Geometry of Phases
in Quantum Solids

by

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Abstract

We apply the lower bound method of reduced density matrix theory in one dimensional rings, using a restricted class of hamiltonians. We implement the calculation in MATLAB using routines for solving positive semi-definite programming problems.

The class of model specific hamiltonians is defined and shown to have a set of good quantum numbers. These determine invariant subspaces which we present as the definition of phase. The phase structure of these hamiltonians is investigated theoretically and we present a theorem on the dimensions of the phases and phase boundaries. Finally, the three body density matrix is parameterized and we obtain by calculation the relative sizes of the different phases.

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Chapter 1

Introduction

In this chapter we introduce superconductivity and the quantum phases. We also review the lower bound method of reduced density matrix theory. Finally, SeDuMi, a MatLab program used for solving semi-definite programming problems is introduced.

1.1 Superconductivity

There are two fields of research into superconductivity which are differentiated by the critical temperature at which the materials become superconductors, T_c. The first involves the study of superconducting metals or alloys with low critical temperatures, such as mercury (the first superconductor to be discovered in 1911, $T_c = 4.19K$ [1]). The second field is high-T_c superconductivity and involves the study of materials with much higher T_c's. The most widely studied high-T_c superconductors are a class of cuprates which have Cu-O planes in parallel. An example is optimally doped $HgBa_2Ca_2Cu_3O_{8+x}$ which has $T_c = 164K$ [2]. Since the interaction between adjacent planes is very weak, the material properties, including the phase structure, are due to interactions within a plane. It is this two-dimensional square lattice which is of interest, but this thesis examines a one-dimensional square lattice. As they become available, results from one, two and three dimensional calculations will be compared to show a dimension effect: that the superconducting phase is most stable in a two-dimensional system.

A material acts as a superconductor when it is in a superconducting phase; there are other possible phases for square lattices, such as the ferromagnetic phase where all electrons have their spins aligned. The most studied model for interactions on square lattices is the Hubbard model [3]. The corresponding hamiltonian is:

$$H_{Hub} = t \sum_i (a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i + b_i^\dagger b_{i+1} + b_{i+1}^\dagger b_i) + U \sum_i a_i^\dagger a_i b_i^\dagger b_i, \qquad (1.1)$$

where a_i, b_i are annihilation operators for spin-up and spin-down electrons on site i respectively. The first term of the Hubbard hamiltonian is known as the hopping term and describes the movement of one electron between two nearest neighbour sites

while the second corresponds to the Coulomb repulsion between two electrons on a single site (when $U > 0$).

1.2 Two-body Hamiltonians

The most important terms of the hamiltonians for atomic, molecular and solid systems are sums of interactions between at most two identical particles. These are one and two-body interactions. For example, the attractive potential of atomic nuclei is a one-body operator and the Coulomb repulsion of two electrons interacting is a two-body term. The physical properties of a system can be obtained from the expectation values of one-body and two-body operators alone.

In atomic systems, shell structure is the result of the Pauli Principle interacting with one-body operators. Introducing the two-body and higher order terms perturbs the solution, but does not completely destroy the shell structure. In solid systems, the Pauli Principle interacts with the two-body terms to give phase structure.

Chapter 2 will show that two-body hamiltonians separate the Hilbert space into invariant subspaces and hence define a set of good quantum numbers. Including one-body terms in the hamiltonian combines many of these subspaces. Chapter 3 presents a definition of phase in terms of these subspaces. In order to study the phase structure directly, the one-body terms are removed and the effect of two-body hamiltonians alone are considered in this thesis.

The first term of the Hubbard hamiltonian is a one-body operator while the second term is two-body. Therefore the Hubbard model is not considered in this thesis. However, a dimension effect is known in the band limit of the Hubbard hamiltonian,

that is when $U = 0$ [5]. In this case the Hubbard hamiltonian is a pure one-body hamiltonian and does not include the interaction between electrons on the same site.

1.3   The Density Operator

The lower bound method of reduced density matrix theory is an alternative to using wave-functions to perform quantum mechanical calculations. Multielectron wave functions, $\psi(1, 2, ..., N)$, are anti-symmetric with respect to exchange of electrons.

$$\psi(1, ..., k, ..., l, ..., N) = -\psi(1, ..., l, ..., k, ..., N). \qquad (1.2)$$

Since physically interesting operators are one-body or two-body operators, most of the information in ψ is redundant. An alternative to the wave function is the von Neumann density operator, p. For an ensemble of k pure states $\psi_1, \psi_2, ...\psi_k$, the density operator is given by

$$p = \sum_{i=1}^{k} c_i p_i = \sum_{i=1}^{k} c_i |\psi_i\rangle\langle\psi_i|, \qquad (1.3)$$

where $\sum_{i=1}^{k} c_i^2 = 1$. The expectation value of any Hermitian operator q on a state ψ_1 can be computed using $p_1 = |\psi_1\rangle\langle\psi_1|$, since

$$\langle q, p_1 \rangle = Tr(q^\dagger p_1) = Tr(q|\psi_1\rangle\langle\psi_1|) = \langle\psi_1|q|\psi_1\rangle. \qquad (1.4)$$

If the equivalence between $\langle q, p \rangle$ and $\langle\psi|q|\psi\rangle$ is not apparent, consider the analog of this in the finite basis $\mathbf{R}^2$ where $|\psi\rangle$ corresponds to a column vector $[a_1, a_2]^T$ and the operator q is a 2×2 symmetric matrix with entries q_{ij}.

$$\langle q, p \rangle = Tr(q^\dagger p) = Tr\left(\begin{bmatrix} q_{11} & q_{12} \\ q_{12} & q_{22} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} [a_1, a_2] \right)$$

$$= Tr\left(\begin{bmatrix} q_{11} & q_{12} \\ q_{12} & q_{22} \end{bmatrix}\begin{bmatrix} a_1^2 & a_1a_2 \\ a_1a_2 & a_2^2 \end{bmatrix}\right)$$

$$= q_{11}a_1^2 + 2q_{12}a_1a_2 + q_{22}a_2^2,$$

$$= [a_1, a_2]\begin{bmatrix} q_{11} & q_{12} \\ q_{12} & q_{22} \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$$

$$= \langle\psi|q|\psi\rangle$$

$$= \langle q\rangle.$$

Thus, the expectation value of any operator q can be calculated using the density operator.

A density operator is a positive semi-definite Hermitian operator with unit trace. Determining the von Neumann density is just as difficult as calculating the wave function for that system. An approximate von Neumann density can be defined by relaxing the condition that it be positive semi-definite. A k-density is an Hermitian operator with unit trace which is positive semi-definite for all operators with degree less than or equal to k in the annihilation and creation operators.

Definition 1.3.1 *An Hermitian operator p is a k-density if:*

1. *$\langle p, q^\dagger q\rangle \geq 0$ for all operators q with $deg(q) \leq k$.*

2. *$Tr(p) = 1$*

The k-density contains all the necessary information to evaluate the expectation value of all j-body operators where $j \leq k$.

1.3.1 Matrix Representations

Let $\mathcal{Q}^k = \{q_1, \ldots, q_s\}$, $s < \infty$, be a basis for the linear space of operators q with $deg(q) \leq k$.

Definition 1.3.2 *Relative to the basis $\mathcal{Q}^k$, the k-matrix corresponding to the k-density p is the matrix $\mathbf{P}$ with entries*

$$p_{ij} = \langle q_i^\dagger q_j, p \rangle. \tag{1.5}$$

The k-matrix contains all of the information of the k-density, since any k-body operator x can be expanded in terms of the basis $\mathcal{Q}^k$:

$$x = \sum_{i,j} x_{ij} q_i^\dagger q_j. \tag{1.6}$$

The matrix representation of x is $\mathbf{X} = [x_{ij}]$. Then the expectation value of x is given by $Tr(\mathbf{PX})$:

$$Tr(\mathbf{PX}) = \sum_{i,j=1}^{s} P_{ij} x_{ij} = \sum_{i,j=1}^{s} \langle p, q_i^\dagger q_j \rangle x_{ij}, \tag{1.7}$$

$$= \langle p, \sum_{i,j=1}^{s} x_{ij} q_i^\dagger q_j \rangle = \langle p, x \rangle. \tag{1.8}$$

Chapter 4 will construct the basis $\mathcal{Q}^3$ to be used in the calculation and determine the entries of $\mathbf{P}$.

Many matrix entries are zero by the commutation relations, and there are many linear relationships between the non-zero matrix entries, since many products $q_i^\dagger q_j$ are equal. For example,

$$(a_1 a_2)^\dagger (b_1 b_2) = a_1^\dagger b_1 a_2^\dagger b_2 = -(a_1 b_2^\dagger)^\dagger (b_1 a_2^\dagger). \tag{1.9}$$

The zeros and linear relationships define the shape of the density matrix, and are necessary conditions for a matrix to be a k-matrix.

1.3.2 n-Representability and the Lower Bound Method

The k-density is positive semi-definite for all operators of degree no greater than k, this is called k-positivity. Not all $s \times s$ positive semi-definite, Hermitian matrices correspond to a positive semi-definite p via (1.5). Those $\mathbf{P}$ with at least one representation p are called k-body reduced density matrices, or n-representable [6].

Searching for solutions by requiring that a positive semi-definite matrix $\mathbf{P}$ be n-representable is not feasible, since necessary and sufficient n-representability conditions cannot be imposed directly. Instead, an approximatation to the actual reduced density matrix is found using the lower bound method.

Approximate reduced density matrices are found by solving the following programming problem:

$$\min E(p) = Tr[\mathbf{HP}], \ \mathbf{P} \in \mathbf{P_0}, \tag{1.10}$$

where $\mathbf{H}$ is the matrix representation of the hamiltonian h, $\mathbf{P}$ is the k-body density matrix and $\mathbf{P_0}$ is the convex set of all positive semi-definite matrices which satisfy the normalization condition $\langle 1, \mathbf{P} \rangle = 1$ and the linear relationships between the matrix entries. These are necessary but not sufficient conditions for a density matrix to be n-representable. Since the variation takes place over a space which contains matrices which are not precisely n-representable, the energy found by this method is less than or equal to the actual ground state energy.

The solutions converge very rapidly with k, the order of positivity. Calculations at the $k = 2$ level are very accurate in atomic and molecular systems [7], [8], [9], but incomplete for the solid system examined here [4]. Calculations at the $k = 3$ level give solutions which are accurate to three figures [4]. Computations at the $k = 4$

level may be accurate to seven figures or more, and may also allow the calculation of excited state energies through the dispersion relation [10], [11].

1.4 SeDuMi

The lower bound method is dependent on restricting the density matrix to be positive semi-definite. There were neither algorithms for solving semi-definite programming problems nor powerful computers when the lower bound method was first developed, therefore only the simplest systems could be examined using the lower bound method. There is now software (SeDuMi [12], SDPT3 [13]) which enforces the semi-definite condition directly. All of these programs exploit the block structure of the matrix to speed up the calculation where possible; organizing the basis so that the density matrix is a block matrix reduces the time required to complete the calculation.

The matrices used in this calculation have a very specialized structure, and these generic programs do not exploit this. Recent results by Mazziotti [9] suggest that routines written specifically for these particular lower bound calculations can decrease the time required for these calculations by a factor of 10 or more.

Chapter 2

Two-Body Hamiltonians

We define a linear space of model two-body hamiltonians for a one-dimensional square lattice and construct a basis for this space of operators. We show that certain subspaces are left invariant by all model hamiltonians and that these can be described by a set of good quantum numbers.

2.1 The Model

The reduced density matrix for the ground state of a system where electrons move on a one-dimensional lattice with periodic boundary conditions will be determined. In one dimension, the infinite lattice is modelled by a finite set of equi-spaced points on a ring, called Λ. $|\Lambda|$, the number of sites on the ring, is even. Let the ring sites be indexed by the integers mod $|\Lambda|$ such that adjacent sites are labelled by consecutive numbers.

The Pauli Principle requires that each site on the lattice be occupied by no electrons, one spin-up electron, one spin-down electron or doubly occupied, with both a spin-up and a spin-down electron. Sites occupied by exactly one electron, either spin-up or spin-down, are called **valence** sites, those which are unoccupied or doubly occupied are **ionic**.[1]

Since each lattice site can be occupied in one of four ways, there are $4^{|\Lambda|}$ distinct configurations for the lattice. A particular configuration can be denoted by

$$| \uparrow\downarrow, \uparrow, \emptyset, \downarrow, \cdots \rangle, \tag{2.1}$$

where, starting on the left, $\uparrow\downarrow$ denotes double occupancy for the first lattice site, $\uparrow$ denotes a spin-up electron on the next lattice site, $\emptyset$ indicates that the third lattice site is unoccupied, $\downarrow$ denotes a spin-down electron on the following lattice site and so on.

Each such configuration corresponds to a basis element of the Hilbert space in the

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[1]This terminology is chosen since, in the high-T_c superconductors, each lattice site corresponds to a valence d orbital of a copper atom. The net charge is zero when the orbital is occupied by one electron but non-zero otherwise.

following way:

$$| \uparrow\downarrow, \uparrow, \emptyset, \downarrow, \cdots \rangle = a_1^\dagger b_1^\dagger a_2^\dagger b_4^\dagger \cdots |0\rangle, \qquad (2.2)$$

where a_i and b_i are the annihilators and $a_i^\dagger$ and $b_i^\dagger$ are the creators of a spin-up (a_i) or spin-down (b_i) electron at site i. The vacuum state $|0\rangle$ has configuration $|\emptyset, \emptyset, \cdots, \emptyset\rangle >$.

2.2   Two-Body Hamiltonians

All operators can also be written as polynomials in $a_i, a_i^\dagger, b_i, b_i^\dagger$, $i = 1, \ldots, |\Lambda|$.

Definition 2.2.1 *An operator q is a k-body operator if and only if it satisfies the following two conditions:*

1. q can be represented as a polynomial of degree $2k$ in $a_i, a_i^\dagger, b_i, b_i^\dagger$, $i = 1, \ldots, |\Lambda|$.

2. q is orthogonal to all operators q' that can be represented as polynomials of degree less than $2k$.

Thus a two-body operator is degree four in the annihilators and creators and orthogonal (with respect to the trace scalar product, $\langle q, p \rangle = Tr(q^\dagger p)$), to all operators of lesser degree. The identity, 1, is the only non-trivial zero-body operator. If q is a k-body operator, then every polynomial representation of q has degree at least $2k$. No operator has a unique polynomial representation because of the commutation relations

$$a_i^\dagger a_i + a_i a_i^\dagger = 1 = b_i^\dagger b_i + b_i b_i^\dagger. \qquad (2.3)$$

An arbitrary two-body hamiltonian measures the interaction of electrons on four sites or fewer. Including only nearest neighbour interactions restricts the model to short range forces. Under nearest neighbour interactions, the hamiltonian operators are restricted to at most two adjacent sites. In this case, an arbitrary hamiltonian h can be written as

$$h = \sum_{i=1}^{|\Lambda|} h_{i\ i+1}, \tag{2.4}$$

where $h_{i\ i+1}$ is the interaction between sites i and $i+1$. Translation invariance is also imposed on the hamiltonian: $\langle h_{i\ i+1}, p \rangle = \langle h_{j\ j+1}, p \rangle$. Thus there is a one-to-one correspondence between the total hamiltonian h and the bond hamiltonian h_{12}, the interaction between sites 1 and 2.

Definition 2.2.1 ignores the lattice structure that underlies the model. A definition for two-body interactions specific to the square lattice can be given in terms of the symmetries of the hamiltonians. Let H be the linear subspace of model hamiltonians on the square lattice. Then $h \in H$ if the bond hamiltonian h_{12} is degree four in annihilation and creation operators and has the following five symmetries:

S1. Self-Adjoint: $h_{12}^{\dagger} = h_{12}$.

S2. Ring Symmetric: $h_{12} = h_{21}$.

S3. Spin Particle Preserving: the interaction preserves the number of spin-up and spin-down electrons separately.

S4. Spin-up, spin-down symmetric: the hamiltonian is invariant with respect to exchange of spin-up and spin-down electrons.

S5. Particle-Hole Invariant: the hamiltonian is invariant under the exchange of
   creators and annihilators for electrons of the same spin.

S1-S5 determine a subspace of operators H_{12} which immediately generates H. The purpose of the present chapter is to find a basis for H_{12}, and hence H, and show that there is a set of good quantum numbers which determine subspaces which are invariant under these hamiltonians.

Interpretation of the Hamiltonian Symmetries

Spin particle preserving hamiltonians are such that the number of spin-up and spin-down electrons are preserved independently. Thus S3 means that h_{12} is a polynomial in the following degree zero and degree two operators, called the **basic** operators:

$$\{1, e_{a_1}, e_{a_2}, e_{b_1}, e_{b_2}, a_1^\dagger a_2, a_1 a_2^\dagger, b_1^\dagger b_2, b_1 b_2^\dagger\}, \qquad (2.5)$$

where $e_{a_i} = a_i^\dagger a_i - a_i a_i^\dagger$ and $e_{b_i} = b_i^\dagger b_i - b_i b_i^\dagger$. The operators e_{a_i} and e_{b_i} measure the occupation of site i. That is, the expectation value of e_{a_i} is 1 if site i is occupied by a spin-up electron, -1 if not. For example,

$$e_{a_i}|\uparrow\downarrow\rangle = (a_i^\dagger a_i - a_i a_i^\dagger)a_i^\dagger b_i^\dagger|0\rangle = a_i^\dagger a_i a_i^\dagger b_i^\dagger|0\rangle - a_i a_i^\dagger a_i^\dagger b_i^\dagger|0\rangle \qquad (2.6)$$

$$= a_i^\dagger(1 - a_i^\dagger a_i)b_i^\dagger|0\rangle = a_i^\dagger b_i^\dagger|0\rangle \qquad (2.7)$$

$$= |\uparrow\downarrow\rangle. \qquad (2.8)$$

The operators e_{a_i} and e_{b_i} are related to the two-body electrostatic operators $(e_{a_i} \pm e_{b_i})(e_{a_j} \pm e_{b_j})$, and are also called electrostatic operators. The last four operators are called transport operators since they necessarily move an electron from site 1 to site 2 or vice-versa.

Consider T_{PH} the transformation which sends particles to holes and vice-versa,

$$T_{PH} : \begin{cases} a \leftrightarrow a^\dagger, \\ b \leftrightarrow b^\dagger. \end{cases} \qquad (2.9)$$

For example,

$$T_{PH}\left[e_{a_1}\right] = T_{PH}\left[a_1^\dagger a_1 - a_1 a_1^\dagger\right] = a_1 a_1^\dagger - a_1^\dagger a_1 = -e_{a_1}. \qquad (2.10)$$

Invariance under T_{PH} is specific to the $2k$-body operators; thus it is S5 which restricts this investigation to the two-body operators. All operators which are invariant under S1-S4 will be determined. These will be divided into two groups, the one-body and the two-body operators according to definition 2.2.1. In section 2.3.3 the action of T_{PH} on these two classes will be examined to show that it distinguishes between one and two-body operators.

2.3 A Basis for H_{12}

Finding a basis for H is equivalent to finding a basis for H_{12}. The basis for H_{12} will be found in two steps, first finding all one and two-body S1-S4 invariant operators and then determining which of these are invariant under S5.

To determine all of the hamiltonians which satisfy S1-S4, polynomials of the basic operators, excluding the identity, are formed. The k-body operators are degree k polynomials in the basic operators, excluding the identity. All possible polynomials are symmeterized with respect to S1-S4 and the lower order components are removed by orthogonal projection.

2.3.1 One-body Operators

These operators are degree one in the basic operators. The two classes of basic operators, electrostatic and transport, result in two types of one-body operators.

One-body Electrostatic Operator

Consider e_{a_1}. This term is not ring symmetric or spin-up, spin-down symmetric, but the symmetrized term

$$E^1 = e_{a_1} + e_{a_2} + e_{b_1} + e_{b_2} \tag{2.11}$$

is. This term is invariant under S1-S4, and is a pure one-body term since it is traceless,

$$Tr(E^1) = 2 + 0 + 0 - 2 = 0, \tag{2.12}$$

and hence orthogonal to the identity. Choosing any electrostatic term results in the same one-body operator.

One-body Transport Operator

Consider next the basic transport operator $a_1^\dagger a_2$. After symmetrization over the ring and the spin, this term becomes

$$T^1 = a_1^\dagger a_2 + a_2^\dagger a_1 + b_1^\dagger b_2 + b_2^\dagger b_1 = a_1^\dagger a_2 - a_1 a_2^\dagger + b_1^\dagger b_2 - b_1 b_2^\dagger, \tag{2.13}$$

the one-body transport term. It is already orthogonal to the identity. These two terms are the only S1-S4 invariant one-body operators.

2.3.2 Two-body Operators

Two-body operators are degree two in the basic operators and there are three types of products that can be formed. The first are the classic two-body electrostatic operators which result from the product of two electrostatic basic operators. The second type are the transport terms, these are the product of two basic transport operators. Finally one basic electrostatic and one basic transport term can be combined to form a mixed operator.

Note that many products of pairs of basic operators, including all squares, are contained in the span of the basic operators by the commutation relations.

$$e_{a_i} e_{a_i} \quad = 1 = \quad e_{b_i} e_{b_i} \tag{2.14}$$

$$a_1^\dagger a_2 a_1^\dagger a_2 \quad = 0 = \quad b_1^\dagger b_2 b_1^\dagger b_2 \tag{2.15}$$

$$a_1 a_2^\dagger a_1 a_2^\dagger \quad = 0 = \quad b_1 b_2^\dagger b_1 b_2^\dagger \tag{2.16}$$

$$e_{a_1} a_1^\dagger a_2 = a_1^\dagger a_2 \qquad e_{b_1} b_1^\dagger b_2 = b_1^\dagger b_2 \tag{2.17}$$

$$e_{a_1} a_1 a_2^\dagger = -a_1 a_2^\dagger \qquad e_{b_1} b_1 b_2^\dagger = -b_1 b_2^\dagger \tag{2.18}$$

$$e_{a_2} a_1^\dagger a_2 = -a_1^\dagger a_2 \qquad e_{b_2} b_1^\dagger b_2 = -b_1^\dagger b_2 \tag{2.19}$$

$$e_{a_2} a_1 a_2^\dagger = a_1 a_2^\dagger \qquad e_{b_2} b_1 b_2^\dagger = b_1 b_2^\dagger \tag{2.20}$$

Notice also that the order of multiplication does not matter since the basic operators are degree two in the annihilators and creators.

Electrostatic Terms

Consider the four basic electrostatic operators $e_{a_1}, e_{a_2}, e_{b_1}, e_{b_2}$. There are $4^2 = 16$ possible pairs, but only $\binom{4}{3} = 6$ do not collapse under the commutation relations.

These are

$$e_{a_1}e_{b_1}, \ e_{a_2}e_{b_2}, \ e_{a_1}e_{a_2}, \ e_{b_1}e_{b_2}, \ e_{a_1}e_{b_2}, \ e_{b_1}e_{a_2}, \tag{2.21}$$

which can be divided into three pairs of operators, as above. The first pair are permuted by the translation symmetry and the other two pairs are permuted by S4. By summing the pairs together, invariant operators are formed. The operator

$$E_0^2 = e_{a_1}e_{b_1} + e_{a_2}e_{b_2} \tag{2.22}$$

is known as the on site electrostatic operator since it is degree four on each site.

The other two operators, $e_{a_1}e_{a_2} + e_{b_1}e_{b_2}$ and $e_{a_1}e_{b_2} + e_{b_1}e_{a_2}$, are combined in the following linear combination which simplifies their interpretation:

$$E_I^2 = \frac{1}{4}(e_{a_1}e_{a_2} + e_{b_1}e_{b_2}) + \frac{1}{4}(e_{a_1}e_{b_2} + e_{b_1}e_{a_2}) = e_1 e_2, \tag{2.23}$$

$$E_V^2 = \frac{1}{4}(e_{a_1}e_{a_2} + e_{b_1}e_{b_2}) - \frac{1}{4}(e_{a_1}e_{b_2} + e_{b_1}e_{a_2}) = f_1 f_2, \tag{2.24}$$

where $e_i = \frac{1}{2}(e_{a_i} + e_{b_i})$ and $f_i = \frac{1}{2}(e_{a_i} - e_{b_i})$. These terms are known as the ionic and valence electrostatic operators repectively.

The eigenvalues of the operators e_i and f_i on each configuration of site i are listed in the following table.

	$\lvert\uparrow\downarrow\rangle$	$\lvert\emptyset\rangle$	$\lvert\uparrow\rangle$	$\lvert\downarrow\rangle$
e_i	+1	-1	0	0
f_i	0	0	+1	-1

Thus E_I^2 is zero unless sites 1 and 2 are ionic and E_V^2 is zero unless both sites are valence. Both are traceless and are also orthogonal to the one-body operators.

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Ionic and Valence Transport Terms

In addition to the simplifications due to 2.14, the four products

$$\{a_1^\dagger a_2 a_1 a_2^\dagger,\ a_1 a_2^\dagger a_1^\dagger a_2,\ b_1^\dagger b_2 b_1 b_2^\dagger,\ b_1 b_2^\dagger b_1^\dagger b_2\} \tag{2.25}$$

need not be considered since they simplify to become electrostatic terms. For example,

$$a_1^\dagger a_2 a_1 a_2^\dagger \;=\; -a_1^\dagger a_1 a_2 a_2^\dagger \tag{2.26}$$

$$=\; -\frac{1}{4}(1 + e_{a_1})(1 - e_{a_2}) \tag{2.27}$$

$$=\; -\frac{1}{4}(1 - e_{a_1} e_{a_2}) - \frac{1}{4}(e_{a_1} - e_{a_2}) \tag{2.28}$$

$$\rightarrow\; -\frac{1}{4}(1 - e_{a_1} e_{a_2}) \tag{2.29}$$

after symmetrizing over S1.

Consider the products $a_1^\dagger a_2 b_1^\dagger b_2$ and $a_1^\dagger a_2 b_1 b_2^\dagger$. These are not ring symmetric or self-adjoint. However the terms

$$-a_1^\dagger b_1^\dagger a_2 b_2 - a_1 b_1 a_2^\dagger b_2^\dagger,\qquad -a_1^\dagger b_1 a_2 b_2^\dagger - a_1 b_1^\dagger a_2^\dagger b_2, \tag{2.30}$$

do satisfy S1-S4. The first is zero unless one site is doubly occupied and the other site is unoccupied, in which case the pair of electrons is transported from site to site. The second is zero unless one site is spin-up occupied and the other is spin-down occupied, in which case the electrons are exchanged between the sites. For this reason, the terms

$$T_I^2 \;=\; -a_1^\dagger b_1^\dagger a_2 b_2 - a_1 b_1 a_2^\dagger b_2^\dagger, \tag{2.31}$$

$$T_V^2 \;=\; -a_1^\dagger b_1 a_2 b_2^\dagger - a_1 b_1^\dagger a_2^\dagger b_2, \tag{2.32}$$

are known as the ionic and valence transport operators respectively.

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Two Site Hamiltonians: Mixing Transport Terms

The final family of products that must be investigated are those where one basic polynomial is electrostatic while the other is a transport operator. The only non-zero terms are of the form $e_{a_1} b_1^\dagger b_2$, where the spins of the electrostatic and transport operators differ. This term is not hermitian symmetric, ring symmetric or spin-up, spin-down symmetric, so a multiple of the average

$$
\begin{aligned}
e_{a_1} b_1^\dagger b_2 \quad &+ \quad e_{a_1} b_2^\dagger b_1 + e_{a_2} b_2^\dagger b_1 + e_{a_2} b_1^\dagger b_2 + e_{b_1} a_1^\dagger a_2 + e_{b_1} a_2^\dagger a_1 + e_{b_2} a_2^\dagger a_1 + e_{b_2} a_1^\dagger a_2 \\
&= \quad (e_{a_1} + e_{a_2})(b_1^\dagger b_2 - b_1 b_2^\dagger) + (e_{b_1} + e_{b_2})(a_1^\dagger a_2 - a_1 a_2^\dagger)
\end{aligned}
\tag{2.33}
$$

is used. This term, called the mixing transport term, T_M^2, transports a single electron from a doubly occupied site to a valence site or a single electron from a valence site to an unoccupied site, swapping the location of the ionic and the valence sites on the lattice.

This completes the search for one and two-body operators which satisfy S1-S4. There are two one-body operators, an electrostatic and a transport operator, and five two-body operators. The two-body operators can be divided further, there are two electrostatic terms, one ionic and one valence, and three transport terms, ionic, valence and mixed.

2.3.3 Particle-Hole Transformation

Invariance under the particle-hole transformation, T_{PH}, is the final property of the hamiltonians to be studied. It was omitted from the criteria that were used to determine the set of hamiltonians, so it is necessary to verify which terms satisfy S5. It

will be shown that the action of T_{PH} gives an easy way to distinguish one-body and two-body operators: requiring an operator to be invariant under T_{PH} is equivalent to requiring that operator be two-body.

Lemma 2.3.1 *The operators* $\{e_{a_1}, e_{b_1}, e_1, f_1\}$ *are anti-symmetric with respect to* T_{PH}.

Proof: By direct computation,

$$T_{PH}[e_{a_i}] \;=\; T_{PH}[a_i^\dagger a_i - a_i a_i^\dagger] = a_i a_i^\dagger - a_i^\dagger a_i = -e_{a_i}, \tag{2.34}$$

$$T_{PH}[e_{b_i}] \;=\; T_{PH}[b_i^\dagger b_i - b_i b_i^\dagger] = b_i b_i^\dagger - b_i^\dagger b_i = -e_{b_i}, \tag{2.35}$$

$$T_{PH}[e_i] \;=\; T_{PH}[\tfrac{1}{2}(e_{a_i} + e_{b_i})] = \tfrac{1}{2}(-e_{a_i} - e_{b_i}) = -e_i, \tag{2.36}$$

$$T_{PH}[f_i] \;=\; T_{PH}[\tfrac{1}{2}(e_{a_i} - e_{b_i})] = \tfrac{1}{2}(-e_{a_i} + e_{b_i}) = -f_i. \tag{2.37}$$

$\square$

Theorem 2.1 *The one-body operators* T^1 *and* E^1 *are anti-symmetric with respect to* T_{PH}.

Proof:

$$T_{PH}[E^1] \;=\; T_{PH}[e_1 + e_2] = -e_1 - e_2 = -E^1, \tag{2.38}$$

$$T_{PH}[T^1] \;=\; T_{PH}[a_1^\dagger a_2 - a_1 a_2^\dagger + b_1^\dagger b_2 - b_1 b_2^\dagger]$$

$$\;=\; a_1 a_2^\dagger - a_1^\dagger a_2 + b_1 b_2^\dagger - b_1^\dagger b_2$$

$$\;=\; -T^1. \tag{2.39}$$

$\square$

Theorem 2.2 *The two-body operators $E_0^2, E_I^2, E_V^2, T_I^2, T_V^2, T_M^2$ are invariant with respect to T_{PH}.*

Proof:

$$T_{PH}[E_0^2] = T_{PH}[e_{a_1}e_{b_1} + e_{a_2}e_{b_2}]$$

$$= (-e_{a_1})(-e_{b_1}) + (-e_{a_2})(-e_{b_2}) = E_0^2, \tag{2.40}$$

$$T_{PH}[E_I^2] = T_{PH}[e_1 e_2] = (-e_1)(-e_2) = E_I^2, \tag{2.41}$$

$$T_{PH}[E_V^2] = T_{PH}[f_1 f_2] = (-f_1)(-f_2) = E_V^2, \tag{2.42}$$

$$T_{PH}[T_I^2] = T_{PH}[a_1^\dagger a_2 b_1^\dagger b_2 + a_1 a_2^\dagger b_1 b_2^\dagger]$$

$$= a_1 a_2^\dagger b_1 b_2^\dagger + a_1^\dagger a_2 b_1^\dagger b_2 = T_I^2 \tag{2.43}$$

$$T_{PH}[T_V^2] = T_{PH}[a_1^\dagger a_2 b_1 b_2^\dagger + a_1 a_2^\dagger b_1^\dagger b_2] = T_V^2 \tag{2.44}$$

$$T_{PH}[T_M^2] = T_{PH}[(e_{a_1} + e_{a_2})(b_1^\dagger b_2 - b_1 b_2^\dagger) + (e_{b_1} + e_{b_2})(a_1^\dagger a_2 - a_1 a_2^\dagger)]$$

$$= (-e_{a_1} - e_{a_2})(b_1 b_2^\dagger - b_1^\dagger b_2) + (-e_{b_1} - e_{b_2})(a_1 a_2^\dagger - a_1^\dagger a_2)$$

$$= T_M^2. \tag{2.45}$$

$\square$

Thus the two-body operators are symmetric with respect to T_{PH} while the one-body operators are anti-symmetric. That is, S5, that h_{12} be invariant under T_{PH} is equivalent to requiring $h = \sum_i^{|\Lambda|} h_{i\ i+1}$ be a two-body operator. This conclusion is generally valid, as expressed by the following theorem.

Theorem 2.3 *All self-adjoint two-body operators are invariant under T_{PH} and all self-adjoint one-body operators are anti-symmetric.*

The proof is omitted since it has been shown directly for the operators used in this thesis.

2.3.4 Basis of Hamiltonians

Every degree one and degree two combination of the basic operators

$$\{e_{a_1}, e_{a_2}, e_{b_1}, e_{b_2}, a_1^\dagger a_2, a_1 a_2^\dagger, b_1^\dagger b_2, b_1 b_2^\dagger\}, \tag{2.46}$$

has been formed, and each was checked for invariance under S1-S4. Furthermore, it has been shown that all of the one-body operators are anti-symmetric under T_{PH} while all of the two-body operators are invariant.

Therefore the set of six operators $\{E_I^2, T_I^2, E_V^2, T_V^2, T_M^2, E_0^2\}$ spans H_{12}. Any $h \in H$ can be expressed as $h = \sum_{i=1}^{|\Lambda|} h_{i\ i+1}$ where the bond hamiltonian h_{12} is given by

$$h_{12} = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \beta_M T_M^2 + \alpha_0 E_0^2. \tag{2.47}$$

In addition, the following theorem shows that these operators are orthogonal and that H_{12} and hence H are in fact six-dimensional. The proof can be done by checking the eigenvalues of each operator on all sixteen possible bonds, but follows easily from the next section.

Theorem 2.4 *The operators $\{E_0^2, E_I^2, E_V^2, T_I^2, T_V^2, T_M^2\}$ form an orthogonal basis for* H_{12}.

2.4 Good Quantum Numbers

Superconducting and other quantum states are stable if they persist under arbitrary perturbations of the hamiltonian. This section shows that all model hamiltonians

leave certain subspaces invariant and that these can be labelled by the quantum numbers

$$\mathbf{N} = \{\mathbf{n} | \mathbf{n} = (n_{\uparrow\downarrow}, n_{\emptyset}, n_{\uparrow}, n_{\downarrow}), \; n_{\emptyset} + n_{\uparrow\downarrow} + n_{\uparrow} + n_{\downarrow} = |\Lambda|\}, \qquad (2.48)$$

where $n_{\uparrow\downarrow}, n_{\emptyset}, n_{\uparrow}$ and $n_{\downarrow}$ are the numbers of doubly occupied, unoccupied, spin-up occupied and spin-down occupied sites on the ring.

2.4.1 Two-body Operators

Electrostatic Operators

The effect of any electrostatic operator is to multiply a configuration basis element by a constant, adding a scale factor. This factor depends on the occupation of the sites; however, all electrostatic operators preserve the number of sites of each occupation.

Transport Operators

The transport operators necessarily change the occupation of a site. However, it will be shown that all two-body transport operators permute the configurations of two sites, preserving the total number of sites of each occupation. Without loss of generality, consider the actions of $\{T_I^2, \; T_V^2, \; T_M^2\}$ on sites 1 and 2. The Hilbert space on these two sites is $4^2 = 16$ dimensional and the configuration basis elements are labelled by the configurations on these two sites. The effect of these hamiltonians is summarized in table 2.1.

In each case, at least two transport operators map the state to zero. The effect of any non-zero interaction is to permute the configurations on sites 1 and 2, possibly adding a scale factor, and hence to preserve the number of sites of each type of occupation.

	T_I^2	T_V^2	T_M^2
$\mid\emptyset>$	0	0	0
$\mid\uparrow,\uparrow>$	0	0	0
$\mid\downarrow,\downarrow>$	0	0	0
$\mid\uparrow\downarrow,\uparrow\downarrow>$	0	0	0
$\mid\uparrow,\emptyset>$	0	0	$-2\mid\emptyset,\uparrow>$
$\mid\downarrow,\emptyset>$	0	0	$-2\mid\emptyset,\downarrow>$
$\mid\emptyset,\uparrow>$	0	0	$-2\mid\uparrow,\emptyset>$
$\mid\emptyset,\downarrow>$	0	0	$-2\mid\downarrow,\emptyset>$
$\mid\uparrow\downarrow,\uparrow>$	0	0	$-2\mid\uparrow,\uparrow\downarrow>$
$\mid\uparrow\downarrow,\downarrow>$	0	0	$-2\mid\downarrow,\uparrow\downarrow>$
$\mid\uparrow,\uparrow\downarrow>$	0	0	$-2\mid\uparrow\downarrow,\uparrow>$
$\mid\downarrow,\uparrow\downarrow>$	0	0	$-2\mid\uparrow\downarrow,\downarrow>$
$\mid\uparrow\downarrow,\emptyset>$	$\mid\emptyset,\uparrow\downarrow>$	0	0
$\mid\emptyset,\uparrow\downarrow>$	$\mid\uparrow\downarrow\,\emptyset>$	0	0
$\mid\uparrow,\downarrow>$	0	$\mid\downarrow,\uparrow>$	0
$\mid\downarrow,\uparrow>$	0	$\mid\uparrow,\downarrow>$	0

Table 2.1: Interactions of T_I^2, T_V^2, T_M^2 on sites 1 and 2.

Good Quantum Numbers

Since any $h_{12} \in H_{12}$ preserves the quantum numbers $\mathbf{n} = (n_\emptyset,\ n_{\uparrow\downarrow},\ n_\uparrow,\ n_\downarrow)$, these are also preserved by the action of any $h \in H$. Let $V_{\mathbf{n_1}} = \{\psi | \mathbf{n}(\psi) = \mathbf{n_1}\}$ be the set of states with quantum numbers $\mathbf{n_1}$.

Theorem 2.5 *The numbers $(n_\emptyset,\ n_{\uparrow\downarrow},\ n_\uparrow,\ n_\downarrow)$ are good quantum numbers for two-body interactions on the lattice.*

Proof: Any $h \in H$ can be written

$$h = \sum_i h_{i\ i+1},\tag{2.49}$$

where $h_{i\ i+1}$ satisfies S1-S5. As presented above, any $h_{i\ i+1}$ that satisfies S1-S5 preserves the quantum numbers $(n_\emptyset, n_{\uparrow\downarrow}, n_\uparrow, n_\downarrow)$,

$$\psi \in V_{\mathbf{n}} \Rightarrow h_{i\ i+1}(\psi) \in V_{\mathbf{n}}. \qquad (2.50)$$

Thus,

$$\psi \in V_{\mathbf{n}} \Rightarrow h(\phi) = \sum_i h_{i\ i+1}(\phi) = \sum_i \phi_i \in V_{\mathbf{n}}, \qquad (2.51)$$

since $\phi_i = h_{i\ i+1}(\psi) \in V_{\mathbf{n}}$.

Therefore, given any ψ_1 and ψ_2, such that $\mathbf{n}(\psi_1) \neq \mathbf{n}(\psi_2)$, and any $h \in H$,

$$\langle \psi_1 | h | \psi_2 \rangle = 0. \qquad (2.52)$$

Therefore the quantum numbers $(n_\emptyset,\ n_{\uparrow\downarrow},\ n_\uparrow,\ n_\downarrow)$ define invariant subspaces and are good quantum numbers.

$\square$

All possible sets of quantum numbers $\mathbf{n}$ satisfy

$$n_\emptyset + n_{\uparrow\downarrow} + n_\uparrow + n_\downarrow = |\Lambda|. \qquad (2.53)$$

There are $\frac{1}{6}|\Lambda|^3 + |\Lambda|^2 + \frac{11}{6}|\Lambda| + 1$ ways to choose these quantum numbers, and each choice determines an invariant subspace of states. Let $\mathbf{N}$ be the set of all possible sets of quantum numbers. The set of all states V is decomposed into a direct sum,

$$V = \oplus_{\mathbf{n} \in \mathbf{N}} V_{\mathbf{n}}. \qquad (2.54)$$

Since every hamiltonian is invariant under S4 and S5, states with $\mathbf{n}_0 = (n_1, n_2, n_3, n_4)$ are degenerate with states which have quantum sets (n_1, n_2, n_4, n_3), (n_2, n_1, n_3, n_4) and (n_2, n_1, n_4, n_3). For example, the configuration where every site is unoccupied,

$(|\Lambda|, 0, 0, 0)$, is equivalent to the configuration where every site is doubly occupied $(0, |\Lambda|, 0, 0)$. The expectation value of all model interactions, $h \in H$, is the same on these two configurations; no perturbation by any $h \in H$ can distinguish between them and remove the degeneracy. Thus it is more accurate to consider the subsets $N \subset \mathbf{N}$ which are invariant under S4 and S5 when describing the ground states of $h \in H$.

2.4.2 One-body Operators

The quantum numbers $(n_\emptyset, n_{\uparrow\downarrow}, n_\uparrow, n_\downarrow)$ do not split the ground states into non-interacting subspaces when one-body interactions are included in the hamiltonian. This is because of the action of the transport operator. For example,

$$
\begin{aligned}
T_{12}^1 \, a_1^\dagger b_1^\dagger |0> &= (a_1 a_2^\dagger + b_1 b_2^\dagger) \, a_1^\dagger b_1^\dagger |0> \\
&= a_1 a_1^\dagger b_1^\dagger a_2^\dagger |0> - a_1^\dagger b_1 b_1^\dagger b_2^\dagger |0> \\
&= b_1^\dagger a_2^\dagger |0> - a_1^\dagger b_2^\dagger |0> .
\end{aligned}
\tag{2.55}
$$

In this example the transport operator takes a configuration basis element with quantum numbers $(1, 1, 0, 0)$ and returns a linear combination of basis elements, all of which have quantum numbers (0,0,1,1). In general, the one-body transport operator changes adjacent doubly occupied and unoccupied sites into one spin-up occupied and one spin-down occupied site or vice-versa. Thus it does not preserve the quantum numbers $(n_\emptyset, n_{\uparrow\downarrow}, n_\uparrow, n_\downarrow)$. However, it does preserve the difference between the number of unoccupied and doubly occupied sites, $n_\emptyset - n_{\uparrow\downarrow}$, and the difference between the number of spin-up and spin-down sites, $n_\uparrow - n_\downarrow$. These are good quantum numbers for systems with one-body interactions.

Theorem 2.6 *Subspaces which are invariant under the action of all S1-S4 one-body and two-body operators can be labelled by the one-body quantum numbers*

$$(d_I, d_V) = (n_\emptyset - n_{\uparrow\downarrow}, n_\uparrow - n_\downarrow). \tag{2.56}$$

The one-body quantum numbers (d_I, d_V) satisfy $|d_I| + |d_V| = 2n \leq |\Lambda|$ for some integer n. There are only $|\Lambda|^2 + 2|\Lambda| + 1$ invariant subspaces when the one-body transport term is included.

The effects of including one-body interactions in the hamiltonian are as follows. Non-interacting subspaces under the pure two-body hamiltonians coalesce to form larger subspaces. This result is analagous to the atomic case where one-body terms interact with the Pauli principle to create shell structure which is perturbed by the inclusion of two-body terms. In the case of solid systems, the two-body terms alone split the states into subspaces which are mixed by the inclusion of one-body interactions.

Chapter 3

Quantum Phases

In this chapter we introduce notation to characterize the important sets of quantum numbers. The definition of phase is presented and the existence of phases using two-body hamiltonians alone is demonstrated. Some results of Erdahl and Jin, [14], relating to ionic hamiltonians are extended to the case of arbitrary hamiltonians and used to prove a theorem characterizing the phase boundaries.

3.1 Phase Structure

Recall H, the linear space of model hamiltonians and $\mathbf{N}$, the set of all possible quantum numbers $\mathbf{n} = (n_\emptyset, n_{\uparrow\downarrow}, n_\uparrow, n_\downarrow)$:

$$\mathbf{N} = \{\mathbf{n} | n_\emptyset + n_{\uparrow\downarrow} + n_\uparrow + n_\downarrow = |\Lambda|\}. \tag{3.1}$$

The Hilbert space of states, V, has an orthogonal decomposition by $\mathbf{n} \in \mathbf{N}$,

$$V = \bigoplus_{\mathbf{n} \in \mathbf{N}} V_\mathbf{n}. \tag{3.2}$$

Consider V^h, the space of ground state eigenvectors of h. These are the states which minimize $\langle h \rangle$, and h may have a unique ground state or degenerate ground states. In either case, V^h has an orthogonal decomposition by quantum number:

$$V^h = \oplus_\mathbf{n} V_\mathbf{n}^h = \oplus_\mathbf{n} V^h \cap V_\mathbf{n}. \tag{3.3}$$

Each $V_1 \subset V$ defines a set of quantum numbers, $N(V_1) = \{\mathbf{n} \in \mathbf{N} | V_1 \cap V_\mathbf{n} \neq \emptyset\}$. For every $h \in H$, the subset $N(h) = N(V^h) \subset \mathbf{N}$ is called the **quantum set** of h. Finally, for every subset $N \subset \mathbf{N}$, let

$$H(N) = \{h \in H | N(h) = N\}. \tag{3.4}$$

It is possible that $H(N) = \emptyset$ for some $N \in \mathbf{N}$. Those subsets are excluded by restricting to $N \in \mathbf{M}$, where

$$\mathbf{M} = \{N \subset \mathbf{N} | H(N) \neq \emptyset\} \tag{3.5}$$

is the collection of all quantum sets.

For each N, the dimension of $H(N)$ is its most important characteristic.

Definition 3.1.1 *A hamiltonian h is generic if, for every perturbation h', there exists $\delta > 0$ such that $|\epsilon| < \delta$ implies $h + \epsilon h' \in H(N(h))$.*

A quantum set N is called **locally minimal** if there exists a generic hamiltonian h such that $N = N(h)$. If a hamiltonian is not generic, an arbitrarily small perturbation can change the quantum numbers of the ground state. Non-generic hamiltonians are degenerate between two or more quantum sets; the perturbation lifts the degeneracy, and the quantum set of the perturbed hamiltonian is contained in the quantum set of the unperturbed hamiltonian. That is, there exists an $\delta > 0$ such that $N(h + \epsilon h') \subset N(h)$, for every h', whenever $\epsilon < \delta$.

The set $H(N(h))$ has full dimension for every generic h. These full dimensional subsets may or may not be connected. They are labelled by generic hamiltonians or locally minimal sets of quantum numbers and have an interpretation as quantum phases. The term quantum phase is used to describe both the characteristics of the ground states and the hamiltonians which generate them. That is, a ground state ϕ is in a phase P if it has the quantum numbers associated with P and a hamiltonian h is a P-phase hamiltonian if all of its ground states $\phi \in V^h$ are in P.

Definition 3.1.2 *For every locally minimal $N \in \mathbf{M}$, the set $H(N)$ is a* **quantum phase***.*

The generic h determine full dimensional regions where $N(h)$ is constant. These N are the locally minimal sets, and each one corresponds to a set $H(N)$. If $N \in \mathbf{M}$ is not locally minimal, then $h \in H(N)$ is not generic and $H(N)$ does not have full dimension. These are the phase boundaries. Two phases N_1 and N_2 share a boundary

if and only if there exists a hamiltonian h such that

$$V_{N_1} \cap V^h \neq \emptyset \qquad V_{N_2} \cap V^h \neq \emptyset, \qquad (3.6)$$

and $N_1 \cup N_2 \subset N(h)$. The boundary of k phases is defined similarly.

There are a finite number of quantum sets, $|\mathbf{N}| < \infty$ since the quantum numbers are integers and bounded by the lattice size. Therefore there is at least one N such that $H(N)$ has full dimension. Let S^5 be the unit sphere in a six-dimensional space. Then $H \cap S^5$, the set of hamiltonians with unit length, is tiled by the sets $H(N) \cap S^5$ for locally minimal N. Thus $h \in H \cap S^5$ is either in a phase or on the boundary of two phases, $H(N)$ is a phase boundary for all non-minimal N. The restriction to hamiltonians with unit length does not affect the phase structure, since each hamiltonian can be multiplied by a positive constant without changing the ground state.

The chance of creating a hamiltonian h which has ground states labelled by N is proportional to the area of $H(N)$. If $H(N)$ does not have full dimension, the chance of finding $h \in H(N)$ is zero. Therefore phases are experimentally observable, while phase boundaries are not. However, a phase transition between two phases is possible only if the boundary between them has co-dimension one. Therefore co-dimension one boundaries are experimentally detectable.

Further Remarks

The hamiltonian encodes the environment in which the electrons interact. There are two very different types of change to the environment which can occur. The first is that the external fields can be adjusted and the phase of the ground state may

change. The second is that the material under investigation can be changed, as long as the lattice structure is maintained. Since these two cannot be distinguished by the model used here, there could be phases which theoretically share a boundary, but for which a phase transition from one to the other is not possible since it would require changing the material in question.

The locally minimal sets N are such that there exist hamiltonians $h \in H(N)$ with a degeneracy in their ground states that can not be removed by local perturbation. However, this does not guarantee that the degeneracy cannot be removed by perturbing very far in one direction. Let N be globally minimal if there is no hamiltonian h such that $N(h) \subset N$. Although the equivalence of the globally minimal and locally minimal sets is not established theoretically, it and some related hypotheses will be re-examined in section 3.4.1 using results specific to H.

3.2 The Quantum Phases

It will be shown that there are five phases which occur as ground states for hamiltonians in H. These are the vacuum phase (VAC), superconducting phase (SC), ferromagnetic phase (FM), the anti-ferromagnetic phase (AFM) and the mixed phase.

Every square lattice can be thought of as a set of bonds instead of a set of sites. This is convenient, since the hamiltonians describe the interaction between sets of electrons on sites separated by exactly one bond. In one dimension, the lattice is a sequence of bonds, the kth bond is between sites k and $k + 1$ and the last bond is between site $|\Lambda|$ and site 1.

There are 10 types of bonds, which are classified as follows. Any bond between an

ionic site and a valence site is a mixed bond; there are four possibilities. The on site, ionic and valence operators are zero on these bonds, and the mixed operator is constant: the expectation of T_M^2 is the same, no matter which type of mixed bond is present. There are two types of ionic and two types of valence bonds, called types I and II. Type I bonds are between sites with the same occupation and type II bonds are between sites with different occupations. Thus there is one type I ionic and one type I valence bond but two type II ionic bonds and two type II valence bonds.

The Vacuum Phase

Consider $h_{12} = -E^I$. The expectation value of E^I on a bond is zero unless that bond is ionic; it is positive ($+1$) if the bond is type I, negative (-1) on type II bonds.

Theorem 3.1 *The vacuum state and all-filled state are ground states for $h_{12} = -E_I^2$.*

Proof: Let k_1, k_2, k_3, k_4 be the number of type I ionic, type II ionic, valence and mixed bonds respectively in a configuration. The expectation value of $-E_I^2$ is

$$-(k_1) + (k_2) + 0(k_3) + 0(k_4) = -(k_1 - k_2). \tag{3.7}$$

The energy is lowest when k_1 is as large as possible and k_2 is as small as possible. This occurs when $k_1 = |\Lambda|$ and $k_2 = k_3 = k_4 = 0$. Thus the ground state configuration of $-E_I^2$ has each site occupied by the same ionic configuration, either the vacuum state, where every site is unoccupied, or the all-filled state, where every site is doubly occupied.

$\square$

The quantum set corresponding to these two configurations,

$$N = \{(|\Lambda|, 0, 0, 0), (0, |\Lambda|, 0, 0)\}, \tag{3.8}$$

may or may not define a phase. To see that it does, i.e. that this quantum set is locally minimal, observe that the vacuum and all-filled configurations are exchanged by the particle hole transformation. Since all $h \in H$ are invariant under T_{PH}, there is no perturbation $h' \in H$ which lifts the degeneracy between these two configurations. Therefore these configurations define a phase, called the vacuum phase.

The characteristics of the vacuum and all filled states that determine their common properties are that every site is ionic and has the same occupation. This means all transport terms have expectation value zero, as does the valence electrostatic operator. The other electrostatic operators act as the identity.

The Mixed Phase

The ground states of the transport operators are superpositions of configuration basis elements and, as such, are more difficult to describe. However, the mixed transport operator is closely related to a one-body operator whose ground states can be described by a Slater determinant.

Conisder $h_{12} = \pm T_M^2$. The expectation value of T_M^2 is the same on each type of mixed bond. Therefore any ground state of $\pm T_M^2$ is degenerate with another in which all ionic sites are unoccupied and all valence sites are spin-up occupied. In the subspace of states where these are the only occupations, the hamiltonian corresponding to T_M^2 is equivalent to the hamiltonian

$$h_{12} = T_M^1 = a_1^\dagger a_2 + a_1 a_2^\dagger. \tag{3.9}$$

This one-body term can be diagonalized and the ground state eigenvectors and eigen-values can be determined. Due to the ring symmetry, the eigenvectors are determined by a discrete Fourier Transform,

$$\alpha_p = \sum_{q=0}^{|\Lambda|-1} e^{i\frac{2\pi}{|\Lambda|}pq}(a_q^\dagger a_{q+1} + a_q a_{q+1}^\dagger), \tag{3.10}$$

for $0 \le p, q \le |\Lambda| - 1$. Each α_p corresponds to the creation of a spin-up electron or valence site on the ring, like the original term $a_1^\dagger a_2 + a_1 a_2^\dagger$. If the corresponding eigenvalues are given by ϵ_p, then $h = \sum_i h_{i\ i+1}$, where $h_{12} = T_M^1$, can be diagonalized,

$$h = \sum_i^{|\Lambda|} (a_i^\dagger a_{i+1} + a_i a_{i+1}^\dagger) = \sum_i^{|\Lambda|} \epsilon_i \alpha_i. \tag{3.11}$$

The eigenvalues ϵ_i are easily calculated knowing the eigenvectors. For even $|\Lambda|$, all are non-zero and for every i, there exists j such that $\epsilon_i = -\epsilon_j$.

The ground state of $h = T_M^1$ is given by including only those terms whose eigenvalues are negative,

$$\phi_+ = \prod_{i,\epsilon_i<0} \alpha_i. \tag{3.12}$$

Similarly, the ground state of $h = -T_M^1$ is

$$\phi_- = \prod_{i,\epsilon_i>0} \alpha_i. \tag{3.13}$$

Since there are an equal number of positive and negative eigenvalues, ϕ_+ and ϕ_- are both given by the product of $\frac{|\Lambda|}{2}$ valence creation operators, and thus are states which have an equal number of ionic and valence sites. The same is true for $\pm T_M^2$, the ground states have an equal number of ionic and valence sites. However, in this case, both ionic occupations and both valence occupations are allowed. Therefore there is a $2^{|\Lambda|}$ fold degeneracy in the ground state of $h_{12} = \pm T_M^2$.

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The quantum set associated with the ground state of $h_{12} = \pm T_M^2$ contains all quantum numbers where the number of ionic and valence sites are equal. In the context of the mixed hamiltonian, this is called half-filled. This subset of quantum numbers is locally minimal, however these states are closely related to other states with both ionic and valence sites. Therefore the definition of the mixed phase is slightly different from 3.1.2, it is defined as the set of all hamiltonians whose ground states have some ionic and some valence sites. The quantum set corresponding to the mixed phase is

$$N_M = \left\{ (n_{\uparrow\downarrow}, n_{\emptyset}, n_{\uparrow}, n_{\downarrow}) \in \mathbf{N} | n_{\uparrow\downarrow} + n_{\emptyset}, n_{\uparrow} + n_{\downarrow} > 0 \right\}. \tag{3.14}$$

The half filled ground states where $n_{\uparrow\downarrow} + n_{\emptyset} = n_{\uparrow} + n_{\downarrow}$ occur only near $h_{12} = \pm T_M^2$. The term pure phase is used to distinguish the other phases from the mixed phase, the pure phases do not consist of unrelated (under T_{PH} and T_S) subspaces grouped together.

Constant and Alternating Subphases

The difference between the ground states of T_M^2 and $-T_M^2$ is the following. Consider ϕ_1 and ϕ_2, two configurations which differ only in that site 1 is unoccupied and site 2 is spin-up occupied in ϕ_1 but these occupations are reversed in ϕ_2. Thus

$$\langle \phi_2 | T_M^2 | \phi_1 \rangle > 0. \tag{3.15}$$

To lower the energy of the ground state wave function of $h = T_M^2$, the signs of the coefficients of these two configurations should differ, (alternating phase) while for $h = -T_M^2$ the signs should agree (constant phase). For example, in the state

$$|\alpha_0\rangle = \sum_{i=1}^{|\Lambda|} \left(a_i^\dagger a_{i+1} |0\rangle + a_i a_{i+1}^\dagger |0\rangle \right) \tag{3.16}$$

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every term has coefficient $+1$ and this state is part of the ground state of $-T_M^2$ since

$$\langle \alpha_0 | - T_M^2 | \alpha_0 \rangle = -2 \langle \alpha_0 | \alpha_0 \rangle = -2 < 0. \tag{3.17}$$

Similarly, the state $|\alpha_{\frac{|\Lambda|}{2}}\rangle$, with $\epsilon_{\frac{|\Lambda|}{2}} = 2$, is an alternating phase ground state. Assigning a parity to each configuration so that they interact only to lower the energy is possible only for bipartite lattices, of which the n-dimensional square lattices are a sub-class. Bipartite lattices are those whose sites can be divided into two groups such that all bonds are between an even site and an odd site. The two groups are called even and odd or positive and negative (since $(-1)^n$ is positive if and only if n is even).

The n-dimensional square lattice sites are labelled by integers $(i_1, i_2, \ldots, i_n)$. The sites are assigned the parity of $i_1 + i_2 + \ldots + i_n$. In the one-dimensional lattice, site i is an even site if and only if i is even. Consider a configuration ϕ and all of those other configurations with which it interacts through the transport operator. Each of these configurations differs from ϕ only on two nearest neighbour sites, where a spin-up electron on one site is moved to an unoccupied site. Since adjacent sites have opposite parities, the number of odd sites occupied by an electron is changed by one. If the parity of a configuration ϕ is determined by the number of valence occupied odd sites, then the interaction between any two configurations under T_M^2 is negative. Since the only important feature is the relative parity of two configurations, an equivalent system is developed by counting the unoccupied sites or by reversing the parity assigned to each site.

The mixed phase is divided into two subphases, the constant mixed subphase and the alternating mixed subphase. A state ϕ must have the correct parity as well as

quantum numbers in order to be included in the subphase.

The SC Phase

Consider $h_{12} = \pm T_I^2$, the ionic transport operator. Only ionic bonds contribute to the energy, therefore the ground states will be ionic ground states. In fact, only bonds between an unoccupied site and a doubly occupied site contribute. The action of T_I^2 on the subspace where all sites are ionic is equivalent to the action of T_M^2 on the unoccupied, spin-up occupied subspace discussed above. Therefore the ground states of $h_{12} = \pm T_I^2$ have an equal number of unoccupied and doubly occupied sites. In the ionic context, these states are half-filled, since the number of electrons is equal to the number of sites on the lattice.

The term half-filled, when referring to pure phases, means that the number of electrons is equal to the number of sites and that the number of spin-up and spin-down electrons is equal. The first condition is automatically fulfilled by valence states while the second is always true for ionic states. This is different from the meaning for mixed states, where half-filled means that the number of ionic and valence sites are equal. In general, the term half-filled refers to the pure phase definition unless otherwise stated.

Like the mixed phase, the superconducting phase is divided into constant and alternating subphases, depending on the sign of the coefficient of T_I^2. In this case, the parity of a configuration is calculated by counting the number of doubly occupied odd sites.

The perturbation of $\pm T_I^2$ by any valence or mixed hamiltonian, or E_0^2 does not change

the ground state since these operators act as constants on the ionic subspace. Perturbation by E_I^2 changes the weighting of the configurations in the wave function, but the quantum numbers are preserved, [14]. Therefore $h_{12} = \pm T_I^2$ defines a phase. This is known as the superconducting phase and is characterized by pair transport.

$$N_{SC} = \left\{ (\frac{|\Lambda|}{2}, \frac{|\Lambda|}{2}, 0, 0) \right\}. \tag{3.18}$$

Pair transport refers to the fact that the transport term T_I^2 moves a pair of electrons from one site to another.

The hamiltonian $h_{12} = E_I^2$ shares the quantum numbers $(\frac{|\Lambda|}{2}, \frac{|\Lambda|}{2}, 0, 0)$ with $h_{12} = \pm T_I^2$. Its ground state is the checkerboard state where the sites alternate between unoccupied and doubly occupied around the ring. This hamiltonian is on the boundary between the constant and alternating superconducting subphases, and arbitrary perturbations by T_I^2 preserve the half-filled property of the ground states.

The Valence Phases

The similarities between the ionic and valence transport and electrostatic terms can be exploited to understand the phase structure. There are two transformations which exchange ionic and valence terms. Since there are three known ionic phases, VAC, ASC and CSC, there are three corresponding valence phases known as the ferromagnetic (FM), alternating anti-ferromagnetic (AAFM) and constant anti-ferromagnetic phases (CAFM).

Consider the following transformations:

$$T_{\pm(I,V)} : \begin{cases} \begin{array}{l} a_i \to a_i^\dagger \\ b_i \to b_i \end{array} & i \text{ even} \\ \begin{array}{l} a_i \to \pm a_i^\dagger \\ b_i \to \pm b_i \end{array} & i \text{ odd.} \end{cases} \tag{3.19}$$

These transformations permute the terms (excluding the mixing term) in the hamiltonian.

$$E_I^2 \xrightarrow{T_{\pm(I,V)}} E_V^2$$

$$T_I^2 \xrightarrow{T_{\pm(I,V)}} \pm T_V^2$$

$$E_0^2 \xrightarrow{T_{\pm(I,V)}} -E_0^2$$

The hamiltonian $-E_I^2$ and its vacuum phase ground states are transformed into $h_V = -E_V^2$ and its ground states. $-E_V^2$ has two degenerate ground states, one where every site is spin-up and another where every site is spin-down. The parallel allignment of spins is the defining characteristic of the ferromagnetic phase.

Under $T_{\pm(I,V)}$ the superconducting phase hamiltonians discussed above become $\pm T_V^2$. All valence ground states are automatically half-filled, but the ground states $\phi \in V^{\pm T_V^2}$ have the additional property that they have same number of spin-up and spin-down sites. This is known as anti-ferromagnetism,

$$N_{AFM} = \left\{ (0, 0, \frac{|\Lambda|}{2}, \frac{|\Lambda|}{2}) \right\}. \tag{3.20}$$

Like the other transport driven phases, the anti-ferromagnetic phase is divided into constant and alternating subphases. By convention, the parity of the configurations

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in the alternating phase are determined by counting the number of odd sites which are occupied by spin-up electrons.

The anti-ferromagnetic subphases are also transport phases. In this case, the action of T_V^2 is to exchange a spin-up electron and a spin-down electron on two sites. This is not pair transport as in the superconducting phases, but two electrons are created and two are destroyed, as was the case for T_I^2.

Thus, for every hamiltonian with an alternating phase superconducting ground state there is a hamiltonian with a constant phase superconducting ground state, a hamiltonian with an alternating phase anti-ferromagnetic ground state and a hamiltonian with a constant phase anti-ferromagnetic ground state. Similarly, to every hamiltonian with a vacuum ground state there corresponds one with a ferromagnetic ground state. This implies that the area covered by the vacuum phase is equal to that covered by the ferromagnetic phase and that each of the other pure phases occupy the same area.

3.3   Ionic Hamiltonian

Instead of considering an arbitrary $h \in H$

$$h_{12} = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \beta_M T_M^2 + \alpha_N E_0^2, \qquad (3.21)$$

consider the ionic hamiltonian

$$h_I = \alpha_I E_I^2 + \beta_I T_I^2 \qquad (3.22)$$

which has been studied extensively by Erdahl and Jin, [14].

The symmetry between the ionic and valence terms means that results which hold for this hamiltonian have conterparts with the valence phases and $h_V = \alpha_V E_V^2 + \beta_V T_V^2$. By decomposing the full hamiltonian into four parts,

$$h = h_I + h_V + \beta_M T_M^2 + \alpha_N E_0^2, \tag{3.23}$$

the phase structure is more easily described and understood.

3.3.1   The Representable Region

The representable region $\mathcal{R}$ is the region filled by

$$\beta = [\beta_E, \beta_T] = [\langle p, E_I^2 \rangle, \langle p, T_I^2 \rangle] \tag{3.24}$$

as $\alpha = [\alpha_I, \beta_I]$ varies. Each von Neumann density is represented by a point in $\mathcal{R}$. Consider the region $\mathcal{R}$ for a ring with eight sites shown in figure 3.1.
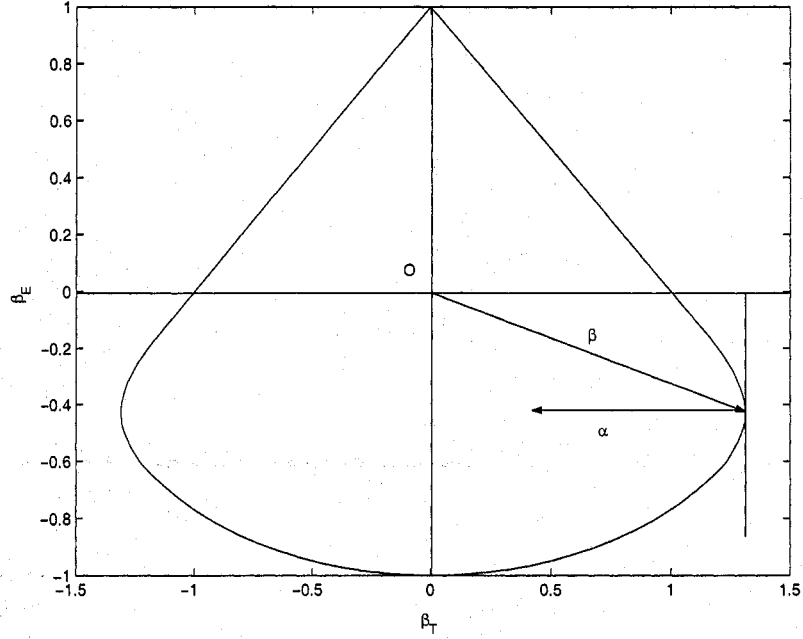
Figure 3.1: The representable region for $|\Lambda| = 8$

Each $\beta \in \mathcal{R}$ corresponds to a quantum state with total energy given by

$$\epsilon = \langle p, h_I \rangle = |\Lambda|\langle p, h_{12} \rangle = |\Lambda|(\alpha_I \langle p, E_I^2 \rangle + \beta_I \langle p, T_I^2 \rangle) = |\Lambda| \; \alpha \cdot \mathbf{a}. \qquad (3.25)$$

Consider the ground state of a hamiltonian with coefficients $\alpha = [0, \beta_T], \beta_T < 0$. This is the vector α in the figure, the ground state parameters are given by the point $\beta \in \mathcal{R}$. This follows since β is a point of tangency for a line that is tangent to $\mathcal{R}$ and perpendicular to α; the energy is constant along the tangent line and the vector α points in the direction of increasing energy.

The regions $\mathcal{R}_{|\Lambda|}$ have certain features in common for all $|\Lambda|$. First, the representable region shrinks as $|\Lambda| \to \infty$,

$$\mathcal{R}_2 \supset \mathcal{R}_4 \supset \mathcal{R}_6 \supset \dots \qquad (3.26)$$

Second, the points $[1,0]$ and $[-1,0]$ are always included. There are also line segments extending from $[1,0]$ to $[\frac{\pm|\Lambda|}{|\Lambda|-1}, \frac{-1}{|\Lambda|-1}]$. These boundary points of $\mathcal{R}$ can be treated theoretically.

Vacuum Phase

Consider the point $[1,0]$. $\langle p, E_I^2 \rangle = 1$ indicates that all of the bonds are in phase (positive) relative to the electrostatic operator. The corresponding configurations are the vacuum and all filled states. These states are both represented by the point $[1,0]$. The hamiltonian $h = -E_I^2$ has tangent vector $T = [0, \pm 1]$ which is tangent to the representable region at $[1,0]$ and $[-1,0]$. Starting from $[1,0]$, $\alpha = [-1,0]$ points to the interior of $\mathcal{R}$, so the vacuum and all filled states are the ground states of $-E_I^2$.

The point $[-1,0]$ represents states which are in phase (negative) for the electrostatic operator. These states are the half filled checkerboard states and are ground states for $h = E_I^2$.

The vacuum phase point $[1,0]$ is also a point of tangency for lines with slope m, $-1 < m < 1$. Each of these hamiltonians, $h = -E_I^2 + \beta T_I^2$, where $-1 < \beta < 1$, has the vacuum phase states as ground states.

VAC and SC Phase Boundaries

When $h = -E_I^2 \pm T_I^2$, the hamiltonian is on one of the boundaries between the vacuum and superconducting phases. There are two line segments which form part of the boundary of $\mathcal{R}$; these extend from $[1,0]$ and have slope ± 1. Consider the segment with slope -1 and the hamiltonian $h = -E_I^2 + T_I^2$ which is close to the ASC subphase,

since the coefficient of T_I^2 is positive. It can be shown, [14], that $1 + h$ is non-negative and that ground states $\Psi = P \, |0\rangle$ satisfy

1. P is homogeneous in the pair creation operators $\sigma_i^\dagger = a_i^\dagger b_i^\dagger$.

2. Pair creators for adjacent lattice sites must have coefficients that differ by sign alone. (Alternating Phase.)

A basis of ground state functions is given by

$$\Psi = \binom{|\Lambda|}{k}^{-\frac{1}{2}} (g^\dagger)^k \, |0\rangle, \quad k = 0, \, 1, \, \ldots, \, |\Lambda|, \tag{3.27}$$

where $g = \sum_{j=1}^{|\Lambda|} e^{-i\pi j} a_j b_j$. The phase factor $e^{-i\pi j} = (-1)^j$ assigns the parity to each configuration.

The entire line segment between $[1, 0]$ and $[\frac{|\Lambda|}{|\Lambda|-1}, \frac{-1}{|\Lambda|-1}]$ is tangent to $\alpha = [-1, +1]$. The point $[1, 0]$ corresponds to the empty and all filled states, $k = 0$ and $k = |\Lambda|$. The point $[\frac{\pm|\Lambda|}{|\Lambda|-1}, \frac{-1}{|\Lambda|-1}]$ is a half filled state, $k = \frac{|\Lambda|}{2}$. All other values of k correspond to points which are interior to the line segment, Ψ for k and $|\Lambda| - k$ are related by particle hole symmetry. Since the vacuum and all filled states are ground states of $h = -E_I^2 + T_I^2$ and a half filled state with alternating phase is another ground state for h, this hamiltonian is on the boundary between the VAC and ASC phases.

The case $h = -E_I^2 - T_I^2$ is treated by symmetry. The operator g becomes

$$g = \sum_{j=1}^{|\Lambda|} a_j b_j \tag{3.28}$$

and all states have the same parity. This shows how the SC phase is divided into the alternating and constant superconducting subphases, depending on the sign of the transport term.

3.3.2 Summary

Some results relating to the ionic hamiltonians can now be presented. Understanding the phase structure in the space of ionic hamiltonians is a prerequisite to developping a good picture of the phases for the full hamiltonian.

Theorem 3.2 *There are only three phases resulting from the use of ionic two-body hamiltonians, the VAC, ASC and CSC phases, and each of these share a boundary of co-dimension one.*

Proof: An ionic hamiltonian can be written

$$h_I = \alpha_I E_I^2 + \beta_I T_I^2, \tag{3.29}$$

where α_I and β_I are not both zero. When $\alpha_I < -|\beta_I| \leq 0$, h has a vacuum ground state. When $\alpha_I = \pm \beta_I < 0$, h is on the boundary between the vacuum and alternating superconducting phases ($\beta_I > 0$) or the boundary between the vacuum and constant superconducting phases ($\beta_I < 0$). When $-|\beta_I| < \alpha_I < 0$ or $\alpha_I > 0$, $\beta_I \neq 0$, the ground state of h is a superconducting phase, alternating or constant depending on the sign of β_I. Finally, in the last case, when $\alpha_I > 0$, $\beta_I = 0$, h has a checkerboard ground state which is on the boundary between the alternating and constant superconduting phases.

Therefore only the VAC, ASC and CSC phases occur as ground states, and there is a two-dimensional family of ionic hamiltonians which share each phase as a ground state. There is a one-dimensional boundary between any pair of states, and, since this space is two-dimensional, this boundary has co-dimension one.

□

A parallel result for the valence hamiltonians holds as well: ground states of $h_V = \alpha_V E_V^2 + \beta_V T_V^2$ are either FM, CAFM or AAFM states and the intersection of any two of these phases has codimension one.

Theorem 3.3 h_I *determines the 'phase' of the ionic molecules of a mixed state.*

Proof: Suppose $h = h_I + h_V + \alpha_0 E_0^2 + \beta_M T_M^2$, $h_I \neq 0$ is such that it has a mixed state ψ as a ground state. If the configurations that make up ψ are such that they have at least two nearest neighbour ionic sites, then ψ contains ionic bonds and the action of h_I on these bonds affects the energy. The hamiltonian terms h_V and T_M^2 have expectation value zero on these bonds, and E_0^2 acts as a constant. Therefore, the only contribution to the energy made by these bond interactions is through h_I. Therefore the energy is lowest when the electrons on these bonds are arranged in the pattern of the ground state of h_I.

$\square$

Thus there are only eight possible phases and subphases for the two-body hamiltonians on the square lattice. A generic hamiltonian $h = h_I + h_V + \alpha_0 E_0^2 + \beta_M T_M^2$ either has an ionic, valence or mixed ground state. If it is ionic, it is determined by h_I, and there are only three possibilities. If it is valence, it is determined by h_V and again it is in one of three subphases. Finally, if h has a mixed ground state, it is either constant or alternating, giving a total of eight subphase possiblilties.

3.4 $H(N)$ for Phase Boundaries

In the case of the general hamiltonian h with corresponding bond hamiltonian

$$h_{12} = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \beta_M T_M^2 + \alpha_0 E_0^2, \qquad (3.30)$$

the mixed phase occurs when the mixing term dominates the hamiltonian,

$$|\beta_M| >> \sqrt{\alpha_I^2 + \beta_I^2 + \alpha_V^2 + \beta_V^2 + \alpha_0^2}. \qquad (3.31)$$

Since all of the pure phases have full dimension, all ground states are pure states or degenerate between pure states when the mixing parameter is small. To understand the phase structure it suffices to examine the phase structure that occurs when $\beta_M = 0$. Each phase which occurs here will extend into the T_M^2 direction, although all phases may not extend equally.

If and only if two basins share a boundary of co-dimension one is a phase transition from one to the other possible. Any phase boundary between pure phases intersects the great circle where $\beta_M = 0$. Let $H_P = \{h | h = h_I + h_V + \alpha_0 E_0^2\}$ be the space of pure hamiltonians.

Let the quantum set of the intersection of k subphases be given by N_k. The goal is to describe the dimension of $H_P \cap H(N_k)$. Let $H_0(N_k) = 1$ if α_0 can be adjusted without changing the phase of the ground state, otherwise $H_0(N_k) = 0$. Similarly, let $H_I(N_k)$ be the number of directions which h_I can be perturbed without affecting the ground state phase. Since $h_I = \alpha_I E_I^2 + \beta_I T_I^2$, $0 \leq H_I(N_k) \leq 2$; the corresponding valence term is $H_V(N_k)$.

Theorem 3.4 *Let N_k be the quantum set associated with the intersection of k ionic subphases. Then $H_I(N_k) = 3 - k$ for $1 \leq k \leq 3$ and $H_I(N_k) = 2$ when $k = 0$.*

Proof: Let $h_{12} = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \alpha_0 E_0^2$. If h has an ionic (possibly degenerate) ground state, then decreasing α_0 does not change the phase since $\langle E_0^2 \rangle = n_I - n_V$. If N_k is the intersection of one or two phases, $H_I(N_k)$ has been described in 3.3. By definition, all phases have full dimension; thus for $k = 1$, $H_I(N_1) = 2$. It was also shown that any two ionic phases share a boundary of co-dimension one, $H_I(N_2) = 1$.

Suppose h is on the boundary of all three ionic phases, $k = 3$. The boundary between the ASC and CSC subphases occurs at $\beta_I = 0$ and the boundary between the vacuum phase and the superconducting subphases occurs when $\alpha_I = \pm \beta_I$. Thus, if h intersects all three ionic subphases siumultaneously, then $h_I = 0$ and $H_I(N_3) = 0$. It is possible for $h_{12} = h_V + \alpha_0 E_0^2$ to have an ionic ground state when $\alpha_0 < 0$ dominates the hamiltonian. In this case, all ionic states have the same energy, lower than that for any mixed or valence state.

Finally, if h is not on the boundary of any ionic phases, $k = 0$, and the ground state of h is valence since $h \in H_P$. Both α_I and β_I can be perturbed without moving onto an ionic boundary, $H_I(N_0) = 2$ in this case.

$\square$

The same results also hold for $H_V(N_k)$. A general $h \in H$ is represented by the bond hamiltonian

$$h_{12} = h_I + h_V + \alpha_0 E_0^2 + \beta_M T_M^2. \tag{3.32}$$

$H_0(N)$, the degress of freedom in choosing α_0, is all that is required to give a complete description of the pure phase structure, since perturbations by T_M^2 will never affect the pure ground states.

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Theorem 3.5 *Let N be the quantum set associated with the intersection of k pure phases. $H_0(N) = 1$ if and only if N is associated with the intersection of only ionic or only valence phases. Otherwise $H_0(N) = 0$.*

Proof: Since E_0^2 treats all ionic states equally and all valence states equally, if h is degenerate between only ionic or only valence states, adding a multiple of E_0^2 does not destroy the degeneracy, so α_0 can be perturbed arbitrarily. Thus $H_0(N) = 1$. If h is degenerate between at least one ionic and at least one valence state, changing α_0 would destroy the degeneracy. Hence $H_0(N) = 0$.

$\square$

The proof that the intersection of any $k < 6$ pure phases has dimension $7 - k$ follows.

Theorem 3.6 *Let N_k be the quantum set associated with the intersection of k pure phases. Then $dim(H(N_k)) = 7 - k$ if $k < 6$.*

Proof: Since $h_{12} = h_I + h_V + \alpha_0 E_0^2 + \beta_m T_M^2$, the dimension of $H(N)$ is given by

$$dim(H(N)) = H_I(N) + H_V(N) + H_0(N) + 1, \tag{3.33}$$

since the expectation value of T_M^2 is zero on all pure phases implies that β_M can be adjusted arbitrarily without changing the ground state.

Case 1, $k = 5$. There are two equivalent possibilities. Either h is in the intersection of three ionic and two valence phases or three valence and two ionic phases. In either case,

$$dim(H(N)) = 0 + 1 + 0 + 1 = 1 + 0 + 0 + 1 = 2 = 7 - k. \tag{3.34}$$

Case 2, $k = 4$. There are three possibilities, but two are equivalent. Either h intersects three phases of one type and one of the other, in which case $dim(H(N)) =$

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$0 + 2 + 0 + 1 = 3 = 7 - k$, or we have two ionic states and two valence states, $\dim(H(N)) = 1 + 1 + 0 + 1 = 3 = 7 - k$.

Case 3, $k = 3$. Again there are two distinct combinations. Either h contacts all three ionic or valence phases and none of the other type, or we have two of one and one of the other. In the first case, $\dim(H(N)) = 0 + 2 + 1 + 1 = 4 = 7 - k$, and in the second case $\dim(H(N)) = 1 + 2 + 0 + 1 = 4 = 7 - k$.

Case 4, $k = 2$. The first possibility is that h is in the intersection of two phases of the same type. In this case, $\dim(H(N)) = 1 + 2 + 1 + 1 = 5 = 7 - k$. Otherwise, h is in the intersection of one ionic and one valence phase, $\dim(H(N)) = 2 + 2 + 0 + 1 = 5 = 7 - k$. This shows that every pair of phases share a boundary of co-dimension one.

Case 5, $k = 1$. h is in a single phase, either ionic or valence. In either case, $\dim(h) = 2 + 2 + 1 + 1 = 6 = 7 - k$. This is equivalent to the earlier result that the pure phases have full dimension since the space of hamiltonains is six-dimensional.

$\square$

The case $k = 6$ must be handled separately. The only hamiltonian which has a degenerate ground state in all six pure phases is the identity, $h = \lambda 1$, which is also degenerate with mixed states. The hamiltonian $h = \beta_M T_M^2$ does not prefer any pure state over the others, but its ground state is a mixed state.

In practice, the normalization condition $\alpha_I^2 + \beta_I^2 + \alpha_V^2 + \beta_V^2 + \beta_M^2 + \alpha_N^2 = 1$ is enforced. This is equivalent to restricting $h \in H \cap S^5$. Projecting h onto S^5 affects the energy of all ground states equally, and hence does not affect the phase of the ground state. This is very helpful in visualizing the six-dimensional space of hamiltonians since it reduces the dimension by one.

3.4.1 Summary

The quantum sets of the of all hamiltonians $h \in H$ have been determined above. The most striking property is that the locally minimal sets are distinct, $N_i \cap N_j = \emptyset$ whenever N_i and N_j are locally minimal. This implies that there is no locally minimal set contained in another, and hence each locally minimal set is globally minimal in the sense that there is no perturbation of the hamiltonian (large or small) which will reduce the quantum set. Thus the phases are in a one-to-one correspondence with the locally minimal quantum sets and the generic hamiltonians.

The quantum set of the boundary between k phases contains the union of the corresponding k quantum sets, but is not necessarily equal to this union. The vacuum and superconducting phase boundaries give an example. Consider $h = -E_I^2 + T_I^2$ with its basis of ground states,

$$\Psi = \left(\frac{|\Lambda|}{k} \right)^{-\frac{1}{2}} (g^\dagger)^k \, |0\rangle, \quad k = 0, 1, \ldots, |\Lambda|, \tag{3.35}$$

where $g = \sum_{j=1}^{|\Lambda|} e^{-i\pi j} a_j b_j$. The wave functions with $k = 0$ and $k = |\Lambda|$ correspond to the vacuum and all-filled states respectively, while those with $k = \frac{|\Lambda|}{2}$ are ASC states.

$$\cup_i N_i = \left\{ (|\Lambda|, 0, 0, 0), (0, |\Lambda|, 0, 0), (\frac{|\Lambda|}{2}, \frac{|\Lambda|}{2}, 0, 0) \right\}. \tag{3.36}$$

The others are neither VAC phase nor ASC phase ground states, they have $\mathbf{n}(\Psi) = (|\Lambda| - k, k, 0, 0)$. Therefore

$$N(h) = \left\{ (|\Lambda| - k, k, 0, 0) | 0 \leq k \leq |\Lambda| \right\}. \tag{3.37}$$

Since $N(h) \neq \cup_i N_i$, this example shows that the quantum set of a hamiltonian on the boundary of k pure phases is not equal to the union of the quantum sets of those pure phases.

Finally, the region H_N is connected for every pure phase but not the mixed phase. It fails for the mixed phase because the two mixed subphases are not connected. The constant mixed phase and the alternating mixed phase occur for different signs of the mixed transport operator. If these subphases had a boundary, then they would be connected. However, the only boundary between $\beta_M > 0$ and $\beta_M < 0$ is $\beta_M = 0$. At this point, the ground state of h is necessarilly pure, and is not affected by small perturbations from T_M^2. Therefore, the mixed phase is disconnected. This does not prevent the other subphase pairs from being adjacent. Consider the boundary between the constant and alternating superconducting subphases. This boundary occurs at $T_I^2 = 0$, but there is a half-filled ionic state which forms part of this boundary, the checkerboard state. As β_I goes to zero, as long as α_I is large (positive) enough, the ground state of h will remain a half-filled (ionic) state, passing through the checkerboard state and going through a transition from the constant to the alternating phase (or vice versa). (ionic) state, passing through the checkerboard state and going through a transition from the constant to the alternating phase (or vice versa).

Chapter 4

The Density Matrix

In this chapter we construct the density matrix and determine the relationships between its entries. First, the parameters which appear in the density matrix are determined. Then the basis which is used to represent the density matrix is chosen so that $\mathbf{P}$ is a block matrix. The entries of the density matrix are $p_{ij} = \langle q_i^\dagger q_j, p \rangle$ and can be expressed in terms of the parameters.

4.1 The k-matrix

The reduced density matrix is a very large, sparse matrix and the effectiveness of the lower bound method depends on the basis of operators. The density matrix is block diagonal if the correct basis and ordering is chosen.

Let $\{q_1, q_2, \ldots, q_s\}$ be a basis for all polynomials in the creation and annihilaion operators with degree less than or equal to k. Any k-body hamiltonian h has a matrix representation relative to this basis given by $\mathbf{H} = [h_{ij}]$ where the h_{ij} are determined by

$$h = \sum_{i,j} h_{ij} q_i^\dagger q_j. \tag{4.1}$$

The k-matrix, $\mathbf{P}$, can also be expressed in this basis. It has entries p_{ij} given by

$$p_{ij} = \langle q_i^\dagger q_j, p \rangle. \tag{4.2}$$

The energy is found using

$$E(p) = \langle h, p \rangle = \sum_{i,j} h_{ij} \langle q_i^\dagger q_j, p \rangle = Tr[\mathbf{H}^\dagger \mathbf{P}]. \tag{4.3}$$

Density matrix calculations provide approximate solutions, and the order of accuracy of the approximation must be considered. The density matrix $\mathbf{P}$ defined above is k-positive: it is positive semi-definite with respect to all operators of degree less than or equal to k. However, since the reduced density matrix is positive semi-definite with respect to all operators, the level of approximation is measured by k. The size of the basis and the density matrix, and hence the complexity of the calculation increase with the order of approximation k. For calculations in solid systems using two-body interactions, $k \geq 3$ is required to obtain meaningful results; when $k = 3$ the results

are accurate to three figures, [4], and this is the order of approximation that will be used here.

4.2 Parameters

The many entries of the density matrix are parameterized by a small number of parameters. Each parameter $\mathbf{q}$ is the expectation value of an operator q on the ground state, $\mathbf{q} = \langle q, p \rangle$, and $\mathbf{q}$ has a given symmetry if and only if q does. The ground states will share the symmetries S1-S5 of the hamiltonian, therefore the density matrix entries will also satisfy S1-S5, but not necessarily the nearest neighbour condition. In this case, the operators q are invariant under S1-S5 and may correspond to interactions on up to four sites. Therefore the operators q are products of pairs of the six basic operators:

$$\{e_{a_i}, e_{b_i}, a_i^\dagger a_j, a_i a_j^\dagger, b_i^\dagger b_j, b_i b_j^\dagger\}, \tag{4.4}$$

where $i < j$.

By forming linear combinations of the above operators, six independent operators which are symmetric or anti-symmetric under S4 and S5 are created. Since the products of pairs of the basic operators must by symmetric under S4 and S5, only operators with the same parity under these two transformations interact. Therefore

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the operators are grouped together according to their parity under S4 and S5:

S4	S5	
$+$	$-$	e_i, and $(a_i^\dagger a_j - a_i a_j^\dagger) + (b_i^\dagger b_j - b_i b_j^\dagger)$
$-$	$-$	f_i, and $(a_i^\dagger a_j - a_i a_j^\dagger) - (b_i^\dagger b_j - b_i b_j^\dagger)$
$+$	$+$	$(a_i^\dagger a_j + a_i a_j^\dagger) + (b_i^\dagger b_j + b_i b_j^\dagger)$
$-$	$+$	$(a_i^\dagger a_j + a_i a_j^\dagger) - (b_i^\dagger b_j + b_i b_j^\dagger)$

$$(4.5)$$

The parameters are sorted into different types, according to the number of sites which are occupied. The basis operators q_i have degree less than or equal to three and the products $q_i^\dagger q_j$ have degree less than or equal to six. Since the parameters must be invariant under S5, they must be degree zero or degree four: they occupy four sites or fewer.

The parameters must be translationally invariant, so indexing by the offset between the occupied sites is natural. The parameters have both local and global representations, for example,

$$\alpha(j) = \frac{1}{|\Lambda|} \sum_{i=1}^{|\Lambda|} \alpha_i(j) \qquad (4.6)$$

where $\alpha_i(j) = \langle e_i e_{i+j}, p \rangle$. The global $\alpha(j)$ corresponds to a general ionic electrostatic interaction between two sites separated by distance j.

Zero and One Site Parameters

Of the two-body, S1-S5 invariant operators, only the identity is a zero-site operator, and $e_{a_i} e_{b_i}$ is the only single site operator. The corresponding parameters are

$$1 = \langle 1, p \rangle, \qquad N_i = \langle e_{a_i} e_{b_i}, p \rangle. \qquad (4.7)$$

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The parameter $N = \frac{1}{|\Lambda|} \sum N_i$ corresponds to the operator $e_{a_1} e_{b_1} + e_{a_2} e_{b_2} = E_0^2 \in H_{12}$ since

$$N = \frac{1}{|\Lambda|} \sum_{i=1}^{|\Lambda|} \langle e_{a_i} e_{b_i}, p \rangle = \frac{1}{2|\Lambda|} \sum_{i=1}^{|\Lambda|} \langle e_{a_i} e_{b_i} + e_{a_{i+1}} e_{b_{i+1}}, p \rangle. \qquad (4.8)$$

Two Site Parameters

The operators on two nearest neighbour sites have been enumerated in chapter 2, extending these to the case of two arbitrary sites is straight forward, and involves the addition of different scale factors for the different operators. The five two site parameters are given by

$$\alpha_i(j) = \frac{1}{4} \langle e_i e_{i+j}, p \rangle, \qquad \beta_i(j) = 2 \langle \sigma_i^\dagger \sigma_{i+j} + \sigma_i \sigma_{i+j}^\dagger, p \rangle, \qquad (4.9)$$

$$\gamma_i(j) = \frac{1}{4} \langle f_i f_{i+j}, p \rangle, \qquad \delta_i(j) = 2 \langle \tau_i^\dagger \tau_{i+j} + \tau_i \tau_{i+j}^\dagger, p \rangle, \qquad (4.10)$$

and

$$\mu_i(j) = \langle (e_{a_i} + e_{a_{i+j}})(b_i^\dagger b_{i+j} - b_i b_{i+j}^\dagger) + (e_{b_i} + e_{b_{i+j}})(a_i^\dagger a_{i+j} - a_i a_{i+j}^\dagger), p \rangle, \quad (4.11)$$

where $1 \le j \le \frac{|\Lambda|}{2}$. The offsets $j > \frac{|\Lambda|}{2}$ do not correspond to new parameters since

$$\alpha_i(j) = \langle e_i e_{i+j}, p \rangle = \langle e_{i+j} e_i, p \rangle = \langle e_{i+j} e_{i+j+(|\Lambda|-j)}, p \rangle = \alpha_{i+j}(|\Lambda| - j). \qquad (4.12)$$

That is, any parameter with offset $j > |\Lambda|/2$ can be written as a parameter with offset $|\Lambda| - j < |\Lambda|/2$.

Three Site Parameters

There are two types of products which result in three site operators: the products of an electrostatic operator and a transport operator or the product of two transport operators where two sites overlap.

The three site parameters have two unpaired spin operators, say on sites i_1 and i_2, and a paired operator, say on site i_3. There are two possible arrangments of the paired and unpaired operators. The first arrangement corresponds to the situation where the paired operator is between the unpaired operators, $i_1 < i_3 < i_2$, while the second arrangment corresponds to the case when the paired spin is outside the unpaired spins, $i_1 < i_2 < i_3$. Let $j_1 = |i_2 - i_1|$ be the offset between the unpaired spin sites and let $j_2 = |i_3 - i_1|$. Then $1 \leq j_2 \leq j_2/2$ if $i_1 < i_3 < i_2$ or $j_1 + 1 \leq j_2 \leq (\Lambda + j_2)/2$ if $i_1 < i_2 < i_3$.

There are four types of paired operator, e_i, f_i, σ_i and τ_i, and each of these correspond to a different type of three-site parameter, E, F, S or T repectively. Once the paired operator has been specified, the possible unpaired operators are known. Since there are two arrangments for each type of operator, there are eight three-site parameters. Symmetrizing the parameters over S1-S5 is straightforward. The only special case is S2, which reflects the paired spin through the transport bond j_1. The three-site parameters are given below.

$$E_i(j_1, j_2) = \langle (a_i^\dagger a_{i+j_1} - a_i a_{i+j_1}^\dagger + b_i^\dagger b_{i+j_1} - b_i b_{i+j_1}^\dagger)(e_{i+j_2} + e_{i+j_1-j_2}), p \rangle,$$

$$F_i(j_1, j_2) = \langle (a_i^\dagger a_{i+j_1} - a_i a_{i+j_1}^\dagger - b_i^\dagger b_{i+j_1} + b_i b_{i+j_1}^\dagger)(f_{i+j_2} + f_{i+j_1-j_2}), p \rangle,$$

$$S_i(j_1, j_2) = \langle (a_i^\dagger b_{i+j_1}^\dagger - b_i^\dagger a_{i+j_1}^\dagger)(\sigma_{i+j_2}^\dagger + \sigma_{i+j_1-j_2}^\dagger), p \rangle$$
$$+ \langle (b_i a_{i+j_1} - a_i b_{i+j_1})(\sigma_{i+j_2} + \sigma_{i+j_1-j_2}), p \rangle,$$

$$T_i(j_1, j_2) = \langle (a_i^\dagger b_{i+j_1} - b_i a_{i+j_1}^\dagger)(\tau_{i+j_2} + \tau_{i+j_1-j_2}), p \rangle$$
$$+ \langle (b_i^\dagger a_{i+j_1} - a_i b_{i+j_1}^\dagger)(\tau_{i+j_2}^\dagger + \tau_{i+j_1-j_2}^\dagger), p \rangle,$$

Four Site Parameters

Degree four operators on four sites always involve four unpaired operators. There are two different cases to be considered, when all four operators share the same spin and when there is one spin-up and one spin-down creator-annihilator pair. The latter case will be treated first - it is more general since there are additional symmetries when all spins are alike. In total, there are four types of operator, A, B, C and D.

Let the sites $i_1 < i_2 < i_3 < i_4$ be ordered so that

$$i_k = i + j_1 + j_2 + \ldots j_{k-1}, \tag{4.13}$$

where $j_1 \leq j_3$ and $|i_4 - i_1| \geq j_1, j_2, j_3$. There is no ambiguity in doing this as long as the two largest gaps are not equal and adjacent. The parameters are indexed by j_1, j_2 and j_3, but they will be written using i_1, i_2 and i_3 to simplify their presentation.

To index the parameters which are invariant with respect to S4 and S5, label them by operators where i_1 is occupied by $a^\dagger$. The following notation is used for the parameter: if the first spin-down occupied site is a creator, the parameter is type C, if it is an annihilator, the parameter is type D. There are three subtypes within each these, depending on the location of the spin-up annihilator, a.

$$C1_i(j_1, j_2, j_3) = \langle a_i^\dagger a_{i_2} b_{i_3}^\dagger b_{i_4} + a_i a_{i_2}^\dagger b_{i_3} b_{i_4}^\dagger + b_i^\dagger b_{i_2} a_{i_3}^\dagger a_{i_4} + b_i b_{i_2}^\dagger a_{i_3} a_{i_4}^\dagger, p \rangle,$$

$$C2_i(j_1, j_2, j_3) = \langle a_i^\dagger b_{i_2}^\dagger a_{i_3} b_{i_4} + a_i b_{i_2} a_{i_3}^\dagger b_{i_4}^\dagger + b_i^\dagger a_{i_2}^\dagger b_{i_3} a_{i_4} + b_i a_{i_2} b_{i_3}^\dagger a_{i_4}^\dagger, p \rangle,$$

$$C3_i(j_1, j_2, j_3) = \langle a_i^\dagger b_{i_2}^\dagger b_{i_3} a_{i_4} + a_i b_{i_2} b_{i_3}^\dagger a_{i_4}^\dagger + b_i^\dagger a_{i_2}^\dagger a_{i_3} b_{i_4} + b_i a_{i_2} a_{i_3}^\dagger b_{i_4}^\dagger, p \rangle.$$

$$D1_i(j_1, j_2, j_3) = \langle a_i^\dagger a_{i_2} b_{i_3} b_{i_4}^\dagger + a_i a_{i_2}^\dagger b_{i_3}^\dagger b_{i_4} + b_i^\dagger b_{i_2} a_{i_3} a_{i_4}^\dagger + b_i b_{i_2}^\dagger a_{i_3}^\dagger a_{i_4}, p \rangle,$$

$$D2_i(j_1, j_2, j_3) = \langle a_i^\dagger b_{i_2} a_{i_3} b_{i_4}^\dagger + a_i b_{i_2}^\dagger a_{i_3}^\dagger b_{i_4} + b_i a_{i_2}^\dagger b_{i_3}^\dagger a_{i_4} + b_i^\dagger a_{i_2} b_{i_3} a_{i_4}^\dagger, p \rangle,$$

$$D3_i(j_1, j_2, j_3) = \langle a_i^\dagger b_{i_2} b_{i_3}^\dagger a_{i_4} + a_i b_{i_2}^\dagger b_{i_3} a_{i_4}^\dagger + b_i a_{i_2}^\dagger a_{i_3} b_{i_4}^\dagger + b_i^\dagger a_{i_2} a_{i_3}^\dagger b_{i_4}, p \rangle.$$

When the two largest gaps are equal and adjacent, it is always possible to write the parameter as a C type parameter. Thus, there are six parameters of this type except when $j_3 = (|\Lambda| - j_1 - j_2)/2$, in which case there are only three.

When all operators have the same spin, the parameters, called A and B and corresponding to the parameters C and D respectively, simplify due to the additional symmetry, meaning that there are only three independent parameters. For example,

$$B3_i(j_1, j_2, j_3) = (a^\dagger_{i_1} a_{i_4})(a_{i_2} a^\dagger_{i_3}) = (a^\dagger_{i_1} a_{i_2})(a^\dagger_{i_3} a_{i_4}) = A1_i(j_1, j_2, j_3). \qquad (4.14)$$

Similarly,

$$A3_i(j_1, j_2, j_3) = A2_i(j_1, j_2, j_3) \text{ and } B2_i(j_1, j_2, j_3) = B1_i(j_1, j_2, j_3). \qquad (4.15)$$

Whenever $j_3 = (|\Lambda| - j_1 - j_2)/2$, there are fewer parameters since $B1_i(j_1, j_2, j_3) = A2_i(j_1, j_2, j_3)$. Thus there are nine parameters on four sites, except when $j_3 = (|\Lambda| - j_1 - j_2)/2$, in which case there are only five.

4.2.1 Restricted Parameters

This is a complete list of parameters needed to express the three-positive density matrix. However, restricting the density matrix so that only two-site parameters appear gives a significant simplification without affecting the accuracy of approximation of the ionic or valence ground states.

Any degree four term $q^\dagger_i q_j$ which occupies three or more sites necessarily has one site occupied by a single annihilator or creator. This **unpaired spin** sends everything to zero or changes the occupation of the site. There are four possible operators and

occupations on this site.

$$a_i|\emptyset\rangle = 0, \quad a_i|\uparrow\downarrow\rangle = |\downarrow\rangle, \quad a_i|\uparrow\rangle = |\emptyset\rangle, \quad a_i|\downarrow\rangle = 0,$$

$$b_i|\emptyset\rangle = 0, \quad b_i|\uparrow\downarrow\rangle = -|\uparrow\rangle, \quad b_i|\uparrow\rangle = 0, \quad b_i|\downarrow\rangle = |\emptyset\rangle,$$

$$a_i^\dagger|\emptyset\rangle = |\uparrow\rangle, \quad a_i^\dagger|\uparrow\downarrow\rangle = 0, \quad a_i^\dagger|\uparrow\rangle = 0, \quad a_i^\dagger|\downarrow\rangle = |\uparrow\downarrow\rangle,$$

$$b_i^\dagger|\emptyset\rangle = |\downarrow\rangle, \quad b_i^\dagger|\uparrow\downarrow\rangle = 0, \quad b_i^\dagger|\uparrow\rangle = -|\uparrow\downarrow\rangle, \quad b_i^\dagger|\downarrow\rangle = 0. \tag{4.16}$$

Therefore the operator $q_i^\dagger q_j$ changes the occupation of the site and necessarily changes the subspace of the ground state if it is a pure ionic or valence state. For any ionic or valence states ψ_1^I, ψ_2^I or ψ_1^V, ψ_2^V,

$$\langle q \rangle = \langle \psi_1^I | q_i^\dagger q_j | \psi_2^I \rangle = \langle \psi_1^V | q_i^\dagger q_j | \psi_2^V \rangle = 0. \tag{4.17}$$

Thus $p_{ij} = \langle p, q_i^\dagger q_j \rangle = \langle q \rangle = 0$ when p corresponds to a pure ground state. Therefore restricting the density matrix so that all three and four site parameters are zero does not affect the accuracy of the approximation of the ionic and valence ground states.

If ψ is not pure, then there are $q = q_i^\dagger q_j$ such that $q\psi$ is in the same subspace as ψ. However, the reduction in the size of the density matrix justifies setting the three and four-site parameters equal to zero for all calculations. Since these interactions model long range correlations, and the hamiltonians are nearest neighbour, the effect of excluding these terms is small.

The entries of the density matrix are parameterized by the expectation values of all operators which are invariant under S1-S5 and can be expressed as linear combinations of terms which occupy at most two sites. This restriction does not compromise the ionic or valence ground state solutions, but greatly reduces the complexity of the calculation. In this case there are $\frac{5}{2}|\Lambda| + 2$ parameters.

4.3   Symmetries of the Hamiltonians

Particle Number

Each operator q_i has an associated two-vector called the Particle Number. $PN(q_i) = [x, y]$, where $x, y \in \mathbb{Z}$ are the net change in spin-up and spin-down electrons respectively. For example, $PN(a_i b_j a_k^\dagger) = [0, -1]$. Since all terms in the hamiltonian are spin particle preserving, $PN(h) = [0, 0]$, operators q_i and q_j will interact if and only if

$$[0, 0] = PN(q_i^\dagger q_j) = PN(q_i^\dagger) + PN(q_j) = -PN(q_i) + PN(q_j), \qquad (4.18)$$

or $PN(q_i) = PN(q_j)$. By ordering the basis according to particle number the density matrix becomes a block diagonal matrix.

Particle-Hole and Spin Symmetries

All pure two-body hamiltonians are invariant with respect to the Particle-Hole transformation, $T_{PH}(h) = h$, and spin-up, spin-down symmetric, $T_S(h) = h$. Suppose $PN(q_i) = [x, y]$, then

$$PN(T_{PH}(q_i)) \quad = \quad [-x, -y] \qquad (4.19)$$

$$PN(T_S(q_i)) \quad = \quad [y, x]. \qquad (4.20)$$

These symmetries mean the blocks with particle number

$$[x, y], [-x, -y], [y, x] \text{ or } [-y, -x] \qquad (4.21)$$

are identical; removing duplicates does not affect the accuracy of the solution. Without loss of generality, include only those basis elements q_i such that $PN(q_i) = [x, y]$

where $x < y$ and $x + y < 0$ in the basis. In this way, the size of the density matrix is reduced by a factor of 4.

Operators on 2 or 3 sites

There are two types of operators in the basis for three-body operators, those which occupy three distinct sites, and those which occupy less than three. An operator on three sites (i, j, k) interacts only with other (i, j, k) operators, since the product of two three sites operators on different sites would occupy more than two sites, but the parameters are restricted to less than two sites. Thus, the matrix breaks apart into blocks: one large block for the operators on two sites and one block for each set of three sites (i, j, k).

With this information, more can be said about the blocks which appear in the reduced density matrix. These blocks are either three sites or two sites, and they are separated by particle number. For the three-body case, all blocks have one of four possible particle numbers:

$$PN(q_i) \in \{[-3, 0], [-2, -1], [-2, +1], [-1, 0]\}. \tag{4.22}$$

4.4 Three Sites Operators

Consider the three sites (i, j, k). There are a total of $4^3 = 64$ operators on those three sites (choice of a, $a^\dagger$, b, $b^\dagger$ at each site). However, only 16 of these are needed to construct the matrices, due to the paricle-hole and spin symmetries. The following table shows how these 16 are sorted by particle number.

PN	Operators	Size
$[-3,0]$	$\{a_i a_j a_k\}$	1
$[-2,-1]$	$\{a_i a_j b_k,\ a_i b_j a_k,\ b_i a_j a_k\}$	3
$[-2,+1]$	$\{a_i a_j b_k^\dagger,\ a_i b_j^\dagger a_k,\ b_i^\dagger a_j a_k\}$	3
$[-1,0]$	$\{a_i a_j a_k^\dagger,\ a_i b_j^\dagger b_k,\ b_i^\dagger a_j b_k,\ a_i b_j b_k^\dagger,\ a_i a_j^\dagger a_k,$ $b_i^\dagger b_j a_k,\ b_i a_j b_k^\dagger,\ b_i b_j^\dagger a_k,\ a_i^\dagger a_j a_k\}$	9

The density matrix contains four blocks for each set of three sites (i, j, k). The number of sets of sites grows quadratically with $|\Lambda|$, and adds significantly to the size of the density matrix.

Weights

By ring symmetry, the parameters which appear in the blocks for sites $(i_1, i_1 + j_1, i_1 + j_1 + j_2)$ and $(i_2, i_2 + j_1, i_2 + j_1 + j_2)$ are equal since the offsets j_1 and j_2 are equal. Thus the blocks themselves are identical. Instead of including the same block repeatedly in the density matrix, each block is multiplied by a weight according to its frequency in order to preserve the trace scalar product. For example, on a ring of size $|\Lambda| = 6$ there are only three different arrangements of offsets: $(1, 1)$, $(1, 2)$ and $(2, 2)$. The first occurs 6 times, since the central site can be any one on the ring. This block is multiplied by a factor of $wt = \sqrt{6/2} = \sqrt{3}$. The second occurs $2 \times 6 = 12$ times, because the central site can be any site on the ring, and for each choice we can decide to have the nearest neighbour site to the left or to the right. In this case, $wt = \sqrt{6}$. The last only occurs twice, for $(1, 3, 5)$ and $(2, 4, 6)$, $wt = 1$.

Matrix Entries

The matrix entries for these blocks can now be determined. For example, consider the operators with $PN = [-2, -1]$ on sites i, j, k. There are three operators of this type, $\{b_i a_j a_k, a_i b_j a_k, a_i a_j b_k\}$; they form a 3×3 block.

The $(1, 1)$ entry is given by:

$$
\begin{aligned}
\langle (b_i a_j a_k)^\dagger (b_i a_j a_k), p \rangle &= \langle b_i^\dagger b_i a_j^\dagger a_j a_k^\dagger a_k, p \rangle \\
&= \tfrac{1}{8} \ \langle (1 + e_i - f_i)(1 + e_j + f_j)(1 + e_k + f_k), p \rangle \\
&= \tfrac{1}{8} \ (\langle 1, p \rangle + \langle e_i e_j, p \rangle - \langle f_i f_j, p \rangle + \langle e_i e_k, p \rangle \\
&\qquad - \langle f_i f_k, p \rangle + \langle e_j e_k, p \rangle + \langle f_j f_k, p \rangle) \\
&= \tfrac{1}{8} \ (1 + \alpha_{ij} - \gamma_{ij} + \alpha_{ik} - \gamma_{ik} + \alpha_{jk} + \gamma_{jk}),
\end{aligned}
$$

since one-body (e_i, f_i) and three-body $(e_i e_j e_k, \ldots)$ do not satisfy S5.

The coefficient of the identity is $\tfrac{1}{8}$, but will be normalized to 1. All 3-site operators are multiplied by a factor of $\sqrt{8} = 2\sqrt{2}$. A normalizing constant is also be added to the two-site operators, see section 4.5.

The first entry is given by

$$
\langle (2\sqrt{2} b_i a_j a_k)^\dagger (2\sqrt{2} b_i a_j a_k), p \rangle = 1 + \alpha_{ij} - \gamma_{ij} + \alpha_{ik} - \gamma_{ik} + \alpha_{jk} + \gamma_{jk}, \tag{4.23}
$$

and the $(1, 2)$ entry is given by:

$$
\begin{aligned}
\langle (2\sqrt{2} b_i a_j a_k)^\dagger (2\sqrt{2} a_i b_j a_k), p \rangle &= 8 \langle b_i^\dagger a_i a_j^\dagger b_j a_k^\dagger a_k, p \rangle \\
&= 4 \langle \tau_i \tau_j^\dagger (1 + e_k + f_k), p \rangle = \delta_{ij}. \tag{4.24}
\end{aligned}
$$

The complete 3×3 block for $PN = [-2, -1]$ on sites (i, j, k) is:

$$\begin{bmatrix} 1 + \alpha_{ij} + \gamma_{ij} + \alpha_{ik} - \gamma_{ik} + \alpha_{jk} - \gamma_{jk} & \delta_{ij} & \delta_{ik} \\ \delta_{ij} & 1 + \alpha_{ij} - \gamma_{ij} + \alpha_{ik} + \gamma_{ik} + \alpha_{jk} - \gamma_{jk} & \delta_{jk} \\ \delta_{ik} & \delta_{jk} & 1 + \alpha_{ij} - \gamma_{ij} + \alpha_{ik} - \gamma_{ik} + \alpha_{jk} + \gamma_{jk} \end{bmatrix}$$

$$(4.25)$$

4.5   Two Site Operators

If there are two sites, and three anihilation or creation operators, one site has an unpaired spin. The other site must have one of the following operators, defined in chapter 2:

$$e_i = (e_{a_i} + e_{b_i}), \quad f_i = (e_{a_i} - e_{b_i}), \tag{4.26}$$

$$\sigma_i = a_i b_i, \quad \tau_i = a_i b_i^\dagger. \tag{4.27}$$

These are the paired operators, and the basis for the two-sites operators is formed by taking the product of a single annihilation or creation operator and one of these paired operators.

The operators e_i and σ_i act on ionic sites and f_i and τ_i act on valence sites. Two large non-interacting blocks are formed by grouping the operators whose paired spins are ionic together and those whose paired spins are valence together.

The two sites basis elements are then ordered by particle number. Both the ionic and valence cases contain a block with particle number $PN = [-1, 0]$. These blocks are formed from elements of the like $\{a_i e_j, b_i^\dagger \sigma_j\}$ and $\{a_i f_j, b_i^\dagger \tau_j\}$ respectively. The other ionic elements, $\{a_i \sigma_j\}$ form a $PN = [-2, -1]$ block, while the other valence elements, $\{a_i \tau_j\}$ form a $PN = [-2, +1]$ block.

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4.5.1 The $[-2, \pm 1]$ operators

The $PN = [-2, \pm 1]$ operators split into $|\Lambda|$ blocks depending on the site of the unpaired spin. By ring symmetry, any arrangement of sites can be translated so that the offsets are preserved but the unpaired spin is on site 1. The parameters in the block are unchanged by this translation. Thus this block need be included only once.

In all of the two-sites blocks there is one more adjustment to the basis elements to be made. Because of ring symmetry, terms such as $a_i e_{i+1}$ and $a_i e_{i-1}$ are related. To use this symmetry, include in the basis terms of the form $a_i(e_{i+1} \pm e_{i-1})$. There are now two non-interacting blocks for each particle number, one of which includes all terms whose paired spin coefficients are $+1$, and one block containing those terms where one paired spin has coefficient -1.

The basis elements for the different blocks are given below:

$$
\begin{array}{c|l}
PN & \\
\hline
[-2,-1] & 2a_1(\sigma_2 + \sigma_{|\Lambda|}),\ 2a_1(\sigma_3 + \sigma_{|\Lambda|-1}),\ \ldots,\ 2\sqrt{2}a_1\sigma_{1+\frac{|\Lambda|}{2}}, \\
[-2,-1] & \qquad 2a_1(\sigma_2 - \sigma_{|\Lambda|}),\ 2a_1(\sigma_3 - \sigma_{|\Lambda|-1}),\ \ldots, \\
[-2,+1] & 2a_1(\tau_2 + \tau_{|\Lambda|}),\ 2a_1(\tau_3 + \tau_{|\Lambda|-1}),\ \ldots,\ 2\sqrt{2}a_1\tau_{1+\frac{|\Lambda|}{2}}, \\
[-2,+1] & \qquad 2a_1(\tau_2 - \tau_{|\Lambda|}),\ 2a_1(\tau_3 - \tau_{|\Lambda|-1}),\ \ldots.
\end{array}
\tag{4.28}
$$

Matrix Entries

As an example, the matrix entries corresponding to the $PN = [-2, -1]$ operators

$$
\{2a_1(\sigma_2 - \sigma_{|\Lambda|}),\ 2a_1(\sigma_3 - \sigma_{|\Lambda|-1}),\ \ldots\}
\tag{4.29}
$$

for a ring with six sites will be formed. In this cases, there are only two operators, $2a_1(\sigma_2 - \sigma_6)$ and $2a_1(\sigma_3 - \sigma_5)$. The diagonal entries are

$$
\begin{aligned}
\langle [2a_1(\sigma_2 - \sigma_6)]^\dagger [2a_1(\sigma_2 - \sigma_6)], p \rangle &= \langle 2(1 + e_1 + f_1)(\sigma_2^\dagger \sigma_2 + \sigma_6^\dagger \sigma_6 - \sigma_2^\dagger \sigma_6 - \sigma_6^\dagger \sigma_2), p \rangle \\
&= 1 + \alpha_1 - \frac{\beta_2}{2}, \quad \text{and} \tag{4.30}
\end{aligned}
$$

$$
\langle [2a_1(\sigma_3 - \sigma_5)]^\dagger [2a_1(\sigma_3 - \sigma_5)], p \rangle = 1 + \alpha_1 - \frac{\beta_2}{2}. \tag{4.31}
$$

The off-diagonal term is

$$
\langle 2(1 + e_1 + f_1)(\sigma_2^\dagger \sigma_3 + \sigma_6^\dagger \sigma_5 - \sigma_2^\dagger \sigma_5 - \sigma_6^\dagger \sigma_3), p \rangle = \frac{\beta_1 - \beta_3}{2}. \tag{4.32}
$$

4.5.2 The $[-1, 0]$ operators

All of the $PN = [-1, 0]$ operators are necessary, even though the sub-blocks generated by operators with different unpaired spin sites are identical as in the $PN = [-2, \pm 1]$ case. All operators are required due to non-zero interactions between operators with different unpaired spin sites because of the mixing terms. These two large blocks are of the order $O(|\Lambda|^2)$. It is still possible to exploit the ring symmetry in this case, by introducing global (or symmetry adapted) basis elements for this part of the basis. Using a discrete Fourier transform to symmetrize over the site of the unpaired spin, this matrix breaks into $|\Lambda|$ diagonal blocks. The symmetry adapted operators for ionic pairings are

$$
A_p^0 = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} \, 2a_q e_q, \tag{4.33}
$$

$$
A_p^{\pm k} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} \, \sqrt{2} a_q (e_{q+k} \pm e_{q-k}), \tag{4.34}
$$

$$A_p^{\frac{|\Lambda|}{2}} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2a_q e_{q+\frac{|\Lambda|}{2}}, \tag{4.35}$$

$$B_p^{\pm k} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2b_q^\dagger (\sigma_{q+k} \pm \sigma_{q-k}), \tag{4.36}$$

$$B_p^{\frac{|\Lambda|}{2}} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2\sqrt{2} b_q^\dagger \sigma_{q+\frac{|\Lambda|}{2}}, \tag{4.37}$$

and for valence pairings are

$$C_p^0 = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2a_q f_q, \tag{4.38}$$

$$C_p^{\pm k} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} \sqrt{2} a_q (f_{q+k} \pm f_{q-k}), \tag{4.39}$$

$$C_p^{\frac{|\Lambda|}{2}} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2a_q f_{q+\frac{|\Lambda|}{2}}, \tag{4.40}$$

$$D_p^{\pm k} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2b_q^\dagger (\tau_{q+k} \pm \tau_{q-k}), \tag{4.41}$$

$$D_p^{\frac{|\Lambda|}{2}} = \frac{1}{\sqrt{|\Lambda|}} \sum_{q=1}^{|\Lambda|} e^{-ipq\pi'} 2\sqrt{2} b_q^\dagger \tau_{q+\frac{|\Lambda|}{2}}, \tag{4.42}$$

where $\pi' = \frac{2\pi}{|\Lambda|}$ and $k = 1, \ldots, \frac{|\Lambda|}{2} - 1$.

4.6 Summary

A basis of degree three operators has been constructed and ordered. The basis elements fall into two general types, three sites and two sites operators. There are four blocks for every arrangement of three sites, each with a different particle number. For three sites (i, j, k), the subbases of operators are given in the following table.

PN	Operators
$[-3, 0]$	$\{2\sqrt{2}a_i a_j a_k\}$
$[-2, -1]$	$\{2\sqrt{2}a_i a_j b_k,\ 2\sqrt{2}a_i b_j a_k,\ 2\sqrt{2}b_i a_j a_k\}$,
$[-2, +1]$	$\{2\sqrt{2}a_i a_j b_k^\dagger,\ 2\sqrt{2}a_i b_j^\dagger a_k,\ 2\sqrt{2}b_i^\dagger a_j a_k\}$,
$[-1, 0]$	$\{2\sqrt{2}a_i a_j a_k^\dagger,\ 2\sqrt{2}a_i b_j^\dagger b_k,\ 2\sqrt{2}b_i^\dagger a_j b_k,\ 2\sqrt{2}a_i b_j b_k^\dagger,\ 2\sqrt{2}a_i a_j^\dagger a_k$,
	$2\sqrt{2}b_i^\dagger b_j a_k,\ 2\sqrt{2}b_i a_j b_k^\dagger,\ 2\sqrt{2}b_i b_j^\dagger a_k,\ 2\sqrt{2}a_i^\dagger a_j a_k\}$.

Table 4.1: Subbases for the three-site blocks.

The two sites operators can also be grouped to give the density matrix block diagonal structure. The subbases for the two local blocks, those with $PN = [-2, \pm 1]$ are

PN	
$[-2,-1]$	$2a_1(\sigma_2 + \sigma_{|\Lambda|}),\ 2a_1(\sigma_3 + \sigma_{|\Lambda|-1}),\ \ldots,\ 2\sqrt{2}a_1\sigma_{1+\frac{|\Lambda|}{2}}$,
$[-2,-1]$	$2a_1(\sigma_2 - \sigma_{|\Lambda|}),\ 2a_1(\sigma_3 - \sigma_{|\Lambda|-1}),\ \ldots,$
$[-2,+1]$	$2a_1(\tau_2 + \tau_{|\Lambda|}),\ 2a_1(\tau_3 + \tau_{|\Lambda|-1}),\ \ldots,\ 2\sqrt{2}a_1\tau_{1+\frac{|\Lambda|}{2}}$,
$[-2,+1]$	$2a_1(\tau_2 - \tau_{|\Lambda|}),\ 2a_1(\tau_3 - \tau_{|\Lambda|-1}),\ \ldots.$

$$\text{(4.43)}$$

The organizational structure for the $PN = [-1, 0]$ blocks is given in table 4.2. The block type is notation included to link this table with table 4.3 where the basis elements for the different blocks are presented.

From this table it is clear that the number of $PN = [-1, 0]$ two-site blocks,

$$2 \times (2 + 2 + (|\Lambda| - 2)) = |\Lambda| + 4, \qquad (4.44)$$

grows linearly with the lattice size $|\Lambda|$. The largest block has size $2|\Lambda| - 1$ which is linear in $|\Lambda|$. The subbases for the different blocks with $PN = [-1, 0]$ are given in table 4.2.

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I / V	Valence			Ionic		
Subphase	Const/Alt		Other	Other	Const/Alt	
+ / -	+	-			-	+
Block Type	$V^{C/A+}$	$V^{C/A-}$	V^O	I^O	$I^{C/A-}$	$I^{C/A+}$
Block Size	$\|\Lambda\|+1$	$\|\Lambda\|-2$	$2\|\Lambda\|-1$	$2\|\Lambda\|-1$	$\|\Lambda\|-2$	$\|\Lambda\|+1$
Number	2	2	$\|\Lambda\|-2$	$\|\Lambda\|-2$	2	2

Table 4.2: Types of $PN = [-1, 0]$ two-site operators and the size of the blocks.

The Full Hamiltonian

Early calculations by Jin ([4]) were confined to hamiltonians $h_I = \alpha_I E^I + \beta_I T^I$. Extending this to the case of an arbitrary hamiltonian $h \in H$ increases the number of parameters in the density matrix, the size of the density matrix and the time required to find solutions.

The most important distinction between these two cases is the number of parameters which are needed. For the case of ionic hamiltonians, only $\frac{|\Lambda|}{2} + 2$ parameters are required, while the number of parameters grows as $|\Lambda|^3$ in the case of an arbitrary hamiltonian $h \in H$. By restricting to parameters on less than two sites, the number of parameters is reduced to $\frac{5}{2}|\Lambda| + 2$.

If all parameters are used, the density matrix is made up of four large, diagonal blocks. By excluding those parameters on more than two sites, these blocks are divided into

Block Type	Operators
V^{C+}	$C_0^0, C_0^1, \ldots, C_0^{\frac{|\Lambda|}{2}}, D_0^1, \ldots, D_0^{\frac{|\Lambda|}{2}}$
V^{C-}	$C_0^{-1}, \ldots, C_0^{-(\frac{|\Lambda|}{2}-1)}, D_0^{-1}, \ldots, D_0^{-(\frac{|\Lambda|}{2}-1)}$
V^{A+}	$C_{\frac{|\Lambda|}{2}}^0, C_{\frac{|\Lambda|}{2}}^1, \ldots, C_{\frac{|\Lambda|}{2}}^{\frac{|\Lambda|}{2}}, D_{\frac{|\Lambda|}{2}}^1, \ldots, D_{\frac{|\Lambda|}{2}}^{\frac{|\Lambda|}{2}}$
V^{A-}	$C_{\frac{|\Lambda|}{2}}^{-1}, \ldots, C_{\frac{|\Lambda|}{2}}^{-(\frac{|\Lambda|}{2}-1)}, D_{\frac{|\Lambda|}{2}}^{-1}, \ldots, D_{\frac{|\Lambda|}{2}}^{-(\frac{|\Lambda|}{2}-1)}$
V^p	$C_p^0, C_p^1, C_p^{-1}, \ldots, C_p^{\frac{|\Lambda|}{2}}, D_p^1, D_p^{-1}, \ldots, D_p^{\frac{|\Lambda|}{2}}, \quad p = 1, \ldots, \frac{|\Lambda|}{2} - 1,$
I^p	$A_p^0, A_p^1, A_p^{-1}, \ldots, A_p^{\frac{|\Lambda|}{2}}, B_p^1, B_p^{-1}, \ldots, B_p^{\frac{|\Lambda|}{2}} \quad p = 1, \ldots, \frac{|\Lambda|}{2} - 1,$
I^{C-}	$A_0^{-1}, \ldots, A_0^{-(\frac{|\Lambda|}{2}-1)}, B_0^{-1}, \ldots, B_0^{-(\frac{|\Lambda|}{2}-1)}$
I^{C+}	$A_0^0, A_0^1, \ldots, A_0^{\frac{|\Lambda|}{2}}, B_0^1, \ldots, B_0^{\frac{|\Lambda|}{2}}$
I^{A-}	$A_{\frac{|\Lambda|}{2}}^{-1}, \ldots, A_{\frac{|\Lambda|}{2}}^{-(\frac{|\Lambda|}{2}-1)}, B_{\frac{|\Lambda|}{2}}^{-1}, \ldots, B_{\frac{|\Lambda|}{2}}^{-(\frac{|\Lambda|}{2}-1)}$
I^{A+}	$A_{\frac{|\Lambda|}{2}}^0, A_{\frac{|\Lambda|}{2}}^1, \ldots, A_{\frac{|\Lambda|}{2}}^{\frac{|\Lambda|}{2}}, B_{\frac{|\Lambda|}{2}}^1, \ldots, B_{\frac{|\Lambda|}{2}}^{\frac{|\Lambda|}{2}}$

Table 4.3: Subbases for different $PN = [-1, 0]$ blocks.

smaller and smaller blocks and the largest block grows only linearly with the ring size.

Even when using only the two-site parameters, the increase in size of the density matrix when moving to the full hamiltonian poses serious computational problems. The full matrix is ten times the size of the ionic matrix alone, and the largest block is twice the size. The use of symmetrized basis elements gives a significant simplification, but the increase in size means that calculations with the full hamiltonian require much more memory than those for the ionic hamiltonians alone.

In the two sites case, the ionic and valence blocks are such that they have the same structure, the only difference being that where the ionic block has ionic parameters, the valence block has valence parameters and that the mixing parameters and the

number parameter change sign. In the three sites blocks, the corresponding ionic and valence parameters also appear together. In the 1×1 block, the parameters always appear together in a sum. Where one 3×3 block has valence parameters, the other has ionic parameters. The 9×9 block can be rearranged so that the ionic parameters appear where the valence parameters once did and vice-versa. Thus for every ionic ground state there is a corresponding valence ground state with the same energy. When the ionic and valence coefficients are exchanged in the hamiltonian, the ground state will have the ionic and valence parameter values exchanged but the energy will be equal. Thus, the size of the basin of attraction for the constant and alternating superconducting phases is equal to that for the constant and alternating anti-ferromagnetic phases. This is the same result obtained in chapter 2.

Chapter 5

The Calculation

In this chapter we present the programming problem to be solved and explain the MatLab routines which are used. The results of the calculations are presented, including the effects of requiring a half-filled shell structure. The phase structure is examined using $h_{12} = \beta_I T_I^2 + \beta_V T_V^2 + \beta_M T_M^2$ and $h_{12} = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \alpha_0 E_0^2$ for fixed α_I and α_V. Finally, the conclusions are summarized and we discuss the next steps in density matrix research.

5.1 Formulation

The ground state reduced density matrix is found by minimizing the energy over all possible density matrices.

$$\min E(p) = \langle h, p \rangle = Tr[\mathbf{HP}], \ \mathbf{P} \in \mathbf{P}_0 \tag{5.1}$$

where $\mathbf{H}$ is a matrix representation for h and $\mathbf{P}_0$ is the space of positive semi-definite matrices with the same structure as the density matrix.

Let $\mathcal{H}$ be the space of matrices with the same block structure as the density matrix. Let $\mathcal{H}_+$ be the set of positive semi-definite matrices in $\mathcal{H}$. Not all elements of $\mathcal{H}_+$ are possible density matrices, only those with the same linear relationships between their entries. There are thousands of entries in the matrix, but only $\frac{5}{2}|\Lambda| + 2$ parameters, so there are many of these linear relationships. Let the Pauli Space, S, be the space such that all $x \in \mathcal{H}$ which satisfy these relationships satisfy $x \in \mathcal{H} \cap S^\perp$. The solution satisfies $\mathbf{P} \in H_+ \cap S^\perp$; therefore projecting h onto $S^\perp$ will not affect the solution. Assume $h \perp S$, and assume $h \perp 1$. (This last condition is equivalent to a translation of the spectrum, so the lower bound method is still applicable.) Thus $H = h \cup 1 \cup S \cup K$ where K is the space of matrices which do satisfy all the required linear relationships and are orthogonal to h and 1. Then $\mathbf{P}_0 = \{\mathbf{P} \in h \cup 1 \cup K | \mathbf{P} \text{ is psd.}\}$. The problem is solved using the following theorem which gives necessary and sufficient conditions for the optimum, [4].

Theorem 5.1 *At the minimum, there exist positive semi-definite matrices x_* and y_* such that*

$$x_* \in H_+ \cap S^\perp, \quad \langle 1, x_* \rangle = 1; \tag{5.2}$$

$$y_* \in H_+ \cap K^\perp, \quad \langle 1, y_* \rangle = 1; \tag{5.3}$$

and $x_* y_* = 0.$

K is much smaller than S, so solving the dual problem is much faster than solving the primal problem. The dual problem is given by

$$
\begin{aligned}
min \quad & \langle h, y \rangle \\
s.t. \quad & \langle 1, y \rangle = 1 \\
& \langle k_i, y \rangle = 0 \quad \forall \quad k_i \in K \\
& y \quad \text{is positive semi-definite.}
\end{aligned}
\tag{5.4}
$$

The problem is now to find a basis for K in order to express the linear conditions on y. The positive semi-definite condition will be handled by the software.

5.2 Solution

There are many variations on the optimization problem which may be solved. These involve changes in ring size, whether to adapt for half-filled shells and whether to include all interactions or only those between ionic sites. Only after that information is known can the hamiltonian coefficients be specified.

To solve the problem, a basis for K is required. To this end, a natural basis for all matrices in $H \cap S^\perp$ is created. This space is spanned by $h \cup 1 \cup K$ and contains matrices which may or may not be positive semi-definite. The natural basis is created by setting each parameter equal to 1 while the others are 0 in the formula for the density matrix. These will satisfy the required linear relationships and span K. There

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are $\frac{5}{2}|\Lambda| + 2$ elements in this basis when all interactions are used and $|\Lambda| + 1$ elements when only the ionic interactions are used. This natural basis is converted into an orthogonal basis using QR decomposition.

Imposing Half-Filled Shells

It is possible to restrict the problem so that all solutions will satisfy the half-filled shell condition for pure states, $n_\emptyset = n_{\uparrow\downarrow}$ and $n_\uparrow = n_\downarrow$. This was originally done to speed up the convergence, and while it does not affect the ground states of the superconducting or anti-ferromagnetic hamiltonians, it does impact on the ground states of the other phases.

If a half-filled shell structure is being imposed, the first basis element b_1 is chosen so that $\langle b_1, d^p \rangle = 0$ guarantees a half-filled shell. Since the basis set is orthogonal, and since $\mathbf{P} \in span\{b_1 \ldots b_k\}$, $\mathbf{P}$ is guaranteed to be a ground state with a half-filled shell if $\mathbf{P} \in span\{b_2 \ldots b_k\}$. If the element b_1 is removed from the basis the denstiy matrix will satisfy the half-filled condition automatically. The remaining basis elements are ordered so that the first two elements are the identity and the hamiltonian and the rest span K.

Consider $\langle \sum_{i=1}^{|\Lambda|} e_i, d \rangle = n_{\uparrow\downarrow} - n_\emptyset$ and $\langle \sum_{i=1}^{|\Lambda|} f_i, d \rangle = n_\uparrow - n_\downarrow$. Then

$$n_{\uparrow\downarrow} = n_\emptyset \;\Rightarrow\; \langle \sum_{i=1}^{|\Lambda|} e_i, d \rangle = 0 \Rightarrow \langle (\sum_{i=1}^{|\Lambda|} e_i)^2, d \rangle = 0, \tag{5.5}$$

$$n_\uparrow = n_\downarrow \;\Rightarrow\; \langle (\sum_{i=1}^{|\Lambda|} f_i)^2, d \rangle = 0, \tag{5.6}$$

and

$$(\sum_{i=1}^{|\Lambda|} e_i)^2 \;=\; e_1 e_1 + e_1 e_2 + \ldots + e_1 e_{|\Lambda|} + e_2 e_1 + \ldots + e_{|\Lambda|} e_{|\Lambda|}$$

$$\langle(\sum_{i=1}^{|\Lambda|} e_i)^2, d\rangle \;=\; |\Lambda|(\frac{1}{2}(1+N) + 2\alpha_1 + \ldots + 2\alpha_{\frac{|\Lambda|}{2}-1} + \alpha_{\frac{|\Lambda|}{2}}).$$

Enforcing the half-filled shell condition is accomplished by requiring

$$\langle(\sum_{i=1}^{|\Lambda|} e_i)^2 + (\sum_{i=1}^{|\Lambda|} f_i)^2, d\rangle = 0. \tag{5.7}$$

That is,

$$\langle d, 1 + 2\alpha_1 + \ldots + \alpha_{\frac{|\Lambda|}{2}} + 2\gamma_1 + \ldots + 2\gamma_{\frac{|\Lambda|}{2}-1} + \gamma_{\frac{|\Lambda|}{2}}\rangle = 0. \tag{5.8}$$

By removing $b_1 = 1 + 2\alpha_1 + \ldots + \alpha_{\frac{|\Lambda|}{2}} + 2\gamma_1 + \ldots + 2\gamma_{\frac{|\Lambda|}{2}-1} + \gamma_{\frac{|\Lambda|}{2}}$ from the basis for K, the density matrix will satisfy the half-filled condition.

Determining the Phase

Once a basis for K has been found, the problem is converted into standard form and solved. The results which are recorded are the hamiltonian coefficients and the values of the parameters. The reduced density matrix itself can be recreated by subsituting the parameter values into the formula for the density matrix.

The phase can easily be determined from the parameters. If $N = 1$ the ground state is ionic, if $N = -1$ the ground state is valence, and if $|N| < 1$, the ground state is mixed. If the ground state is ionic or valence, the corresponding transport parameter is either positive, negative or zero. If it is positive, the ground state is an alternating subphase state; if it is negative, the ground state is a constant subphase. The mixed transport term is never zero when $|N| < 1$. If $N = 1$ but the ionic transport term is zero, $\beta_1 = 0$, then the ground state is the vacuum state. If $N = -1$ and $\delta_1 = 0$, the ferromagnetic ground state is present.

5.3 Calculational Results

This method was first tested on the case of the ionic hamiltonian alone, $h_I = \alpha_I E^I + \beta_I T^I$, where data is known from Jin, [4]. The results agree with Jin and the convergence is very fast. Rings up to size $|\Lambda| = 100$ were tested, far surpassing earlier calculations.

The method was then extended to calculate ground state energies for arbitrary two-body spin-invariant nearest neighbour hamiltonians. The amount of memory needed to store the form of the density matrix and the basis for the K space increased dramatically and this limited the size of the rings which were usable to $|\Lambda| \leq 16$. The time also increased and rings with $|\Lambda| \leq 12$ sites were the largest that could be used to extract useful results on the phases. The results for ionic hamiltonians agreed with our earlier results and parallel results for valence hamiltonians were also obtained.

Half-filled Shells

The half-filled condition affects the ground states of the electrostatic and mixed operators. The ground state of $h = \alpha_I E_I^2$ is a half-filled checkerboard state when $\alpha_I > 0$ or the vacuum state when $\alpha_I < 0$. Thus, when $\alpha_I < 0$ the half-filled condition is not satisfied. When the half-filled condition is not enforced, the ground state returned by the program for all hamiltonians $h = \alpha_I E_I^2 + \beta_I T_I^2$, where $\alpha_I < -|\beta_I| < 0$, is the degenerate gound state between the vacuum and all filled states. If $|\alpha_I| > -\beta_I$, the program returns a half-filled state whether the half-filled condition is enforced or not, confirming other results which show that the superconducting phase is half-filled.

When the half-filled condition is enforced, no mixed phase ground states are observed.

To understand this, consider the case of a pure mixed hamiltonian, $h = T_M^2$. As presented in section 3.2, the mixed states do not satisfy the half-filled condition for pure phases and the program terminates with errors if the half-filled condition is enforced when $h = T_M^2$.

Since enforcing the half-filled condition does not improve the accuracy of the solution, nor the speed of convergence, this condition is not used in the calculations.

Removing Blocks

Some blocks remain positive definite, no matter which hamiltonians are used. These blocks can be removed from the denstiy matrix calculation without changing the accuracy of approximation. The three sites blocks for non-adjacent sites are an example. Since the hamiltonians are all nearest neighbour, ignoring the interactions between three distant sites affects the energy very little, the approximation is equally accurate whether these blocks are included or not. Removing these blocks simplifies the density matrix greatly, especially for large $|\Lambda|$, since the number of three sites blocks grows quadratically with $|\Lambda|$.

It was expected that the global blocks for the higher phase factors would be removeable, but this is not true. This means that the number of blocks in the matrix grows linearly with the ring size and that the number of non-zero entries in the matrix is $O(|\Lambda|^3)$. Compare this with the case of the ionic interactions where the number of blocks is constant (6) and the number of entries is $O(|\Lambda|^2)$.

5.4 Computational Results on Phases

An arbitrary, hamiltonian $h \in H$ coresponds to a given bond hamiltonian

$$h_{12} = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \alpha_0 E_0^2 + \beta_M T_M^2. \qquad (5.9)$$

By varying the coefficients $\alpha_I, \beta_I, \alpha_V, \beta_V, \alpha_0$ and β_M, the ground state for any two-body hamiltonian can be determined by calculation. The space of hamiltonains is six dimensional, but hamiltonians which are related by a positive constant have the same ground states. The hamiltonians $h \in H \cap S^5$ satisfy the normalization condition

$$\alpha_I^2 + \beta_I^2 + \alpha_V^2 + \beta_V^2 + \alpha_0^2 + \beta_M^2 = 1 \qquad (5.10)$$

and form a five dimensional space which contains all of the information of the full space. That is, $H(N)$ has dimension n in this space if and only if $H(N)$ has dimension $n + 1$ in the space of full hamiltonians.

A minimum of 50 data points in each dimension is required to obtain reasonable approximations to the locations of the phase boundaries. Exploring the five-dimensional space of hamiltoninans is not practical. Instead, three dimensional families of hamiltonians which intersect at least two subsets $H(N_1)$ and $H(N_2)$, and hence contain a phase boundary, are plotted individually.

The phase boundary of greatest interest is the boundary between the pure phases and the mixed phase. If the location of this boundary changes with the dimension of the lattice such that the pure phases occupy more area in two dimensions than in three, this would explain why certain oxides are high temperature superconductors. Although this boundary is not determined exactly by the approximate solutions returned by the program, the results obtained here provide a lower bound on the area occupied by the pure phases.

5.4.1 Transport Hamiltonians

Consider the transport hamiltonians

$$h_{12} = \beta_I T_I^2 + \beta_V T_V^2 + \beta_M T_M^2, \quad \text{where } \beta_I^2 + \beta_V^2 + \beta_M^2 = 1. \qquad (5.11)$$

This space of hamiltonians is two dimensional and can be considered the surface of the unit sphere with the three axes x, y, z labelled by $\beta_I, \beta_V, \beta_M$. In this case, let $h(\theta, \phi)$ be the hamiltonian as a function of the polar coordinates ϕ, θ where

$$\beta_M = \cos(\phi), \ \beta_I = \sin(\phi)\cos(\theta), \ \beta_V = \sin(\phi)\sin(\theta). \qquad (5.12)$$

There are six subphases which are ground states for hamiltonians in this family, as listed in the following table.

h	T^I	$-T^I$	T^V	$-T^V$	T^M	$-T^M$
Phase	ASC	CSC	AAFM	CAFM	AM	CM

$h(\theta, \frac{\pi}{2})$ has $\beta_M = 0$ and must have a superconducting or an anti-ferromagnetic ground state. The same holds for small values of $|\beta_M|$, since these phases have full dimension. Let M^1 be the supremum of numbers M such that $0 < |\beta_M| < M$ implies N_h is pure. Let $\phi^1 = \arccos(M^1)$. This region of pure states, $-M_1 < \beta_M < M_1$, surrounds the equator of the sphere of hamiltonians.

Since the ground state of $\pm T^M$ is a mixed ground state, as $|\phi - \frac{\pi}{2}|$ is increased, all hamiltonians, regardless of θ, cross a boundary into the mixed phase. Let M^2 be the infimum of numbers M such that $|\beta_M| > M$ implies h has a mixed ground state. Let $\phi^2 = \arccos(M^2) < \phi^1$. The values of ϕ^1 and ϕ^2 are important in determining a dimension effect in square lattices. $\phi^1 - \phi^2$ describes the relative strength of the

coherence in the pure versus the mixed phases. The values of ϕ^1 and ϕ^2 are given in the following table for rings of size 4, 8 and 12.

$|\Lambda|$	ϕ^1	ϕ^2
4	0.9081	0.7363
8	1.2640	1.1413
12	1.2885	1.1658

The pure states and their boundaries have been described in chapter 3. When $\beta_I > |\beta_V|$, h has an alternating superconducting ground state, while hamiltonians with $-\beta_I > |\beta_V|$ have constant superconducting ground states. When $|\beta_V| > |\beta_I|$ the ground states are anti-ferromagnetic. The ionic-valence boundaries lie along the curves $|\beta_I| = |\beta_V|$.

The ground states of $h(\theta, \frac{\pi}{2}) = \cos(\theta)T_I^2 + \sin(\theta)T_V^2$ are the same ASC states for all $-\frac{\pi}{4} \leq \theta \leq \frac{\pi}{4}$, since $|\cos(\theta)| > |\sin(\theta)| > 0$ for all of these θ. However, the expectation value of T_V^2 is zero on the ASC states, therefore the total energy is lower when $\theta = 0$ than when $\theta \approx \frac{\pi}{4}$, since $\beta_I = \cos(\theta)$ has a maximum at $\theta = 0$. This makes the hamiltonians with $|\beta_I| \approx |\beta_V|$ much more susceptible to perturbations, not only from T_V^2, but also from T_M^2. As β_M is increased past M^1, the hamiltonians near the ionic-valence boundaries, $\theta = \frac{\pi}{4}, \frac{3\pi}{4}, \frac{5\pi}{4}, \frac{7\pi}{4}$ have ground states which are mixed while the hamiltonians with $\theta = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}$ will have pure ground states until $\beta_M > M^2$.

Consider the figure 5.1 which displays the different phases by different colours. This figure only displays a small portion of the surface; all possible transport hamiltonians can be obtained from these hamiltonians and the transformations $T_{\pm I/V}$ and $T_M^2 \rightarrow -T_M^2$. The portion displayed is for $0 \leq \theta \leq \pi/4$; $\beta_I > \beta_V > 0$ throughout this region. It does, however, show that the ionic to mixed boundary is not constant.
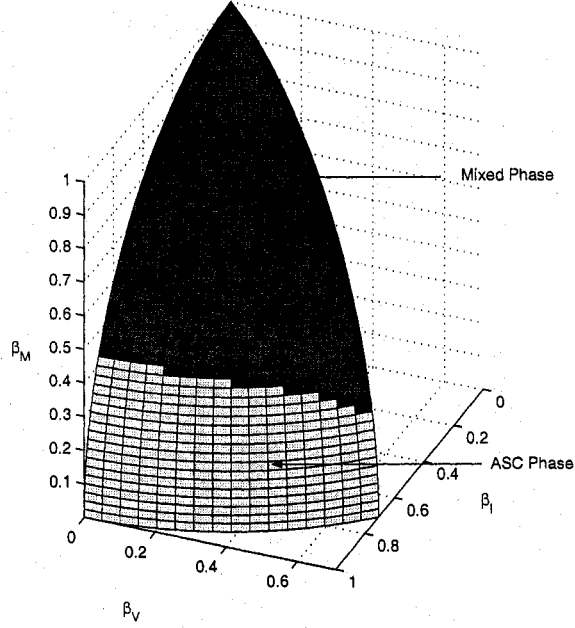
Figure 5.1: The phase structure for $h = \beta_I T_I^2 + \beta_V T_V^2 + \beta_M T_M^2$

The quantum numbers of the mixed phase states are not determined correctly by this level of approximation, except at the poles $h = \pm T_M^2$. The parameter N should take on discrete values since $N = \frac{n_I - n_V}{|\Lambda|}$ and there are a finite number of sites. However, the values returned for N range between -1 and 1 and are not discrete. This may occur since the level of approximation being used ($k = 3$) is not accurate enough, because the parameters with unpaired spins have been removed or because of the very large degeneracy in the mixed ground states.

5.4.2 Ionic to Mixed Phase Transition

To understand this phase transition in greater detail, including the effect of the electrostatic terms, consider the hamiltonians

$$h(\theta, \phi) = \alpha_I(\theta, \phi)E_I^2 + \beta_I(\theta, \phi)T_I^2 + \beta_M(\phi)T_M^2, \tag{5.13}$$

where $\alpha_I(\theta, \phi) = \sin(\phi)\cos(\theta)$, $\beta_I(\theta, \phi) = \sin(\phi)\sin(\theta)$ and $\beta_M(\phi) = \cos(\phi)$. The results which hold for this ionic-mixed phase transition will also hold for the valence-mixed phase transition because of the symmetry between the ionic and valence terms.

The ground state energy of $h(\theta, \frac{\pi}{2})$ is proportional to the stability of the pure phase as $|\beta_M|$ is increased. $h(\theta, \frac{\pi}{2})$ has its lowest ground state energy when $\theta \approx 1.2252$ or $\theta \approx \pi - 1.2252$, and its highest ground state energy when $\theta = \frac{\pi}{4}$ or $\theta = \frac{3\pi}{4}$. Let M^3 be the infimum of numbers M such that $h(\frac{\pi}{4}, M)$ has a pure ground state and M^4 be the supremum of numbers M such that $h(1.2252, M)$ has a mixed ground state. The values of $\phi^i = \arccos(M^i)$ are given in the following table for three different ring sizes.

$|\Lambda|$	ϕ^3	ϕ^4
4	1.2027	0.6995
8	1.1781	1.0308
12	1.1781	1.0799

In the two tables above, the values for the $|\Lambda| = 4$ case stand out as being very different than those of the other two cases. In fact, $\phi^1 < \phi^3$ in this case, while $\phi^1 > \phi^3$ in the others. This suggests that the four sites case does not accurately capture the physics of the system. Note that $\phi^3 > \phi^2 > \phi^4$ for every ring size. This

is because the ϕ^2 corresponds to $\beta_V = \alpha_V = \alpha_I = 0$ while ϕ^3 and ϕ^4 correspond to the minimum and maximum over hamiltonians with $\beta_V = \alpha_V = 0$.

Using the data from the 12 sites case, the area occupied by the pure phases is between 27% and 47% of the total. This is divided equally between the four subphases.

5.4.3 Phase Boundary Results

To visualize the phases and phase boundaries which exist, consider the three dimensional space of hamiltonians

$$h = \alpha_I E_I^2 + \beta_I T_I^2 + \alpha_V E_V^2 + \beta_V T_V^2 + \alpha_0 E_0^2, \tag{5.14}$$

with α_I, α_V fixed. The three spheres

$$\alpha_I = \alpha_V = -1, \quad \alpha_I = \alpha_V = -0.5, \quad \alpha_I = \alpha_V = 0 \tag{5.15}$$
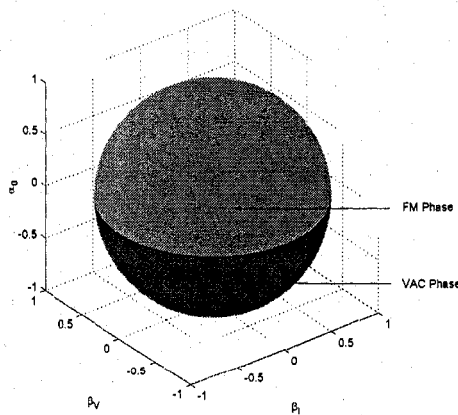
will be discussed in detail.

Figure 5.2: Phase structure for $h \in H_P$ when $\alpha_I = \alpha_V = -1$

When $\alpha_I = \alpha_V = -1$, there are no superconducting or anti-ferromagnetic states since $\alpha_I = \alpha_V < -|\beta_I|, |\beta_V| < 0$ for all hamiltonians. The boundary between the vacuum and ferromagnetic phases occurs at $\alpha_0 = 0$, the equator. If α_I or α_V is decreased from -1, the phase structure remains unchanged, while the location of the phase boundary moves off the equator whenever $\alpha_I \neq \alpha_V$.
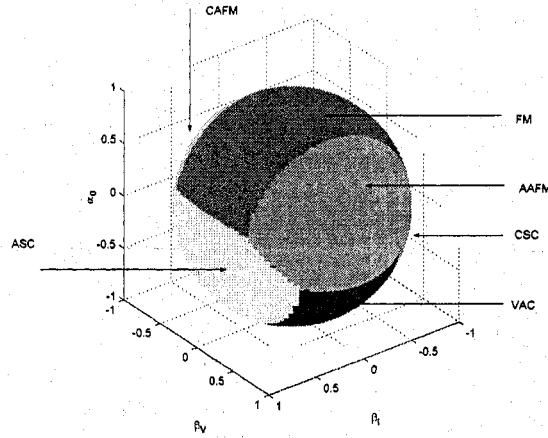

Figure 5.3: Phase structure for $h \in H_P$ when $\alpha_I = \alpha_V = -0.5$

To examine $-1 < \alpha_I = \alpha_V < 0$, consider $\alpha_I = \alpha_V = -0.5$. The phase boundaries between ionic and valence phases are centered at the equator, $\alpha_0 = 0$, but do not occur there for all β_I and β_V. For $|\beta_I| > |\alpha_I|$, the ground state is a superconducting ground state. Therefore changing the coefficient β_I affects the energy and increasing β_I at the expense of β_V causes the ionic-valence phase boundaries to move off of the equator with the ionic phses occupying more space. Similarly for the valence cases. The boundary between the vacuum phase and the superconducting subphases always occurs at $\beta_I = \pm\alpha_I = \pm0.5$.
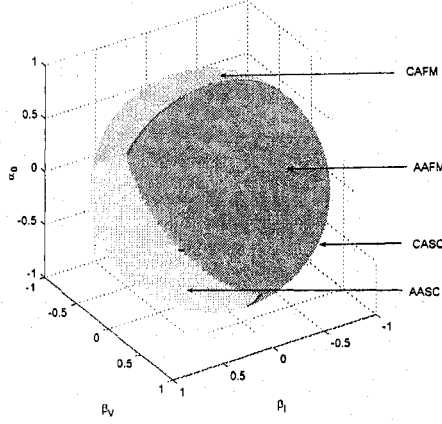
Finally, consider $\alpha_I = \alpha_V = 0$.

Figure 5.4: Phase structure for $h \in H_P$ when $\alpha_I = \alpha_V = 0$

When $\alpha_I = \alpha_V = 0$, there are no vacuum or ferromagnetic phase ground states, since $|\beta_I| > \alpha_I$ and $|\beta_V| > \alpha_V$. The phase boundary between the superconducting states to the anti-ferromagnetic states is centered at the equator, however the exact location fluctuates as β_I and β_V change. The boundary between the alternating and constant phase superconducting states occurs at $\beta_I = 0$. Since $\alpha_I = 0$, this boundary is degenerate between all ionic ground states. When $\alpha_I > 0$, this boundary is the checkerboard state and is not degenerate with the vacuum and all-filled states. The checkerboard state does not have full dimension and the entire ionic portion of the sphere is occupied by the superconducting subphases when $\alpha_I > 0$.

For all hamiltonians, adjusting α_I and α_V so that they are not equal will move the ionic-valence phase boundaries away from $\alpha_0 = 0$. However, the phase structure in the ionic and valence regions is unchanged.

5.5 Conclusions

Theoretical results on the possible phases and the dimensions of their intersections were obtained. Any $k < 6$ pure phases share a boundary of dimension $7 - k$ and this shows that any two phases share a boundary of co-dimension one, since H is six dimensional. That is, a phase transition between any two pure phases is possible.

To implement the lower bound method, the basis of all degree three polynomials in the annihilation and creation operators was ordered to give the density matrix the simplest block structure. By restricting to parameters on two sites or fewer, the blocks are further divided, greatly simplifying the calculation without sacrificing the accuracy of the approximation of the pure ground states. Global basis elements were used to reduce the size of the largest block by a factor equal to the ring size. The size of this block grows linearly with the ring size, but the number of blocks of this type also grows linearly, so that the size of the density matrix as a whole is quadratic in $|\Lambda|$.

The work of Jin was extended by implementing software routines which are capable of enforcing positive semi-definite conditions and by using arbitrary nearest neighbour, two-body hamiltonians. SeDuMi, a software program written in MatLab for solving semi-definite programming problems was tested. The results were in agreement with the results from [4]. Calculations on rings up to $|\Lambda| = 100$ were carried out using the pure ionic hamiltonian and up to $|\Lambda| = 12$ were carried out using the full hamiltonian.

The mixed phase contains states which have equal numbers of ionic and valence sites and states which do not. A complete analysis of the mixed phase was impossible due to the degeneracy of the mixed states. However, useful results about the location of its

boundary with the pure phases were obtained and provide a method to compare the sizes of the superconducting phases in one, two, and three dimensional square lattices. In the one-dimensional lattices, the two superconducting phases occupy more than 7.5% of the surface each and all pure phases together occupy at least 30%.

5.5.1 Future Work

This thesis is one step on the way to replacing the wave-function method with the lower bound method of reduced density matrix theory.

This calculation is limited by the amount of memory needed to store the conditions on the dual matrix, so any advance in computing power will help. Using the full set of parameters makes this problem much more difficult, and powerful computers such as the HPCVL (High Performance Computing Virtual Laboratory) will be needed to do these calculations. This will also allow larger lattices to be used. Recent results by Mazzioti [9] show that programs that exploit the particular structure of the density matrix can significantly decrease the time and memory used over SeDuMi .

The next step is to use the 4-body density matrix in place of the 3-body matrix. This would likely give very accurate results without increasing the number of constraints significantly. Solving the dispersion problem (see [11]) can only done using the k-body density matrix with $k \geq 4$. The dispersion problem calculates the energies of excited states as well as ground states. However, the calculation at any level of approximation is simplified by the restriction to two-site parameters without affecting the accuracy.

The most physically interesting extension of this work will be to apply these methods to two and three-dimensional square lattices. This would allow the detection of a

dimension effect which is a key problem in superconductivity.

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