $x \mapsto f_n(g^{-1} \bullet x)$ is continuous for each fixed g and the continuous image of a compact set (the support of f_n in this case) is compact. Also, $f_n(g^{-1} \bullet x) \in \mathsf{L}^2_\nu(S)$ because, by a change of variables/Radon-Nikodym theorem and the group invariance of the measure ν, we have that:

$$\begin{aligned}\int_S |f_n(g^{-1} \bullet x)|^2 \, d\nu = \int_{g \bullet S} |f_n(g^{-1} \bullet (g \bullet y))|^2 \, d\nu = \int_S |f_n(y)|^2 \, d\nu = \int_{\text{spt.}(f_n)} |f_n(y)|^2 \, d\nu \\ \leq \big(\sup_{y \in \text{spt.}(f_n)} |f_n(y)|^2 \big) \times \nu(\text{spt.}(f_n)) < \infty \end{aligned} \tag{3.6}$$

By a computation very similar to the one above, we also conclude that $\{f_n(g^{-1} \bullet x)\}_{n \in \mathbb{N}}$ is a Cauchy sequence in $\mathsf{L}^2_\nu(S)$ and so, by completeness, the limit in (3.5) and hence the

proposed group action is well defined.[8]

We now need to confirm that this limit satisfies the two laws of group action. For the first law, we need to verify that $(g \circ h) \bullet f = g \bullet (h \bullet f)$. So, let $\{f_n(x)\}_{n \in \mathbb{N}} \subset \mathsf{C_c}(S)$ be convergent to $f \in \mathsf{L}^2_\nu(S)$. Then, by definition of the action and the calculations in Proposition 3.1.3, we have:

$$(g \circ h) \bullet f = \lim_{n \to \infty} f_n((g \circ h)^{-1} \bullet x) = \lim_{n \to \infty} f_n((h^{-1} \circ g^{-1}) \bullet x) \quad . \tag{3.7}$$

On the other hand, to evaluate $g \bullet (h \bullet f)$, let $\{\phi_n(x)\}_{n \in \mathbb{N}} \subset \mathsf{C_c}(S)$ converge to $(h \bullet f) \in \mathsf{L}^2_\nu(S)$. So, $g \bullet (h \bullet f) = \lim_{n \to \infty} \phi_n(g^{-1} \bullet x)$. Since $\{f_n(x)\}_{n \in \mathbb{N}} \to f$ in $\mathsf{L}^2_\nu(S)$, by definition of the group action, we must have that $\{f_n(h^{-1} \bullet x)\}_{n \in \mathbb{N}} \to h \bullet f$ in $\mathsf{L}^2_\nu(S)$. Thus, by choosing the sequence $\{\phi_n(x)\}_{n \in \mathbb{N}}$ to be equal to $\{f_n(h^{-1} \bullet x)\}_{n \in \mathbb{N}}$, we get that:

$$g \bullet (h \bullet f) = \lim_{n \to \infty} f_n(h^{-1} \bullet (g^{-1} \bullet x)) = \lim_{n \to \infty} f_n((h^{-1} \circ g^{-1}) \bullet x) \quad . \tag{3.8}$$

Comparing (3.7) and (3.8), the first law of group action is verified. Finally, we also have:

$$e \bullet f(x) = \lim_{n \to \infty} f_n(e^{-1} \bullet x) = \lim_{n \to \infty} f_n(x) = f(x). \tag{3.9}$$

This completes the proof. ■

An immediate corollary of the above is the following result on unitary representations:

Theorem 3.2.3. *With the setting of Lemma 3.2.2, let* $\bullet : \mathcal{G} \times \mathsf{L}^2_\nu(S) \to \mathsf{L}^2_\nu(S)$ *denote the action of* $\mathcal{G}$ *on functions in* $\mathsf{L}^2_\nu(S)$ *as defined by* (3.5)*. For each* $g \in \mathcal{G}$ *we consider an operator* $\mathcal{T}_g : \mathsf{L}^2_\nu(S) \to \mathsf{L}^2_\nu(S)$ *such that for any* $f \in \mathsf{L}^2_\nu(S)$, $\mathcal{T}_g[f] = g \bullet f$*. Let the set* $L_\mathcal{G}$ *denote the collection* $\{\mathcal{T}_g : g \in \mathcal{G}\}$*. Then the map* $\zeta : \mathcal{G} \to L_\mathcal{G}$ *forms a unitary representation of the group* $\mathcal{G}$ *on the carrier space* $\mathsf{L}^2_\nu(S)$*.*

Proof: We first note that $\forall g \in \mathcal{G}$, the action of $\mathcal{T}_g$ on any function $f \in \mathsf{L}^2_\nu(S)$ is well defined via Lemma 3.2.2. Each $\mathcal{T}_g$ is easily verified to be a linear operator on $\mathsf{L}^2_\nu(S)$ and $\mathcal{T}_g \in \mathcal{L}(\mathsf{L}^2_\nu(S), \mathsf{L}^2_\nu(S))$ because, by the continuity of the norm and the change of variables

[8] The action is also unambiguous in the sense that one can choose *any* approximating sequence for the purpose - two different sequences will necessarily produce results that differ from each other only on a set of ν-measure zero.

calculation in (3.6), we have:

$$\begin{aligned}\|\mathcal{T}_g[f]\|_{\mathsf{L}^2_\nu(S)} = \|g \bullet f\|_{\mathsf{L}^2_\nu(S)} = \|\lim_{n\to\infty} f_n(g^{-1} \bullet x)\|_{\mathsf{L}^2_\nu(S)} = \lim_{n\to\infty} \|f_n(g^{-1} \bullet x)\|_{\mathsf{L}^2_\nu(S)} \\ = \lim_{n\to\infty} \|f_n(x)\|_{\mathsf{L}^2_\nu(S)} = \|\lim_{n\to\infty} f_n(x)\|_{\mathsf{L}^2_\nu(S)} = \|f\|_{\mathsf{L}^2_\nu(S)} \quad .\end{aligned} \tag{3.10}$$

Further, the fact that $\bullet : \mathcal{G} \times \mathsf{L}^2_\nu(S) \to \mathsf{L}^2_\nu(S)$ is an action on functions in $\mathsf{L}^2_\nu(S)$, leads to:

$$(\mathcal{T}_g \cdot \mathcal{T}_h)[f] = \mathcal{T}_g[\mathcal{T}_h[f]] = \mathcal{T}_g[h \bullet f] = g \bullet (h \bullet f) = (g \circ h) \bullet f = \mathcal{T}_{g\circ h}[f] \quad . \tag{3.11}$$

Also, $\mathcal{T}_e$ is the identity operator on $\mathsf{L}^2_\nu(S)$. Hence, the map $\zeta : \mathcal{G} \to L_{\mathcal{G}}$ is a homomorphism and so the operators $\mathcal{T}_g$ form a representation of $\mathcal{G}$ on $\mathsf{L}^2_\nu(S)$.

To see that each operator $\mathcal{T}_g$ is unitary, we consider $\phi, \psi \in \mathsf{L}^2_\nu(S)$ and the inner product $\langle \phi, \psi \rangle_{\mathsf{L}^2_\nu(S)} = \int_S \phi(x)\overline{\psi(x)} d\nu$. Let $\{\phi_m\}_{m\in\mathbb{N}}$ and $\{\psi_n\}_{n\in\mathbb{N}}$ be sequences in $\mathsf{C}_\mathsf{c}(S)$ that converge to ϕ and ψ respectively. Then, by definition of the action on $\mathsf{L}^2_\nu(S)$ functions, continuity of the inner product and a change of variables, we have:

$$\begin{aligned}\langle \mathcal{T}_g\phi, \mathcal{T}_g\psi \rangle_{\mathsf{L}^2_\nu(S)} = \langle g \bullet \phi, g \bullet \psi \rangle_{\mathsf{L}^2_\nu(S)} = \langle \lim_{m\to\infty} \phi_m(g^{-1} \bullet x), \lim_{n\to\infty} \psi_n(g^{-1} \bullet x) \rangle_{\mathsf{L}^2_\nu(S)} \\ = \lim_{m,n\to\infty} \langle \phi_n(g^{-1} \bullet x), \psi_m(g^{-1} \bullet x) \rangle_{\mathsf{L}^2_\nu(S)} = \lim_{m,n\to\infty} \int_S \phi_m(g^{-1} \bullet x)\, \overline{\psi_n(g^{-1} \bullet x)}\, d\nu \\ = \lim_{m,n\to\infty} \int_{g\bullet S} \phi_m(g^{-1} \bullet (g \bullet y))\, \overline{\psi_n(g^{-1} \bullet (g \bullet y))}\, d\nu = \lim_{m,n\to\infty} \int_S \phi_m(y)\, \overline{\psi_n(y)}\, d\nu \\ = \lim_{m,n\to\infty} \langle \phi_m, \psi_n \rangle_{\mathsf{L}^2_\nu(S)} = \langle \lim_{m\to\infty} \phi_m, \lim_{n\to\infty} \psi_n \rangle_{\mathsf{L}^2_\nu(S)} = \langle \phi, \psi \rangle_{L^2_\nu(S)} \quad .\end{aligned} \tag{3.12}$$

Thus each $\mathcal{T}_g$ is an isometry. Furthermore, $(\mathcal{T}_g)^{-1} = \mathcal{T}_{g^{-1}}$ is well defined on and so, the range $\mathcal{T}_g$ is easily seen to be $\mathsf{L}^2_\nu(S)$. Hence, each $\mathcal{T}_g$ is a unitary operator [9] and $\zeta : \mathcal{G} \to L_{\mathcal{G}}$ forms a unitary representation of $\mathcal{G}$. ■

We now move onto ideas related to the irreducibility of representations.

[9] A surjective linear isometry is a unitary map [Folland, 1999].

3.2.2 Irreducible Representations and Completely Reducible Representations

Given two unitary representations ζ_1 and ζ_2 of $\mathcal{G}$ on the Hilbert spaces H_1 and H_2 respectively, we may introduce the set of intertwining operators for ζ_1 and ζ_2:

$$\mathcal{C}(\zeta_1, \zeta_2) = \{T \in \mathcal{L}(\mathsf{H}_1, \mathsf{H}_2) : T \cdot \zeta_1(g) = \zeta_2(g) \cdot T, \forall g \in \mathcal{G}\} \tag{3.13}$$

In particular, we refer to $\mathcal{C}(\zeta) = \mathcal{C}(\zeta, \zeta)$ as the commutant of the unitary representation $\zeta : \mathcal{G} \to \mathcal{L}(\mathsf{H}, \mathsf{H})$. Clearly, this is the set of bounded operators on H that commute with $\zeta(g)$ for every $g \in \mathcal{G}$.

We say that the representations ζ_1 and ζ_2 are unitarily equivalent if $\mathcal{C}(\zeta_1, \zeta_2)$ contains a unitary operator $U : \mathsf{H}_1 \to \mathsf{H}_2$ since in this case we have an isomorphism between the representations given as $\zeta_2(g) = U \cdot \zeta_1(g) \cdot U^{-1}, \forall g \in \mathcal{G}$. This motivates us to introduce an equivalence relation $\sim$ between unitary representations of $\mathcal{G}$ by specifying that $\zeta_1 \sim \zeta_2$ iff ζ_1 is unitarily equivalent to ζ_2. This equivalence relation clearly partitions the set of all unitary representations of $\mathcal{G}$ into equivalence classes of unitarily equivalent representations. The question that arises at this point then, is that, given a particular equivalence class of unitary representations, is there a specific representative in the given equivalence class that has a relatively simpler structure than the others? It turns out that the answer to this question is intimately tied to the notion of invariant subspaces of representations. So we introduce:

Definition 3.2.4. Let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be a unitary representation of the group $\mathcal{G}$ on the carrier space H and let $\mathcal{M}$ be a closed subspace of H. We say that $\mathcal{M}$ is an invariant subspace for the representation ζ or that $\mathcal{M}$ is group invariant if:

$$\zeta(g)[f] \in \mathcal{M}, \ \forall f \in \mathcal{M}, \forall g \in \mathcal{G}. \tag{3.14}$$

If $\mathcal{M} \neq \{0\}$ or H we say that the invariant subspace is non trivial and that the representation ζ is reducible. If ζ does not admit any non-trivial invariant subspaces, we say that the representation is irreducible. □

The above ideas lead us to the following important result:

Theorem 3.2.5. *Let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be a unitary representation of the group $\mathcal{G}$ over the carrier space H and let $\mathcal{M}$ be a closed subspace of H. Let $\mathcal{P}^{\mathcal{M}}$ be the projection operator on H whose range is $\mathcal{M}$. Then:*

1. *The orthogonal complement $\mathcal{M}^{\perp}$ of $\mathcal{M}$ is group invariant if and only if $\mathcal{M}$ is group invariant.*

2. *Any $f \in \mathsf{H}$ admits the unique representation $f = f_1 + f_2$, with $f_1 \in \mathcal{M}, f_2 \in \mathcal{M}^\perp$.*

3. *$\mathcal{M}$ is group invariant if and only if $\mathcal{P}^{\mathcal{M}} \in \mathcal{C}(\zeta)$ i.e., $\mathcal{P}^{\mathcal{M}} \cdot \zeta(g) = \zeta(g) \cdot \mathcal{P}^{\mathcal{M}},\ \forall g \in \mathcal{G}$.*

4. *The restriction of ζ to $\mathcal{M}$, that is, $\zeta^{\mathcal{M}}(g) = \zeta(g)|_{\mathcal{M}}$, defines a representation of $\mathcal{G}$ on $\mathcal{M}$. Similarly, the restriction of ζ to $\mathcal{M}^\perp$ defines a representation of $\mathcal{G}$ on $\mathcal{M}^\perp$. (These are the so called sub-representations of ζ over the invariant subspaces $\mathcal{M}$ and $\mathcal{M}^\perp$ respectively.)*

Proof: 1. We begin by recalling that $\mathcal{M}^\perp = \{f \in \mathsf{H} : \langle f, \phi \rangle_{\mathsf{H}} = 0,\ \forall \phi \in \mathcal{M}\}$. This definition automatically implies that $\mathcal{M}^\perp$ is closed, since for any convergent sequence $\{f_n\}_{n=1}^{\infty} \subset \mathcal{M}^\perp$ with $f = \lim_{n\to\infty} f_n$ and $\phi \in \mathcal{M}$, we have by the continuity of the inner product:

$$\langle f, \phi \rangle_{\mathsf{H}} = \langle \lim_{n\to\infty} f_n, \phi \rangle_{\mathsf{H}} = \lim_{n\to\infty} \langle f_n, \phi \rangle_{\mathsf{H}} = 0 \tag{3.15}$$

So $f \in \mathcal{M}^\perp$.

Now, if $\mathcal{M}$ is group invariant, then $\forall f \in \mathcal{M}, \forall \phi \in \mathcal{M}^\perp$ and $\forall g \in \mathcal{G}$ we have:

$$\langle \zeta(g)\phi, f \rangle_{\mathsf{H}} = \langle \phi, \zeta(g)^* f \rangle_{\mathsf{H}} = \langle \phi, \zeta(g^{-1}) f \rangle_{\mathsf{H}} = 0, \tag{3.16}$$

because $\zeta(g^{-1})f \in \mathcal{M}$ and ζ is a unitary representation. Hence, $\mathcal{M}^\perp$ is also group invariant. The opposite implication follows readily by exchanging the roles of $\mathcal{M}$ and $\mathcal{M}^\perp$ and noting that $\{\mathcal{M}^\perp\}^\perp = \bar{\mathcal{M}} = \mathcal{M}$ since $\mathcal{M}$ is closed.

2. This result is a consequence of the Hilbert projection theorem from linear functional analysis and it may be found in various standard references such as Folland [1999] and Naylor and Sell [1971]. However, because of the important role that this result plays, we derive a proof of it in Appendix A, Section A.1.

3. We first notice that for any $\phi \in \mathsf{H}$, we have $\phi \in \mathcal{M}$ if and only if $\mathcal{P}^{\mathcal{M}}\phi = \phi$. Now, if $\mathcal{P}^{\mathcal{M}} \in \mathcal{C}(\zeta)$ and if $f \in \mathcal{M}$ then $\mathcal{P}^{\mathcal{M}} f = f$ and so,

$$\forall g \in \mathcal{G},\ \zeta(g)f = \zeta(g)[\mathcal{P}^{\mathcal{M}} f] = \mathcal{P}^{\mathcal{M}}[\zeta(g)f]. \tag{3.17}$$

Thus $\zeta(g)f \in \mathcal{M},\ \forall g \in \mathcal{G}, \forall f \in \mathcal{M}$. Hence, $\mathcal{M}$ is a group invariant subspace.

Conversely, we suppose that $\mathcal{M}$ is a group invariant subspace and we let $f \in \mathsf{H}$. We use the result in part(2) to write $f = f_1 + f_2$ where, $f_1 \in \mathcal{M}, f_2 \in \mathcal{M}^\perp$. Now, for

any $g \in \mathcal{G}$, we have $\zeta(g)[\mathcal{P}^{\mathcal{M}} f] = \zeta(g) f_1$. On the other hand,

$$\mathcal{P}^{\mathcal{M}}[\zeta(g) f] = \mathcal{P}^{\mathcal{M}}[\zeta(g) f_1] + \mathcal{P}^{\mathcal{M}}[\zeta(g) f_2]. \tag{3.18}$$

But since $\mathcal{M}^{\perp}$ is also group invariant, $\zeta(g) f_2 \in \mathcal{M}^{\perp}$ and so, $\mathcal{P}^{\mathcal{M}}(\zeta(g) f_2) = 0$. Finally, since $\mathcal{M}$ is group invariant, $\zeta(g) f_1 \in \mathcal{M}$ and so, $\mathcal{P}^{\mathcal{M}}[\zeta(g) f_1] = \zeta(g) f_1$. Hence, for any $f \in \mathsf{H}, g \in \mathcal{G}$, we have that:

$$(\mathcal{P}^{\mathcal{M}})[\zeta(g) f] = \zeta(g)[\mathcal{P}^{\mathcal{M}} f] = \zeta(g) f_1. \tag{3.19}$$

Hence $\mathcal{P}^{\mathcal{M}} \in \mathcal{C}(\zeta)$.

4. The definition of the map $\zeta^{\mathcal{M}}$ is such that for each $g \in \mathcal{G}$, we have a bounded linear operator $T_g^{\mathcal{M}} : \mathcal{M} \to \mathcal{M}$. The range of each T_g is $\mathcal{M}$ by group invariance. It is now easy to check that $\zeta^{\mathcal{M}}$ is an identity preserving homomorphism and so, it is a representation of $\mathcal{G}$ over $\mathcal{M}$. The proof for the case of $\mathcal{M}^{\perp}$ is exactly similar.

■

By part (2) of Theorem 3.2.5 above, since any $f \in \mathsf{H}$ admits the representation $f = f_1 + f_2$ with $f_1 \in \mathcal{M}, f_2 \in \mathcal{M}^{\perp}$, we may introduce the direct sum notation to write $\mathsf{H} = \mathcal{M} \oplus \mathcal{M}^{\perp}$. Part (4) of the theorem then motivates the notion of direct sums of representations and we may formally write $\zeta = \zeta^{\mathcal{M}} \oplus \zeta^{\mathcal{M}^{\perp}}$ to mean that the unitary representation $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ has invariant subspaces $\mathcal{M}$ and $\mathcal{M}^{\perp}$ and that $\zeta^{\mathcal{M}}$ and $\zeta^{\mathcal{M}^{\perp}}$ are the restrictions of ζ to these invariant subspaces. We call $\zeta^{\mathcal{M}}$ and $\zeta^{\mathcal{M}^{\perp}}$ the sub-representations of ζ. We may now repeat this procedure by looking at the invariant subspaces of $\zeta^{\mathcal{M}}$ on $\mathcal{M}$ as well as the invariant subspaces of $\zeta^{\mathcal{M}^{\perp}}$ on $\mathcal{M}^{\perp}$ and so on. Thus, this recursive procedure can be used to yield a decomposition of the given Hilbert space in terms of group invariant subspaces. The usefulness of this arises from the fact that a problem posed on the original Hilbert space may often be solved more conveniently on the "smaller" invariant subspaces.

To make these ideas concrete, we first need to introduce the general notion of direct sums of Hilbert spaces. Since this involves an extra bit of work and so, we do it separately in Appendix A, Section A.2. With the ideas presented in the appendix in place, we are now ready to define the direct sum of representations:

Definition 3.2.6. For each $\alpha \in \mathcal{A}$, let ζ_α be a unitary representations of the group $\mathcal{G}$ on the Hilbert space H_α. Then the direct sum of representations is the representation ζ of $\mathcal{G}$ on

$\mathsf{H} = \bigoplus_{\alpha\in\mathcal{A}} \mathsf{H}_\alpha$ defined by

$$\zeta(g)(\sum_{\alpha\in\mathcal{A}} v_\alpha) = \sum_{\alpha\in\mathcal{A}} \zeta_\alpha(g)v_\alpha \tag{3.20}$$

with $v_\alpha \in \mathsf{H}_\alpha$. We express this symbolically as $\zeta = \bigoplus_{\alpha\in\mathcal{A}} \zeta_\alpha$. □

We may easily verify that for each $g \in \mathcal{G}$, the operator $\zeta(g)$ defined in the above manner is indeed a unitary operator on H. Further, the H_α are invariant subspaces under the representation ζ and that each ζ_α is a sub-representation of ζ, i.e., $\zeta_\alpha(g) = \zeta(g)|_{\mathsf{H}_\alpha}$.

The above definition of direct sums of representations is from the perspective of building newer representations on "larger" spaces from given ones on "smaller spaces". As mentioned a little earlier, from the point of view of applications, we would in fact like to turn this procedure around by expressing a given representation on a "larger" space as the direct sum of sub-representations on "smaller" spaces. In fact, we may define:

Definition 3.2.7. Let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be a unitary representation of the group $\mathcal{G}$ on the carrier space H and let us suppose that we have:

$$\mathsf{H} = \bigoplus_{\alpha\in\mathcal{A}} \mathcal{M}_\alpha, \quad \zeta = \bigoplus_{\alpha\in\mathcal{A}} \zeta_\alpha, \tag{3.21}$$

as defined in Appendix A and Definition 3.2.6. We say that the unitary representation ζ of $\mathcal{G}$ on H is completely reducible if each sub-representation ζ_α on $\mathcal{M}_\alpha$ is irreducible. □

From this perspective, it is apparent that irreducible unitary representations of a given $\mathcal{G}$ are the "building blocks" of all other (completely reducible) unitary representations of $\mathcal{G}$ since, the process of breaking down representations using invariant subspaces has to terminate when irreducible representations appear. Hence, irreducible representations assume a central role in the representation theory of $\mathcal{G}$.[10] Irreducible representations of many of the common discrete groups of isometries (particularly, the crystallographic space groups and point groups) are well known and are easily obtainable as tabulated data [Miller, 1967; Aroyo et al., 2006; Serre, 1977]. For the purpose of this work, we will have the occasion to refer to these tables when dealing with finite groups of isometries. We demonstrate in

[10]Technical remark: It is not clear apriori however, that a given group will have any irreducible representations except the trivial identity representation. However, the Gelfand-Raikov Theorem [Folland, 1994] assures us that every locally compact group admits sufficiently many irreducible unitary representations on Hilbert spaces so that points can be separated. More specifically, for any locally compact group G and $x, y \in G, x \neq y$, there exists an irreducible representation ζ of G such that $\zeta(x) \neq \zeta(y)$. Thus, in case of discrete groups of isometries for example, we are assured of the existence of non-trivial representations.

the next few sections that it is possible to prove a few qualitative features of irreducible representations of some particular groups without referring to these tables.

3.2.3 Reducibility and Irreducibility Criteria

Given a particular representation of $\mathcal{G}$ on $\mathcal{U}(\mathsf{H},\mathsf{H})$ the results of Theorem 3.2.5 can be used to identify if the given representation is reducible or not. However, the criteria suggested in that theorem are not necessarily easy to verify and so we would like to formulate criteria which are easier to check. The following result for example, provides a characterization of completely reducible representations when the carrier space H is a finite dimensional and so this result is important from the perspective of numerical algorithms that employ symmetry:

Proposition 3.2.8. *A finite dimensional unitary representation of any group is completely reducible. In particular, there exists an orthonormal basis of* H *in which the (finite) matrix representation corresponding to any (and every) group element appears block diagonal.*

Proof: If H_1 is a proper invariant subspace of H, then by part (1) of Theorem 3.2.5, $\mathsf{H}_1^\perp$ is also invariant and we have $\mathsf{H} = \mathsf{H}_1 \oplus \mathsf{H}_1^\perp$. If H_1 or $\mathsf{H}_1^\perp$ contains a proper invariant subspace, then we use the same result again, to obtain a decomposition and we continue this procedure until we obtain a decomposition of H into irreducible invariant subspaces. The finite dimensionality of H assures us that this procedure will terminate to yield the required decomposition.

Now, for the sake of definiteness, let dim.$(\mathsf{H}) = n < \infty$. For some $m < n$, let $\{\mathcal{M}_j\}_{j=1}^m$, denote the collection of invariant subspaces of H obtained by the above procedure, i.e., $\mathsf{H} = \bigoplus_{j=1}^m \mathcal{M}_j$. For each $j = 1,\ldots,m$, let $\mathcal{E}_j = \{e_k^j\}_{k=1}^{n_j}$ be an orthonormal basis of $\mathcal{M}_j$. Clearly, the set $\mathcal{E} = \bigcup_j \mathcal{E}_j$ is an orthonormal basis of H and $\displaystyle\sum_{j=1}^{m} n_j = n$. We denote $\mathcal{E} = \{\tilde{e}_i\}_{i=1}^n$ and we let this be an ordering of $\mathcal{E}$ in which the first n_1 basis vectors belong to $\mathcal{E}_1$, the next n_2 basis vectors belong to $\mathcal{E}_2$ and so on. Thus, the first n_1 vectors in $\mathcal{E}$ are basis vectors of $\mathcal{M}_1$, the next n_2 vectors are basis vectors of $\mathcal{M}_2$, etc. For any $g \in \mathcal{G}$, we now consider the matrix representation of $\zeta(g) = \mathcal{T}_g$ in this basis. For any $i,k \in \{1,2,\ldots,n\}$, if $\tilde{e}_i \in \mathcal{M}_j$ and $\tilde{e}_k \in \mathcal{M}_{j'}$, with $j \neq j'$, then $T_g\tilde{e}_i \in \mathcal{M}_j$ while $\tilde{e}_k \in \mathcal{M}_j^\perp$ and so, $D_{i,k}(g) = \langle T_g\tilde{e}_i, \tilde{e}_k\rangle_{\mathsf{H}} = 0$. On the other hand, if both $\tilde{e}_i, \tilde{e}_k \in \mathcal{M}_j$, then $T_g\tilde{e}_i \in \mathcal{M}_k$ as well, and so $D_{i,k}(g) \neq 0$ in general. Hence, in this basis, the matrix form of $\mathcal{T}_g$ assumes

the following block diagonal form:

$$D_{n\times n}(g) = \begin{bmatrix} D^1_{n_1\times n_1}(g) & 0 & \dots & 0 \\ 0 & D^2_{n_2\times n_2}(g) & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & D^m_{n_m\times n_m}(g) \end{bmatrix}, \tag{3.22}$$

with each $D^j(g)$ an irreducible block of size $n_j \times n_j$, for $j \in \{1, \dots, m\}$. The rest of the entries of $D(g)$ are zero. In general however, some of the subspaces $\mathcal{M}_j$ may just be related to each other by orthogonal transformations. Thus, an irreducible representation can appear more than once in the given representation through unitarily equivalent representations. ■

Remark 3.2.9. If, in particular $\mathsf{H} = \mathbb{C}^n$, and we are working with a given basis $\mathcal{E}'$ of H such that the matrix representation of $\zeta(g)$ in this basis is $D(g)$, then the block diagonal structure of $D(g)$ is revealed by the change of basis to $\mathcal{E} = \{\tilde{e}_i\}_{i=1}^{i=n}$. This can be done by the unitary transformation $Q^\dagger D(g)Q$ with $Q = [\tilde{e}_1 \ \tilde{e}_2 \ \dots \ \tilde{e}_n]$, with each $\tilde{e}_i$ expressed in the basis $\mathcal{E}'$. □

One of the most fundamental and widely used irreducibility criteria is Schur's Lemma [Folland, 1994; Barut and Raczka, 1986]. We will have the occasion to use this result quite extensively in some of the following material and so, we briefly outline a proof of this result here:

Theorem 3.2.10 (Schur's Lemma)**.** *A representation $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ is irreducible if and only if the only operator commuting with all $\zeta(g), g \in \mathcal{G}$ is a scalar multiple of the identity operator (that is, $\mathcal{C}(\zeta)$ is one-dimensional).*

Proof: We suppose first that the given representation ζ is reducible. Then clearly, ζ has a non-trivial group invariant subspace $\mathcal{M}$. By part 3 of Theorem 3.2.5, the projection operator $\mathcal{P}^{\mathcal{M}} \in \mathcal{C}(\zeta)$ and so, $\mathcal{C}(\zeta)$ is not one-dimensional.

On the other hand, we suppose that ζ is irreducible and let $A \in \mathcal{C}(\zeta)$ such that $A \neq cI_{\mathsf{H}}$. First, let A be a symmetric (Hermitian) operator. Then, by the spectral theorem for such operators [Raskin, 2006; Folland, 1994], there exists a spectral measure E such that $A = \int \lambda \, dE_\lambda$. At this point, it simply remains to observe that $A \in \mathcal{C}(\zeta)$ would have to imply that $\zeta(g)$ commutes with all projections E_λ. This would violate irreducibility because the ranges of the projections E_λ would be left invariant by ζ. If A is not Hermitian, then

$A_1 = \frac{A+A^*}{2}$ and $A_1 = \frac{A-A^*}{2i}$ are Hermitian and both lie in $\mathcal{C}(\zeta)$ since $A \in \mathcal{C}(\zeta)$. Applying the spectral theorem arguments presented above to both A_1 and A_2, we get:

$$A_1 = \lambda_1 I_{\mathsf{H}}, \quad A_2 = \lambda_2 I_{\mathsf{H}}, \quad A = (A_1 + iA_2) = (\lambda_1 + i\lambda_2) I_{\mathsf{H}} \quad . \tag{3.23}$$

This completes the proof. Further details of this calculation, using spectral measures and the spectral theorem for symmetric operators may be found in Raskin [2006]. ■

There is an immediate corollary of Schur's Lemma that turns out to be particularly useful in many situations. Its statement and proof are as follows:

Corollary 3.2.11. *If $\zeta_1 : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ and $\zeta_2 : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ are two irreducible representations of $\mathcal{G}$ then $\mathcal{C}(\zeta_1, \zeta_2) = \{0\}$ if ζ_1 and ζ_2 are inequivalent.*

Proof: If $T \in \mathcal{C}(\zeta_1, \zeta_2)$, then the adjoint $T^* \in \mathcal{C}(\zeta_1, \zeta_2)$ as for any $g \in \mathcal{G}$ we have:

$$T^* \cdot \zeta_2(g) = [\zeta_2(g^{-1}) \cdot T]^* = [T \cdot \zeta_1(g^{-1})]^* = \zeta_1(g) \cdot T^* \quad . \tag{3.24}$$

Hence we have that $T^* \cdot T \in \mathcal{C}(\zeta_1)$ while $T \cdot T^* \in \mathcal{C}(\zeta_2)$. By Schur's Lemma, we then have that $T \cdot T^* = T^* \cdot T = c\, I_{\mathsf{H}}$. Thus, either $T = 0$ or $c^{-\frac{1}{2}} T$ is unitary. In particular, therefore, $\mathcal{C}(\zeta_1, \zeta_2) = \{0\}$ if ζ_1 and ζ_2 are inequivalent since in that case the possibility of $c^{-\frac{1}{2}} T$ being unitary is ruled out. ■

We will end this chapter by analyzing the consequences of Schur's Lemma for the particular case of finite (compact) groups of isometries which may or may not be Abelian.

3.2.4 Irreducible Representations of Finite Groups

Whether or not a finite group of isometries (which is necessarily discrete) is Abelian, it obeys the following result:

Proposition 3.2.12. *Let $\mathcal{G}$ be a finite group of isometries and let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be an irreducible unitary representation of $\mathcal{G}$ on the carrier space H. Then, ζ is finite dimensional.*

Proof: We fix a unit vector $u \in \mathsf{H}$ and we define an operator T on H as follows:

$$\text{For any } v \in \mathsf{H}, Tv = \int_{\mathcal{G}} \langle v, \zeta(g)u \rangle_{\mathsf{H}}\, \zeta(g)\, u\, d\mu = \sum_{g \in \mathcal{G}} \langle v, \zeta(g)u \rangle_{\mathsf{H}}\, \zeta(g)\, u \quad . \tag{3.25}$$

We then notice the properties that $T \in \mathcal{L}(\mathsf{H}, \mathsf{H})$, T is a finite rank operator and $T \in \mathcal{C}(\zeta)$. Let us now prove each of these statements.

The linearity property of T is easily verified since the inner product is linear in it's first argument. Next, for any $v \in \mathsf{H}$, using the Cauchy Schwarz inequality,

$$\begin{aligned} \|Tv\|_{\mathsf{H}} &= \|\sum_{g\in\mathcal{G}} \langle v, \zeta(g)u\rangle_{\mathsf{H}}\, \zeta(g)\, u\|_{\mathsf{H}} \\ &\leq \sum_{g\in\mathcal{G}} |\langle v, \zeta(g)u\rangle_{\mathsf{H}}|\ \|\zeta(g)\, u\|_{\mathsf{H}} \leq \sum_{g\in\mathcal{G}} \|v\|_{\mathsf{H}} \|\zeta(g)u\|_{\mathsf{H}}^2 \end{aligned} \tag{3.26}$$

Since $\zeta(g)$ is unitary, we have that $\|\zeta(g)u\|_{\mathsf{H}} = \|u\|_{\mathsf{H}} = 1$ and so:

$$\|Tv\|_{\mathsf{H}} \leq |\mathcal{G}|\ \|v\|_{\mathsf{H}} \quad , \tag{3.27}$$

where $|\mathcal{G}|$ is the group order. Thus, $T \in \mathcal{L}(\mathsf{H}, \mathsf{H})$. Next, the operator T is of finite rank (that is, it's range is finite dimensional) since by construction, the v appears only as a complex coefficient and so:

$$\text{Ran}\,(T) \subset \text{span}\{\zeta(g)u : g \in \mathcal{G}\} \quad . \tag{3.28}$$

To check that $T \in \mathcal{C}(\zeta)$, we have for any $g \in \mathcal{G}$:

$$\begin{aligned} \zeta(h)[Tv] &= \sum_{g\in\mathcal{G}} \langle v, \zeta(g)u\rangle_{\mathsf{H}}\, \zeta(h)[\zeta(g)\, u] = \sum_{g\in\mathcal{G}} \langle v, \zeta(g)u\rangle_{\mathsf{H}}\, \zeta(h\circ g)\, u \\ &= \sum_{(h^{-1}\circ g)\in\mathcal{G}} \langle v, \zeta(h^{-1}\circ g)u\rangle_{\mathsf{H}}\, \zeta(h\circ(h^{-1}\circ g))\, u \\ &= \sum_{g\in\mathcal{G}} \langle v, \zeta(h^{-1})[\zeta(g)u]\rangle_{\mathsf{H}}\, \zeta(g)\, u \\ &= \sum_{g\in\mathcal{G}} \langle v, \zeta(h)^*[\zeta(g)u]\rangle_{\mathsf{H}}\, \zeta(g)\, u \\ &= \sum_{g\in\mathcal{G}} \langle \zeta(h)v, \zeta(g)u\rangle_{\mathsf{H}}\, \zeta(g)\, u = T[\zeta(h)v] \quad . \end{aligned} \tag{3.29}$$

By Schur's Lemma (Theorem 3.2.10), since ζ is irreducible, it must be that $T = cI_{\mathsf{H}}$. But since T is of finite rank so must be I_{H} and hence, we must have that H is finite dimensional. Thus, ζ is a finite dimensional unitary representation. ■

The most important consequence of this result is that every unitary representation ζ of a finite group of isometries is completely reducible as the following result shows:

Theorem 3.2.13. *Let $\mathcal{G}$ be a finite group of isometries and let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be a*

unitary representation of $\mathcal{G}$ on the carrier space H*. Then, ζ is expressible as the direct sum of irreducible representations.*

Proof: Given an arbitrary unitary representation ζ of $\mathcal{G}$, we define the operator $T \in \mathcal{L}(H, H)$ as in Proposition 3.2.12. Then T is self-adjoint because for any $v, w \in \mathsf{H}$ we have:

$$\begin{aligned}\langle Tv, w\rangle_{\mathsf{H}} &= \left\langle \sum_{g\in\mathcal{G}} \langle v, \zeta(g)u\rangle_{\mathsf{H}}\, \zeta(g)u\,, w \right\rangle_{\mathsf{H}} = \sum_{g\in\mathcal{G}} \langle v, \zeta(g)u\rangle_{\mathsf{H}}\, \langle \zeta(g)u, w\rangle_{\mathsf{H}} \\ &= \sum_{g\in\mathcal{G}} \langle \zeta(g)^* v, u\rangle_{\mathsf{H}}\, \langle u, \zeta(g)^* w\rangle_{\mathsf{H}} = \sum_{g\in\mathcal{G}} \langle \zeta(g^{-1})v, u\rangle_{\mathsf{H}}\, \langle u, \zeta(g^{-1})w\rangle_{\mathsf{H}} \\ &= \left\langle \sum_{g\in\mathcal{G}} \langle u, \zeta(g)w\rangle_{\mathsf{H}} \zeta(g)v\,, u \right\rangle_{\mathsf{H}} = \langle v, Tw\rangle_{\mathsf{H}} \quad , \end{aligned} \tag{3.30}$$

as well as the fact that both T and T^* are defined on all of H. Hence, T is a finite rank self adjoint operator on H. So the spectral theorem for compact self-adjoint operators [Naylor and Sell, 1971] says that T has a nonzero eigenvalue λ with a finite dimensional eigenspace $\mathcal{M}$. But $T \in \mathcal{C}(\zeta)$ by the calculations in Proposition 3.2.12 and so, $\mathcal{M}$ is a group invariant subspace by part 3 of Theorem 3.2.5. Thus, ζ has a finite dimensional sub-representation on $\mathcal{M}$. By Proposition 3.2.8, every finite dimensional representation is completely reducible. Hence, ζ has an irreducible sub-representation.

Now we consider families of mutually orthogonal irreducible invariant subspaces of ζ. We can partially order these families by set inclusion and use Zorn's Lemma [Folland, 1999; Naylor and Sell, 1971] to conclude that there is a maximal family $\{\mathcal{M}_\alpha\}_{\alpha\in\mathcal{A}}$. Let $\mathsf{H}_\mathcal{A} = \oplus_{\alpha\in\mathcal{A}}\mathcal{M}_\alpha$ and let $\mathcal{N}$ be the orthogonal complement of $\mathsf{H}_\mathcal{A}$. By part 1 of Theorem 3.2.5, it must be that $\mathcal{N}$ is group invariant since $\mathsf{H}_\mathcal{A}$ is group invariant. By the maximality of $\{\mathcal{M}_\alpha\}_{\alpha\in\mathcal{A}}$, it must be that $\mathcal{N}$ is irreducible, otherwise it should have been part of the family $\{\mathcal{M}_\alpha\}_{\alpha\in\mathcal{A}}$. Hence it must be that $\mathcal{N} = \{0\}$. Thus, we are led to the conclusion $\mathsf{H} = \mathsf{H}_\mathcal{A} = \oplus_{\alpha\in\mathcal{A}}\mathcal{M}_\alpha$ with each $\mathcal{M}_\alpha$ a finite dimensional irreducible invariant subspace. Thus, introducing $\zeta_\alpha = \zeta|_{\mathcal{M}_\alpha}$ we see that ζ is expressible as $\zeta = \oplus_{\alpha\in\mathcal{A}}\zeta_\alpha$, with each ζ_α an irreducible representation of $\mathcal{G}$, thus proving the theorem. ■

We find it quite remarkable that there is in fact a systematic method to carry out the direct sum decomposition that the above theorem proves the existence of. That is, there is actually an explicit formula that one can use for constructing the invariant subspaces associated with the irreducible representations of a finite group. In the context of investigating the effects

of symmetry on a boundary value problem, this is perhaps the single most useful result. To prove this result, we first need the following:

Lemma 3.2.14 (Orthogonality Relations)**.** *Let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ and $\zeta' : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be any two irreducible unitary representations of $\mathcal{G}$ on the carrier space H. Let $D_{ij}(g)$ and $D'_{ij}(g)$ denote respectively, the the matrix elements of $\zeta(g)$ and $\zeta'(g)$. Let d_ζ be the matrix dimension of the representation D_{ij}. Then, the matrix elements satisfy the relations:*

$$\frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} D_{ij}(g)\overline{D'_{mn}(g)} = \begin{cases} 0 & \text{if} \quad \zeta \text{ and } \zeta' \text{are not equivalent.} \\ \frac{1}{d_\zeta}\,\delta_{im}\delta_{jn} & \text{if} \quad \zeta \text{ and } \zeta' \text{are unitarily equivalent.} \end{cases} \tag{3.31}$$

Proof: We introduce the operators:

$$E_{ij} = \frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} \zeta(g)\mathcal{E}_{ij}\zeta'(g^{-1}) \;, \tag{3.32}$$

with $(\mathcal{E}_{ij})^{mn} = \delta_{i,m}\delta_{j,n};\ i,m = 1,2,\ldots,d_\zeta$ and $j,n = 1,2,\ldots,d_{\zeta'}$. [11] For every $h \in \mathcal{G}$, the operators (3.32) satisfy the relation:

$$\begin{aligned} \zeta(h)E_{ij} &= \frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} \zeta(h\circ g)\mathcal{E}_{ij}\zeta'(g^{-1}) \\ &= \frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} \zeta(g')\,\mathcal{E}_{ij}\,\zeta'(g'^{-1}\circ h) = E_{ij}\zeta'(h) \;. \end{aligned} \tag{3.33}$$

Hence, if ζ is not equivalent to ζ', then Schur's lemma (in the form of Corollary 3.2.11) implies $E_{ij} = 0$, or in terms of matrix components:

$$\frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} D_{li}(g)D'_{jk}(g^{-1}) = \frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} D_{li}(g)\overline{D'_{jk}(g)} = 0 \;. \tag{3.34}$$

On the other hand, if ζ and ζ' are equivalent, then by Schur's Lemma (Theorem 3.2.10), we have $E_{ij} = \lambda_{ij}I$. Thus, for $(l,i) \neq (k,j)$, the orthogonality relations (3.33) are still satisfied. If, however, $(l,i) = (k,j)$, then using (3.32) and $E_{ii} = \lambda_{ii}I$ (no summation), we obtain:

$$(E_{ii})_{ll} = \frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} D_{li}(g)D_{il}(g^{-1}) = \frac{1}{|\mathcal{G}|}\sum_{g\in\mathcal{G}} |D_{li}(g)|^2 = \lambda_{ii} \;. \tag{3.35}$$

[11] Due to Proposition 3.2.12, we know that both ζ and ζ' must be equivalent to finite dimensional matrices of dimension d_ζ and $d_{\zeta'}$ respectively. The operator $\mathcal{E}_{ij}$ is a linear transformation on the space of $d_{\zeta'} \times d_{\zeta'}$ matrices, with range in the space of $d_\zeta \times d_\zeta$ matrices.

To evaluate the constant λ_{ii}, we set $i = j$ in (3.32) and take the trace on both sides to obtain:

$$\text{Tr.}(E_{ii}) = d_\zeta \, \lambda_{ii} = \frac{1}{|\mathcal{G}|} \sum_{g \in \mathcal{G}} \text{Tr.}(\zeta(g) \, \mathcal{E}_{ii} \, \zeta'(g^{-1})) = \text{Tr.}(\mathcal{E}_{ii}) = 1 \ . \tag{3.36}$$

In the above, we have used the fact that the trace remains invariant under cyclic permutations. Thus, by (3.36), we finally conclude that $\lambda_{ii} = \frac{1}{d_\zeta}$, thus completing the proof. ■

A common statement of the above orthogonality relations [Bossavit, 1986] involves identifying equivalent representations by a Kronecker delta and then rewriting (3.31) as:

$$\frac{d_\nu}{|\mathcal{G}|} \sum_{g \in \mathcal{G}} D^\mu_{ij}(g) D^\nu_{lk}(g^{-1}) = \delta_{ik} \delta_{jl} \delta_{\mu\nu} \ . \tag{3.37}$$

Let us point out that the total number of inequivalent irreducible representations of a finite group equals the number of conjugacy classes [Serre, 1977] in the group, and so it is necessarily finite. Hence, we may think of numbering all the inequivalent irreducible representations associated with $\mathcal{G}$ by $\nu = 1, \ldots, \ell$ and denoting them as ζ^ν, $\nu = 1, \ldots, \ell$. We now have the following result:

Theorem 3.2.15 (Projection Operators)**.** *Let $\zeta : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be an arbitrary unitary representation of the finite group of isometries $\mathcal{G}$ on the carrier space H. Let $\zeta^\nu : \mathcal{G} \to \mathcal{U}(\mathsf{H}, \mathsf{H})$ be an irreducible representation of $\mathcal{G}$ on the same carrier space and let d_ν be the dimension of the representation ζ^ν. Let the matrix elements of $\zeta^\nu(h)$ be denoted as $D^\nu_{ij}(h)$ and let us set:*

$$P^\nu_{ij} = \frac{d_\nu}{|\mathcal{G}|} \sum_{h \in \mathcal{G}} \overline{D^\nu_{ij}(h)} \zeta(h) \quad . \tag{3.38}$$

Then the P^ν_{ii} are projection operators on H, their ranges $V^\nu_{ii} = P^\nu_{ii}(\mathsf{H})$ are mutually orthogonal closed subspaces of H and we have the direct sum decomposition:

$$\mathsf{H} = \bigoplus_{\nu,i} V^\nu_{ii} \quad , \tag{3.39}$$

the direct sum being taken over $\nu = 1 \ldots, \ell$ and $i = 1, \ldots, d_\nu$.

Proof: We define P^ν_{ij} as in (3.38) and observe, that since $\zeta(g)$ and $D^\nu(g)$ are unitary operators, the operators P^ν_{ii} obey $P^\nu_{ii} = (P^\nu_{ii})^*$. Thus the operators P^ν_{ii} are self-adjoint. By direct

computation, we have for every $g \in \mathcal{G}$:

$$\begin{aligned}
\zeta(g) P^{\nu}_{ij} &= \zeta(g)\, \frac{d_\nu}{|\mathcal{G}|} \sum_{h\in\mathcal{G}} D^{\nu}_{ji}(h^{-1})\zeta(h) \\
&= \frac{d_\nu}{|\mathcal{G}|} \sum_{h\in\mathcal{G}} D^{\nu}_{ji}(h^{-1})\zeta(g\circ h) = \frac{d_\nu}{|\mathcal{G}|} \sum_{h\in\mathcal{G}} D^{\nu}_{ji}(h^{-1}\circ g)\zeta(h) \\
&= \sum_{k=1}^{d_\nu} \frac{d_\nu}{|\mathcal{G}|} \sum_{h\in\mathcal{G}} D^{\nu}_{jk}(h^{-1}) D^{\nu}_{ki}(g)\zeta(h) = \sum_{k=1}^{d_\nu} D^{\nu}_{ki}(g)\, \frac{d_\nu}{|\mathcal{G}|} \sum_{h\in\mathcal{G}} D^{\nu}_{jk}(h^{-1})\zeta(h) \\
&= \sum_{k=1}^{d_\nu} D^{\nu}_{ki}(g)\, P^{\nu}_{kj}\ . \qquad (3.40)
\end{aligned}$$

Now, by use of the orthogonality relations (3.37) and (3.40), we conclude that:

$$P^{\mu}_{kl} P^{\nu}_{ij} = \frac{d_\mu}{|\mathcal{G}|} \sum_{g\in\mathcal{G}} D^{\mu}_{lk}(g^{-1}) \sum_{m=1}^{d_\mu} D^{\nu}_{mi}(g) P^{\nu}_{mj} = \delta_{li}\, \delta_{\mu\nu}\, P^{\nu}_{kj}\ . \qquad (3.41)$$

The above expression immediately yields a few results. First, we conclude that $P^{\mu}_{ii}\, P^{\nu}_{jj} = \delta_{ij}\, \delta_{\mu\nu}\, P^{\nu}_{ij}$. Therefore, if V^{ν}_{ii} denotes the image of H under P^{ν}_{ii}, then the V^{ν}_{ii} are mutually orthogonal. The formulas also show that $P^{\nu}_{ii} P^{\nu}_{ii} = P^{\nu}_{ii}$ and since P^{ν}_{ii} are self-adjoint, we conclude that the P^{ν}_{ii} are in fact orthogonal projectors onto the ranges V^{ν}_{ii}.

To see that we actually obtain the decomposition (3.39), we can argue by contradiction. We introduce the projection operators associated with the irreducible representations, that is:

$$Q^{\nu} = \sum_{i=1}^{d_\nu} P^{\nu}_{ii} = \frac{d_\nu}{|\mathcal{G}|} \sum_{g\in\mathcal{G}} \overline{\mathrm{Tr.}(\zeta^{\nu}(g))}\, \zeta(g) \quad . \qquad (3.42)$$

clearly, for $\nu = 1, \ldots, \ell$, the range of the operators Q^{ν} is obtained as:

$$V^{\nu} = Q^{\nu}(\mathsf{H}) = \bigoplus_i V^{\nu}_{ii} \quad . \qquad (3.43)$$

We may easily check using (3.41) that the operators Q^{ν} obey:

$$Q^{\nu} Q^{\mu} = \delta_{\mu\nu} Q^{\mu} \quad , \qquad (3.44)$$

and so, V^ν form mutually orthogonal subspaces of H. Let us form:

$$W = \bigoplus_{\nu} V^\nu = \bigoplus_{i,\nu} V_{ii}^\nu \quad . \tag{3.45}$$

For the sake of contradiction, if $W \neq \mathsf{H}$, then the orthogonal complement $W^\perp$ of W in H would be an invariant subspace (by Theorem 3.2.5) and so the restriction of ζ to $W^\perp$ would be a sub-representation. Then, we would be able to find $Y \subseteq W^\perp$, such that Y is an irreducible subspace. But this would contradict the fact that the list of irreducible representations $\zeta^\nu, \nu = 1, \ldots, \ell$, which are the restrictions of ζ to all possible irreducible subspaces, is exhaustive.[12] ■

Remark 3.2.16. As a consequence of the above results, we may obtain an interpretation of the operators P_{ij}^ν as isomorphisms. Specifically, the operator P_{ji}^ν maps the space V_{ii}^ν onto the space V_{jj}^ν injectively. The proof of this result follows directly from the identities $P_{ii}^\nu P_{ij}^\nu = P_{ij}^\nu$, $P_{ij}^\nu P_{jj}^\nu = P_{ij}^\nu$ and $P_{ij}^\nu P_{ji}^\nu = P_{ii}^\nu$, all of which follow from (3.41). We note that these formulas also imply that the image of H under P_{ij}^ν is in V_{ii}^ν and that P_{ij}^ν maps to zero outside V_{jj}^ν. Thus, given $w \in \mathsf{H}$, we observe that P_{ij}^ν will "pick out" the component of w in V_{jj}^ν and it will map this component to its counterpart in V_{ii}^ν.

Armed with the large body of results developed in this chapter, we now turn back to the electronic structure computation problem. In the next chapter, we will apply the ideas developed in this chapter, to the electronic structure computation problem, for objective structures generated by finite groups of isometries.

[12] In essence, this is a restatement of Theorem 3.2.13.

Chapter 4

Calculations on Finite Groups

In this chapter, we analyze the electronic structure computation problem of objective structures generated by finite groups of isometries. We use the tools developed in the previous chapter to characterize the effect of symmetry on a simplified version of the Kohn-Sham equations (2.19-2.21). We begin with a discussion of these simplifications. The strategy that we use for obtaining the simplifications is to look at the generic form of the numerical problem that we aim to solve as an approximation of the problem (2.19-2.21). As we shall see, this will involve simplifying the domain on which the problem is set up, simplification of the potentials that appear in the Kohn-Sham equations, as well as replacement of these equations themselves by a self consistent iteration procedure that solves a linear eigenvalue problem at each stage.

4.1 Problem Set Up and Simplification

Let $\mathcal{S}$ be a fixed point free objective structure generated by the finite group of isometries $\mathcal{G}$ acting on the finite set M. A finite group of isometries consists of (proper or improper) rotations which have at least one common fixed point Dayal et al. [2010], and we may assume that this fixed point is the origin, without any loss of generality.

We suppose that M consists of the points $\{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_m\} \subset \mathbb{R}^3$. We suppose further that $\{Z_1, Z_2, \ldots, Z_m\}$ are the respective nuclear charges associated with these points and we let $|\mathcal{G}|$ denote the group order. We are interested in computing the electronic structure of $\mathcal{S}$ and we intend to use the Kohn-Sham model of Density Function Theory (outlined in Chapter 2, Section 2.2.3) for doing so. For the purpose of this calculation, we assume that the objective structure consists of $m|\mathcal{G}|$ nuclei and n electrons. The electronic structure

associated with the objective structure is therefore obtained by the solving the variational problem:

$$I_n^{KS} = \inf_{\phi_i \in \mathsf{H}^1(\mathbb{R}^3)} \left\{ \frac{1}{2} \sum_{i=1}^{n} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho V_{nu} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \, d\mathbf{x}\, d\mathbf{y} \right.$$
$$\left. + E_{xc}(\rho) : \langle \phi_i, \phi_j \rangle_{L^2} = \delta_{ij} \right\} \quad . \tag{4.1}$$

The electronic density ρ and the nuclear potential V_{nu} are respectively given as:

$$\rho(\mathbf{x}) = \sum_{i=1}^{n} |\phi_i(\mathbf{x})|^2, \quad V_{nu}(\mathbf{x}) = -\sum_{\Upsilon \in \mathcal{G}} \sum_{i=1}^{m} \frac{Z_i}{|\mathbf{x} - \Upsilon(\mathbf{x}_i)|} \quad . \tag{4.2}$$

Since we are only interested in bound states of the system, that is, states in which the electrons do not escape to infinity, we will typically need to enforce the condition on the total nuclear charge Z:

$$Z = |\mathcal{G}| \sum_{i=1}^{m} Z_i \geq n \quad . \tag{4.3}$$

Under these conditions, for commonly used approximations of $E_{xc}(\rho)$ (such as those discussed in Section 2.2.3, it is possible to show that problem (4.1) admits the existence of a minimizer [Le Bris, 1993]. The question of uniqueness however, is unknown [Le Bris, 2003].

4.1.1 Simplification of Domain and Boundary Conditions on Electronic Density

One of the key difficulties that one has to overcome while analyzing (4.1) is that it is a locally compact problem posed on a noncompact domain in the following sense [Defranceschi and Le Bris, 1997]: if one restricts the problem to one posed on an open subset of $\mathbb{R}^3$ that has compact closure, then proving existence of solutions is relatively straightforward. The problem posed on the whole space on the other hand, is much more difficult to deal with. As far as numerical computations are concerned however, we will always be interested in computing solutions on a connected, bounded open set with a regular boundary. Hence the first simplification that we will assume is that the objective structure $\mathcal{S}$ is embedded in a large sphere of radius R centered at the origin and we will apply the boundary condition $\rho(\mathbf{x}) = 0$ on the surface of the sphere to account for the fact that the electronic density of a finite system is known to have exponential decay far away from the system. This will automatically imply via (4.2) that the $\phi_i(\mathbf{x})$ that appear in the Kohn-Sham model will also obey $\phi_i(\mathbf{x}) = 0$ whenever $|\mathbf{x}| = R$.

The particular choice of R is to be dictated by the decay properties of the exact electronic density (defined via equation 2.12) associated with the structure. Specifically, it is known from Hoffmann-Ostenhof et al. [1980] and Ahlrichs et al. [1981] for example, that at large distances from any nucleus the square root of the electronic density of an n-electron system with total nuclear charge Z and first ionization potential ϵ obeys:

$$\sqrt{\rho(\mathbf{x})} \leq C\,(1+|\mathbf{x}|)^{(Z-n+1)/\sqrt{2\epsilon}-1}\ \exp\left(-\sqrt{2\epsilon}\,|\mathbf{x}|\right) \quad . \tag{4.4}$$

Thus, as far as the analysis of the problem is concerned, we will not make any particular specification of R other than it has to be finite but "sufficiently large" in the sense that the $\rho(\mathbf{x}) = 0$ boundary condition is commensurate with (4.4). The computational domain however will be limited by computational resources and so, in general it will be a somewhat smaller sphere of radius R_c. This situation is illustrated in Figure 4.1. It is not uncommon

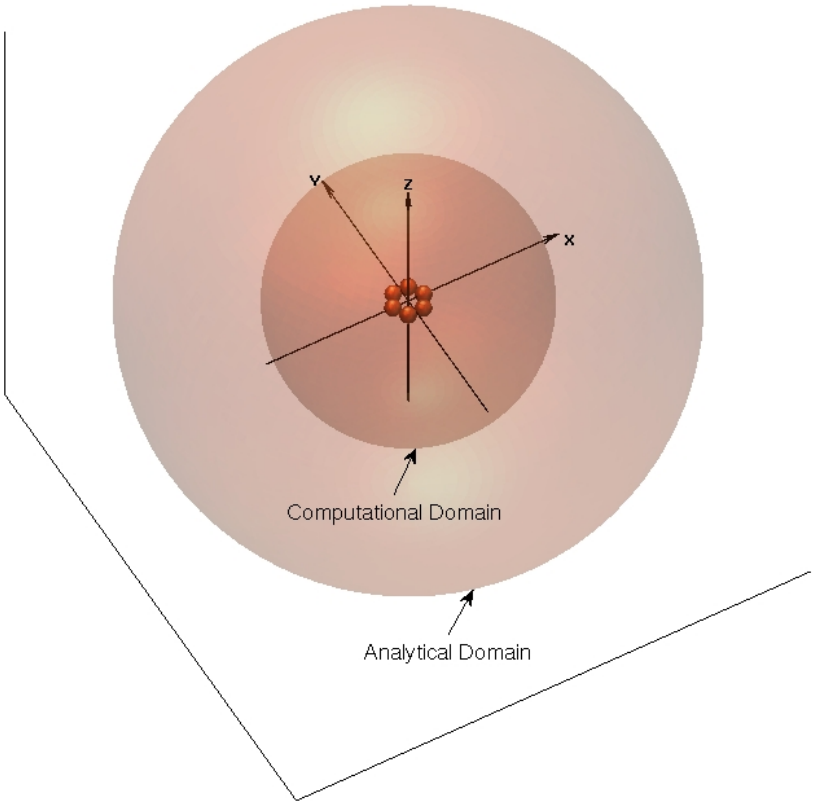

Figure 4.1: Schematic of Problem set up: An objective structure (ring of atoms) embedded in a spherical computational domain of radius R_c. The analytical domain is a sphere of much larger radius R. (Figure not to scale.)

in the DFT literature to encounter real space codes which embed the molecular system of interest in a sphere of a large radius [for example, Chelikowsky et al., 1994; Jing et al., 1994]. As far as the analysis of the problem is concerned, the choice of a spherical domain is particularly useful to us because such a domain possesses a C^∞ boundary and the isometric group action of any finite set of rotations is well defined for points belonging to a sphere.

4.1.2 Linearization via Self Consistent Field Iterations

Let $\mathcal{B}_R$ denote the open ball of radius R centered at the origin. Based on the above discussion, the problem at hand now reads as:

$$\tilde{I}_n^{KS} = \inf_{\phi_i \in \mathsf{H}_0^1(\mathcal{B}_R)} \left\{ \frac{1}{2} \sum_{i=1}^{n} \int_{\mathcal{B}_R} |\nabla \phi_i|^2 + \int_{\mathcal{B}_R} \rho V_{nu} + \frac{1}{2} \int_{\mathcal{B}_R} \int_{\mathcal{B}_R} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \, d\mathbf{x}\, d\mathbf{y} \right.$$
$$\left. + E_{xc}(\rho) : \langle \phi_i, \phi_j \rangle_{L^2(\mathcal{B}_R)} = \delta_{ij} \right\} \quad . \tag{4.5}$$

Since each ϕ_i lies in the space $\mathsf{H}_0^1(\mathcal{B}_R)$ (this is simply the closure of $\mathsf{C}_c^\infty(\mathcal{B}_R)$ in the H^1 norm), we need to interpret the boundary conditions $\phi_i(\mathbf{x}) = 0, \forall \mathbf{x} \in \partial\mathcal{B}_R$ in the trace sense. Let us remark at this stage that a standard line of argument employing the direct method in the calculus of variations can be used to prove the existence of solutions to problem (4.5) for E_{xc} given by common parametrizations of the Local Density Approximation. Thus, a systematic check of the weak lower semicontinuity and the coercivity properties of the functional suffice to show that $\mathsf{H}_0^1(\mathcal{B}_R)$ solutions to (4.5) exist. Details of such an argument may be found in Suryanarayana et al. [2010].

Like many of the standard real space algorithms of Kohn-Sham Density Functional Theory (see for example Chelikowsky et al. [1994] or Martin [2004]), we now choose to work with the Euler-Lagrange equations of the variational problem (4.5), that is the Kohn-Sham equations posed on the ball with Dirichlet boundary conditions:

$$\left(-\frac{1}{2}\Delta + V_{nu}(\mathbf{x}) + \left(\int_{\mathcal{B}(R)} \frac{\rho(\mathbf{x})}{|\mathbf{y}-\mathbf{x}|} \, d\mathbf{x} \right) + V_{xc}(\rho(\mathbf{x})) \right) \phi_i(\mathbf{x}) = \lambda_i \phi_i(\mathbf{x}) \quad , \tag{4.6}$$

$$\langle \phi_i, \phi_j \rangle_{L^2(\mathcal{B}(R))} = \delta_{ij}, \quad \rho(\mathbf{x}) = \sum_{i=1}^{n} |\phi_i(\mathbf{x})|^2 \quad , \tag{4.7}$$

$$\text{and for } \mathbf{x} \in \partial\mathcal{B}(R), \quad \phi_i(\mathbf{x}) = 0 \quad . \tag{4.8}$$

As we remarked earlier, the usual method of solution of this set of non-linear equations is

to introduce a self-consistent iteration scheme. Let us make this a little more precise since this is effectively the process by which we achieve a linearization of (4.6). First, we may lump all but the first term that appears on the left hand of (4.6) into a single term $\tilde{V}(\mathbf{x}, \rho(x))$ to write:

$$\Big(-\frac{1}{2}\Delta + \tilde{V}(\mathbf{x}, \rho(x))\Big)\phi_i(\mathbf{x}) = \lambda_i \phi_i(\mathbf{x}) \quad . \tag{4.9}$$

To solve this iteratively, we suppose that we have a guess for the ground state electronic density of the system $\rho^k(\mathbf{x})$ at some stage of the iteration. We may now define the following update scheme for $0 < \tilde{\alpha} < 1$:

$$V^k(\mathbf{x}) = \tilde{V}(\mathbf{x}, \rho^k(\mathbf{x})) \quad , \tag{4.10}$$

$$\Big(-\frac{1}{2}\Delta + V^k(\mathbf{x})\Big)\phi_i^{k+1}(\mathbf{x}) = \lambda_i^{k+1}\phi_i^{k+1}(\mathbf{x}), \text{ (for } i = 1, \ldots, n) \quad , \tag{4.11}$$

$$\rho^{k+1}(\mathbf{x}) = \tilde{\alpha}\left(\sum_{i=1}^{n} |\phi_i^{k+1}(\mathbf{x})|^2\right) + (1 - \tilde{\alpha})\,\rho^k(\mathbf{x}) \quad . \tag{4.12}$$

We could now hope that for a good enough initial guess $\rho^1(\mathbf{x})$, the above iteration would converge to an actual solution of (4.6-4.7) and satisfy the boundary condition (4.8). Thus, (4.10-4.12) form a linear approximation of the original problem in this sense. In an actual simulation, a typical choice for $\rho^1(\mathbf{x})$ would be to obtain it from the atomic orbitals of the constituent atoms [Le Bris, 2003].

The above discussion motivates the study of the following linearized eigenvalue problem (posed on the open ball of radius R) for a suitable class of "effective" potentials $V(\mathbf{x})$:

$$\Big(-\frac{1}{2}\Delta + V(\mathbf{x})\Big)\phi_i(\mathbf{x}) = \lambda_i \phi_i(\mathbf{x}), \quad \phi_i(\mathbf{x}) = 0 \text{ on } \partial\mathcal{B}_R \quad (i = 1, \ldots, n). \tag{4.13}$$

We aim to study how the above eigenvalue problem interacts with the symmetry group of a finite objective structure later in this chapter. First however, we need to characterize the relevant class of effective potentials and the generic properties of the above eigenvalue problem (4.13). We carry out this study next.

4.1.3 Characterization of the Effective Potential

Let us assume for the moment that the electronic density ρ is a known function and that ρ is continuous and compactly supported on the closure of $\mathcal{B}_R$, that is, we let $\rho \in \mathsf{C}_c^0(\mathcal{B}_R)$.

The effective potential is given as:

$$V(\mathbf{x}) = \tilde{V}(\rho, \mathbf{x}) = V_{xc}(\rho(\mathbf{x})) + \int_{\mathcal{B}_R} \frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} + V_{nu}(\mathbf{x}) \quad . \tag{4.14}$$

Let us examine the above expression term by term. One of the most common parametrizations of the Local Density Approximation form for V_{xc} is due to Perdew and Zunger [1981] and Ceperley and Alder [1980] and it is of the following form:

$$\begin{aligned}
V_{xc}(\rho) &= V_x(\rho) + V_c(\rho) \quad . \\
V_x(\rho) &= \Big(\epsilon_x(\rho) + \rho \frac{d\,\epsilon_x(\rho)}{d\rho}\Big), \quad V_c(\rho) = \Big(\epsilon_c(\rho) + \rho \frac{d\,\epsilon_c(\rho)}{d\rho}\Big) \quad . \\
\epsilon_x(\rho) &= -\frac{3}{4}\Big(\frac{3}{\pi}\Big)^{1/3} \rho^{1/3} \quad . \\
\epsilon_c(\rho) &= \begin{cases} \frac{\gamma}{1+\beta_1\sqrt{r_s}+\beta_2 r_s} & \text{for } r_s \geq 1 \quad . \\ A\log r_s + B + C r_s \log r_s + D r_s & \text{for } r_s < 1 \quad . \end{cases} \\
\text{where, } r_s &= \Big(\frac{3}{4\pi\rho}\Big)^{1/3} \quad .
\end{aligned} \tag{4.15}$$

The coefficients $A, B, C, D, \gamma, \beta_1, \beta_2$ are chosen such that, among other things, $\epsilon_c(\rho)$ has a continuous first derivative at $r_s = 1$. It is quite clear that $V_x(\rho)$ is a continuous function. If we make the additional hypothesis that $\epsilon_c(0) = 0$, we see that $V_c(\rho)$ also becomes a continuous function thus making V_{xc} continuous in our region of interest. Unfortunately however, we can't say that V_{xc} is any more regular than this, since the first derivative of V_x blows up near zero.

The second term, that is, the Coulombic interaction between the electrons is better behaved. We may invoke results from potential theory [Gilbarg and Trudinger, 2001] to tell us that if ρ is Hölder continuous, then for $V_H(\mathbf{x}) = \int_{\mathcal{B}_R} \frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, dy$, we must have $V_H \in \mathsf{C}^2(\mathcal{B}_R)$ and and that it must satisfy the boundary value problem:

$$\begin{aligned}
-\Delta V_H &= 4\pi\rho \quad \text{for } \mathbf{x} \in \mathcal{B}_R \quad , \\
V_H(\mathbf{x}) &= \int_{\mathcal{B}_R} \frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \quad \text{for } \mathbf{x} \in \partial\mathcal{B}_R \quad .
\end{aligned} \tag{4.16}$$

Apart from demonstrating the above regularity property, this result is also quite useful to use at the numerical level, especially when large numerical simulations are involved: the integral expression for V_H is often much more expensive computationally, than solving the Poisson problem (4.16) by a conjugate gradient solver [Chelikowsky et al., 1994].

The last term arises due to the nuclear interaction and it is also of a Coulombic nature. The standard Coulombic term is not continuous at the location of the nuclei. It is therefore, very common in the DFT literature to replace this term by a smooth approximation [Le Bris, 2003; Martin, 2004] for the purpose of numerical simulation.[1] We will adopt this approximation in this work. One of the simplest ways to achieve this is to assume that a nuclear charge is not concentrated at a specific point but that it is smeared out as a smooth function supported on a small ball B_δ centered on the location of the nucleus. The expression for V_{nu} in (4.2) gets replaced by:

$$V_{nu}(\mathbf{x}) = \sum_{\Upsilon \in \mathcal{G}} \sum_{i=1}^{m} \int_{B_\delta(\Upsilon(\mathbf{x}_i))} \frac{Z_i \, b(|\mathbf{y} - \Upsilon(\mathbf{x}_i)|)}{|\mathbf{x} - \mathbf{y}|} \, d\mathbf{y} \quad , \tag{4.17}$$

where, $b(|\mathbf{y} - \mathbf{x}_i|)$ is a smooth radially symmetric charge distribution such that:

$$\int_{B_\delta(\mathbf{x}_i)} b(|\mathbf{y} - \mathbf{x}_i|) \, d\mathbf{y} = 1 \quad . \tag{4.18}$$

Since $b \in \mathsf{C}_c^\infty(B_\delta)$, it must be that $V_{nu}(\mathbf{x})$ is smooth [Gilbarg and Trudinger, 2001].

We will now prove a rather simple result which in some sense, forms the basis for the rest of the work presented in this thesis:

Lemma 4.1.1. *Let us suppose that the electronic density of the objective structure $\mathcal{S}$ is continuous, and that it inherits the symmetry of the structure, that is:*

$$\forall \mathbf{x} \in \mathcal{B}_R, \forall \Upsilon \in \mathcal{G}, \rho(\Upsilon(\mathbf{x})) = \rho(\mathbf{x}) \quad . \tag{4.19}$$

Then, the effective potential $V(x)$ is also continuous on $\mathcal{B}_R$ and it inherits the symmetry of the objective structure.

Proof: The continuity of V is required to ensure that we may investigate the behavior of $V(\mathbf{x})$ pointwise. From the preceding discussion, since V_{xc} is continuous in ρ, and ρ has been assumed continuous, $V_{xc}(\mathbf{x})$ must be a continuous function of $\mathbf{x}$. The nuclear contribution through (4.17) is also continuous. That, V_H is continuous if ρ is continuous, can be easily justified by potential theory results [Gilbarg and Trudinger, 2001]. Hence, the sum of V_{xc}, V_{nu} and V_H is a continuous function of $\mathbf{x}$.

[1] This is the commonly referred to as the pseudopotential approximation. Another motivation for using a pseudopotential is that they can be formulated in a way such that only valence electrons have to be solved for in the resulting Kohn-Sham equations. The core electrons are usually chemically inert and do not play an important role in most chemical and physical processes.

Now, for arbitrary $\mathbf{x} \in \mathcal{B}_R, \forall \Upsilon \in \mathcal{G}$, we can investigate the effect of the change $\mathbf{x} \mapsto \Upsilon(\mathbf{x})$ by looking at how $V_{xc}(\mathbf{x}), V_H(\mathbf{x})$ and $V_{nu}(\mathbf{x})$ behave. From the parametrizations presented in (4.15), it is clear that V_{xc} respects the symmetry of the objective structure since it is an explicit function of ρ and $\rho(\mathbf{x})$ respects the symmetry of the objective structure. Considering now, the representation formula for V_H, we have, by the change of variables $\mathbf{y} = \Upsilon(\mathbf{z})$:

$$\begin{aligned} V_H(\Upsilon(\mathbf{x})) = \int_{\mathcal{B}_R} \frac{\rho(\mathbf{y})}{|\Upsilon(\mathbf{x}) - \mathbf{y}|}\, d\mathbf{y} &= \int_{\Upsilon^{-1}(\mathcal{B}_R)} \frac{\rho(\Upsilon(\mathbf{z}))}{|\Upsilon(\mathbf{x}) - \Upsilon(\mathbf{z})|}\, d\mathbf{z} \\ &= \int_{\mathcal{B}_R} \frac{\rho(\mathbf{z})}{|\mathbf{x} - \mathbf{z}|}\, d\mathbf{z} = V_H(\mathbf{x}) \quad . \end{aligned} \tag{4.20}$$

This verifies that this contribution to the potential also inherits the symmetry of the objective structure. Finally, considering the nuclear contribution through (4.17), we have by the same change of variables $\mathbf{y} = \Upsilon(\mathbf{z})$:

$$\begin{aligned} V_{nu}(\Upsilon(\mathbf{x})) &= \sum_{\Upsilon_1 \in \mathcal{G}} \sum_{i=1}^{m} \int_{B_\delta(\Upsilon_1(\mathbf{x}_i))} \frac{Z_i\, b(|\mathbf{y} - \Upsilon_1(\mathbf{x}_i)|)}{|\Upsilon(\mathbf{x}) - \mathbf{y}|}\, d\mathbf{y} \\ &= \sum_{\Upsilon_1 \in \mathcal{G}} \sum_{i=1}^{m} \int_{\Upsilon^{-1}(B_\delta(\Upsilon_1(\mathbf{x}_i)))} \frac{Z_i\, b(|\Upsilon(\mathbf{z}) - \Upsilon(\Upsilon^{-1} \circ \Upsilon_1(\mathbf{x}_i))|)}{|\Upsilon(\mathbf{x}) - \Upsilon(\mathbf{z})|}\, d\mathbf{z} \\ &= \sum_{\Upsilon_1 \in \mathcal{G}} \sum_{i=1}^{m} \int_{(B_\delta(\Upsilon^{-1} \circ \Upsilon_1(\mathbf{x}_i)))} \frac{Z_i\, b(|\mathbf{z} - \Upsilon^{-1} \circ \Upsilon_1(\mathbf{x}_i)|)}{|\mathbf{x} - \mathbf{z}|}\, d\mathbf{z} \\ &= \sum_{(\Upsilon^{-1} \circ \Upsilon_1) \in \mathcal{G}} \sum_{i=1}^{m} \int_{(B_\delta(\Upsilon^{-1} \circ \Upsilon_1(\mathbf{x}_i)))} \frac{Z_i\, b(|\mathbf{z} - \Upsilon^{-1} \circ \Upsilon_1(\mathbf{x}_i)|)}{|\mathbf{x} - \mathbf{z}|}\, d\mathbf{z} \\ &= V_{nu}(\mathbf{x}) \quad . \end{aligned} \tag{4.21}$$

Thus, the effective potential $V(\mathbf{x})$ inherits the symmetry of the objective structure. ■

In our simplified framework therefore, we are led to the study of the a Schrödinger operator with an effective potential which is continuous and group invariant. We next summarize some results related to this eigenvalue problem.

4.2 Study of the simplified eigenvalue problem

The Kohn Sham equations (and its simplifications considered in this work) require that we evaluate the lowest n eigenvalues and corresponding eigenfunctions of the Kohn Sham operator. Even for the simplified eigenvalue problem however, it is not clear apriori that there

exist eigenvalues and corresponding eigenfunctions since, from the material in Appendix A.3 there exist numerous possibilities in an infinite dimensional setting. In particular, it is quite possible to have linear operators that do not possess eigenfunctions at all. In the langauage of Appendix A.3, we find it necessary to investigate existence of a point spectrum in our simplified problem. The canonical approach to this, is to use the weak theory of elliptic equations [Gilbarg and Trudinger, 2001; Evans, 1998; Renardy and Rogers, 2004] as discussed below.

4.2.1 Existence of Eigenvalues & Eigenfunctions

In light of the discussion in the previous section, our starting point is the consideration of the operator $\mathfrak{H} = -\frac{1}{2}\Delta + V$, on the function space $\mathsf{L}^2(\mathcal{B}_R)$, with $V(\mathbf{x})$ a continuous and group invariant potential. It turns out that $\mathfrak{H}$ is an unbounded operator which is is densely defined on the domain $\mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}_0^1(\mathcal{B}_R)$ [2]. The operator is clearly symmetric, since for any $u, v \in \mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}_0^1(\mathcal{B}_R)$, we can show, using integration by parts:

$$\langle \mathfrak{H}u, v\rangle_{\mathsf{L}^2(\mathcal{B}_R)} = \langle u, \mathfrak{H}v\rangle_{\mathsf{L}^2(\mathcal{B}_R)} \, . \tag{4.22}$$

Study of the weak form of the eigenvalue problem (4.13) allows us to establish the existence of eigenvalues and associated eigenvectors. To interpret the eigenvalue problem associated with $\mathfrak{H}$ in a weak sense, we have to introduce the sesquilinear form $\mathfrak{B} : \mathsf{H}_0^1(\mathcal{B}_R) \times \mathsf{H}_0^1(\mathcal{B}_R) \to \mathbb{C}$ associated with $\mathfrak{H}$. For any $u, v \in \mathsf{H}_0^1(\mathcal{B}_R)$, we let:

$$\mathfrak{B}[u, v] = \int_{\mathcal{B}_R} \frac{1}{2}\nabla u.\nabla \overline{v} + V u \overline{v} \, d\mathbf{x} \quad , \tag{4.23}$$

and we say that $\{\lambda \in \mathbb{C}, v \in \mathsf{H}_0^1(\mathcal{B}(R))\}$ is an eigenvalue-eigenvector pair for the operator $\mathfrak{H}$ in the weak sense if:

$$\mathfrak{B}[u, v] = \lambda \langle u, v\rangle_{\mathsf{L}^2(\mathcal{B}_R)} \quad \forall v \in \mathsf{H}_0^1(\mathcal{B}_R) \quad . \tag{4.24}$$

Using the Poincaré inequality, the Lax-Milgram lemma and the Rellich-Kondrachov theorem [Evans, 1998; Renardy and Rogers, 2004; Kato, 1995] we can show that the resolvent operator $R_\kappa = (\mathfrak{H} - \kappa I)^{-1}$ of $\mathfrak{H}$ (for κ belonging to the resolvent set of $\mathfrak{H}$), is a compact self-adjoint operator on $\mathsf{L}^2(\mathcal{B}_R)$. The spectral theorem for compact-self adjoint operators [Naylor and Sell, 1971; Kato, 1995] can therefore, be used on R_κ to prove the existence of

[2] Refer to Evans [1998] or Renardy and Rogers [2004] for the standard definitions of the Sobolev spaces $\mathsf{H}^2(\mathcal{B}_R)$ and $\mathsf{H}_0^1(\mathcal{B}_R)$

an increasing sequence of real eigenvalues and associated eigenfunctions[3], which form an orthonormal basis of $\mathsf{L}^2(\mathcal{B}_R)$. This finally allows us to conclude that $\mathfrak{H}$ indeed has a point spectrum, and that there exist weak solutions to the problem (4.24). We may summarize the above discussion as follows:

Theorem 4.2.1. *For $V(\mathbf{x}) \in \mathsf{C}(\mathcal{B}_R)$, the operator $\mathfrak{H} = -\frac{1}{2}\Delta + V$ has a compact self-adjoint resolvent $R_\kappa : \mathsf{L}^2(\mathcal{B}_R) \to \mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}^1_0(\mathcal{B}_R)$. The operator $\mathfrak{H}$ therefore, has an increasing sequence of real eigenvalues of finite multiplicity $\lambda_1 \leq \lambda_2 \leq \ldots \leq \lambda_i \leq \ldots$ such that $\lambda_i \to \infty$ as $i \to \infty$. Further, there is an orthonormal basis $\{\phi_i\}_{i\in\mathbb{N}}$ of $\mathsf{L}^2(\mathcal{B}_R)$ consisting of the eigenfunctions $\{\phi_i\}_{i\in\mathbb{N}} \in \mathsf{H}^1_0(\mathcal{B}_R)$ such that $\mathfrak{H}\phi_i = \lambda_i\phi_i$ holds in the weak sense.*

We now move on to the issue of regularity of the eigenfunctions since they play some role in the self-consistent iterations.

4.2.2 Comments on the Regularity of Eigenfunctions

The next natural question that we need to concern ourselves with is, how regular the eigenfunctions of the operator $\mathfrak{H}$ are. In the light of self-consistent iterations, this is very important, since regularity of the eigenfunctions of $\mathfrak{H}$ dictate the regularity of the resulting density and hence, the regularity of the effective potential that appears in the next step of the self consistent iterations. Fortunately, theorems from the theory of elliptic partial differential equations can again be invoked to acquire this information. Since $V \in \mathsf{C}(\mathcal{B}_R) \subset \mathsf{L}^\infty(\mathcal{B}_R)$ and we are working on a domain with a smooth boundary, we may conclude that any eigenfunction $\phi \in \mathsf{H}^2(\mathcal{B}_R)$ [Theorem 4 in Chapter 6 of Evans, 1998]. We may then invoke general Sobolev inequalities [Theorem 6 in Chapter 5 of Evans, 1998] to conclude that ϕ Hölder continuous on $\mathcal{B}_R$ with the Hölder exponent $= 0.5$. As far as the self-consistent scheme is concerned, this is already quite good since this means that the density obtained from these eigenfunctions will be regular enough to yield a continuous effective potential for the next step of the iterations. We may however, sharpen the above regularity results considerably by using theorems from potential theory [specifically, Theorem 3.1 in Chapter 3 of Han and Lin, 2000] to conclude that even the gradient of ϕ is actually Hölder continuous. Among other things therefore, these theorems tell us that it makes sense to interpret values of the eigenfunctions and their gradients pointwise. This is useful from the perspective of implementation of boundary conditions in numerical methods as well as the analysis of convergence properties of these numerical methods.

[3]Refer to Appendix A, section A.3 for some relevant definitions.

4.3 Symmetry and the Simplified Eigenvalue Problem

We are now ready to analyze the interaction of the isometry group $\mathcal{G}$, of the given objective structure $\mathcal{S}$, with the simplified eigenvalue problem associated with electronic structure calculation of $\mathcal{S}$. Most of the abstract theory worked out in Chapter 3 works for *any* unitary representations of a discrete group of isometries on *any* Hilbert space. As far as the simplified eigenvalue problem associated with electronic structure calculation is concerned, the function space that is of most interest to us is $\mathsf{L}^2(\mathcal{B}_R)$. Here again, results from Chapter 3 (specifically, Lemma 3.2.2 and Theorem 3.2.3) already tell us how to obtain group representations. We need to focus mainly on the consequences of Schur's Lemma (Theorem 3.2.10) as it applies to our problem.

4.3.1 Representations on $\mathsf{L}^2(\mathcal{B}_R)$: Block Diagonalization of the Resolvent

In the context of Lemma 3.2.2 let us consider $S = \mathcal{B}_R$ and equip $\mathcal{B}_R$ with the Lebesgue measure[4]. Then Theorem 3.2.3 allows us to construct a unitary representation ζ of $\mathcal{G}$ on the carrier space $\mathsf{L}^2(\mathcal{B}_R)$. We denote the set of unitary operators associated with this unitary representation as $L_{\mathcal{G}} = \{T_g = \zeta(g) : g \in \mathcal{G}\}$. As in Chapter 3, let us denote the unitary irreducible representations of $\mathcal{G}$ as $\zeta^\nu, \nu = 1, \ldots, \ell$ and let us denote the matrix components of ζ^ν as $D^\nu_{ij}\ , i, j = 1, \ldots, \delta_\nu$.

We will first show that for a potential that is associated with the objective structure, the operator $\mathfrak{H}$ on its domain $\mathrm{Dom.}(\mathfrak{H}) = \mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}^1_0(\mathcal{B}_R)$ commutes with each of the operators in $L_{\mathcal{G}}$. To see this, let us consider any $f \in \mathsf{C}^2_c(\mathcal{B}_R), g \in \mathcal{G}$ and observe that since the mapping $\mathbf{x} \mapsto \mathbf{R}_g^T\mathbf{x} - \mathbf{c}_g = g^{-1} \bullet \mathbf{x}$ leaves the Laplacian invariant. [5] The potential V is also group invariant by Lemma 4.1.1, and so we have:

$$\begin{aligned} T_g \cdot \mathfrak{H}[f(\mathbf{x})] &= T_g[(-\frac{1}{2}\Delta f)(\mathbf{x}) + (Vf)(\mathbf{x})] = (-\frac{1}{2}\Delta f)(g^{-1} \bullet \mathbf{x}) + (Vf)(g^{-1} \bullet \mathbf{x}) \\ &= (-\frac{1}{2}\Delta f)(g^{-1} \bullet \mathbf{x}) + V(\mathbf{x}) f(g^{-1} \bullet \mathbf{x}) \quad . \end{aligned} \tag{4.25}$$

On the other hand, we also have:

$$\mathfrak{H} \cdot T_g[f(\mathbf{x})] = (-\frac{1}{2}\Delta + V)[f(g^{-1} \bullet \mathbf{x})] = (-\frac{1}{2}\Delta f)(g^{-1} \bullet \mathbf{x}) + V(\mathbf{x}) f(g^{-1} \bullet \mathbf{x}) \quad . \tag{4.26}$$

Hence, $T_g \cdot \mathfrak{H}[f(\mathbf{x})] = \mathfrak{H} \cdot T_g[f(\mathbf{x})]$. By the density of $\mathsf{C}^2_c(\mathcal{B}_R)$ in $\mathrm{Dom.}(\mathfrak{H}) = \mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}^1_0(\mathcal{B}_R)$, we may now extend the above calculation to the domain of $\mathfrak{H}$ to conclude that $\mathfrak{H}$

[4] The Lebesgue measure is a Radon measure and it is group invariant.

[5] This is easily verified by a change of variables calculation.

commutes with each of the operators in $L_{\mathcal{G}}$. [6]

At this point, we would like to invoke Schur's Lemma and its results from Chapter 3 to come to conclusions about the structure of $\mathfrak{H}$. The technical issue however, is that $\mathfrak{H}$ is an unbounded operator on $\mathsf{L}^2(\mathcal{B}_R)$. On the other hand Schur's Lemma concerns bounded operators. [7] We may avoid this annoying technicality by dealing with the resolvent operator of $\mathfrak{H}$[8]. This suits our purpose particularly well since the resolvent $R_\kappa : \mathsf{L}^2(\mathcal{B}_R) \to \mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}^1_0(\mathcal{B}_R)$ of the operator $\mathfrak{H}$ is self-adjoint and compact for any κ belonging to the resolvent set (by Theorem 4.2.1). To proceed further, we first note the following two results:

Proposition 4.3.1. *Let A : Dom.$(A) \subset \mathcal{X} \to \mathcal{X}$ be a closed linear operator[9] on the Banach space $\mathcal{X}$, such that the resolvent set of A is non-empty. Let B be a bounded linear operator on $\mathcal{X}$. Then, A commutes with B if and only if the resolvent $\mathcal{R}(\kappa, A)$ of A, commutes with B for some, and hence every κ in the resolvent set of A.*

Proof: We recall that A commutes with B means that $B\big(\text{Dom.}(A)\big) \subset \text{Dom.}(A)$ and that for every $y \in \text{Dom.}(A)$, we have $BAy = ABy$. Clearly, this happens if and only if $(A - \kappa I)$ and B commute for any $\kappa \in \mathbb{C}$. Now, for $y \in \text{Dom.}(A)$, and any κ in the resolvent set of A, we consider the expression $(A - \kappa I)By = B(A - \kappa I)y$. Since κ is in the resolvent set, $(A - \kappa I)^{-1}$ is a bounded linear operator. So we may operate on the above expression with $(A - \kappa I)^{-1}$ to conclude that A commutes with B if and only if $By = (A - \kappa I)^{-1}B(A - \kappa I)y$ for every $y \in \text{Dom.}(A)$. Now, since A is a closed operator, the closed graph theorem [Folland, 1999] can be used to extend $(A - \kappa I)^{-1} : \text{Ran.}(A - \kappa I) \to \text{Dom.}(A)$ to $(A - \kappa I)^{-1} : \mathcal{X} \to \text{Dom.}(A)$. Hence, we may express every $y \in \text{Dom.}(A)$ as $y = (A - \kappa I)^{-1}z$ for some $z \in \mathcal{X}$. Hence we expressing y in this form, we conclude that A commutes with B if and only if $B(A-\kappa I)^{-1}z = (A-\kappa I)^{-1}Bz$ for every $z \in \mathcal{X}$. Thus, we conclude, that A and B commute if and only if the resolvent $\mathcal{R}(\kappa, A)$ of A, commutes with B for some κ in the resolvent set of A. Since nothing special about κ, other than that it belongs to the resolvent set of A, was used, we may infer that A commutes with B if and only if $\mathcal{R}(\kappa, A)$ commutes with B for every κ in the resolvent set of A. ■

We now apply this abstract result to the operator $\mathfrak{H}$, to obtain:

[6] Technically, to make the leap from $\mathsf{C}^2_c(\mathcal{B}_R)$ to Dom.$(\mathfrak{H}) = \mathsf{H}^2(\mathcal{B}_R) \cap \mathsf{H}^1_0(\mathcal{B}_R)$, it suffices to observe that the sesquilinear form $\mathfrak{B}[u, v]$ associated with $\mathfrak{H}$, obeys $\mathfrak{B}[u, v] = \mathfrak{B}[T_g(u), T_g(v)]$ for every $u, v \in \mathsf{H}^1_0(\mathcal{B}_R)$ and every $T_g \in L_{\mathcal{G}}$.This calculation is shown in (4.29).

[7] In any case, it is quite awkward to interpret what commutation of an unbounded operator with a bounded operator such as T_g means and so it is customary in Functional Analysis to replace an unbounded operator by its resolvent while looking at commuting operators [Teschl, 2009]. This is what we do here as well.

[8] Refer to Appendix A for a definition of the resolvent operator and the resolvent set.

[9] As is customary in the literature, for an unbounded operator A on $\mathcal{X}$, the domain of A is denoted as Dom.(A)

Lemma 4.3.2. *For every κ in the resolvent set of $\mathfrak{H}$, the resolvent operator R_κ of $\mathfrak{H}$ commutes with every operator in $L_{\mathcal{G}}$.*

Proof: This result follows easily from the above proposition. It is not difficult to verify that the operator $\mathfrak{H}$, on $\mathcal{X} = \mathsf{L}^2(\mathcal{B}_R)$ is indeed, a closed operator, and that the resolvent set of $\mathfrak{H}$ is non-empty [Kato, 1995; Renardy and Rogers, 2004]. The calculations above already show that $\mathfrak{H}$ commutes with every operator in $L_{\mathcal{G}}$. Since each operator in $L_{\mathcal{G}}$ is a bounded operator on $\mathcal{X}$, the sought result follows. ■

With the above results in place, we are now in a position to use Schur's Lemma and it's consequences. Since R_κ is a bounded operator and $R_\kappa \in \mathcal{C}(\zeta)$, the basic idea is that we may perform a "block-diagonalization" of the operator R_κ in a precise sense described below.

Let us fix κ in the resolvent set of $\mathfrak{H}$ [10] and consider the resolvent operator R_κ. Let v be an eigenvector of R_κ and let $\sigma \in \mathbb{R}$ be the associated eigenvalue[11]. Since this implies that v is also an eigenvector of $\mathfrak{H}$ with the associated eigenvalue $1/\sigma$, many of the things which we discuss now hold for the operator $\mathfrak{H}$ as well. Now, since $R_\kappa v = \sigma v$, operating with any $T_g = \zeta(g), g \in \mathcal{G}$, we get that $T_g R_\kappa v = T_g\, \sigma v$. Lemma 4.3.2 implies that $R_\kappa(T_g v) = \sigma(T_g v)$, that is, $T_g v$ is also an eigenvector of R_κ, with the same eigenvalue. Thus, the eigen-space associated with a given eigenvalue σ, that is, the set $Y_\sigma = \{v : R_\kappa v = \sigma v\}$ carries a representation of the group $\mathcal{G}$. The natural question that arises, is if the representation carried by Y_σ reducible. The general belief, seems to be that such a representation will be irreducible in general [McWeeny, 2002; Bossavit, 1986]. Since the question of reducibility is basically the same as finding invariant subspaces, and in this case, the subspaces have already been distinguished according to eigenvalue, two non-symmetry related eigenvectors sharing the same eigenvalue are very unlikely to occur. Any such, non-symmetry related degeneracy is termed *accidental* in the literature [McWeeny, 2002], with the understanding that such degeneracies would vanish under small perturbations of the system[12]. Thus, assuming that accidental degeneracies do not exist, we may conclude that every degenerate group of eigenfunctions Y_σ of R_κ provides an irreducible representation of the group $\mathcal{G}$. Since the eigenvectors of R_κ provide a complete orthonormal basis of $\mathsf{L}^2(\mathcal{B}_R)$, we may now summarize the above discussions as follows:

[10] In particular, a detailed proof of Theorem 4.2.1 reveals that the resolvent set of $\mathfrak{H}$ is not empty. Any sufficiently large κ actually belongs to the resolvent set. The symmetry related arguments presented here work for any κ in the resolvent set.

[11] Since R_κ is self-adjoint, every eigenvalue of R_κ must be real.

[12] If it is found that such "accidental" degeneracies are stable under perturbations, then the usual interpretation is that the system under question has generic un-accounted for symmetries [Bossavit, 1986].

Theorem 4.3.3. *Suppose, that the (unbounded) operator $\mathfrak{H} = -\frac{1}{2} + V(\mathbf{x})$ on $\mathsf{L}^2(\mathcal{B}_R)$ is such that the potential $V \in \mathsf{C}(\mathcal{B}_R)$ is invariant under the finite group of isometries $\mathcal{G}$. Then, for every d_ν-dimensional irreducible representation of the group $\mathcal{G}$, we can find d_ν-fold degenerate sets of eigenfunctions of $\mathfrak{H}$. Any further degeneracies should be viewed as accidental.*

Since a non-Abelian group necessarily has irreducible representations which have dimension more than one, we may conclude that in such cases, we would necessarily encounter symmetry related degenerate eigenfunctions.

As mentioned earlier, for a finite group $\mathcal{G}$, the dimension of irreducible representations of $\mathcal{G}$ is finite (Proposition 3.2.12) and the number of non-equivalent representations of $\mathcal{G}$ is finite as well. On the other hand, $\mathsf{L}^2(\mathcal{B}_R)$ is infinite dimensional. We therefore conclude that the number of degenerate sets eigenfunctions must be infinite. Let us look at this a little more carefully from the point of view of the symmetry related projection operators introduced in Chapter 3.

Let S denote the spectrum of R_κ and as before, let $\mathsf{H} = \mathsf{L}^2(\mathcal{B}_R)$. Let Y_σ denote the eigenspace associated with $\sigma \in S$. The spectral theorem for compact operators [Naylor and Sell, 1971; Helmberg, 2008] tells us that we may write:

$$\mathsf{H} = \bigoplus_{\sigma \in S} Y_\sigma \quad . \tag{4.27}$$

On the other hand, from Chapter 3, we have the following projectors, for $\nu = 1, \ldots, \ell$:

$$\begin{aligned} \mathsf{H} &= \bigoplus_{\nu=1}^{l} V^\nu \ , \\ V^\nu = Q^\nu(\mathsf{H}) \ , \ Q^\nu &= \frac{d_\nu}{|\mathcal{G}|} \sum_{g \in \mathcal{G}} \overline{\text{Tr.}(\zeta^\nu(g))}\, \zeta(g) \quad . \end{aligned} \tag{4.28}$$

The natural question is, how the subspaces V^ν are related to the subspaces Y_σ. As alluded to in the above discussion, the relationship is that, in the absence of accidental degeneracies, for every $\sigma \in S$, we have $Y_\sigma \subset V^\nu$ for some $\nu = 1, \ldots, \ell$. Provided there are no accidental degeneracies, this amounts to the claim that if $\exists v \in V^\nu \cap Y_\sigma$ with $v \neq 0$, then $Y_\sigma \subset V^\nu$. Thus, in the absence of accidental degeneracy, we have a partition of the spectrum S into the form $S = \cup_{\nu=1}^{d_\nu} S_\nu$, such that $Y_\sigma \subset V^\nu$ whenever $\sigma \in S_\nu$. The subspaces $V^\nu_{ii} \subset V^\nu, i = 1, \ldots, d_\nu, \nu = 1, \ldots, \ell$ correspond to choosing one eigenvector at a time (out of the d_ν ones available) from each $Y_\sigma \subset V^\nu$ (with $\sigma \in S_\nu$) and forming the closed linear span of these

eigenvectors.[13]

Intuitively, it also makes sense to look at the matrix coefficients of R_κ in an orthonormal basis obtained from the basis functions of V^ν. First, we observe that R_κ commutes with each of the projectors Q^ν since it commutes with each operator in $L_\mathcal{G}$. This implies that R_κ has each V^ν as an invariant subspace. This is because, if $v \in V^\nu$, that is, if $Q^\nu v = v$, we have $R_\kappa v = R_\kappa(Q^\nu v) = Q^\nu(R_\kappa v) \in V^\nu$. Since R_κ has each V^ν as an invariant subspace, the matrix coefficient $\langle R_\kappa e_\alpha, e_\gamma \rangle_{\mathsf{L}^2(\mathcal{B}_R)}$ is non-zero or zero depending on whether e_α and e_γ are from the same invariant subspace or not. Since any compact operator is the norm limit of a sequence of finite rank operators [Naylor and Sell, 1971], we may think of R_κ as an "infinite matrix" with block diagonal entries corresponding to these non-zero matrix coefficients in the symmetry adapted basis.

We conclude therefore that the use of the theory developed in Chapter 3 allows the original eigenvalue problem to be broken into independent symmetry adapted subproblems. Specifically, there are ℓ subproblems, each associated with one of the irreducible representations of $\mathcal{G}$. The subproblems are obtained by restriction of the original problem to the subspaces $V^\nu, \nu = 1, \ldots, \ell$. In the next section, we will try to obtain a concrete formulation of these restricted subproblems. Later, we will show that see that these restricted subproblems can be interpreted as boundary value problems posed on the fundamental domain. [14]

[13] We note however, that while the subspaces V^ν can be specified irrespective of the choice of basis vectors, the spaces V^ν_{ii} can only be obtained as the linear span of a set of basis vectors that are chosen specially. If accidental degeneracies are absent, the irreducible subspace associated with a particular eigenvalue can be specified without a particular choice of basis vectors as well.

[14] We recall, that every group action has a fundamental set (Proposition 3.1.2). However, usual formulations of boundary value problems require that the set on which the problem is being posed has some topological regularities. Therefore, we need to introduce the idea of a fundamental domain, since having a fundamental set is not adequate for discussing boundary value problems. This is done in Section 4.3.3.

4.3.2 Formulation of Symmetry Adapted Subproblems

Let us begin by observing that for every $T_g \in L_{\mathcal{G}}, g = (\mathbf{R}_g|\mathbf{0}) \in \mathcal{G}$ and for every $u, v \in \mathsf{H}^1_0(\mathcal{B}_R)$, the sesquilinear form $\mathfrak{B}[u, v]$ associated with our problem, obeys the condition:

$$\begin{aligned}
&\mathfrak{B}[T_g u, T_g v] \\
&= \int_{\mathcal{B}_R} \frac{1}{2} \nabla u(g^{-1} \bullet \mathbf{x}).\nabla \overline{v(g^{-1} \bullet \mathbf{x})} + V(\mathbf{x}) u(g^{-1} \bullet \mathbf{x}) \overline{v(g^{-1} \bullet \mathbf{x})}\, d\mathbf{x} \\
&= \int_{\mathcal{B}_R} \frac{1}{2} \big(\mathbf{R}_g^T \nabla u(\mathbf{x})\big).\big(\mathbf{R}_g^T \nabla \overline{v(\mathbf{x})}\big)\, d\mathbf{x} + \int_{\mathcal{B}_R} V(g^{-1} \bullet \mathbf{x}) u(g^{-1} \bullet \mathbf{x}) \overline{v(g^{-1} \bullet \mathbf{x})}\, d\mathbf{x} \\
&= \int_{\mathcal{B}_R} \frac{1}{2} \big(\nabla u(\mathbf{x})\big).\big(\mathbf{R}_g \mathbf{R}_g^T \nabla \overline{v(\mathbf{x})}\big)\, d\mathbf{x} + \int_{\mathcal{B}_R} V(g^{-1} \bullet \mathbf{x}) u(g^{-1} \bullet \mathbf{x}) \overline{v(g^{-1} \bullet \mathbf{x})}\, d\mathbf{x} \\
&= \int_{\mathcal{B}_R} \frac{1}{2} \nabla u(\mathbf{x}).\nabla \overline{v(\mathbf{x})}\, d\mathbf{x} + \int_{\mathcal{B}_R} V(\mathbf{x}) u(\mathbf{x}) \overline{v(\mathbf{x})}\, d\mathbf{x} \\
&= \mathfrak{B}[u, v]\ . \qquad (4.29)
\end{aligned}$$

In the above calculation, we have used the group invariance of the potential V, the group invariance of the Lebesgue measure and the invariance of $\mathcal{B}_R$ under the group action. The property (4.29) is often referred to as equivariance in the literature [Bossavit, 1993] and we see that it implies:

$$\mathfrak{B}[T_g u, v] = \mathfrak{B}[T_g u, T_g T_g^* v] = \mathfrak{B}[u, T_g^* v] = \mathfrak{B}[u, T_{g^{-1}} v]\ . \qquad (4.30)$$

This, in turn, by the sesquilinearity of $\mathfrak{B}$, implies that for each of the operators P^ν_{ij}, introduced in (3.38), we have:

$$\begin{aligned}
\mathfrak{B}[P^\nu_{ij} u, v] &= \frac{d_\nu}{|\mathcal{G}|} \sum_{g \in \mathcal{G}} \overline{D^\nu_{ij}(g)} \mathfrak{B}[T_g u, v] = \sum_{g \in \mathcal{G}} D^\nu_{ji}(g^{-1}) \mathfrak{B}[u, T_{g^{-1}} v] \\
&= \mathfrak{B}[u, \sum_{g \in \mathcal{G}} \overline{D^\nu_{ji}(g^{-1})} T_{g^{-1}} v] = \mathfrak{B}[u, P^\nu_{ji} v]\ . \qquad (4.31)
\end{aligned}$$

In particular, this implies that $\mathfrak{B}[P^\nu_{ii} u, v] = \mathfrak{B}[u, P^\nu_{ii} v]$. Summing over $i = 1, \ldots, d_\nu$, this also gives us, $\mathfrak{B}[Q^\nu u, v] = \mathfrak{B}[u, Q^\nu v]$. The fact that each operator T_g is unitary, implies that $\langle T_g u, T_g v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} = \langle u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)}$ for every $u, v \in \mathsf{H}^1_0(\mathcal{B}_R)$. Since, the inner product is a sesquilinear form on $\mathsf{H}^1_0(\mathcal{B}_R) \times \mathsf{H}^1_0(\mathcal{B}_R)$, this automatically implies, $\langle P^\nu_{ij} u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} = \langle u, P^\nu_{ji} v \rangle_{\mathsf{L}^2(\mathcal{B}_R)}$. Together, these results now imply the following about the weak form of the symmetry adapted subproblems[15]:

[15] A technical point here is that the representation theory tools (projection operators, etc) developed were for functions in $\mathsf{L}^2(\mathcal{B}_R)$ and the result in Proposition 4.3.4 concerns functions in $\mathsf{H}^1_0(\mathcal{B}_R)$. This is alright, because the group action associated with the operators in

Proposition 4.3.4. *A function $u \in \mathsf{H}^1_0(\mathcal{B}_R)$ satisfies the eigenvalue problem* (4.24) *if and only if, for some $\nu = 1 \ldots, \ell$, it satisfies:*

$$\mathfrak{B}[u, w] = \lambda \langle u, w \rangle_{\mathsf{L}^2(\mathcal{B}_R)}, \quad \forall w \in W^\nu = Q^\nu(\mathsf{H}^1_0(\mathcal{B}_R)) \ . \tag{4.32}$$

Thus, solving the problem (4.24) *is equivalent to solving the ℓ subproblems listed in* (4.32).

Proof: Given $u \in \mathsf{H}^1_0(\mathcal{B}_R)$ which satisfies $\mathfrak{B}[u, v] = \lambda \langle u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)}, \ \forall v \in \mathsf{H}^1_0(\mathcal{B}_R)$, we must have that $u \in W^\nu = Q^\nu(\mathsf{H}^1_0(\mathcal{B}_R))$ for some $\nu = 1 \ldots, \ell$.[16] Thus, we have, $Q^\nu u = u$, for this value of ν. So, we may write, $\forall v \in \mathsf{H}^1_0(\mathcal{B}_R)$:

$$\mathfrak{B}[u, v] = \mathfrak{B}[Q^\nu u, v] = \mathfrak{B}[u, Q^\nu v] = \lambda \langle u, Q^\nu v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} \ . \tag{4.33}$$

In particular, if $v \in W^\nu$, this immediately gives us (4.32).

On the other hand, suppose that we have found $u \in \mathsf{H}^1_0(\mathcal{B}_R)$, which satisfies (4.32). It suffices to consider the case in which $u \in W^\nu = Q^\nu(\mathsf{H}^1_0(\mathcal{B}_R))$.[17] Given any $v \in \mathsf{H}^1_0(\mathcal{B}_R)$, we write, using Theorem 3.2.15 and equation (3.45), $v = v^\parallel + v^\perp$ with $v^\parallel \in W^\nu, v^\perp \in (W^\nu)^\perp$. We have therefore, using $\langle u, v^\perp \rangle_{\mathsf{L}^2(\mathcal{B}_R)} = 0$ and $Q^\nu v^\perp = 0$:

$$\begin{aligned} \mathfrak{B}[u, v] =& \mathfrak{B}[u, v^\parallel] + \mathfrak{B}[u, v^\perp] = \lambda \langle u, v^\parallel \rangle_{\mathsf{L}^2(\mathcal{B}_R)} + \mathfrak{B}[Q^\nu u, v^\perp] \\ =& \lambda \langle u, v^\parallel \rangle_{\mathsf{L}^2(\mathcal{B}_R)} + \lambda \langle u, v^\perp \rangle_{\mathsf{L}^2(\mathcal{B}_R)} + \mathfrak{B}[u, Q^\nu v^\perp] \\ =& \lambda \langle u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} \ . \end{aligned} \tag{4.36}$$

Thus, (4.24) is established.[18] ■

$L_{\mathcal{G}}$ work for both the Hilbert spaces. Indeed, we may verify that $P^\nu_{ii}(\mathsf{H}^1_0(\mathcal{B}_R)) = P^\nu_{ii}(\mathsf{L}^2(\mathcal{B}_R)) \cap \mathsf{H}^1_0(\mathcal{B}_R)$. As mentioned earlier, the operator theoretic interpretation of the eigenvalue problem is associated with the space $\mathsf{L}^2(\mathcal{B}_R)$, while it's equivalent weak interpretation is associated with the space $\mathsf{H}^1_0(\mathcal{B}_R)$.

[16] Following the discussion in Section 4.3.1, this assertion is certainly true provided accidental degeneracies are absent. In case an accidental degeneracy is present, we may choose our basis such that the eigenspace associated with a given eigenvalue σ, Y_σ can be written as $Y_\sigma = S_1 \cup S_2$, with $S_1 \subset W^{\nu_1}$ and $S_2 \subset W^{\nu_2}$. The rest of the theorem now works as outlined.

[17] Absence of accidental degeneracy in fact, requires that $u \in W^\nu$, for some ν. In any case, the condition (4.32) implies that the part of u that lies in W^ν also obeys the same condition. To see this, we write for $u \in \mathsf{H}^1_0(\mathcal{B}_R), v \in W^\nu$:

$$\mathfrak{B}[u, v] = \mathfrak{B}[u, Q^\nu v] = \mathfrak{B}[Q^\nu u, v] \ . \tag{4.34}$$

On the other hand, we also have:

$$\langle u, Q^\nu v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} = \langle Q^\nu u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} \ . \tag{4.35}$$

Thus, we must have $\mathfrak{B}[Q^\nu u, v] = \lambda \langle Q^\nu u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)}$ for every $v \in W^\nu$.

[18] We may observe that the well posedness of problem (4.32) follows easily since the subspaces W^ν are closed and therefore they are Hilbert spaces in their own right.

Thus, we have obtained an interpretation of the symmetry adapted subproblems that can be obtained by restriction of the operator R_κ to the subspaces $V^\nu = Q^\nu(\mathsf{L}^2(\mathcal{B}_R)), \nu = 1, \ldots, \ell$, associated with the irreducible representations of $\mathcal{G}$.

4.3.3 Interpretation of Symmetry Adapted Subproblems

The naive interpretation of the use of symmetry in a boundary value problem would be that the problem can somehow be recast into smaller problems on the fundamental domain. It becomes necessary therefore, to interpret the problems associated with the symmetry adapted subspaces, mentioned in the earlier section, in terms of problems associated with the fundamental domain. As in Bossavit [1986, 1993], we use the notion of ν-symmetric families of vectors (functions in this case) to achieve this goal. We introduce:

Definition 4.3.5. A ν-symmetric set of vectors in H is a d_ν-tuple $\{v_i\}_{i=1}^{d_\nu} \subset \mathsf{H}$ such that $v_i = P^\nu_{ij}\, v_j, \forall i, j = 1, \ldots, d_\nu$. As a consequence of Remark 3.2.16, this definition requires that $v_i \in V^\nu_{ii}$. □

To systematically build a ν-symmetric set of vectors, we may start with any $v \in \mathsf{H}$ and we may set $v^\nu_{i,(j)} = P^\nu_{ij}\, v, \forall i, j = 1, \ldots, d_\nu$. Then, the set $\{v^\nu_{i,(j)}\}_{i=1}^{d_\nu}$ is ν-symmetric for every fixed $j = 1, \ldots, d_\nu$. Thus, every $\nu = 1, \ldots, \ell$ contributes to d_ν ν-symmetric sets and each set is of size d_ν. The elements of the ν-symmetric sets so formed $v^\nu_{i,(j)}$, are referred to as the generalized Fourier components of $v \in \mathsf{H}$ [Bossavit, 1986, 1993]. Conversely, given d_ν ν-symmetric sets, $\{v^\nu_{i,(j)}\}_{i=1}^{d_\nu}, j = 1, \ldots, d_\nu$, we may reconstruct $v = \sum_{\nu=1}^{l} \sum_{i=1}^{d_\nu} v^\nu_{i,(i)}$. Next, we may use the relation (3.41) to verify that this vector $v \in \mathsf{H}$ will generate the same generalized Fourier components that it was created from.

A ν-symmetric set of vectors transforms in a very special way under the group action. In fact, we may show [Bossavit, 1986]:

Proposition 4.3.6. *A d_ν-tuple of vectors $\{v_j\}_{i=1}^{d_\nu} \subset \mathsf{H}$ is a ν-symmetric set if and only if for every $j = 1, \ldots, d_\nu$, we have:*

$$\zeta(g) v_j = \sum_{k=1}^{d_\nu} D^\nu_{kj}(g) v_k \ , \ \forall g \in \mathcal{G}. \tag{4.37}$$

Proof: Given a ν-symmetric set of vectors, we may use (3.40) to conclude that (4.37) holds. On the other hand, given a d_ν-tuple of vectors that obey (4.37), we may multiply by

$d_\nu D^\nu_{ji}(g^{-1})$, sum over the group and use the orthogonality relations (3.37) to conclude that Definition 4.3.5 holds. ■

The above characterization of a ν-symmetric set basically tells us that the linear span of such a set is a group invariant subspace (in the sense of Definition 3.2.4) and that this subspace is in fact irreducible. Using this, and the discussion following Theorem 4.3.3, we are immediately led to the important result that, in the absence of accidental degeneracies, the eigenspace Y_σ associated with any eigenvalue of the resolvent R_κ is a ν-symmetric set.[19] We may conclude therefore that, degenerate eigenvectors of $\mathfrak{H}$ obey the relation (4.37). We will now see, how this special structure of the eigenvectors of $\mathfrak{H}$, can be used to simplify the boundary value problem associated with the computation of the eigenvectors.

To proceed, we will first show that a ν-symmetric set of functions posed on the ball $\mathcal{B}_R$ can be interpreted in terms of their restriction to the fundamental domain. We need to formalize the notion of a fundamental domain and therefore, we introduce the following[20]:

Definition 4.3.7. Suppose that $\mathcal{G}$ is a finite group of isometries. A fundamental domain (or symmetry cell) of $\mathcal{G}$ relative to the open ball $\mathcal{B}_R$ is a set $\mathcal{D} \subset \mathcal{B}_R$ such that it is open, connected, possesses a regular boundary[21] and has the properties:

$$\mathcal{B}_R \subset \text{cl.}\left(\bigcup_{\Upsilon\in\mathcal{G}} \Upsilon(\mathcal{D})\right) \quad , \quad \Upsilon_1(\mathcal{D}) \cap \Upsilon_2(\mathcal{D}) = \emptyset\,, \forall \Upsilon_1, \Upsilon_2 \in \mathcal{G}, \Upsilon_1 \neq \Upsilon_2. \tag{4.38}$$

Given a fundamental domain $\mathcal{D}$, we will call the set $\partial_{\mathcal{O}}(\mathcal{D}) = \partial\mathcal{D}\backslash\partial\mathcal{B}_R$, the objective boundary of $\mathcal{D}$ and the set $\partial_D(\mathcal{D}) = \partial\mathcal{D} \cap \partial\mathcal{B}_R$, the original boundary of $\mathcal{D}$.

Roughly speaking, the fundamental domain is a well behaved set containing one point per orbit, with respect to the group action of $\mathcal{G}$ on points in $\mathcal{B}_R$. Based on the properties in (4.38), we may see that $\bigcup_{\Upsilon\in\mathcal{G}} \Upsilon\Big(\partial_D(\mathcal{D})\Big) = \partial\mathcal{B}_R$. It follows that, whenever $\mathbf{x} \in \partial_{\mathcal{O}}(\mathcal{D})$, there exists $g \in \mathcal{G}, g \neq e$ such that $g \bullet \mathbf{x} \in \partial_{\mathcal{O}}(\mathcal{D})$ and that for almost every $\mathbf{x} \in \partial_{\mathcal{O}}(\mathcal{D})$, this $g \in \mathcal{G}$ must be unique [Bossavit, 1986]. To say this in a somewhat different way, we may define, for $g \in \mathcal{G}, g \neq e$:

$$\partial^g_{\mathcal{O}}(\mathcal{D}) = \left\{\mathbf{x} \in \text{cl.}(\mathcal{D}) : g \bullet \mathbf{x} \in \text{cl.}(\mathcal{D})\right\}, \tag{4.39}$$

[19] If accidental degeneracies are present, the eigenspace Y_σ consists of the union over ν-symmetric sets.

[20] We use the standard notation cl.(Ω) to denote the closure, and $\partial\Omega$ to denote the boundary of a set Ω.

[21] We say that a domain, that is, a bounded, connected, open subset of $\mathbb{R}^3$, has a regular boundary Γ, if Γ is the union of a finite number of differentiable closed surfaces.

and we may then notice that each point $\mathbf{x} \in \partial_{\mathcal{O}}(\mathcal{D})$ lies in $\partial^g_{\mathcal{O}}(\mathcal{D})$, for some $g \in \mathcal{G}, g \neq e$. Further, each point in $\mathbf{x} \in \partial_{\mathcal{O}}(\mathcal{D})$ lies in only one such $\partial^g_{\mathcal{O}}(\mathcal{D})$, except for a subset of $\partial\mathcal{D}$, of relative measure zero [Bossavit, 1993].

Now that we have established the notion of the fundamental domain, we may proceed further. We let $\mathcal{W}$ denote the restriction to $\mathcal{D}$, of functions in $\mathsf{H}^1(\mathcal{B}_R)$ and we further let:

$$\mathcal{W}_0 = \left\{ f \in \mathcal{W} : f = 0 \text{ on } \partial_D(\mathcal{D}) \right\}. \tag{4.40}$$

We introduce the space $\mathcal{W}_0$, so as to be able to establish an isomorphism between the subspaces $W^\nu_{ii} = P^\nu_{ii}(\mathsf{H}^1_0(\mathcal{B}_R)), \nu = 1, \ldots, \ell; i = 1, \ldots, d_\nu$ and the space:

$$\mathcal{W}_0^{d_\nu} = \mathcal{W}_0 \times \cdots \times \mathcal{W}_0 \ (d_\nu \text{ times}) . \tag{4.41}$$

We can define a natural trace operator on the d_ν-tuples of functions in $\mathcal{W}_0^{d_\nu}$. Specifically, let $\tilde{\mathbf{v}} \in \mathcal{W}_0^{d_\nu}$, with $\tilde{\mathbf{v}} = \{\tilde{v}_i\}_{i=1}^{d_\nu}$. For $\mathbf{x} \in \partial_{\mathcal{O}}(\mathcal{D})$, let $g \in \mathcal{G}, g \neq e$, be such that $\mathbf{x} \in \partial^g_{\mathcal{O}}(\mathcal{D})$. We set:

$$\big(\Gamma_\nu \tilde{\mathbf{v}}\big)(\mathbf{x}) = \left\{ \tilde{v}_i(\mathbf{x}) - \sum_{k=1}^{d_\nu} D^\nu_{ki}(g) \tilde{v}_k(g \bullet \mathbf{x}) \right\}_{i=1}^{d_\nu}, \tag{4.42}$$

and we may now observe the following result:

Proposition 4.3.8 (Characterization of ν-symmetric sets using fundamental domain)**.** *A d_ν-tuple of functions $\tilde{\mathbf{v}} = \{\tilde{v}_i\}_{i=1}^{d_\nu}$ is the restriction of a ν-symmetric set to cl.$(\mathcal{D})$ if and only if $\big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0$. Hence, the space W^ν_{ii} is isomorphic to the space $\left\{ \tilde{\mathbf{v}} \in \mathcal{W}_0^{d_\nu} : \big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0 \right\}$.*

Proof: Since compactly supported continuous functions form a dense subspace of $\mathsf{H}^1_0(\mathcal{B}_R)$, it suffices to establish the above result for such functions. So, given $\tilde{\mathbf{v}}$, a d_ν-tuple of functions on $\mathcal{D}$, we may form $\mathbf{v}^\nu = \{v^\nu_i\}_{i=1}^{d_\nu}$, the continuous extension of this tuple of functions to all of $\mathcal{B}_R$ as follows: we define, for every $\mathbf{x} \in \mathcal{D}, g \in \mathcal{G}$:

$$\mathbf{v}^\nu(g \bullet \mathbf{x}) = \{v^\nu_i(g \bullet \mathbf{x})\}_{i=1}^{d_\nu} = \left\{ \sum_{k=1}^{d_\nu} D^\nu_{ki}(g^{-1}) \tilde{v}_k(\mathbf{x}) \right\}_{i=1}^{d_\nu} \tag{4.43}$$

The condition $\big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0$, ensures that $\mathbf{v}^\nu$ is continuous across the boundaries $\partial_{\mathcal{O}}(\mathcal{D})$ and the conditions laid out in Proposition 4.3.6 now indicate that $\mathbf{v}^\nu$ forms a ν-symmetric set.

On the other hand, if $\mathbf{v} = \{v_i\}_{i=1}^{d_\nu}$ is a given ν-symmetric set, then, its components obey the

conditions of Proposition 4.3.6. Therefore, (4.43) holds, and consequently, the restriction to cl.$(\mathcal{D})$ of these functions obey $\big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0$.

In the light of the above discussion, the isomorphism between the spaces W^ν_{ii} is and $\Big\{\tilde{\mathbf{v}} \in \mathcal{W}_0^{d_\nu} \,:\, \big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0\Big\}$ is easy to see. Starting form $v_i \in W^\nu_{ii}$, we may generate the corresponding ν-symmetric set (for instance, using the operators P^ν_{ji}) and then, consider the restrictions of these d_ν functions to cl.$(\mathcal{D})$. This way, we will end up with a vector of functions $\tilde{\mathbf{v}} \in \mathcal{W}_0^{d_\nu}$ which obeys the relation $\big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0$. On the other hand, given a vector of functions $\tilde{\mathbf{v}} \in \mathcal{W}_0^{d_\nu}$ which obey $\big(\Gamma_\nu \tilde{\mathbf{v}}\big) = 0$, we may extend this set of functions to all of $\mathcal{B}_R$ via (4.43) and consider the i^{th} component of the vector of functions so formed to get an element of W^ν_{ii}. ■

With the above result in place, we can interpret the symmetry adapted problems in Proposition 4.3.4 as problems posed on the fundamental domain. We have, for $u, v \in \mathsf{H}^1_0(\mathcal{B}_R)$, the left hand side of (4.32):

$$\begin{aligned}
\mathfrak{B}[u,v] &= \int_{\mathcal{B}_R} \frac{1}{2}\nabla u(\mathbf{x}).\nabla\overline{v(\mathbf{x})}\, d\mathbf{x} + \int_{\mathcal{B}_R} V(\mathbf{x})u(\mathbf{x})\overline{v(\mathbf{x})}\, d\mathbf{x} \\
&= \sum_{g\in\mathcal{G}} \int_{g(\mathcal{D})} \frac{1}{2}\nabla u(\mathbf{x}).\nabla\overline{v(\mathbf{x})}\, d\mathbf{x} + \sum_{g\in\mathcal{G}} \int_{g(\mathcal{D})} V(\mathbf{x})u(\mathbf{x})\overline{v(\mathbf{x})}\, d\mathbf{x} \\
&= \sum_{g\in\mathcal{G}} \int_{\mathcal{D}} \frac{1}{2}\nabla u(g\bullet\mathbf{y}).\nabla\overline{v(g\bullet\mathbf{y})}\, d\mathbf{y} + \sum_{g\in\mathcal{G}} \int_{\mathcal{D}} V(g\bullet\mathbf{y})u(g\bullet\mathbf{y})\overline{v(g\bullet\mathbf{y})}\, d\mathbf{y} \\
&= \sum_{g\in\mathcal{G}} \int_{\mathcal{D}} \frac{1}{2}\nabla\big(\zeta(g)u(\mathbf{y})\big).\nabla\big(\overline{\zeta(g)v(\mathbf{y})}\big)\, d\mathbf{y} + \sum_{g\in\mathcal{G}} \int_{\mathcal{D}} V(\mathbf{y})\big(\zeta(g)u(\mathbf{y})\big)\overline{\big(\zeta(g)v(\mathbf{y})\big)}\, d\mathbf{y}
\end{aligned} \tag{4.44}$$

In the light of the discussion in Section 4.3.2, we know that the eigenvalue problem posed on $\mathsf{H}^1_0(\mathcal{B}_R)$ only needs to be posed on the symmetry adapted subspaces W^ν. Indeed, let $u, v \in W^\nu_{ii} \subset \mathsf{H}^1_0(\mathcal{B}_R)$ for some $\nu = 1, \ldots, \ell$ and $i = 1, \ldots, d_\nu$, and let $\{u_j\}_{j=1}^{d_\nu}, \{v_k\}_{k=1}^{d_\nu}$ be the corresponding ν-symmetric families. Since $u_i \equiv u$ and $v_i \equiv v$, using (4.37), we may rewrite (4.44) as:

$$\begin{aligned}
\mathfrak{B}[u,v] = \sum_{g\in\mathcal{G}} \int_{\mathcal{D}} \frac{1}{2}\nabla\Big(\sum_{j=1}^{d_\nu} D^\nu_{ji}(g)u_j\Big).\nabla\overline{\Big(\sum_{k=1}^{d_\nu} D^\nu_{ki}(g)v_k\Big)}\, d\mathbf{y} \\
+ \sum_{g\in\mathcal{G}} \int_{\mathcal{D}} V(\cdot)\Big(\sum_{j=1}^{d_\nu} D^\nu_{ji}(g)u_j\Big)\overline{\Big(\sum_{k=1}^{d_\nu} D^\nu_{ki}(g)u_k\Big)}\, d\mathbf{y}\ .
\end{aligned} \tag{4.45}$$

To be able to simplify (4.45) further, we need to introduce the sesquilinear form over the fundamental domain. Accordingly, for any $u, v \in \mathsf{H}^1_0(\mathcal{B}_R)$, let $\tilde{u}, \tilde{v}$ denote the restriction of these functions to $\mathcal{D}$. Then, let us define:

$$\tilde{\mathfrak{B}}[\tilde{u}, \tilde{v}] = \int_{\mathcal{D}} \frac{1}{2} \nabla \tilde{u}(\mathbf{x}) . \nabla \overline{\tilde{v}(\mathbf{x})} \, d\mathbf{x} + \int_{\mathcal{D}} V(\mathbf{x}) \tilde{u}(\mathbf{x}) \overline{\tilde{v}(\mathbf{x})} \, d\mathbf{x} \tag{4.46}$$

With this notation in hand, and denoting the restrictions of the ν-symmetric families associated with u and v to the fundamental domain as $\{\tilde{u}_j\}_{j=1}^{d_\nu}$ and $\{\tilde{v}_k\}_{k=1}^{d_\nu}$ respectively, we rewrite (4.45) as:

$$\begin{aligned} \mathfrak{B}[u, v] =& \sum_{g \in \mathcal{G}} \sum_{j,k=1}^{d_\nu} D^\nu_{ji}(g) \overline{D^\nu_{ki}(g)} \tilde{\mathfrak{B}}[\tilde{u}_j, \tilde{v}_k] \\ =& \frac{|\mathcal{G}|}{d_\nu} \sum_{k=1}^{d_\nu} \tilde{\mathfrak{B}}[\tilde{u}_k, \tilde{v}_k] \ , \end{aligned} \tag{4.47}$$

using the orthogonality relations (3.37). A similar calculation for the right hand side of (4.32) yields:

$$\langle u, v \rangle_{\mathsf{L}^2(\mathcal{B}_R)} = \frac{|\mathcal{G}|}{d_\nu} \sum_{k=1}^{d_\nu} \langle \tilde{u}_k, \tilde{v}_k \rangle_{\mathsf{L}^2(\mathcal{D})} \tag{4.48}$$

Thus, for every irreducible representation of the the group, we arrive at d_ν coupled subproblems over the fundamental domain:

$$\sum_{k=1}^{d_\nu} \tilde{\mathfrak{B}}[\tilde{u}_k, \tilde{v}_k] = \lambda \sum_{k=1}^{d_\nu} \langle \tilde{u}_k, \tilde{v}_k \rangle_{\mathsf{L}^2(\mathcal{D})} \ . \tag{4.49}$$

If the eigenfunctions are sufficiently regular, we may perform integration by parts to obtain the strong form of the equations in (4.49). This calculation leads us to the following symmetry adapted version of the problem laid out in (4.13), over the fundamental domain:

$$\begin{aligned} &\text{For every irreducible representation } \nu = 1, \dots, \ell \text{ and } i = 1, \dots, d_\nu : \\ &-\frac{1}{2} \Delta \tilde{u}^i(\mathbf{x}) + V(\mathbf{x}) \tilde{u}^i(\mathbf{x}) = \lambda \tilde{u}^i(\mathbf{x}) \text{ for } \mathbf{x} \in \mathcal{D}. \\ &\tilde{u}^i(\mathbf{x}) = 0 \text{ , for } \mathbf{x} \in \partial_D\big(\mathcal{D}\big), \\ &\text{and } \big(\Gamma_\nu \tilde{\mathbf{u}}\big) = 0 \text{ on } \partial_{\mathcal{O}}\big(\mathcal{D}\big), \text{ with } \tilde{\mathbf{u}} = \{\tilde{u}^i\}_{i=1}^{d_\nu}. \end{aligned} \tag{4.50}$$

As before, each irreducible representation yields d_ν coupled subproblems. Once the above

problems have been solved on the the fundamental domain, we may extend the solutions to all of $\mathcal{B}_R$ by means of (4.37).

4.3.4 Self Consistent Field Iterations and Symmetry Based Reduction

So far, we have seen that, if at some stage of the self-consistent field iterations, the electronic density ρ is continuous and it is invariant under a finite group of isometries $\mathcal{G}$, then the problem of computing the Kohn Sham eigenstates admits symmetry based simplifications through (4.50) or (4.32). The natural question to ask, then, is if the newly computed set of eigenfunctions yields an electronic density that is continuous and invariant under the same group of isometries $\mathcal{G}$. It is important for us to know the answer to this question because it gives us an indication whether the self consistent iterations can be carried out in a consistent manner while computing the electronic properties of an objective structure. In the absence of this consistency, it is quite possible that an objective structure with an underlying symmetry group $\mathcal{G}$ has a ground state electronic density that is not commensurate with $\mathcal{G}$, but with some subgroup of $\mathcal{G}$. Such examples of symmetry breaking in physical systems tends to occur whenever there are degenerate energy minima.

In the case of electronic structure computation using the Kohn-Sham equations, it is easy to appreciate why symmetry breaking is likely to be observed in some cases.[22] We recall, that the self consistent method of solution, requires us to form the electronic density using the lowest few eigenstates of the Kohn-Sham operator. If the highest occupied Kohn-Sham state happens to be degenerate, then each of the eigenfunctions associated with the degenerate level are likely to lead to different electronic densities. While studying objective structures, this might be particularly problematic, because objective structures with an underlying non-Abelian group of symmetries will always have symmetry related degeneracies.

There are special circumstances, under which, it can be guaranteed that the electronic density resulting from symmetry adapted schemes, are commensurate with the symmetry of the objective structure. Specifically, we have:

Theorem 4.3.9. *Let $\mathcal{G}$ denote the finite group of isometries underlying a given fixed point free objective structure $\mathcal{S}$. Suppose that, we are computing the ground state electronic properties of $\mathcal{S}$, by means of a self consistent field iteration scheme for the Kohn-Sham equations (as in 4.10-4.12) and that the starting guess for the electronic density, ρ^1, is continuous and commensurate with the group $\mathcal{G}$. If, at each stage of the iteration, the*

[22] See Prodan [2005] for a specific example.

entire eigenspace associated with the highest occupied Kohn-Sham level, λ_n^k, is used for computing the electronic density, ρ^k, then, the ground state electronic density resulting from the above iteration scheme will be continuous and commensurate with the group $\mathcal{G}$.

Proof: The continuity of the electronic density at each stage of the iteration, follows from Lemma 4.1.1 and the comments in Section 4.2.2. To see, that under the hypothesis of the theorem, the resulting electronic density is commensurate with the symmetry group $\mathcal{G}$, let us proceed by induction. Therefore, let ρ^{k-1} be commensurate with the symmetry group $\mathcal{G}$. Based on the results developed in Section 4.3, this now implies that the eigenspace $Y_{\lambda_n^k}$ associated with λ_n^k must be a ν-symmetric set, if accidental degeneracies are absent; or that $Y_{\lambda_n^k}$ is a combination of more than one ν-symmetric set, if accidental degeneracies are present. We first assume, that the highest occupied level has no accidental degeneracy. The ν-symmetric eigenspace $Y_{\lambda_n^k}$, contributes a term of the form $\sum_{l=1}^{d_\nu} |\phi_l^k|^2$ to the electronic density ρ^k, with each $\phi_l^k \in Y_{\lambda_n^k}$. Now, for any $g \in \mathcal{G}$, the eigenspace $Y_{\lambda_n^k}$ must transform as in (4.37), and we may write this as:

$$\Phi(g^{-1} \bullet \mathbf{x}) = [\mathbf{D}^\nu(g)]^T \Phi(\mathbf{x}) \ . \tag{4.51}$$

Here, $\Phi(\cdot)$ is the d_ν dimensional vector field over the ball $\mathcal{B}_R$, formed by lining up the eigenfunctions $\{\phi_l^k\}_{l=1}^{d_\nu}$ that lie in $Y_{\lambda_n^k}$ and $\mathbf{D}^\nu(g)$ denotes the matrix of unitary irreducible representations that appears in (4.37). In this notation, the contribution to the electronic density can be expressed as:

$$\rho_{Y_{\lambda_n^k}}(\mathbf{x}) = \|\Phi(\mathbf{x})\|^2_{\mathbb{C}^{d_\nu}} = \langle \Phi(\mathbf{x}), \Phi(\mathbf{x}) \rangle_{\mathbb{C}^{d_\nu}} \ . \tag{4.52}$$

Hence, we have, for any $g \in \mathcal{G}$:

$$\begin{aligned} \rho_{Y_{\lambda_n^k}}(g^{-1} \bullet \mathbf{x}) &= \langle \Phi(g^{-1} \bullet \mathbf{x}), \Phi(g^{-1} \bullet \mathbf{x}) \rangle_{\mathbb{C}^{d_\nu}} \\ &= \langle [\mathbf{D}^\nu(g)]^T \Phi(\mathbf{x}), [\mathbf{D}^\nu(g)]^T \Phi(\mathbf{x}) \rangle_{\mathbb{C}^{d_\nu}} \\ &= \langle \Phi(\mathbf{x}), \overline{[\mathbf{D}^\nu(g)]} [\mathbf{D}^\nu(g)]^T \Phi(\mathbf{x}) \rangle_{\mathbb{C}^{d_\nu}} \\ &= \langle \Phi(\mathbf{x}), \Phi(\mathbf{x}) \rangle_{\mathbb{C}^{d_\nu}} = \rho_{Y_{\lambda_n^k}}(\mathbf{x}) \ . \end{aligned} \tag{4.53}$$

Thus, the contribution to the electronic density, at the highest occupied level is commensurate with the group $\mathcal{G}$, provided accidental degeneracy is absent at this level. On the other hand, if there is accidental degeneracy, we may apply the above argument to each of the ν-symmetric sets that constitute $Y_{\lambda_n^k}$, to reach the same conclusions as (4.53). For

the Kohn-Sham states that lie below the highest occupied level, we are anyway forced to consider the entire eigenspace associated with any eigenvalue, and therefore, the above argument works for the contributions from these levels too. In summary therefore, provided the conditions of the theorem are met, we may always write $\sum_{i=1}^{n}|\phi_i^k|^2(g \bullet \mathbf{x}) = \sum_{i=1}^{n}|\phi_i^k|^2(\mathbf{x})$ for any $g \in \mathcal{G}$. It follows by (4.12), that we have $\rho^k(g \bullet \mathbf{x}) = \rho^k(\mathbf{x}), \forall g \in \mathcal{G}$, thus proving the theorem. ■

The above result gives us an indication of the circumstances under which one might have to study symmetry breaking bifurcations in the ground state electronic properties of objective structures. If the conditions of the above theorem are not met, and the highest occupied Kohn-Sham level is degenerate at some stage of the Kohn-Sham iterations, it would, perhaps, be desirable to fork off multiple calculations, each one corresponding to the usage of one of the degenerate eigenstates. We find it useful to mention, that in the setting of the so called extended Kohn Sham scheme [Le Bris, 2003], these situations can never occur. In particular, finite temperature Kohn-Sham theory [Mermin, 1965; Martin, 2004] will always result in electronic densities commensurate with the symmetry of the objective structure[Prodan, 2005]. The reason for this is that these modified theories consider averaged out contributions from all degenerate eigenstates.

In the next chapter, we will work through two numerical setups for implementation of some of the symmetry adaptation techniques developed in this chapter.

Chapter 5

Numerical Solution Schemes

We will now, work through the set up of Kohn-Sham Density Functional Theory calculations that employ some of the techniques developed in the previous chapter. First, we will discuss a simple, but illustrative finite difference approach that is geared toward exploiting the particular symmetry group D_{2h}. We will then work through the setup of a more general spectral scheme using spherical basis functions, that can handle any objective structure generated by a finite group of isometries.

5.1 Set up of a Simple Numerical Example Using Finite Differences

For setting up our computations, we will use a rectangular grid and a high order finite difference algorithm [Chelikowsky et al., 1994] on that grid. The specific objective structure that we have in mind is a ring of atoms that displays the symmetry group D_{2h}. The reason for choosing this particular case is that this symmetry group is compatible with rectangular grids and that it is an Abelian group.

Let us consider the situation in Figure 5.1. Let the cubic computational domain, into which the objective structure is embedded, be denoted as $\mathcal{K}$. Any finite $\mathcal{O} \subset \mathcal{K}$ will be called an objective grid if it respects the symmetry of the group D_{2h}. Specifically, this means that, if $(x, y, z) \in \mathcal{O}$, then the points $(-x, y, z)$, $(x, -y, z)$, $(x, y, -z)$, $(-x, -y, z)$, $(x, -y, -z)$, $(x, -y, -z)$ and $(-x, -y, -z)$ all belong to $\mathcal{O}$. Let us suppose that the objective grid $\mathcal{O}$ consists of the finite set of points $\mathbf{p}_i \in \mathbb{R}^3, i = 1, \ldots, \mathcal{N}$. We consider an indexing function on $\mathcal{O}$, that is a bijection $\mathcal{S} : \mathcal{O} \to \{1, 2, \ldots, \mathcal{N}\}$ (for example, $\mathcal{S}(\mathbf{p}_i) = i$). The group action on $\mathcal{O}$ is a bijection from $\mathcal{O}$ to $\mathcal{O}$ and so we may associate with each $g \in \mathcal{G}$, a bijection $\pi_g : \mathcal{O} \to \mathcal{O}$, so that the set of permutations $\Pi_{\mathcal{G}} = \{\pi_g : g \in \mathcal{G}\}$ is a group

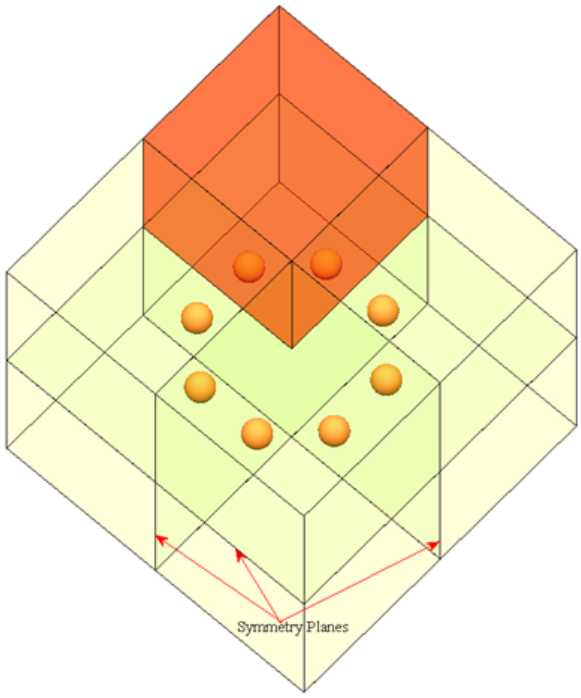

Figure 5.1: Schematic of Problem set up: An objective structure (ring of atoms) embedded in a cubic computational domain. The reflection planes and the fundamental domain have been shown. (Figure not to scale.)

under composition of functions and is in fact an isomorphism of the group $\mathcal{G}$. Thus, we have $\forall g \in \mathcal{G}, \mathbf{x} \in \mathcal{O},\ g(\mathbf{x}) = \pi_g(\mathbf{x})$. So, if $\mathbf{x} = \mathbf{p}_i$, with $i = \mathcal{S}(x)$, then $g(\mathbf{x}) = \mathbf{p}_j$ with $j = \mathcal{S}(g(\mathbf{x})) = \mathcal{S}(\pi_g(\mathbf{x}))$. This adequately specifies the group action of $\mathcal{G}$ on $\mathcal{O}$. Now, we consider any function $f : \mathcal{O} \to \mathbb{C}$, defined over the grid. We are interested in the group action on such functions.[1] Each such function is really a vector $\tilde{f} \in \mathbb{C}^{\mathcal{N}}$ with components $\tilde{f}(i), i = 1, \ldots, \mathcal{N}$, and in fact, $\forall \mathbf{x} \in \mathcal{O}, f(\mathbf{x}) = \tilde{f}(\mathcal{S}(\mathbf{x}))$. By the Lemma 3.2.2 we have that the group action on f can be given as $g \bullet f(\mathbf{x}) = f(g^{-1} \bullet \mathbf{x})$. Thus, in terms of the vector $\tilde{f}$, $g \in \mathcal{G}$ acts on $\tilde{f}$ to give the vector $\tilde{v}_g \in \mathbb{C}^{\mathcal{N}}$ whose components satisfy, for $i = 1, \ldots, \mathcal{N}, \tilde{v}_g(i) = \tilde{f}(\mathcal{S}(g^{-1}(\mathcal{S}^{-1}(i))))$. We may now investigate the linear transformations that take the vector $\tilde{f}$ into corresponding vector $\tilde{v}_g$ for each $g \in \mathcal{G}$. Clearly the set of such linear transformations $\mathcal{R}_{\mathcal{G}} = \{R_g : g \in \mathcal{G}\}$ is in one to one correspondence with the set $\Pi_{\mathcal{G}}$, by the following definition of the matrix representation of each R_g: for $i, j \in \{1, \ldots, \mathcal{N}\},\ R_g(i, j) = 1$, if $\mathcal{S}^{-1}(i) = \pi_g(\mathcal{S}^{-1}(j))$ and $R_g(i, j) = 0$ otherwise. Theorem 3.2.3 indicates that the mapping $\zeta : \mathcal{G} \to \mathcal{R}_{\mathcal{G}}$ must form a unitary representation of $\mathcal{G}$ on $\mathbb{C}^{\mathcal{N}}$. By direct calculation, we can indeed check that each R_g is a unitary matrix,

[1] We note that any such function is trivially square integrable with respect to the counting measure because $\mathcal{O}$ is finite.

since, if $A = R_g R_g^*$, then we have, for the components of A:

$$A(i,j) = \sum_{k=1}^{\mathcal{N}} R_g(i,k) R_g^*(k,j) = \sum_{k=1}^{\mathcal{N}} R_g(i,k) R_g(j,k) \tag{5.1}$$

Clearly, $A(i,j) \neq 0$ if and only if $R_g(i,k)R_g(j,k) \neq 0$ for some $k \in \{1,2,\ldots,\mathcal{N}\}$, that is, if and only if $\mathcal{S}^{-1}(i) = \pi_g(\mathcal{S}^{-1}(k)) = \mathcal{S}^{-1}(j)$ for some k. But the summation in (5.1) makes $\pi_g(\mathcal{S}^{-1}(k))$ eventually take on every value in $\{1,2,\ldots,\mathcal{N}\}$. Thus, we see that $A(i,j) \neq 0$ if and only if $i = j$ and in fact, $A(i,j) = 1$ when $i = j$. Thus, $A = I$. Similarly, we also have $R_g^* R_g = I$. Further, using the fact that $\Pi_{\mathcal{G}}$ is a group under the operation of composition of functions, it is easy to check (via a calculation similar to (5.1)) that the matrix representations of R_g form a matrix group isomorphic to $\mathcal{G}$ (i.e, for $g, h \in \mathcal{G}, R_g R_h = R_{gh}, R_{g^{-1}} = R_g^{-1}$). This confirms the conclusions we drew in Lemma 3.2.2, as adapted to this special case and it also presents us with a suitable representation theory on the objective grid $\mathcal{O}$ in terms of permutations of the grid points.

To obtain the discretized version of the Kohn-Sham equations over the grid, we proceed as in [Chelikowsky et al., 1994], and we write the Laplace operator as a high order finite difference of the form:

$$h^2 \Delta\psi(x,y,z) \approx$$
$$\left(\sum_{j=-N}^{N} C_j \psi(x+jh,y,z) + \sum_{j=-N}^{N} C_j \psi(x,y+jh,z) + \sum_{j=-N}^{N} C_j \psi(x,y,z+jh) \right). \tag{5.2}$$

Here, h is the uniform mesh spacing in all three directions and the coefficients C_j are symmetric with respect to zero, that is $C_j = C_{-j}$. Evaluating the effective potential at each grid point (x,y,z) and adding this to the Laplace operator therefore, gives us a way of discretizing the linearized eigenvalue problem associated with the Kohn-Sham iterations. By Lemma 4.1.1, the computation of the potential itself needs to be only done over the fundamental domain in these calculations since it can then be extended to the rest of the computational domain by symmetry.

We notice, that the discretized Hamiltonian operator so obtained, commutes with the group action. This is due to the symmetry of the coefficients appearing in the Laplace operator, and the symmetry in the effective potential V. Thus, the discretized Hamiltonian will commute with each of the matrices R_g associated with the representation of the group D_{2h} over $\mathcal{O}$. By the discussion in Section 4.3.1, we conclude that the discretized Hamiltonian can be put into block diagonal form by a suitable choice of basis vectors. To obtain these

basis vectors, we first need to obtain the projectors onto the invariant subspaces, as given in Theorem 3.2.15. For each such projector, we may compute the eigenvectors which are associated with an eigenvalue of 1. We then line up these eigenvectors into a matrix Q and $Q^T \mathfrak{H}_h Q$ gives us the required block diagonal form for the discrete Hailtonian $\mathfrak{H}_h$. In the present case since D_{2h} is Abelian and is of order 8, so there are 8 such projectors. Block diagonalization of the Hamiltonian, as well as computing the effective potential only over the fundamental domain are likely to lead to increased computational efficiency.

The above approach of block diagonalization of the Hamiltonian is very much in line with the material presented in Section 4.3.1. An alternative to this approach, might be to work on the fundamental domain only. As suggested by the developments in Section 4.3.3, we may solve the subproblems corresponding to each irreducible representation of the group D_{2h}, in accordance with equation (4.50), on the fundamental domain. This will lead us to odd or even boundary conditions on the wavefunction. This approach is more attractive than the former one, since the new boundary conditions are easy to implement in the finite difference setting, and because the memory overheads are much lesser. We are in the process of implementing both these strategies at this point of time.

5.2 Set up of a spectral scheme

While the above solution scheme is relatively easy to setup and implement, it is not sufficiently general, in the sense that the rectangular grids only allow some point group symmetries to be exploited. Even with curvilinear grids, setup of problems with non-Abelian symmetry groups is somewhat non trivial because the symmetry adapted boundary conditions result in coupled sub-problems (Section 4.3.3) over the fundamental domain. Moreover, high order finite differences, which are required for getting accurate solutions to the Kohn-Sham equations, do not appear to be an attractive choice in spherical coordinates. Numerical schemes designed for crystals are very often spectral in nature and it appears consistent to us that schemes designed for objective structures, mutatis mutandis, should be spectral as well.

The steps behind solving a governing equation by a spectral approach usually involve, first discovering a good basis set and then working out form of the governing equation in this basis set. We systematically investigate the above steps before looking at how the effects of symmetry can be accounted for.

5.2.1 Obtaining a suitable basis set

For the formulation of the spectral scheme[2], we need an orthonormal basis of $\mathsf{L}^2(\mathcal{B}_R)$. An easy way of obtaining such a basis is to look at the set of eigenfunctions of any self-adjoint operator with a compact resolvent. With this in mind, we look at the Laplace operator on $\mathsf{L}^2(\mathcal{B}_R)$ with Dirichlet boundary conditions. We will work in spherical coordinates since these are the natural coordinates on the sphere and at the same time, the group action on any point in the sphere can be easily expressed in these coordinates. The eigenfunctions of the Dirichlet Laplacian on the sphere which are regular at the origin are expressible in terms of spherical Bessel functions and spherical harmonics.[3] Let us look into this in a little more detail.

The eigenvalue problem for the Laplacian on the sphere with Dirichlet boundary conditions is as follows:

$$-\Delta F = \tilde{\lambda} F \ , \tag{5.3}$$

$$F = 0 \ \text{ on } x \in \partial\mathcal{B}_R \ . \tag{5.4}$$

We first introduce spherical coordinates for $r \in (0, R], \vartheta \in [0, \pi]$ and $\varphi \in [0, 2\pi]$:

$$\begin{aligned} x &= r \sin\vartheta \cos\varphi \\ y &= r \sin\vartheta \sin\varphi \\ z &= r \cos\vartheta \end{aligned} \tag{5.5}$$

Next, we set $\tilde{\lambda} = k^2$ for convenience[4] and note that, the above problem posed in terms of $\hat{F}(r, \vartheta, \varphi)$, that is, $F(\mathbf{x})$ expressed in spherical coordinates reads as:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \hat{F}}{\partial r}\right) + \frac{1}{r^2 \sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta \frac{\partial \hat{F}}{\partial \vartheta}\right) + \frac{1}{r^2 \sin^2\vartheta}\frac{\partial^2 \hat{F}}{\partial \varphi^2} + k^2 \hat{F} = 0 \ , \tag{5.7}$$

$$\hat{F}(r = R, \vartheta, \varphi) = 0 \ . \tag{5.8}$$

[2]Recently, we became aware of a spectral scheme for molecular clusters [Broglia et al., 2004], that employs spherical basis functions and is, in some ways, similar to the scheme presented here.

[3]The spherical harmonics themselves are related to the irreducible representations of SO(3). They form the basis vectors of the invariant subspaces associated with the irreducible representations of SO(3).

[4]Note that the Rayleigh quotient form allows us to write the lowest eigenvalue of the Dirichlet Laplace as:

$$\tilde{\lambda}_1 = \inf_{f \in \mathsf{H}^1_0(\mathcal{B}_R)} \frac{\int_{\mathcal{B}_R} |\nabla f|^2}{\int_{\mathcal{B}_R} |f|^2} \tag{5.6}$$

Hence, the lowest eigenvalue is non-negative. Since the only solution to $-\Delta f = 0$ with Dirichlet boundary conditions is $f = 0$, it must be that $\tilde{\lambda}_1 > 0$. Hence, all eigenvalues of the Dirichlet Laplacian are positive.

We use the canonical approach of separation of variables to write:

$$\hat{F}(r, \vartheta, \varphi) = \mathcal{R}(r)\, \Theta(\vartheta)\, \Phi(\varphi) \ .$$

Substituting this ansatz into (5.7) and multiplying by $r^2/(\mathcal{R}\vartheta\varphi)$ gives us:

$$\frac{1}{\mathcal{R}}\frac{d}{dr}\left(r^2\frac{d\mathcal{R}}{dr}\right) + k^2r^2 + \frac{1}{\Theta \sin\vartheta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right) + \frac{1}{\Phi \sin^2\vartheta}\frac{d^2\Phi}{d\varphi^2} = 0 \ . \tag{5.9}$$

We multiply (5.9) by $\sin^2\vartheta$ and observe that the last term $\dfrac{1}{\Phi}\left(\dfrac{d^2\Phi}{d\varphi^2}\right)$ only involves φ while the first two terms only depend on r and ϑ. This implies, that the last term must be a constant and so we write:

$$\frac{1}{\Phi}\left(\frac{d^2\Phi}{d\varphi^2}\right) = -m^2 \ , \tag{5.10}$$

The solution to (5.10) is $\Phi(\varphi) = e^{im\varphi}$ and to ensure the solution is continuous across the XZ plane, we must have $\Phi(\varphi) = \Phi(\varphi + 2\pi s)$ for $s \in \mathbb{Z}$. Thus, we get:

$$\Phi(\varphi) = e^{im\varphi} \ , \ m \in \mathbb{Z}. \tag{5.11}$$

We substitute this solution into (5.9) and we get:

$$\frac{1}{\mathcal{R}}\frac{d}{dr}\left(r^2\frac{d\mathcal{R}}{dr}\right) + k^2r^2 + \frac{1}{\Theta \sin\vartheta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right) - \frac{m^2}{\sin^2\vartheta} = 0 \ . \tag{5.12}$$

Now, we observe that the last two terms in the above equation are a function of ϑ only while the first two depend on r only. Thus, the last two terms must equal a constant, which we write as $l(l+1)$ (to ensure no divergence for $\cos\vartheta = 1$ or $\cos\vartheta = -1$) and we get:

$$\frac{1}{\Theta \sin\vartheta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right) - \frac{m^2}{\sin^2\vartheta} = -l(l+1) \ . \tag{5.13}$$

We let $\eta = \cos\vartheta$ in the above and obtain the ordinary differential equation:

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{d\tilde{\Theta}}{d\eta}\right] + \left(l(l+1) - \frac{m^2}{1-\eta^2}\right)\tilde{\Theta}(\eta) = 0 \, , \tag{5.14}$$

where $\tilde{\Theta}(\eta) = \Theta(\cos^{-1}\eta)$. Equation (5.14) above is the Associated Legendre equation and

so, its solutions are the Associated Legendre Polynomials:

$$\tilde{\Theta}(\eta) = \mathcal{P}_l^m(\eta) \ , \ l = 0, 1, 2, \dots \text{ and } m = -l, -(l-1), \dots, (l-2), (l-1), l \ . \quad (5.15)$$

The functions Θ and Φ are often combined and normalized on the unit sphere to yield the spherical harmonics for $l = 0, 1, 2, \dots$ and $m = -l, -(l-1), \dots, (l-1), l$:

$$\mathcal{Y}_l^m(\vartheta, \varphi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} \, \mathcal{P}_l^m(\cos\vartheta) \, e^{im\varphi} \ . \quad (5.16)$$

Finally it remains to look at the radial equation, which from (5.12) and (5.13) is:

$$\frac{d}{dr}\left(r^2 \frac{d\mathcal{R}}{dr}\right) + [k^2 r^2 - l(l+1)]\mathcal{R} = 0 \ . \quad (5.17)$$

To see this equation in a more recognizable form, we let $\tilde{r} = kr$ and we set $\mathcal{R}(r) = \tilde{\mathcal{R}}(\tilde{r})$. This gives us:

$$\tilde{r}^2 \frac{d^2\tilde{\mathcal{R}}}{d\tilde{r}^2} + 2\tilde{r}\frac{d\tilde{\mathcal{R}}}{d\tilde{r}} + [\tilde{r}^2 - l(l+1)]\tilde{\mathcal{R}} = 0 \ , \quad (5.18)$$

which is simply, spherical Bessel's differential equation. It's solutions are the so called spherical Bessel and Neumann functions. These functions admit expressions in terms of (the usual) Bessel and Neumann functions (that is, solutions to the usual Bessel equation) and for the purpose of implementation, it is important for us to obtain these expressions. We let $\tilde{\mathcal{R}}(\tilde{r}) = \kappa(\tilde{r})/\sqrt{\tilde{r}}$ and substitute this into the above equation to arrive at (after a bit of algebra):

$$\tilde{r}^2 \frac{d^2\kappa}{d\tilde{r}^2} + \tilde{r}\frac{d\kappa}{d\tilde{r}} + [\tilde{r}^2 - (l + \frac{1}{2})^2]\kappa = 0 \ . \quad (5.19)$$

This is Bessel's equation of order $(l + \frac{1}{2})$. The general solution is:

$$\kappa(\tilde{r}) = c_1 J_{l+\frac{1}{2}}(\tilde{r}) + c_2 N_{l+\frac{1}{2}}(\tilde{r}) \ , \quad (5.20)$$

where $J_\nu(\cdot)$ and $N_\nu(\cdot)$, denote Bessel functions of the first and second kind respectively. Thus, the solutions to the equation (5.18) are given as:

$$\tilde{\mathcal{R}}(\tilde{r}) = c_1 \frac{J_{l+\frac{1}{2}}(\tilde{r})}{\sqrt{\tilde{r}}} + c_2 \frac{N_{l+\frac{1}{2}}(\tilde{r})}{\sqrt{\tilde{r}}} \ , \quad (5.21)$$

and the solutions to the radial equation (5.17) are given by:

$$\mathcal{R}(r) = c_1 \frac{J_{l+\frac{1}{2}}(kr)}{\sqrt{kr}} + c_2 \frac{N_{l+\frac{1}{2}}(kr)}{\sqrt{kr}} \ . \tag{5.22}$$

The boundary conditions for the problem (5.17) are:

$$\mathcal{R}(R) = 0 \text{ and } \mathcal{R}(0) \text{ is finite.} \tag{5.23}$$

The second condition in the above eliminates the second term from (5.22) while keeping the first term since Bessel functions of the first kind are regular at the origin while the Bessel functions of the second kind are not. The first condition, on the other hand gives us:

$$\mathcal{R}(R) = c_1 \frac{J_{l+\frac{1}{2}}(kR)}{\sqrt{kR}} = 0 \ . \tag{5.24}$$

Thus, we must have $J_{l+\frac{1}{2}}(kR) = 0$, that is, $kR = b^n_{l+\frac{1}{2}}$, where $b^n_{l+\frac{1}{2}}$ is the n^{th} zero of the Bessel function of order $(l + \frac{1}{2})$. We may fix the constant c_1 in (5.22) by using a normalization condition. In this case, we require:

$$c_1^2 \int_0^R r^2 \left[J_{l+\frac{1}{2}}\left(\frac{b^n_{l+\frac{1}{2}}}{R} r\right) \Big/ \sqrt{\frac{b^n_{l+\frac{1}{2}}}{R} r} \right]^2 dr = 1 \ , \tag{5.25}$$

$$\text{which implies ,} \quad c_1^2 \frac{R^3}{b^n_{l+\frac{1}{2}}} \int_0^R (r/R) \left[J_{l+\frac{1}{2}}\left(b^n_{l+\frac{1}{2}} \frac{r}{R} \right) \right]^2 d(r/R) = 1 \ ,$$

$$\text{which for } r_1 = r/R \text{ becomes:} \quad c_1^2 \frac{R^3}{b^n_{l+\frac{1}{2}}} \int_0^1 r_1 \left[J_{l+\frac{1}{2}}\left(b^n_{l+\frac{1}{2}} \, r_1 \right) \right]^2 dr_1 = 1 \ ,$$

$$\text{and using properties of Bessel functions this becomes:} \quad c_1^2 \frac{R^3}{b^n_{l+\frac{1}{2}}} \frac{1}{2} J^2_{(l+\frac{3}{2})}\left(b^n_{l+\frac{1}{2}} \right) = 1 \ . \tag{5.26}$$

So, we get finally:

$$\mathcal{R}(r) = \frac{1}{R J_{l+\frac{3}{2}}\left(b^n_{l+\frac{1}{2}} \right)} \sqrt{\frac{2}{r}} J_{l+\frac{1}{2}}\left(\frac{b^n_{l+\frac{1}{2}}}{R} r \right) \ , \tag{5.27}$$

$$\text{and} \quad \tilde{\lambda}_{l,m,n} = k^2 = \left(\frac{b^n_{l+\frac{1}{2}}}{R} \right)^2 \ . \tag{5.28}$$

Thus, a normalized eigenfunction of the Dirichlet Laplacian on the sphere has the form:

$$\hat{F}_{l,m,n}(r,\vartheta,\varphi) = c_{l,m,n}\,\frac{1}{\sqrt{r}} J_{l+\frac{1}{2}}\left(\frac{b^n_{l+\frac{1}{2}}}{R} r\right) \mathcal{P}^m_l(\cos\vartheta)\, e^{im\varphi}\ , \tag{5.29}$$

$$\text{with}\quad c_{l,m,n} = \frac{1}{R J_{l+\frac{3}{2}}\big(b^n_{l+\frac{1}{2}}\big)} \sqrt{\frac{(2l+1)}{2\pi}\frac{(l-m)!}{(l+m)!}}\ . \tag{5.30}$$

5.2.2 Expansion in spherical basis functions

Let $\phi \in \mathsf{L}^2(\mathcal{B}_R)$. Then the density of the basis set discussed above implies that for every $\epsilon > 0$, there exist numbers $\mathcal{L}, \mathcal{N} \in \mathbb{N}$ and complex numbers $\{a_{l,m,n} : (l,m,n) \in \Gamma\}$ with:

$$\| \phi - \sum_{(l,m,n)\in\Gamma} a_{l,m,n}\, F_{l,m,n} \|_{\mathsf{L}^2(\mathcal{B}_R)} < \epsilon\ , \tag{5.31}$$

where, $\Gamma = \{0,1,\ldots,\mathcal{L}\} \times \{-\mathcal{L},\ldots,\mathcal{L}\} \times \{1,\ldots,\mathcal{N}\}$. So, for the purpose of a numerical approximation, we fix $\mathcal{L}, \mathcal{N} \in \mathbb{N}$ and we let:

$$\phi(\mathbf{x}) = \sum_{(l,m,n)\in\Gamma} a_{l,m,n}\, F_{l,m,n}(\mathbf{x})\ . \tag{5.32}$$

We note that this ansatz automatically ensures the Dirichlet boundary conditions are satisfied. To determine the expansion coefficients, we will use the orthonormality of the basis set. To do this, we consider the inner product of ϕ with $F_{l',m',n'}$ in (5.32) and we obtain by orthonormality:

$$a_{l',m',n'} = \langle \phi, F_{l',m',n'} \rangle_{\mathsf{L}^2(\mathcal{D})}\ . \tag{5.33}$$

Let $\hat{\varphi}(r,\vartheta,\varphi)$ denote $\phi(\mathbf{x})$ in spherical coordinates. The inner product of ϕ and $F_{l',m',n'}$ can be evaluated in spherical coordinates by the expression:

$$\langle \phi, F_{l',m',n'} \rangle_{\mathsf{L}^2(\mathcal{D})} = \int_{r=0}^{r=R} \int_{\vartheta=0}^{\vartheta=\pi} \int_{\varphi=0}^{\varphi=2\pi} \hat{\varphi}(r,\vartheta,\varphi)\ \overline{\hat{F}_{l',m',n'}(r,\vartheta,\varphi)}\ r^2 \sin\vartheta\, d\vartheta\, d\varphi\, dr\ . \tag{5.34}$$

By substituting the expression for $\hat{f}_{m',n',k'}(r,\vartheta,\varphi)$, we get:

$$a_{m',n',k'} =$$
$$c_{l,m,n} \times \int_{r=0}^{r=R} \int_{\vartheta=0}^{\vartheta=\pi} \int_{\varphi=0}^{\varphi=2\pi} \hat{\varphi}(r,\vartheta,\varphi)\, J_{l+\frac{1}{2}}\left(\frac{b^n_{l+\frac{1}{2}}}{R} r\right) \mathcal{P}_l^m(\cos\vartheta)\, e^{-im\varphi}\, r\sin\vartheta\, d\vartheta\, d\varphi\, dr \ . \tag{5.35}$$

To obtain a discretization of the linear governing equation (4.13), we substitute (5.32) to get:

$$\frac{1}{2}\sum_{\Gamma} a_{l,m,n}\ \tilde{\lambda}_{l,m,n}\ \hat{F}_{l,m,n}(r,\vartheta,\varphi) + \hat{V}(r,\vartheta,\varphi)\sum_{\Gamma} a_{l,m,n}\ \hat{F}_{l,m,n}(r,\vartheta,\varphi)$$
$$= \lambda \sum_{\Gamma} a_{l,m,n}\ \hat{F}_{l,m,n}(r,\vartheta,\varphi) \ . \tag{5.36}$$

Next, let us suppose that the expansion coefficients of $\hat{V}(r,\vartheta,\varphi)$ are known:

$$\hat{V}(r,\vartheta,\varphi) = \sum_{\Gamma} v_{\tilde{l},\tilde{m},\tilde{n}}\ \hat{F}_{\tilde{l},\tilde{m},\tilde{n}}(r,\vartheta,\varphi) \ . \tag{5.37}$$

The actual computation of these coefficients involves a number of steps and these are outlined in a later section. We can substitute this expression into (5.36) to get:

$$\frac{1}{2}\sum_{\Gamma} a_{l,m,n}\ \tilde{\lambda}_{l,m,n}\ \hat{F}_{l,m,n}(r,\vartheta,\varphi) + \sum_{\Gamma}\sum_{\Gamma}\ a_{l,m,n}\, v_{\tilde{l},\tilde{m},\tilde{n}}\ \hat{F}_{\tilde{l},\tilde{m},\tilde{n}}(r,\vartheta,\varphi)\ \hat{F}_{l,m,n}(r,\vartheta,\varphi)$$
$$= \lambda \sum_{\Gamma} a_{l,m,n}\ \hat{F}_{l,m,n}(r,\vartheta,\varphi) \ . \tag{5.38}$$

We now take the inner product of this equation with $\hat{F}_{l',m',n'}(r,\vartheta,\varphi)$ and use orthonormality of the basis set to obtain the following system of linear equations for $a_{l',m',n'}\ ,\ (l',m',n') \in \Gamma$:

$$\frac{1}{2}\tilde{\lambda}_{l',m',n'}\ a_{l',m',n'} + \sum_{\Gamma}\sum_{\Gamma} \mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}\ v_{\tilde{l},\tilde{m},\tilde{n}}\ a_{l,m,n} = \lambda\, a_{l',m',n'} \ , \tag{5.39}$$

$$\text{where,} \quad \mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} = \langle \hat{F}_{\tilde{l},\tilde{m},\tilde{n}}\ \hat{F}_{l,m,n}\ ,\ \hat{F}_{l',m',n'} \rangle_{\mathsf{L}^2(\mathcal{B}_R)} \ . \tag{5.40}$$

The computation of the scalars $\mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}$ need some further simplifications which we'll discuss shortly. For now, let us discuss the matrix eigenvalue problem set up.

5.2.3 Set up of Matrix Eigenvalue Problem

To make clear sense of (5.39) as a matrix eigenvalue problem, we may introduce the following notation:

$$\text{for any } (l,m,n),(l',m',n') \in \Gamma, \quad \mathcal{Z}^{(l',m',n')}_{(l,m,n)} = \sum_{(\tilde{l},\tilde{m},\tilde{n})\in\Gamma} v_{\tilde{l},\tilde{m},\tilde{n}}\, \mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} \tag{5.41}$$

Then, (5.39) simply reads as:

$$\frac{1}{2}\tilde{\lambda}_{l',m',n'}\, a_{l',m',n'} + \sum_{(l,m,n)\in\Gamma} a_{l,m,n}\, \mathcal{Z}^{(l',m',n')}_{(l,m,n)} = \lambda\, a_{l',m',n'}\ . \tag{5.42}$$

Now, let $P = (\mathcal{L}+1)\times(2\mathcal{L}+1)\times\mathcal{N}$ and let $\mathcal{I} : \Gamma \to \{1,2,\ldots,P\}$ be an indexing map. Let $\mathcal{J} : \{1,2,\ldots,P\} \to \Gamma$ denote the inverse map to $\mathcal{I}$. The spectral method basically converts the infinite dimensional problem posed in (4.13) to a problem posed on the vector space $\mathbb{C}^P$. The discretized problem (5.42) can be converted to a $P\times P$ sized matrix eigenvalue problem with the aid of the above mentioned indexing functions. We may set, for $i,j \in \{1,2,\ldots,P\}$:

$$\begin{aligned} H_{i,j} &= \frac{1}{2}\tilde{\lambda}_{\mathcal{J}(i)} + \mathcal{Z}^{\mathcal{J}(i)}_{\mathcal{J}(i)} = \frac{1}{2}\lambda_{\mathcal{J}(i)} + \sum_{(\tilde{l},\tilde{m},\tilde{n})\in\Gamma} v_{\tilde{l},\tilde{m},\tilde{n}}\, \mathcal{W}^{\mathcal{J}(i)}_{\mathcal{J}(i)\,,\,(\tilde{l},\tilde{m},\tilde{n})}, \quad \text{for } i=j, \\ &= \mathcal{Z}^{\mathcal{J}(i)}_{\mathcal{J}(j)} = \sum_{(\tilde{l},\tilde{m},\tilde{n})\in\Gamma} v_{\tilde{l},\tilde{m},\tilde{n}}\, \mathcal{W}^{\mathcal{J}(i)}_{\mathcal{J}(j)\,,\,(\tilde{l},\tilde{m},\tilde{n})} \quad \text{for } i\neq j. \end{aligned} \tag{5.43}$$

Following the computation of these matrix coefficients, the lowest N eigenvalue eigenvector pairs of the matrix need to be computed to determine the N lowest electronic states. We may note however, that the matrix H is not sparse in general. The Kohn Sham eigenstates must be real, and this is ensured by the fact that the operator in (4.13) is self-adjoint. Accordingly, we can easily check that the matrix in (5.43) only yields real eigenvalues by checking that it is Hermitian. This follows from the facts that the coefficients $\mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}$ and the Laplacian eigenvalues $\tilde{\lambda}_{l',m',n'}$ are all real and further, since the potential $V(\mathbf{x})$ appearing in (4.13) is a real scalar field, it's expansion coefficients obey:

$$\begin{aligned} \overline{v_{\tilde{l},\tilde{m},\tilde{n}}} &= \overline{\int_{\mathcal{B}_R} V(\mathbf{x})\, \overline{\hat{F}_{\tilde{l},\tilde{m},\tilde{n}}}\, d\mathbf{x}} = \int_{\mathcal{B}_R} \overline{V(\mathbf{x})\, \overline{\hat{F}_{\tilde{l},\tilde{m},\tilde{n}}}}\, d\mathbf{x} = \int_{\mathcal{B}_R} V(\mathbf{x})\, \overline{(\overline{\hat{F}_{\tilde{l},\tilde{m},\tilde{n}}})}\, d\mathbf{x} \\ &= \int_{\mathcal{B}_R} V(\mathbf{x})\, \overline{(-1)^{\tilde{m}}\, \hat{F}_{\tilde{l},-\tilde{m},\tilde{n}}}\, d\mathbf{x} = (-1)^{\tilde{m}} \int_{\mathcal{B}_R} V(\mathbf{x})\, \overline{\hat{F}_{\tilde{l},-\tilde{m},\tilde{n}}}\, d\mathbf{x} = (-1)^{\tilde{m}}\, v_{\tilde{l},-\tilde{m},\tilde{n}}\ . \end{aligned} \tag{5.44}$$

The above relation (5.44) should be kept in mind since it can cut the task of computing the expansion coefficients of $V(\mathbf{x})$ in half, that is, we may directly obtain the coefficient $v_{\tilde{l},-\tilde{m},\tilde{n}}$ from the coefficient $v_{\tilde{l},\tilde{m},\tilde{n}}$. As far as implementation is concerned, to fill up the entries of H, we iterate over i and j keeping in mind that H is Hermitian. For each chosen i, j we compute the coefficients $\mathcal{W}^{\mathcal{J}(i)}_{\mathcal{J}(j)\,,\,(\tilde{l},\tilde{m},\tilde{n})}$ and the expansion coefficients $v_{\tilde{l},\tilde{m},\tilde{n}}$. The summations over Γ appearing in (5.43) basically correspond to taking a dot product between the vectors that hold these coefficients once they have been computed.

5.2.4 Computation of the coefficients $\mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}$

To simplify the coefficients, we first note that the complex dependence of the basis functions is only through the spherical harmonics $\mathcal{Y}^m_l(\vartheta,\varphi)$ and therefore the basis functions obey:

$$\overline{\hat{F}_{l',m',n'}} = (-1)^{m'}\,\hat{F}_{l',-m',n'} \tag{5.45}$$

Thus, we must have:

$$\begin{aligned}
&\mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} \\
&= \langle \hat{F}_{\tilde{l},\tilde{m},\tilde{n}}\,\hat{F}_{l,m,n}\,,\,\hat{F}_{l',m',n'}\rangle_{\mathsf{L}^2(\mathcal{B}_R)} \\
&= (-1)^{m'}\int_{\mathcal{B}_R}\hat{F}_{\tilde{l},\tilde{m},\tilde{n}}\hat{F}_{l,m,n}\hat{F}_{l',-m',n'}\;d\mathbf{x} \\
&= \tilde{\kappa}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}\times\int_0^R\left(\frac{1}{\sqrt{r}}\right)^3 J_{l+\frac{1}{2}}\left(\frac{b^n_{l+\frac{1}{2}}}{R}r\right)J_{\tilde{l}+\frac{1}{2}}\left(\frac{b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}}{R}r\right)J_{l'+\frac{1}{2}}\left(\frac{b^{n'}_{l'+\frac{1}{2}}}{R}r\right)r^2\,dr \\
&\qquad\qquad\times\int_0^{2\pi}\int_0^{\pi}\mathcal{Y}^m_l(\vartheta,\varphi)\,\mathcal{Y}^{\tilde{m}}_{\tilde{l}}(\vartheta,\varphi)\,\mathcal{Y}^{-m'}_{l'}(\vartheta,\varphi)\sin\vartheta\;d\vartheta\,d\varphi\;. \qquad (5.46)
\end{aligned}$$

$$\text{where,}\quad \tilde{\kappa}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} = (-1)^{m'}\frac{\sqrt{8}}{R^3}\,\frac{1}{J_{l+\frac{3}{2}}\left(b^n_{l+\frac{1}{2}}\right)}\,\frac{1}{J_{\tilde{l}+\frac{3}{2}}\left(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}\right)}\,\frac{1}{J_{l'+\frac{3}{2}}\left(b^{n'}_{l'+\frac{1}{2}}\right)}\;. \tag{5.47}$$

The integral of the spherical harmonics over the unit sphere can be simplified in terms of the Wigner 3-j symbols or the Clebsch-Gordan coefficients [Messiah, 1962]. We may write:

$$\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi}\mathcal{Y}^m_l(\vartheta,\varphi)\,\mathcal{Y}^{\tilde{m}}_{\tilde{l}}(\vartheta,\varphi)\,\mathcal{Y}^{-m'}_{l'}(\vartheta,\varphi)\sin\vartheta\;d\vartheta\,d\varphi \\
&\qquad = \sqrt{\frac{(2l+1)(2\tilde{l}+1)(2l'+1)}{4\pi}}\begin{pmatrix} l & \tilde{l} & l' \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & \tilde{l} & l' \\ m & \tilde{m} & -m'\end{pmatrix} \qquad (5.48)
\end{aligned}$$

The 3-j symbols themselves are quite expensive to compute. The naive way of evaluating them would be to use Lebedev integrators [Lebedev, 1976] to perform the numerical quadratures on the unit sphere. Alternately, they can be evaluated directly through the Racah formula [Messiah, 1962] or through recursive methods [Schulten and Gordon, 1976; Luscombe and Luban, 1998]. Fortunately, many of the 3-j symbols are zero (the only non-zero 3-j symbols are ones for which $m + \tilde{m} = -m'$ and $|l - \tilde{l}| \leq l' \leq l + \tilde{l}$) and the non-zero ones behave nicely under permutation symmetries. These two restrictions allow us to reduce the storage and computation overheads associated with the 3-j symbols significantly.

On the other hand, the first integral in the radial direction in (5.46) can be made free of R by the substitution $r_2 = r/R$. The integral then becomes:

$$R^{\frac{3}{2}} \int_0^1 J_{l+\frac{1}{2}}\left(b^n_{l+\frac{1}{2}} r_2\right) J_{\tilde{l}+\frac{1}{2}}\left(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}} r_2\right) J_{l'+\frac{1}{2}}\left(b^{n'}_{l'+\frac{1}{2}} r_2\right) \sqrt{r_2}\, dr_2 \;:= R^{\frac{3}{2}}\, I^{(l',n')}_{(l,n),(\tilde{l},\tilde{n})} \quad . \tag{5.49}$$

We can precompute the integrals $I^{(l',n')}_{(l,n),(\tilde{l},\tilde{n})}$ and store them ahead of time so as to speed up computations. The fact that these integrals always appear in multiplication with the 3j-coefficients implies that only certain of the integrals need to be computed. Specifically, we only need to compute the intgrals for which $|l - \tilde{l}| \leq l' \leq l + \tilde{l}$. Furthermore, (5.49) clearly demonstrates that we are allowed to permute between the three pairs of natural numbers $(l, n), (\tilde{l}, \tilde{n})$ and (l', n') while keeping the value of the integral the same. As with the 3-j symbols therefore, these restrictions can be used to obtain computational efficiency.

Based on the above discussion, we can finally write the following expression:

$$\mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} = \kappa^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} I^{(l',n')}_{(l,n),(\tilde{l},\tilde{n})} \begin{pmatrix} l & \tilde{l} & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & \tilde{l} & l' \\ m & \tilde{m} & -m' \end{pmatrix}, \tag{5.50}$$

$$\text{with,} \quad \kappa^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})} = (-1)^{m'} \left(\frac{2}{R}\right)^{\frac{3}{2}} \frac{1}{J_{l+\frac{3}{2}}\left(b^n_{l+\frac{1}{2}}\right)} \frac{1}{J_{\tilde{l}+\frac{3}{2}}\left(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}\right)} \frac{1}{J_{l'+\frac{3}{2}}\left(b^{n'}_{l'+\frac{1}{2}}\right)} \times \sqrt{\frac{(2l+1)(2\tilde{l}+1)(2l'+1)}{4\pi}} \,. \tag{5.51}$$

The above discussion regarding the the expansion of the term $V(\mathbf{x})\phi(\mathbf{x})$ can be summarized by means of the following result:

Proposition 5.2.1. *Let $p(\mathbf{x}), q(\mathbf{x})$ be functions defined on the sphere such that $p, q \in$*

$\mathsf{L}^2(\mathcal{B}_R)$ and let the expansion of these functions in the basis set $\{F_{l,m,n}\}_{(l,m,n)\in\Gamma}$ be:

$$p = \sum_{\Gamma} \breve{p}_{l,m,n}\, F_{l,m,n}\,, \quad q = \sum_{\Gamma} \breve{q}_{l,m,n}\, F_{l,m,n} \quad . \tag{5.52}$$

Then the expansion of the function $g(\mathbf{x}) = p(\mathbf{x})\, q(\mathbf{x})$ in the same basis set [5] *admits the expression:*

$$\begin{aligned} g &= \sum_{\Gamma} \breve{g}_{l',m',n'}\, F_{l',m',n'}\,, \\ \textit{with}, \quad \breve{g}_{l',m',n'} &= \sum_{\Gamma}\sum_{\Gamma} \mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}\, \breve{p}_{\tilde{l},\tilde{m},\tilde{n}}\, \breve{q}_{l,m,n}\,. \end{aligned} \tag{5.53}$$

In the above expressions, $\mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}$ is defined through equations (5.49) , (5.50) *and* (5.51) .

5.2.5 Computation of the expansion coefficients of the electronic density

Once the expansion coefficients of the eigenfunctions have been obtained by means of solving the eigenvalue problem (5.39) , we need to obtain the electronic density ρ for the next cycle of the self-consistent field iteration. To obtain the expansion coefficients of the density, we may proceed as follows. First, let:

$$\rho(\mathbf{x}) = \sum_{\Gamma} \tau_{l,m,n}\, F_{l,m,n}\,. \tag{5.54}$$

The actual expression for the electronic density is:

$$\rho(\mathbf{x}) = \sum_{j=1}^{N} \phi_j(\mathbf{x})\, \overline{\phi_j(\mathbf{x})}\,. \tag{5.55}$$

Thus, we may use Proposition 5.2.1 to obtain the coefficients $\tau_{l,m,n}$ in (5.54) once the expansion coefficients $\phi^{(j)}_{l,m,n}$ of the eigenfunctions ϕ_j, as well as their complex conjugates are known. As mentioned earlier, $\phi^{(j)}_{l,m,n}$ appear as the lowest n_e eigenvectors of the eigenvalue problem (5.39). To compute the expansion coefficients of $\overline{\phi_j}$, we may write:

$$\phi_j = \sum_{\Gamma} \phi^{(j)}_{l,m,n}\, F_{l,m,n}\,. \tag{5.56}$$

[5] This requires that $g \in \mathsf{L}^2(\mathcal{B}_R)$. For this purpose, it is sufficient for instance, if $p, q \in \mathsf{L}^4(\mathcal{B}_R)$. In that case, $p, q \in \mathsf{L}^2(\mathcal{B}_R)$ as well and by the Cauchy-Schwarz inequality, we automatically have $g \in \mathsf{L}^2(\mathcal{B}_R)$.

Then, taking the complex conjugate of this equation, we get:

$$\overline{\phi_j} = \sum_{\Gamma} \overline{\phi^{(j)}_{l,m,n}}\, \overline{F_{l,m,n}} = \sum_{\Gamma} \overline{\phi^{(j)}_{l,m,n}}\, (-1)^m F_{l,-m,n} \ . \tag{5.57}$$

Thus, the coefficient of $F_{l,-m,n}$ is $\overline{\phi^{(j)}_{l,m,n}}\,(-1)^m$. Since (l,m,n) and $(l,-m,n)$ are both present in Γ, it follows that the coefficient of $F_{l,m,n}$ is $\overline{\phi^{(j)}_{l,-m,n}}\,(-1)^{-m} = \overline{\phi^{(j)}_{l,-m,n}}\,(-1)^m$. It now follows from Proposition 5.2.1 that for any $(l',m',n') \in \Gamma$:

$$\tau_{l',m',n'} = \sum_{j=1}^{N} \sum_{\Gamma} \sum_{\Gamma} \mathcal{W}^{(l',m',n')}_{(l,m,n)\,,\,(\tilde{l},\tilde{m},\tilde{n})}\, (-1)^m\, \phi^{(j)}_{\tilde{l},\tilde{m},\tilde{n}}\, \overline{\phi^{(j)}_{l,-m,n}} \ . \tag{5.58}$$

We may note that under continuity assumptions of the pseudopotential and the exchange correlation potential, elliptic regularity theory implies that the eigenfunctions associated with the linearized eigenvalue problem (4.13) will be Hölder continuous. In particular, they are in $\mathsf{L}^4(\mathcal{B}_R)$, and so the use of (5.53) to obtain (5.58) is justified.

The above discussion outlines a potentially expensive computational process which needs to be carried out at each step of the self consistent field iteration. One simplification that we may keep in mind is that, like the potential $V(\mathbf{x})$, the density $\rho(\mathbf{x})$ is a real quantity. Therefore, we must have:

$$\tau_{l',-m',n'} = (-1)^{m'}\, \overline{\tau_{l',m',n'}} \ . \tag{5.59}$$

This can also be directly checked by means of the formula (5.58).

5.2.6 Computation of the expansion coefficients of the effective potential

As in (5.37), we write:

$$\hat{V}(r,\vartheta,\varphi) = \sum_{\Gamma} v_{\tilde{l},\tilde{m},\tilde{n}}\ \hat{F}_{\tilde{l},\tilde{m},\tilde{n}}(r,\vartheta,\varphi) \ ,$$

and we ask if the computation of the coefficients $v_{\tilde{l},\tilde{m},\tilde{n}}$ can be simplified in some manner. To proceed along these lines, we write:

$$V = V_H(\rho) + V_{nu} + V_{xc}(\rho) \ , \tag{5.60}$$

$$\text{with,} \quad V_H(\mathbf{y}) = \int_{\mathcal{B}_R} \frac{\rho(\mathbf{x})}{|\mathbf{y}-\mathbf{x}|}\, d\mathbf{x} \ , \tag{5.61}$$

$$\text{and, for an all-electron calculation,} \quad V_{nu}(\mathbf{y}) = \sum_{i=1}^{M} \frac{Z_k}{|\mathbf{y}-\mathbf{x}_k|} \ . \tag{5.62}$$

The splitting in (5.60) and the linearity of the inner-product allows us to write:

$$v_{\tilde{l},\tilde{m},\tilde{n}} = \langle V_H(\rho), \hat{F}_{\tilde{l},\tilde{m},\tilde{n}} \rangle_{\mathsf{L}^2(\mathcal{B}_R)} + \langle V_{nu}, \hat{F}_{\tilde{l},\tilde{m},\tilde{n}} \rangle_{\mathsf{L}^2(\mathcal{B}_R)} + \langle V_{xc}(\rho), \hat{F}_{\tilde{l},\tilde{m},\tilde{n}} \rangle_{\mathsf{L}^2(\mathcal{B}_R)} \ . \tag{5.63}$$

We will now deal with each of the terms separately and try to see in what way the integrals associated with the computation of the inner products can be simplified so that numerical quadratures can be avoided as much as possible.

- **Hartree Term:** One way of solving the Hartree potential V_H is to solve the associated Poisson problem. In fact, if the electronic density lies in the Hölder space $\mathsf{C}^{0,\alpha}(\mathcal{B}_R)$ for some exponent $0 < \alpha < 1$, then a theorem from potential theory [Gilbarg and Trudinger, 2001, Chapter 4] allows us to conclude that the Hartree potential can be obtained by solving the boundary value problem:

$$\begin{aligned} -\Delta V_H(\mathbf{y}) &= 4\pi\, \rho(\mathbf{y}), \quad \text{for } \mathbf{y} \in \mathcal{B}_R, \\ V_H(\mathbf{y}) &= \int_{\mathcal{B}_R} \frac{\rho(\mathbf{x})}{|\mathbf{y}-\mathbf{x}|}\, d\mathbf{x}, \quad \text{for } \mathbf{y} \in \partial\mathcal{B}_R. \end{aligned} \tag{5.64}$$

  The spectral method under discussion is especially well suited for solving the above problem since the basis set $\{F_{l,m,n}\}$ was derived in connection with the Laplace operator. We need to be careful about a couple of issues however. The first issue is that we are guaranteed that the electronic density that comes out of a step of the self consistency iterations is Hölder continuous provided the terms V_{nu} and V_{xc} lie in $\mathsf{L}^\infty(\mathcal{B}_R)$. Usually we have $V_{xc} \in \mathsf{C}(\mathcal{B}_R)$ and so we are justified in using (5.64) to obtain the Hartree potential provided the Coulumbic singularity in V_{nu} can be regularized. This is usually handled automatically by pseudopotentials and so we probably need some care in all electron calculations. The second issue is related to the boundary conditions obeyed by the Hartree potential on the surface of the sphere. Expansion of the Hartree potential in the basis functions $\{F_{l,m,n}\}$ automatically forces it to obey a

Dirichlet boundary condition on the sphere surface instead of the boundary condition that appears in (5.64). An easy way to correct for this [Suryanarayana et al., 2010] is to solve the Hartree problem on a much larger sphere $\mathcal{B}_{\tilde{R}}$. To this end, we may introduce the basis set $\{E_{l,m,n}\}$ to stand for the same set of functions as in (5.29), but with R replaced by $\tilde{R}$ in (5.29) and (5.30). Recalling that for $r \ll \nu$,

$$J_\nu(r) \sim \sqrt{\frac{2}{\pi r}}\, \cos\left[r - (2\nu+1)\frac{\pi}{4}\right] , \tag{5.65}$$

and that the radial part of $E_{l,m,n}$ goes as $\frac{1}{\sqrt{r}} J_{l+\frac{1}{2}}(\frac{b^n_{l+\frac{1}{2}}}{\tilde{R}} r)$, we may observe that the functions $E_{l,m,n}$ formally have the $1/r$ decay for large r, as (5.61) requires. At $r = \tilde{R}$, however, they are forced to be zero due to the oscillatory nature of the Bessel function. In any case, expansion of the Hartree potential using the set of functions $\{E_{l,m,n}\}_{(l,m,n)\in\Gamma}$ gives us:

$$V_H = \sum_{\Gamma} v^H_{l,m,n}\, E_{l,m,n}\,. \tag{5.66}$$

Applying the Laplace operator on both sides gives us:

$$-\Delta V_H = \sum_{\Gamma} v^H_{l,m,n}\,(-\Delta\, E_{l,m,n}) = \sum_{\Gamma} v^H_{l,m,n} \hat{\lambda}_{l,m,n} E_{l,m,n} = 4\pi\,\rho\,. \tag{5.67}$$

Taking the inner product of this equation with $E_{\tilde{l},\tilde{m},\tilde{n}}$, we arrive at:

$$v^H_{\tilde{l},\tilde{m},\tilde{n}} = \frac{4\pi}{\hat{\lambda}_{\tilde{l},\tilde{m},\tilde{n}}} \left\langle \rho, E_{\tilde{l},\tilde{m},\tilde{n}} \right\rangle_{\mathsf{L}^2(\mathcal{B}_R)} = 4\pi \left(\frac{\tilde{R}^2}{b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}}\right)^2 \tau_{\tilde{l},\tilde{m},\tilde{n}}\,. \tag{5.68}$$

We also have an alternate, more accurate route for arriving at the coefficients $v^H_{\tilde{l},\tilde{m},\tilde{n}}$. This starts from the so called Laplace expansion of the potential [Jackson, 1975]:

$$\frac{1}{|\mathbf{x}-\mathbf{y}|} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} \frac{r^l_<}{r^{l+1}_>}\, \overline{\mathcal{Y}^m_l(\vartheta_\mathbf{x}, \varphi_\mathbf{x})}\, \mathcal{Y}^m_l(\vartheta_\mathbf{y}, \varphi_\mathbf{y})\,. \tag{5.69}$$

In the above, $r_< = \min(r_\mathbf{x}, r_\mathbf{y}), r_> = \max(r_\mathbf{x}, r_\mathbf{y})$ and $(r_\mathbf{x}, \vartheta_\mathbf{x}, \varphi_\mathbf{x})$ and $(r_\mathbf{y}, \vartheta_\mathbf{y}, \varphi_\mathbf{y})$ denote $\mathbf{x}$ and $\mathbf{y}$ in spherical coordinates respectively. In accordance with (5.54), we

now write:

$$\rho(r_{\mathbf{x}}, \vartheta_{\mathbf{x}}, \varphi_{\mathbf{x}}) = \sum_{\Gamma} \tau_{\hat{l},\hat{m},\hat{n}}\, s_{\hat{l},\hat{n}} \sqrt{\frac{2}{r_{\mathbf{x}}}}\, J_{\hat{l}+1}\!\left(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\right) \mathcal{Y}^{\hat{m}}_{\hat{l}}(\vartheta_{\mathbf{x}}, \varphi_{\mathbf{x}}) \ ,$$
$$\text{with,} \quad s_{\hat{l},\hat{n}} = \frac{1}{R J_{\hat{l}+\frac{3}{2}}(b^{\hat{n}}_{\hat{l}+\frac{1}{2}})} \ . \tag{5.70}$$

Let $d\breve{\mathbf{x}}$ to denote the volume element in the sphere $\mathcal{B}_R$, that is,

$$d\breve{\mathbf{x}} = r^2_{\mathbf{x}} \sin\vartheta_{\mathbf{x}}\, dr_{\mathbf{x}} d\vartheta_{\mathbf{x}} d\varphi_{\mathbf{x}} \ .$$

In accordance with (5.61), we have:

$$\begin{aligned}
\hat{V}_H(r_{\mathbf{y}}, \vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}}) &= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} \sum_{\Gamma} s_{\hat{l},\hat{n}} \tau_{\hat{l},\hat{m},\hat{n}} \mathcal{Y}^m_l(\vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}}) \\
&\quad \times \int_{\mathcal{B}_R} \frac{r^l_<}{r^{l+1}_>} \overline{\mathcal{Y}^m_l(\vartheta_{\mathbf{x}}, \varphi_{\mathbf{x}})} \sqrt{\frac{2}{r_{\mathbf{x}}}}\, J_{\hat{l}+1}\!\left(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\right) \mathcal{Y}^{\hat{m}}_{\hat{l}}(\vartheta_{\mathbf{x}}, \varphi_{\mathbf{x}})\, d\breve{\mathbf{x}} \\
&= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} \sum_{\Gamma} s_{\hat{l},\hat{n}}\, \tau_{\hat{l},\hat{m},\hat{n}}\, \mathcal{Y}^m_l(\vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})\, \delta_{l,\hat{l}}\, \delta_{m,\hat{m}} \\
&\quad \times \int_{r_{\mathbf{x}}=0}^{r_{\mathbf{x}}=R} \frac{r^{\hat{l}}_<}{r^{\hat{l}+1}_>} \sqrt{\frac{2}{r_{\mathbf{x}}}}\, J_{\hat{l}+1}\!\left(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\right) r^2_{\mathbf{x}}\, dr_{\mathbf{x}} \\
&= \sum_{\Gamma} \frac{4\pi}{2\hat{l}+1}\, s_{\hat{l},\hat{n}}\, \tau_{\hat{l},\hat{m},\hat{n}}\, \mathcal{Y}^{\hat{m}}_{\hat{l}}(\vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})\, \zeta_{\hat{l},\hat{n}}(r_{\mathbf{y}}) \ .
\end{aligned} \tag{5.71}$$

In the above calculations, $\delta_{\cdot,\cdot}$ denotes the Kronecker delta. The interchange of the integrals and the infinite sums in this calculation is justified by the continuity of the inner product on $\mathsf{L}^2(\mathcal{B}_R)$ and by the fact that $\hat{V}_H \in \mathsf{L}^2(\mathcal{B}_R)$. Next, we see that the

function $\zeta_{\hat{l},\hat{n}}(r_{\mathbf{y}})$ can be written as follows:

$$\begin{aligned}
\zeta_{\hat{l},\hat{n}}(r_{\mathbf{y}}) &= \int_{r_{\mathbf{x}}=0}^{r_{\mathbf{x}}=R} \frac{r_{<}^{\hat{l}}}{r_{>}^{\hat{l}+1}} \sqrt{\frac{2}{r_{\mathbf{x}}}}\, J_{\hat{l}+1}\Big(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\Big)\, r_{\mathbf{x}}^2\, dr_{\mathbf{x}} \\
&= \sqrt{2}\left[\frac{1}{r_{\mathbf{y}}^{\hat{l}+1}} \int_0^{r_{\mathbf{y}}} r_{\mathbf{x}}^{\hat{l}+2} \frac{1}{\sqrt{r_{\mathbf{x}}}} J_{\hat{l}+1}\Big(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\Big)\, dr_{\mathbf{x}} + r_{\mathbf{y}}^{\hat{l}} \int_{r_{\mathbf{y}}}^{R} \frac{1}{r_{\mathbf{x}}^{\hat{l}-1}\sqrt{r_{\mathbf{x}}}} J_{\hat{l}+1}\Big(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\Big)\, dr_{\mathbf{x}}\right] \\
&= \sqrt{2}\left[\frac{1}{r_{\mathbf{y}}^{\hat{l}+1}} \int_0^{r_{\mathbf{y}}} r_{\mathbf{x}}^{\hat{l}+\frac{3}{2}} J_{\hat{l}+1}\Big(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\Big)\, dr_{\mathbf{x}} + r_{\mathbf{y}}^{\hat{l}} \int_{r_{\mathbf{y}}}^{R} \frac{1}{r_{\mathbf{x}}^{\hat{l}-\frac{1}{2}}} J_{\hat{l}+1}\Big(\frac{b^{\hat{n}}_{\hat{l}+\frac{1}{2}}}{R} r_{\mathbf{x}}\Big)\, dr_{\mathbf{x}}\right] \\
&= \sqrt{2}\left[\frac{R^{\hat{l}+\frac{5}{2}}}{r_{\mathbf{y}}^{\hat{l}+1}} \int_0^{(r_{\mathbf{y}}/R)} r_1^{\hat{l}+\frac{3}{2}} J_{\hat{l}+1}\Big(b^{\hat{n}}_{\hat{l}+\frac{1}{2}} r_1\Big)\, dr_1 + \frac{r_{\mathbf{y}}^{\hat{l}}}{R^{\hat{l}-\frac{3}{2}}} \int_{(r_{\mathbf{y}}/R)}^{1} \frac{1}{r_1^{\hat{l}-\frac{1}{2}}} J_{\hat{l}+1}\Big(b^{\hat{n}}_{\hat{l}+\frac{1}{2}} r_1\Big)\, dr_1\right] \\
&= \sqrt{2R^3}\left[\Big(\frac{R}{r_{\mathbf{y}}}\Big)^{\hat{l}+1} \int_0^{(r_{\mathbf{y}}/R)} r_1^{\hat{l}+\frac{3}{2}} J_{\hat{l}+1}\Big(b^{\hat{n}}_{\hat{l}+\frac{1}{2}} r_1\Big)\, dr_1 \right. \\
&\qquad \left. + \Big(\frac{r_{\mathbf{y}}}{R}\Big)^{\hat{l}} \int_{(r_{\mathbf{y}}/R)}^{1} \frac{1}{r_1^{\hat{l}-\frac{1}{2}}} J_{\hat{l}+1}\Big(b^{\hat{n}}_{\hat{l}+\frac{1}{2}} r_1\Big)\, dr_1\right]. \qquad (5.72)
\end{aligned}$$

To determine the expansion coefficients of the Hartree potential as it appears in (5.71), we take the inner product of equation (5.71) with $\hat{F}_{\tilde{l},\tilde{m},\tilde{n}}(r_{\mathbf{y}}, \vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})$ to get:

$$\begin{aligned}
v^H_{\tilde{l},\tilde{m},\tilde{n}} &= \sum_{\Gamma} \frac{4\pi}{2\hat{l}+1}\, s_{\hat{l},\hat{n}}\, \tau_{\hat{l},\hat{m},\hat{n}} \\
&\qquad \times \int_{\mathcal{B}_R} \mathcal{Y}_{\hat{l}}^{\hat{m}}(\vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})\, \zeta_{\hat{l},\hat{n}}(r_{\mathbf{y}}) s_{\tilde{l},\tilde{n}} \sqrt{\frac{2}{r_{\mathbf{y}}}}\, J_{\tilde{l}+1}\Big(\frac{b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}}{R} r_{\mathbf{y}}\Big)\, \overline{\mathcal{Y}_{\tilde{l}}^{\tilde{m}}(\vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})}\, d\breve{\mathbf{y}} \\
&= \sum_{\Gamma} \frac{4\pi}{2\hat{l}+1}\, s_{\hat{l},\hat{n}} \tau_{\hat{l},\hat{m},\hat{n}}\, \delta_{\tilde{l},\hat{l}}\, \delta_{\tilde{m},\hat{m}}\, s_{\tilde{l},\tilde{n}} \int_0^R \zeta_{\hat{l},\hat{n}}(r_{\mathbf{y}}) \sqrt{\frac{2}{r_{\mathbf{y}}}}\, J_{\tilde{l}+1}\Big(\frac{b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}}{R} r_{\mathbf{y}}\Big) r_{\mathbf{y}}^2\, dr_{\mathbf{y}} \\
&= \frac{4\pi\sqrt{2R^5}}{2\tilde{l}+1} s_{\tilde{l},\tilde{n}} \sum_{\hat{n}=0}^{\hat{n}=N} s_{\tilde{l},\hat{n}} \tau_{\tilde{l},\tilde{m},\hat{n}} \int_0^1 \zeta_{\tilde{l},\hat{n}}(R\, r_2)\, J_{\tilde{l}+1}\Big(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}\, r_2\Big) r_2^{\frac{3}{2}}\, dr_2 \\
&= \frac{4\pi\sqrt{2R^5}}{2\tilde{l}+1} s_{\tilde{l},\tilde{n}} \sum_{\hat{n}=0}^{\hat{n}=N} s_{\tilde{l},\hat{n}} \tau_{\tilde{l},\tilde{m},\hat{n}}\, \chi_{\tilde{l},\tilde{n};\hat{n}}\,. \qquad (5.73)
\end{aligned}$$

Let us simplify the term $\chi_{\tilde{l},\tilde{n};\hat{n}}$ a bit. We have:

$$\begin{aligned}
\chi_{\tilde{l},\tilde{n};\hat{n}} &= \int_0^1 \zeta_{\tilde{l},\hat{n}}(R\,r_2)\, J_{\tilde{l}+1}\Big(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}\, r_2\Big) r_2^{\frac{3}{2}}\, dr_2 \\
&= \sqrt{2R^3}\left[\int_0^1 \left\{\int_0^{r_2} r_1^{\tilde{l}+\frac{3}{2}} J_{\tilde{l}+1}\Big(b^{\hat{n}}_{\tilde{l}+\frac{1}{2}} r_1\Big)\, dr_1\right\} J_{\tilde{l}+1}\Big(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}\, r_2\Big) r_2^{\frac{3}{2}} \Big(\frac{1}{r_2}\Big)^{\tilde{l}+1}\, dr_2\right. \\
&\qquad \left. + \int_0^1 \left\{\int_{r_2}^1 \frac{1}{r_1^{\tilde{l}-\frac{1}{2}}} J_{\tilde{l}+1}\Big(b^{\hat{n}}_{\tilde{l}+\frac{1}{2}} r_1\Big)\, dr_1\right\} J_{\tilde{l}+1}\Big(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}\, r_2\Big) r_2^{\tilde{l}+\frac{3}{2}}\, dr_2\right] \qquad (5.74) \\
&:= \sqrt{2R^3}\, \xi_{\tilde{l},\tilde{n};\hat{n}} \qquad (5.75)
\end{aligned}$$

Since $\xi_{\tilde{l},\tilde{n};\hat{n}}$ is independent of R, it can be precomputed and stored. With the above considerations, we finally have:

$$v^H_{\tilde{l},\tilde{m},\tilde{n}} = \frac{8\pi R^2}{2\tilde{l}+1} \frac{1}{\big[J_{\tilde{l}+\frac{3}{2}}(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}})\big]} \sum_{\hat{n}=0}^{\hat{n}=N} \frac{\tau_{\tilde{l},\tilde{m},\hat{n}}\, \xi_{\tilde{l},\tilde{n};\hat{n}}}{J_{\tilde{l}+\frac{3}{2}}(b^{\hat{n}}_{\tilde{l}+\frac{1}{2}})\big]}\ . \qquad (5.76)$$

- **Nuclear Interaction Term:** Let us consider the all-electron case. In this situation, the calculations for the expansion coefficients are somewhat similar to the calculations in case of the Hartree potential. Starting from (5.62) and using the Laplace expansion, we get:

$$\hat{V}_{nu}(r_{\mathbf{y}}, \vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}}) = \sum_{k=1}^{M} Z_k \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} \frac{r^l_{k<}}{r^{l+1}_{k>}} \overline{\mathcal{Y}^m_l(\vartheta_{\mathbf{x}_k}, \varphi_{\mathbf{x}_k})}\, \mathcal{Y}^m_l(\vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})\ , \quad (5.77)$$

with, $r_{k<} = \min(r_{\mathbf{x}_k}, r_{\mathbf{y}}), r_{k>} = \max(r_{\mathbf{x}_k}, r_{\mathbf{y}})$ and $(r_{\mathbf{x}_k}, \vartheta_{\mathbf{x}_k}, \varphi_{\mathbf{x}_k})$ and $(r_{\mathbf{y}}, \vartheta_{\mathbf{y}}, \varphi_{\mathbf{y}})$ denote the points $\mathbf{x}_k$ and $\mathbf{y}$ in spherical coordinates respectively. To compute the expansion coefficients, we proceed by:

$$\begin{aligned}
v^{nu}_{\tilde{l},\tilde{m},\tilde{n}} &= \langle V_{nu}, F_{\tilde{l},\tilde{m},\tilde{n}} \rangle_{\mathsf{L}^2(\mathcal{B}_R)} \\
&= \sum_{k=1}^{M} Z_k \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} \overline{\mathcal{Y}^m_l(\vartheta_{\mathbf{x}_k}, \varphi_{\mathbf{x}_k})}\, s_{\tilde{l},\tilde{n}}\, \delta_{l,\tilde{l}}\, \delta_{m,\tilde{m}} \\
&\qquad \times \int_{r_{\mathbf{y}}=0}^{r_{\mathbf{y}}=R} \frac{r^l_{k<}}{r^{l+1}_{k>}} \sqrt{\frac{2}{r_{\mathbf{y}}}} J_{\tilde{l}+1}\Big(\frac{b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}}}{R} r_{\mathbf{y}}\Big)\, r^2_{\mathbf{y}}\, dr_{\mathbf{y}} \\
&= \frac{(-1)^{\tilde{m}} 4\pi}{R J_{\tilde{l}+\frac{3}{2}}(b^{\tilde{n}}_{\tilde{l}+\frac{1}{2}})} \sum_{k=1}^{M} \frac{Z_k}{2\tilde{l}+1}\, \mathcal{Y}^{-\tilde{m}}_{\tilde{l}}(\vartheta_{\mathbf{x}_k}, \varphi_{\mathbf{x}_k})\, \zeta_{\tilde{l},\tilde{n}}(r_{\mathbf{x}_k})\ . \qquad (5.78)
\end{aligned}$$

Clearly, the coefficients $v^{nu}_{\tilde{l},\tilde{m},\tilde{n}}$ need to be computed only once for every simulation.

- **Exchange Correlation Term**:
  The nonlinear nature of the exchange correlation potential makes it difficult to obtain any generic simplifications of this term. At this point, the only strategy we have is to implement a numerical quadrature of the integral involved in evaluating the expansion coefficients. Accordingly, we may write:

$$v^{xc}_{\tilde{l},\tilde{m},\tilde{n}} = \int_{\mathcal{B}_R} V_{xc}(\rho(\mathbf{y}))\, \overline{F_{\tilde{l},\tilde{m},\tilde{n}}(\mathbf{y})}\, d\mathbf{y} \tag{5.79}$$

  For the purpose of evaluation of the above integral, it is convenient to set up a real space grid in spherical coordinates and then, to perform the integral over this grid.

5.2.7 Symmetry Adaptation

We now briefly outline symmetry adaptation in the spectral scheme. First, we observe that spherical harmonics behave nicely under the action of a discrete groups of rotations. The action of a point group element on a spherical harmonic with a given value of $l \in \{0, 1, \ldots\}$ and $m \in \{-l, \ldots, l\}$ is such that the result is completely expressible in terms of the spherical harmonics with the same value of l.[6] In particular, a rotation about the z-axis for instance, changes a spherical harmonic, by a scalar factor at most. Thus, the basis functions described in (5.29) inherit these nice properties. From the information about the group action on the basis functions, we may easily set up the matrices associated with the representation of the group over the complex vector space $\mathcal{V} = \text{span}\{F_{l,m,n}\}_{(l,m,n)\in\Gamma}$. We may then use the theory in section 3.2.4 to obtain a block diagonalization of the Hamiltonian matrix. This reduces the computational expense of diagonalization of the Hamiltonian.

Calculation of the expansion coefficients of the potentials can be foreseeably simplif the potentials have the symmetry of the full group. Using the projection operator corresponding to the identity representation, we may start with the basis set $\mathcal{F} = F_{l,m,n_{(l,m,n)\in\Gamma}}$ and obtain a basis of the subspace $\mathcal{V}_I \subset \mathcal{V}$, associated with the identity representation. Let this basis set be denoted as $\mathcal{E}_I = \{e_j\}_{j=1}^m$, with $m = \text{Dim.}(\mathcal{V}_I)$. If a function f on the sphere is expressible completely in terms of the basis set $\mathcal{E}_I$, that is, it is invariant under the group $\mathcal{G}$, then the computation of its expansion coefficients in the basis $\mathcal{F}$ can be considerably simplified. For instance, if $f = V_{xc}(\rho(\cdot)) = \sum_{j=1}^{m} \alpha_j e_j$, then, we may compute the coefficients

[6] This follows from the consideration that discrete groups of rotations are subgroups of SO(3) and from the comment in footnote (3) of this chapter.

e_j as follows:

$$\alpha_j = \int_{\mathcal{B}_R} f(\mathbf{y})\overline{e_j(\mathbf{y})}\, d\mathbf{y} = |\mathcal{G}| \int_{\mathcal{D}} f(\mathbf{y})\overline{e_j(\mathbf{y})}\, d\mathbf{y} \ . \tag{5.80}$$

Once the above coefficients have been computed, the expansion of f, using the basis set $\mathcal{F}$, is easy to carry out since the expansion of each function e_j in the basis set $\mathcal{F}$ is also known. Similar symmetry based simplifications can be carried out while computing the expansion coefficients of the electronic density as well as the Hartree and nuclear potentials.

We are in the process of implementing the above numerical scheme as well as its symmetry based simplifications.

Chapter 6

Conclusions and Future Work

In this work, we have taken important steps toward formulating density functional theory methods for studying objective structures. The focus of our work has been on objective structures generated by finite groups of isometries. We have achieved a good theoretical understanding of the role that symmetry plays in the electronic structure computation problem for such objective structures. We have also formulated promising numerical schemes for the solution of the electronic structure problem associated with these objective structures. Currently, we are in the process of developing computer codes based on the schemes developed in this work. This will provide us with a platform for carrying out extensive simulation studies of objective structures generated by finite groups of isometries.

The program that has been carried out in this work, needs to be extended to objective structures generated by helical groups of isometries. We have some ideas about what this program might entail. Since such groups are necessarily infinite, one of the central issues, would be to develop a result analogous to the Bloch theorem in crystals [Bloch, 1929]. This would enable us to reduce the electronic structure computation problem to the fundamental domain. The Bloch theorem for crystals lies at the heart of the single electron band theory of crystals [Le Bris, 2003] and a Bloch theorem for helical groups should hold an analogous role for the case of objective structures generated by helical groups. Once the problem has been reduced to the fundamental domain, we would need to formulate a numerical scheme for solution of the reduced problem. The computation of the electrostatic potentials would have to be carried out carefully due to convergence issues arising from the infinite extent of the system. The most likely method for overcoming this particular issue would be to formulate an Ewald sum method for helical groups. The final stage of the program would be to develop a computer code that can provide us with a platform for studying objective

structures generated by helical groups.

One general issue that we would like to investigate in the course of future work, is the convergence of the Kohn-Sham self consistent field iterations. A first step toward this investigation would be to carry out a linear stability analysis of suitable solutions of the Kohn-Sham equations. The study of the spectrum of the linearized Kohn-Sham operator, evaluated at such solutions would give us an indication of whether the self-consistent field iterations converge in the neighborhood of such solutions. Such studies are likely to provide useful guidelines for carrying out efficient numerical simulations.

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Appendix A

Hilbert Space Miscellany

We present miscellaneous useful concepts and results related to Hilbert spaces in this Appendix.

A.1 Hilbert Projection Theorem

Here we state and prove the Hilbert projection theorem:

Theorem A.1.1. *Let* H *be a Hilbert space with a closed subspace* $\mathcal{M}$*. Let* $\mathcal{M}^\perp$ *denote the orthogonal subspace of* $\mathcal{M}$*. Then any* $f \in \mathsf{H}$ *admits the unique representation* $f = f_1 + f_2$*, with* $f_1 \in \mathcal{M}, f_2 \in \mathcal{M}^\perp$*.*

Proof: Let $f \in \mathsf{H}$ be given. To find $f_1 \in \mathcal{M}, f_2 \in \mathcal{M}^\perp$ such that $f = f_1 + f_2$, we define:

$$f_1 = \text{argmin}_{y \in \mathcal{M}} \|f - y\|_{\mathsf{H}}, \quad f_2 = f - f_1. \tag{A.1}$$

To see the existence and uniqueness of such $f_1 \in \mathcal{M}$, we consider a minimizing sequence $\{y_n\}_{n=1}^\infty \subset \mathcal{M}$ and let $\alpha = \inf_{y \in \mathcal{M}} \|f - y\|_{\mathsf{H}}$. Then by definition of a minimizing sequence, $\|f - y_n\|_{\mathsf{H}} \to \alpha$ as $n \to \infty$ and each $y_n \in \mathcal{M}$. We actually intend to show that $\{y_n\}_{n=1}^\infty$ is a Cauchy sequence since that would imply by the closedness of $\mathcal{M}$ in the complete space H that there exists $x_0 \in \mathcal{M}$ such that $\{y_n\} \to x_0$. The continuity of the norm would then imply that $\|f - x_0\|_{\mathsf{H}} = \lim_{n \to \infty} \|f - y_n\|_{\mathsf{H}} = \alpha$, thus establishing existence. Now, to see that $\{y_n\}_{n=1}^\infty$ is Cauchy, we first observe that $\forall m, n \in \mathbb{N}$, $\frac{y_m + y_n}{2} \in \mathcal{M}$ and so,

$\|f - \frac{y_m+y_n}{2}\|_{\mathsf{H}} \geq \alpha$. We then have, by the parallelogram identity:

$$\begin{aligned}\|y_m - y_n\|_{\mathsf{H}}^2 &= \|(y_m - f) - (y_n - f)\|_{\mathsf{H}}^2 \\ &= 2(\|(y_m - f)\|_{\mathsf{H}}^2 + \|(y_n - f)\|_{\mathsf{H}}^2) - \|(y_m - f) + (y_n - f)\|_{\mathsf{H}}^2 \\ &= 2(\|(y_m - f)\|_{\mathsf{H}}^2 + \|(y_n - f)\|_{\mathsf{H}}^2) - 4\|(f - \frac{y_m + y_n}{2})\|_{\mathsf{H}}^2 \\ &\leq 2(\|(y_m - f)\|_{\mathsf{H}}^2 + \|(y_n - f)\|_{\mathsf{H}}^2) - 4\alpha^2 \end{aligned} \tag{A.2}$$

Clearly, as $m, n \to \infty$ in (A.2) above, we get:

$$\lim_{m,n\to\infty} \|y_m - y_n\|_{\mathsf{H}}^2 = 2(\alpha^2 + \alpha^2) - 4\alpha^2 = 0. \tag{A.3}$$

We can also see easily that uniqueness holds since if x_0, x_0^* are both solutions to the minimization problem, then $\|f - x_0\|_{\mathsf{H}} = \|f - x_0^*\|_{\mathsf{H}} = \alpha$. Then, by a calculation similar to the one above:

$$\begin{aligned}\|x_0 - x_0^*\|_{\mathsf{H}}^2 &= \|(x_0 - f) - (x_0^* - f)\|_{\mathsf{H}}^2 \\ &\leq 2(\|(x_0 - f)\|_{\mathsf{H}}^2 + \|(x_0^* - f)\|_{\mathsf{H}}^2) - 4\alpha^2 = 0. \end{aligned} \tag{A.4}$$

Thus, we have, $x_0 = x_0^*$. It now remains to show that $f_2 = f - f_1$ lies in $\mathcal{M}^\perp$. To see this, we observe that f_1 being the solution of the minimization problem $f_1 = \text{argmin}_{y\in\mathcal{M}}\|f - y\|_{\mathsf{H}}$ implies the first variation condition:

$$\begin{aligned}&\frac{d}{d\eta}\|f - (f_1 + \eta y)\|_{\mathsf{H}}\Big|_{\eta=0} = 0,\ \forall y \in \mathcal{M} \\ &\implies \text{Re}(\langle f - f_1, y\rangle_{\mathsf{H}}) = 0,\ \forall y \in \mathcal{M} \\ &\implies \langle f - f_1, y\rangle_{\mathsf{H}} = 0,\ \forall y \in \mathcal{M} \end{aligned} \tag{A.5}$$

Hence $f_2 \in \mathcal{M}^\perp$. The last step follows since we can multiply y with suitable scalars and make the inner product real valued and since $\mathcal{M}$ is a subspace, it is closed under multiplication by arbitrary scalars. We would also like to point out that the orthogonality condition (A.5) actually characterizes the minimizer: For given $f \in \mathsf{H}$, if $f_1 \in \mathcal{M}$ satisfies (A.5), then f_1 is the unique minimizer to the minimization problem $\inf_{y\in\mathcal{M}} \|f - y\|_{\mathsf{H}}$. This is because, for an arbitrary $y \in \mathcal{M}$, we have that $f_1 - y \in \mathcal{M}$. Now,

$$\begin{aligned}\|f - y\|_{\mathsf{H}}^2 &= \|(f - f_1) - (y - f_1)\|_{\mathsf{H}}^2 \\ &= \|f - f_1\|_{\mathsf{H}}^2 + \|y - f_1\|_{\mathsf{H}}^2 + \langle f - f_1, y - f_1\rangle_{\mathsf{H}} + \langle y - f_1, f - f_1\rangle_{\mathsf{H}}. \end{aligned} \tag{A.6}$$

Since the last two terms are zero by (A.5) we have

$$\forall y \in \mathcal{M}, \|f - y\|_{\mathsf{H}} \geq \|f - f_1\|_{\mathsf{H}}, \tag{A.7}$$

with the equality holding if and only if $y = f_1$.

Finally, if $f = f_1 + f_2 = \tilde{f}_1 + \tilde{f}_2$ with $f_1, \tilde{f}_1 \in \mathcal{M}$ and $f_2, \tilde{f}_2 \in \mathcal{M}^{\perp}$, then $f_1 - \tilde{f}_1 = \tilde{f}_2 - f_2 \in \mathcal{M} \cap \mathcal{M}^{\perp} = \{0\}$. Hence, $f_1 = \tilde{f}_1$ and $f_2 = \tilde{f}_2$, making the decomposition unique. ■

A.2 Direct Sums of Hilbert Spaces

Our primary sources for this material are Folland [1999] and Folland [1994]. We begin by recalling that given an arbitrary collection of sets $\{S_\alpha\}, \alpha \in \mathcal{A}$, the Cartesian product of the sets $S = \prod_{\alpha \in \mathcal{A}} S_\alpha$ is the collection of all functions $f : \mathcal{A} \to \bigcup_{\alpha \in \mathcal{A}} S_\alpha$ such that $f(\alpha) \in S_\alpha, \forall \alpha \in \mathcal{A}$. We may now deifne:

Definition A.2.1. Let $\{\mathsf{H}_\alpha\}_{\alpha \in \mathcal{A}}$ be a family of Hilbert spaces. The direct sum $\bigoplus_{\alpha \in \mathcal{A}} \mathsf{H}_\alpha$ is the set of all $v = (v_\alpha)_{\alpha \in \mathcal{A}}$ in the Cartesian product $\Pi_{\alpha \in \mathcal{A}} \mathsf{H}_\alpha$ such that $\sum_{\alpha \in \mathcal{A}} \|v_\alpha\|^2_{\mathsf{H}_\alpha} < \infty$. Since any uncountable sum of positive quantities is necessarily infinite, it must be that $v_\alpha = 0$ for all but countably many α. □

We express this relationship as $\mathsf{H} = \bigoplus_{\alpha \in \mathcal{A}} \mathsf{H}_\alpha$ and we note that H itself is a Hilbert space with inner product:

$$\langle u, v \rangle_{\mathsf{H}} = \sum_{\alpha \in \mathcal{A}} \langle u_\alpha, v_\alpha \rangle_{\mathsf{H}_\alpha} \tag{A.8}$$

The summands H_α are embedded in H as mutually orthogonal closed subspaces. Conversely, if H is a Hilbert space and $\{\mathcal{M}_\alpha\}_{\alpha \in \mathcal{A}}$ is a family of mutually orthogonal closed subspaces of H whose linear span is dense in H, we may identify $\mathsf{H} = \bigoplus_{\alpha \in \mathcal{A}} \mathcal{M}_\alpha$. Henceforth, when we speak of direct sums of subspaces of a Hilbert space, we will always assume that the subspaces are mutually orthogonal.

A.3 Classification of the Spectra of Operators

We find it instructive to elaborate on the various possibilities that one can encounter while discussing the spectral properties of an arbitrary operator on a Banach Space. We hope that this presentation will also elucidate some of the technical terms used in the thesis. The material in this Appendix has been taken from Renardy and Rogers [2004].

Let $\mathcal{X}$ be a non-empty Banach space over the field of complex numbers. Let A be an arbitrary operator on $\mathcal{X}$ with domain Dom.$(A) \subset \mathcal{X}$ and let I denote the identity operator on $\mathcal{X}$. For any $\lambda \in \mathbb{C}$, we may define the operator $A_\lambda = A - \lambda I$ on $\mathcal{X}$ also with domain Dom.(A). If A_λ has an inverse that is, if it is one to one, then we call the inverse the resolvent of A and we denote it as $R_\lambda(A)$. We now consider the following three conditions:

1. $R_\lambda(A)$ exists.
2. $R_\lambda(A)$ is a bounded operator.
3. The domain of $R_\lambda(A)$ is dense in $\mathcal{X}$.

Accordingly, decompose the complex plane as per the following rules:

1. The resolvent set of A is the set:

$$\mathcal{R}(A) = \{\lambda \in \mathbb{C} : (1),(2) \text{ and } (3) \text{ hold true}\} \quad . \tag{A.9}$$

   We say λ is a regular value of A if $\lambda \in \mathcal{R}(A)$. The operator valued map $R(\lambda, A) : \mathcal{R}(A) \to \mathcal{L}(\mathcal{X})$ is often called the resolvent map.

2. The spectrum of A is the set:

$$\sigma(A) = \mathbb{C} \backslash \mathcal{R}(A) \quad . \tag{A.10}$$

   The spectrum of A can be decomposed into three disjoint sets. The point spectrum of A is the set:

$$\sigma_p(A) = \{\lambda \in \sigma(A) : (1) \text{ does not hold}\} \quad . \tag{A.11}$$

   This is by far the most important set as far as the work in this thesis is concerned. Clearly, if $\lambda \in \sigma_p(A)$, then the null space of $R_\lambda(A)$ is non-trivial. We call the elements of the nullspace of $R_\lambda(A)$ the eigenfunctions of A for the eigenvalue $\lambda \in \sigma_p(A)$ and the dimension of the null space is called the multiplicity of the eigenvalue λ. Finally, continuous spectrum of A is the set:

$$\sigma_c(A) = \{\lambda \in \sigma(A) : (1) \text{ and } (3) \text{ hold, but } (2) \text{ does not hold}\} \quad , \tag{A.12}$$

   while the residual spectrum of A is the set:

$$\sigma_r(A) = \{\lambda \in \sigma(A) : (1) \text{ holds, but } (3) \text{ does not hold}\} \quad . \tag{A.13}$$